MH2006 International Symposium on Metal-Hydrogen Systems

-Fundamentals and Applications-

Technical Program

Symposium Venue: Sheraton Maui Resort Hotel, Maui, Hawaii

Time	Monday 02 Oct	Tuesday 03 Oct	Wednesday 04 Oct	Thursday 05 Oct	Friday 06 Oct
8:30	Plenary I Awards	Tu-O-1a,b,c	We-O-1a,b,c	Th-O-1a,b,c	Fr-O-1a,b
9:00					
9:30					
10:00		**Coffee**	**Coffee**	**Coffee**	**Coffee**
10:30	**Coffee**	Tu-O-2a,b,c	We-O-2a,b,c	Th-O-2a,b,c	Fr-O-2a,b
11:00	Plenary II				
11:30					
12:00			**Box Lunch**		
12:30	**Lunch**	**Lunch**	**Optional** Excursion to Volcano Crater or Free Time	**Lunch**	**END**
13:00					
13:30					
14:00	Mo-O-1a,b,c	Tu-O-3a,b,c		Th-O-3a,b,c	
14:30					
15:00					
15:30					
16:00	**Break**	**Break**		**Break**	
16:30	Mo-O-2a,b,c	Tu-O-4a,b,c		Th-O-4a,b	
17:00					
17:30					
18:00	**Dinner**	**Dinner**		**Break**	
18:30					
19:00			**Dinner**	**Luau**	
19:30					
20:00	**Poster Session I (P-176 to P-244)**	**Poster Session II (P-245 to P-313)**	**Poster Session III (P-314 to P-381)**		
20:30					
21:00					
21:30					
22:00					

SUNDAY, OCTOBER 1			MH2006 SYMPOSIUM SCHEDULE	
14:00			Registration	(until 21:30)
18:00			Welcoming Reception	(until 20:00)
MONDAY, OCTOBER 2				
7:30			Registration	(until 18:00)
	Chairs:	C. Jensen G. Sandrock	Mo - Plenary Session I (Maui Ballroom)	Awards
8:30	O-001	J. J. Reilly (Plenary)	A Retrospective View of Metal Hydride Research at Brookhaven National Laboratory 1966-2006	
9:30	O-002	M. Felderhoff (Plenary)	Complex Metal Hydrides – Potential Hydrogen Storage Materials for Fuel Cell Applications	
10:30			Coffee Break	
	Chair:	T. J. Udovic	Mo - Plenary Session II (Maui Ballroom)	General Overviews
11:00	O-003	P. H. L. Notten (Plenary)	The Electrochemistry and Modelling of Hydrogen Storage Materials	
11:45	O-004	S. W. Jorgensen (Plenary)	Mobile Hydrogen Storage: A Discussion Between Science and Engineering	
12:30			Lunch	
	Chair:	J. Herbst	Mo-O-1a (Kahului+Kihei+Wailea)	Theory Overview
14:00	O-005	C. G. Van de Walle (Invited)	Hydrogen in Semiconductors and Insulators	
14:30	O-006	D. S. Sholl (Invited)	Density Functional Theory Calculations as a Tool for Probing Hydrogen Diffusion and Storage in Metal Hydrides	
15:00	O-007	E. H. Majzoub	Global Optimization of Complex Anionic Hydride Crystal Structures	
15:20	O-008	M. Gupta	Ab Initio Study of the Hydrogenation Properties of Mg-based Binary and Ternary Compounds (Mg_2X, X=Ni,Si and $MgYNi_4$)	
15:40	O-009	P. Vajeeston	A New Series of High Hydrogen Content Hydrogen-Storage Materials – a Theoretical Prediction	
	Chair:	C. C. Ahn	Mo-O-1b (Wailuku)	H-Carbon Overview
14:00	O-010	R. Chahine (Invited)	Comparison of Hydrogen Adsorption in Nanoporous Materials	
14:30	O-011	A. C. Cooper (Invited)	Integrated Hydrogen Storage and Delivery Using Organic Liquid-Phase Carriers	
15:00	O-012	G. L. Powell	Hydriding Kinetics Of Organic Hydrogen Getters	
15:20	O-013	A. Dailly	Hydrogen Physisorption in Crystalline Microporous Materials	
15:40	O-014	M. Krishna Kumar	Pd Functionalized Multiwalled Carbon Nanotube Based Hydrogen Sensor	
	Chair:	Y. Fukai	Mo-O-1c (Kapalua+Napili)	H-Metals
14:00	O-015	M. Kubota (Invited)	Observations of New Features of Hydrogen in Pd: A Phase Transition Originates from O-Site Vacancies and Possible Quantum Phenomena	
14:30	O-016	M. Tkacz (Invited)	Pressure Induced Phase Transformation of REH_3	
15:00	O-017	J. L. Bobet	Crystal Structure and H Sorption Properties of $GdMgNi_{4-x}Al_x$ (Pseudo Laves Phase). Experimental and Theoretical Approach	
15:20	O-018	R. Ahuja	Pressure-induced Phase Transition in YH_3	
15:40	O-019	M. Prina	Degradation Behavior of $LaNi_{4.78}Sn_{0.22}H_x$ during Cycling to Elevated Temperature	
16:00			Break	

	Chair:	M. Fichtner	Mo-O-2a Destabilization (Kahului+Kihei+Wailea)
16:30	O-020	J. J. Vajo (Invited)	Destabilization Strategies and Kinetics Challenges in Light Metal Hydride Systems
17:00	O-021	H. Wu	Neutron Scattering Study of the Structure, Phase Variation, and Properties of Si-Destabilized Calcium Hydrides
17:20	O-022	R. Gupta	First Principles Study of the Destabilization of the Li Amide-Imide Reaction for Hydrogen Storage
17:40	O-023	G. S. Walker	Mechanism of Hydrogen Release for the $LiBH_4/MgH_2$ System
	Chair:	A. Percheron-Guégan	Mo-O-2b Fuel Cells/Catalysts (Wailuku)
16:30	O-024	S. W. Nam (Invited)	Preparation of Ni-Al Alloy Catalyst at Reduced Temperature for Fuel Cell Application
17:00	O-025	E. Jankowska	Electrochemical Properties of Nanocrystalline and Microcrystalline ZrV_2-Type Electrode Materials
17:20	O-026	S. Ramaprabhu	Performance of Polymer Electrolyte Membrane Fuel Cells with Pt/MWNTs as Oxygen Reduction Catalyst
17:40	O-027	S. N. Paglieri	Characterization of V-6Ni-5Co Membranes for Hydrogen Separation
	Chair:	S. Orimo	Mo-O-2c Chemical Hydrides (Kapalua+Napili)
16:30	O-028	T. Autrey (Invited)	Amine Boranes for Chemical Hydrogen Storage
17:00	O-029	S. Kathmann	Computational Studies of Materials for Chemical Hydrogen Storage
17:20	O-030	L.-X. Sun	Hydrolysis of $Al_{80}(CaH_2)_{20-x}Bi_x$ Alloys for Hydrogen Generation
17:40	O-031	Q. Xu	A New Portable Hydrogen Generation System: Catalytic Dissociation and Hydrolysis of Ammonia-Borane
18:00			Dinner
20:00	Poster Session I (P-176 to P-244)		(until 21:30)
TUESDAY, OCTOBER 3			
8:00			Registration (until 18:00)
	Chair:	J. Huot	Tu-O-1a MgH_2/Catalysts (Kahului+Kihei+Wailea)
8:30	O-032	R. Checchetto (Invited)	Catalytic Properties on the Hydrogen Desorption Process of Metallic Additives Dispersed in the MgH_2 Matrix
9:00	O-033	D. D. Graham	Combining Electron Energy Loss Spectroscopy and Energy Dispersive Spectroscopy for Identification of Catalytic Species in Hydrogen Storage Materials
9:20	O-034	R. A. Varin	Hydrogen Desorption Properties of MgH_2 Nanocomposites with Nano-oxides and Special INCO Nano-and-Micro-Ni
9:40	O-035	Y. Yoo	Enhanced Hydrogen Reaction Kinetics of Nanostructured Mg-based Composites with Nanoparticle Metal Catalysts Dispersed on Supports
	Chair:	E. Gray	Tu-O-1b QENS/NPD (Wailuku)
8:30	O-036	M. R. Hartman (Invited)	Quasielastic Neutron Scattering Investigation of the Reorientational Motion of Hydrogen in Na_3AlH_6 and $^7Li^{11}BH_4$
9:00	O-037	T. J. Frankcombe	The Effect of Zero Point Vibration on $LiBH_4$
9:20	O-038	B. C. Hauback	Crystal Structure of Alanates
9:40	O-039	T. J. Udovic	Crystal Structure of a Novel Class of Ternary Hydrides Li_4Tt_2D (Tt=Si and Ge)

	Chair:	P. H. L. Notten	Tu-O-1c Batteries/Thin Films (Kapalua+Napili)
8:30	O-040	J. Chen (Invited)	Studies on Ni-MH Batteries
9:00	O-041	D. M. Borsa	Mg-Ti-H Thin Films with Optimal Properties for Batteries, Solar Collectors and Sensors
9:20	O-042	Y. L. Du	Structural and Hydrogen Storage Properties of MgPrNi Amorphous Alloys with High Glass Formability
9:40	O-043	M. Getzlaff	Hydrogen-Induced Plastic Deformation of Rare Earth Metal Thin Films
10:00			Coffee Break
	Chair:	T. Autrey	Tu-O-2a Amides (Kahului+Kihei+Wailea)
10:30	O-044	P. Chen (Invited)	Formation of NH_3 during the Dehydrogenation of Amide-Hydride Mixtures
11:00	O-045	J. Rijssenbeek (Invited)	Crystal Structure Determination and Reaction Pathway of Amide-Hydride Mixtures
11:30	O-046	M. H. Sørby	Crystal Structure Investigations of Li and Mg Amide and Imide
11:50	O-047	S. Isobe	Characterization of Titanium Based Catalysts in the Li-N-H Hydrogen Storage System by X-ray Absorption Spectroscopy
12:10	O-048	C. M. Araujo	*Ab Initio* Investigation of Li-N-Mg-H Systems for Hydrogen Storage
	Chair:	B. Hjörvarsson	Tu-O-2b Thin Films (Wailuku)
10:30	O-049	B. Dam	Hydrogenography: A Versatile Combinatorial Thin Film Technique to Investigate the Formation of Metal Hydrides
11:00	O-050	J. Schoenes	New Insights from Raman and IR Spectroscopy into the Metal-Insulator Transition of YH_x Switchable Mirrors
11:30	O-051	A. K. Eriksson	Resistivity Changes in Cr/V 14/14 and 7/14 Superlattices during Hydrogen Uptake
11:50	O-052	D. E. Azofeifa	Optical Properties of Hydrided Holmium Thin Films
12:10	O-053	S. Ólafsson	Modelling the Binding Energy Change of Hydrogen in Metals by Interfaces Insertions in Multilayers
	Chair:	R. C. Bowman, Jr.	Tu-O-2c Tritides/Helium/Permeation (Kapalua+Napili)
10:30	O-054	K. L. Shanahan (Invited)	Deuterium, Tritium, and Helium Desorption from Aged Titanium Tritides
11:00	O-055	S. Thiébaut (Invited)	^{3}He Retention in $LaNi_5$ and Pd tritides : Dependence on Stoichiometry, ^{3}He Distribution and Aging Effects
11:30	O-056	A. Fabre	EELS Study of Individual Helium Bubbles in Aged $Pd_{90}Pt_{10}$
11:50	O-057	J. Yang	Effect of H_2S on Hydrogen Permeation of Pd-Cu/V-15Ni Composite Membrane
12:10	O-058	M. Morinaga	Enhanced Hydrogen Embrittlement of Pd-coated Niobium Metal Membrane Detected by In-situ Small Punch Test under Hydrogen Permeation
12:30			Lunch

	Chair:	A. Switendick	Tu-O-3a MH Theory (Kahului+Kihei+Wailea)
14:00	O-059	D. D. Johnson (Invited)	Predicting Accurate Thermodynamic Properties of Reversible Hydrogen-Storage Destabilized Metal Hydrides and their Proper Comparison to Experiment
14:30	O-060	H. Jonsson (Invited)	Theoretical Studies of the Hydrogen Storage Properties of Magnesium-based Hydrides: Stability, H-atom Diffusivity and Hydrogen Release Temperature
15:00	O-061	D. S. Sholl	Accelerating Development of Destabilized Metal Hydrides for Hydrogen Storage Using First Principles Calculations
15:20	O-062	M.-Y. Chou	First-Principles Studies of Phase Stability and Reaction Dynamics in Complex Metal Hydrides
15:40	O-063	P. E. de Jongh	The Effect of Magnesium(hydride) Cluster Size on the Sorption Thermodynamics: a Quantum-Chemical Study
	Chair:	V. E. Antonov	Tu-O-3b Defects in H-M (Wailuku)
14:00	O-064	R. Kirchheim (Invited)	Interaction of Hydrogen with Defects and Their Stabilisation
14:30	O-065	J. Cizek (Invited)	Hydrogen-Induced Defects in Niobium
15:00	O-066	B. Hjörvarsson	Do Diffraction Techniques Give a Reliable Measure of the Hydrogen Induced volume Changes?
15:20	O-067	D. Khatamian	Comparison of the TSSD Results Obtained by Differential Scanning Calorimetry and Neutron Diffraction
15:40	O-068	Y. Fukai	The Defect Structure with Superabundant Vacancies to be Formed from fcc Binary Metal Hydrides: Experiments and Simulations
	Chair:	G. Sandrock	Tu-O-3c AlH_3 (Kapalua+Napili)
14:00	O-069	J. Graetz (Invited)	Kinetics and Thermodynamics of the Aluminum Hydride Polymorphs
14:30	O-070	H. W. Brinks (Invited)	Crystal Structure Investigation of Alane
15:00	O-071	S.-J. Hwang	NMR Studies of the Aluminum Hydride Phases and their Stabilities
15:20	O-072	R. Zidan	Development of Complex Hydrides using Novel Techniques
15:40	O-073	V. A. Yartys	Alane AlH_3 for Hydrogen Storage
16:00			Break
	Chair:	R. Chahine	Tu-O-4a H-MOF (Kahului+Kihei+Wailea)
16:30	O-074	C. C. Ahn (Invited)	H_2 Physisorption in Carbons and Metal Organic Frameworks
17:00	O-075	M. Hirscher (Invited)	Hydrogen Adsorption in Metal-Organic Frameworks
17:30	O-076	M. Latroche	Organometallic Compounds with Very Large Pore Volumes as Hydrogen Storage Materials.
	Chair:	M. H. Mintz	Tu-O-4b H-M Alloys (Wailuku)
16:30	O-077	D. Sun	Hydrogen Storage Properties of AB3-type Compounds
17:00	O-078	M. Sahlberg	Hydrogen Absorption in $Mg_3Y_2Zn_3$
17:20	O-079	W. Sikora	Symmetry Analysis of Hydrogen Related Structural Transformations in Laves Phase Intermetallic Compounds
17:40	O-080	M. Yamaguchi	Compton Scattering Studies on the Electronic and Magnetic Structure of Metal Hydrides

	Chair:	M.-Y. Chou	Tu-O-4c Theory - MH/Alanates (Kapalua+Napili)
16:30	O-081	J. F. Herbst (Invited)	$LaTM_5$ Hydrides (TM = Fe, Co, Ni): Theoretical Perspectives
17:00	O-082	O. M. Løvvik (Invited)	Theory of Complex Hydrides
17:30	O-083	W. Zhou	Vibrational Properties of TiH_n (n=0-8) Complexes Adsorbed on Carbon Nanostructures
17:50	O-084	Q. Ge	A First Principles Study of Active Species in Ti-doped Sodium Aluminum Hydride Surfaces
18:10			Dinner
20:00	Poster Session II (P-245 to P-313)		(until 21:30)
WEDNESDAY, OCTOBER 4			
	Chair:	A. V. Skripov	We-O-1a NMR/Diffusion (Kahului+Kihei+Wailea)
8:30	O-085	M. S. Conradi (Invited)	NMR to Determine Rates of Motion and Structures in Metal-Hydrides
9:00	O-086	T. M. Ivancic	Characterization of H and D Motion in $ZrNiH_x$ and $ZrNiD_x$ by NMR Relaxation Times
9:20	O-087	T. Otsuka	Effect of Inclusions in Steels on Hydrogen Diffusion and Trapping Examined by Tritium Autoradiography
9:40	O-088	V. E. Antonov	Tunnel Splitting of Excited Optical Vibrational States of Hydrogen in α-Mn
	Chair:	K. J. Gross	We-O-1b MgH_x - Applications (Wailuku)
8:30	O-089	P. de Rango (Invited)	Nanostructured Magnesium Hydride for Pilot Tank Development
9:00	O-090	A. S. Ingason	Hydrogen Uptake in Mg:C Multilayers - Interface Effects on the Binding Energy in the Hydride Layer MgH_2
9:20	O-091	J.-G. Roquefere	Use of Super Critical Fluid Process to Deposit Nanoplot of Ni and Pd on Mg Powder Surface - Improvements of the Hydrogen Sorption Cyclability
9:40	O-092	X. Tang	Hydrogen Storage Properties of Na-Li-Mg-Al-H Complex Hydrides
	Chair:	M. Hirscher	We-O-1c H-Carbon Systems (Kapalua+Napili)
8:30	O-093	J. E. Fischer (Invited)	Tailored Nanoscale Porosity in Carbide-Derived Carbons: Optimization for High Capacity Hydrogen Storage
9:00	O-094	V. E. Antonov	Saturated High-Pressure Hydrofullerenes $C_{60}H_{60}$ and $C_{60}D_{60}$
9:20	O-095	P. E. de Jongh	Magnesium-Carbon Nanocomposites for Hydrogen Storage?
9:40	O-096	A. I. Kolesnikov	Neutron Spectroscopy Study of Single-Walled Carbon Nanotubes Hydrogenated under High Pressure
10:00			Coffee Break
	Chair:	V. A. Yartys	We-O-2a Techniques/MH-Theory (Kahului+Kihei+Wailea)
10:30	O-097	T. Blach	Sieverts Apparatus and Methodology for Accurate Determination of Hydrogen Uptake by Light-Atom Hosts
10:50	O-098	N. T. Stetson	An Overview of Analytical Techniques Being Used to Characterize Today's Most Advanced Hydrogen Storage Materials
11:10	O-099	K. Ishikawa	Microstructural Changes in the Multi-Phase $Nb_{40}Ti_{30}Co_{30}$ Alloy by Rorring-Annealing Techniques and Their Hydrogen Permeability
11:30	O-100	H.-K. Lee	Usable Capacity as a Criterion for Searching for Optimal Hydrogen Storage Nanomaterials

	Chair:	J. J. Rush	We-O-2b (Wailuku) Alloy Hydrides
10:30	O-101	M. Ito	Effect of Nb Addition on the Terminal Solid Solubility of Hydrogen for Zr and Zircaloy-4
10:50	O-102	K.-B. Kim	Hydrogen Permeation and Embrittlement of Ni- and Zr-based Amorphous Alloys
11:10	O-103	S. M. Filipek	Novel Hydrides of RMn_2 Laves Phases Synthesized under Hydrogen Pressure
11:30	O-104	Y. Filinchuk	Deuterium Site Occupancies in $Ce_2Ni_7D_4$ and Comparison with $CeNi_3D_{2.8}$
	Chair:	J. J. Vajo	We-O-2c (Kapalua+Napili) H-Carbon Systems/Characterization
10:30	O-105	C. M. Brown	Neutron Scattering Studies of Hydrogen in Carbon Materials
10:50	O-106	J. L. Herberg	NMR Investigations of Hydrogen Interaction with Metal-Containing Carbon Structures
11:10	O-107	B. Panella	New Methods to Study Hydrogen Physisorption in Microporous Materials
11:30	O-108	A. J. Ramirez-Cuesta	Inelastic Neutron Scattering in the Study of Hydrogen Storage Materials
11:50			Box Lunch
12:00			Optional Excursion to Haleakala National Park (until 18:30) or Free Time
18:30			Dinner
20:00	Poster Session III (P-314 to P-381)		(until 21:30)
THURSDAY, OCTOBER 5			
	Chair:	E. Akiba	Th-O-1a (Kahului+Kihei+Wailea) Alanates/Amides
8:30	O-109	M. P. Pitt	Defining the Location of Ti in the Ti-doped $NaAlH_4$ System
8:50	O-110	C. P. Baldé	Evolution of Ti in $TiCl_3$-doped $NaAlH_4$ – Implications for Hydrogen Storage
9:10	O-111	P. Wang	Advantage of TiF_3 over $TiCl_3$ as a Dopant Precursor to Prepare Catalytically Enhanced $NaAlH_4$ System: Functional Flourine Anion
9:30	O-112	Z. T. Xiong	Investigations on Hydrogen Desorption over a $LiNH_2$-$LiAlH_4$ (2/1) Mixture
	Chair:	M. Latroche	Th-O-1b (Wailuku) H_2 Permeation/Separation
8:30	O-113	S. M. Opalka (Invited)	Hydrogen Interactions with the Ordered BCC PdCu Alloy
9:00	O-114	D. E. Nanu	Towards the Design of Stable Pd-based Membranes for Hydrogen Gas Separation: a Statistical Thermodynamics Approach
9:20	O-115	K. Aoki	Alloy Designs for Highly Hydrogen Permeable Nb-Ti-Co Alloys with Large Resistance to Hydrogen Embrittlement
9:40	O-116	J. W. Reiter	Performance and Degradation of Gas Gap Heat Switches in Hydride Compressor Beds
	Chair:	B. C. Hauback	Th-O-1c (Kapalua+Napili) Borohydrides/Amides
8:30	O-117	K. Miwa (Invited)	Theoretical Prediction on Thermodynamical Stabilities of Metal Complex Hydrides
9:00	O-118	Y. Nakamori (Invited)	Thermodynamical Stabilities of Complex Hydrides
9:30	O-119	T. R. Jensen	Dehydrogenation of $LiBH_4$ Investigated using *in-situ* Synchrotron X-ray Diffraction and MAS NMR
10:00			Coffee Break

	Chair:	K. Yvon	Th-O-2a Combinational Complex MH (Kahului+Kihei+Wailea)
10:30	O-120	J. P. Lemmon (Invited)	Combinatorial Techniques and Results for Hydrogen Storage Discovery
11:00	O-121	E. Rönnebro (Invited)	Synthesis of New Metal Hydrides and How to Select New Potential Materials
11:30	O-122	G. J. Lewis	High Throughput Screening of a Novel Ternary Complex Hydride System
11:50	O-123	J. Yang	Hydrogen Storage of Li-based Complex Hydrides Made from a Combination of Known High Capacity Hydrides
12:10	O-124	A. Ludwig	High-throughput Characterization of Hydrogen Storage Materials Using Thin Films on Micromachined Si Substrates
	Chair:	R. Kirchheim	Th-O-2b Defects - II (Wailuku)
10:30	O-125	K. Sakaki (Invited)	Positrons in Hydrogen Storage Materials -AB_5-type Alloys and Alanates
11:00	O-126	R. Cantelli (Invited)	Dynamics of Defects in Alanates
11:30	O-127	Q. Shi	Point Defect Dynamics in Sodium Aluminum Hydrides
11:50	O-128	H. Yukawa	Raman Scattering and Lattice Stability of $NaAlH_4$ and Na_3AlH_6
12:10	O-129	N. Eigen	Ultra-fast Hydrogen Sorption by Tuned Microstructure and Morphology in Sodium Alanates
	Chair:	M. S. Conradi	Th-O-2c Borohydrides (Kapalua+Napili)
10:30	O-130	D. Book (Invited)	Synthesis and Characterisation of Transition-Metal Borohydrides
11:00	O-131	G. Severa (Invited)	Transition Metal Borohydride Complexes as Reversible Hydrogen Storage Materials
11:30	O-132	M. Au	Hydrogen Desorption and Absorption of the Modified $LiBH_4$
11:50	O-133	M. Fichtner	Synthesis and Properties of Magnesium Boranate
12:10	O-134	H. Kabbour	Hydrogen Release and Reversibility in $Ca(AlH_4)_2$-based Systems
12:30			Lunch
	Chair:	J. Graetz	Th-O-3a Amides (Kahului+Kihei+Wailea)
14:00	O-135	T. Ichikawa (Invited)	Role of Ammonia in the Amide-Imide Hydrogen Storage Systems
14:30	O-136	Weifang Luo (Invited)	Li-Mg-N-H: Recent Investigations and Development
15:00	O-137	P. A. Anderson	Synthesis and Characterization of Amide–Borohydrides: New Complex Light Hydrides for Potential Hydrogen Storage
15:20	O-138	T. A. Dobbins	Ultrasmall-Angle X-ray Scattering (USAXS) Studies on High Energy Milled $NaAlH_4$
15:40	O-139	A. R. Akbarzadeh	First-Principles Studies of Thermodynamic and Structural Properties of the Li-Mg-N-H System

	Chair:	N. T. Stetson	Th-O-3b Mg Kinetics (Wailuku)
14:00	O-140	M. Dornheim (Invited)	Reaction Kinetics of Doped Light Weight Hydrides and Reactive Hydride Composites
14:30	O-141	D. M. Grant	The Effect of Mixed Metal Oxide Materials on the Hydrogen Sorption Properties of Milled MgH_2
14:50	O-142	T. Sato	A Series of Hydrogen Rich $[Mg_{\sim.9}TM_{\sim.1}]H_2$ (TM = Ti, Zr, Hf, V, Nb and Ta) Hydrides with an FCC Structure was Found to Have Significantly Better Desorption Kinetics than MgH_2
15:10	O-143	T. Kohno	Structural and Hydriding Properties of New Mg-Li-Ni Alloys
15:30	O-144	I. E. Gabis	The Mechanisms and the Kinetics of Hydride Formation
	Chair:	R. Zidan	Th-O-3c Ball Milling MH (Kapalua+Napili)
14:00	O-145	J. Huot (Invited)	Synthesis of Hydrogen Storage Materials by Ball-milling and Cold Rolling Techniques
14:30	O-146	A. V. Skripov (Invited)	Nuclear Magnetic Resonance Studies of Ball-Milled Hydrides
15:00	O-147	A. Léon	Ageing of $NaAlH_4$ Doped with either $TiCl_3$ or Ti_{13}·6THF by Ball Milling
15:20	O-148	O. Gutfleisch	Effect of Mechanochemical Treatment and Catalyst Addition on the Decomposition of $LiAlH_4$
15:40	O-149	S. Sartori	Synthesis, Structure and Stability of Mixed Alanates
16:00			Break
	Chair:	H. W. Brinks	Th-O-4a Complex MH_x (Kahului+Kihei+Wailea)
16:30	O-150	U. R. Kattner	A Thermodynamic Database for Metal-Hydrogen Systems
16:50	O-151	K. J. Gross	Results of an Investigation on Some Novel Complex Hydrogen Storage Materials
17:10	O-152	K. Komiya	Synthesis and Dehydrogenation of $M(AlH_4)_2$(M=Mg, Ca)
17:30	O-153	G. Streukens	Hydrogen Isotope Scrambling and Thermodynamic Studies on Doped Sodium Alanate
	Chair:	P. Vajda	Th-O-4b MH Magnetism & Other Properties (Wailuku)
16:30	O-154	V. Paul-Boncour	Isotope Effect on the Metamagnetic Transitions in $Y_{1-x}R_xFe_2(H,D)_{4.3}$ Compounds (R=Tb, Er, Lu)
16:50	O-155	L. Havela	5*f* Magnetism Studied in Complex Intermetallic U-based Hydrides
17:10	O-156	G. Srinivas	Hydriding Kinetics of $Ho_{1-x}Mm_xCo_2$-H System
17:30	O-157	P.-R. Cha	Hydrogen Effect on the Structural Stability of an Amorphous Metal
17:50			After-Session Break
19:00			Luau Dinner (until 22:30)

FRIDAY, OCTOBER 6			
	Chair:	S. M. Filipek	Fr-O-1a MH Properties (Kahului+Kihei+Wailea)
8:30	O-158	F. Cuevas	Relationship Between Microstructure and Hydrogenation Properties of $Ti_{0.85}Zr_{0.15}Mn_{1.5}V_{0.5}$ Alloy
8:50	O-159	S. Mitrokhin	Synthesis and Properties of Hydrides Under High Hydrogen Pressure
9:10	O-160	M. Okada	High-pressure Synthesis of Novel Hydride in Mg-TM Systems (TM = Ti, V, Zr, Nb, Hf, Ta)
9:30	O-161	S. Yamanaka	Thermophysical and Thermochemical Properties of Metal Hydrides MH_X (M=Ti, Y, and Zr)
	Chair:	R. Cantelli	Fr-O-1b Surfaces, Clusters, & Membranes (Wailuku)
8:30	O-162	H. Bach	The Effect of Surface State on the Kinetics of Cerium-Hydride Formation
8:50	O-163	Y. Hatano	Effects of Carbide Intermediate Layers on High Temperature Durability of Pd Coating Prepared on Nb and Ta
9:10	O-164	M. Suleiman	Hydrogen Absorption in Palladium Clusters: Does the Structure Matter?
9:30	O-165	J. N. Chotard	A New Example for a Hydrogen Induced Insulating State in the La-Ni-Mg-H System
9:50			Coffee Break
	Chair:	J. J. Reilly	Fr-O-2a MH Applications (Kahului+Kihei+Wailea)
10:15	O-166	K. Hirose (Plenary)	Toyota's Vision of the Development of Hydrogen Storage Materials for Vehicular Applications
11:00	O-167	D. A. Mosher (Invited)	Design, Fabrication and Testing of $NaAlH_4$ Based Hydrogen Storage Systems
11:30	O-168	D. Pearson	The Planck Sorption Cooler: Using Metal Hydrides to Produce 20 K
11:50	O-169	J. I. Abes	Evaluation of Zr_2Fe (SAES St198) and Zr_3Fe for Hydrogen Gettering
12:10	O-170	J. O. Jensen	The Energy Efficiency of On-board Hydrogen Storage
	Chair:	H. Figiel	Fr-O-2b MH_x Phases (Wailuku)
10:15	O-171	Y. Manassen (Invited)	Hydrogen Concentration Fluctuations in the α and β Phases of the Gd(0001)/W(110) – H system: STM Observations
10:45	O-172	I. Goncharenko (Invited)	Crystal Structure and Magnetic Properties of Hydrides Under Very High Pressures
11:15	O-173	T. Kume	Raman and Visible Absorption Study of YH_3 at High Pressure
11:35	O-174	Wei Luo	Pressure-Induced Structural Phase Transition in Metal Dihydrides
11:55	O-175	I. Saita	Hydriding Combustion Synthesis of TiFe

MH2006 Symposium Abstracts

ORAL PRESENTATIONS (O-001 to O-031) **Monday, October 2 (see schedule)**

O-001 **A Retrospective View of Metal Hydride Research at Brookhaven National Laboratory 1966-2006.** J. J. Reilly, – Department of Energy Science & Technology, Brookhaven National Laboratory, Upton, NY, USA

While this lecture will be primarily concerned with the effort at BNL, it will be presented within an overall historical context of the development of metal hydrides as energy storage media. Initial work on the use of readily reversible intermetallic hydrides for use in stationary fuel cell applications will be described. The early work in the development of alloy hydrides for automotive applications will also be discussed. The successful development of the AB_5 class of alloys for use as battery electrodes will be ecounted. The exploitation of hydrogen driven metallurgical reactions to synthesize nano-composite materials will also be a subject of interest. Finally recent work involving the use high capacity, complex, metal hydrides and alane for automotive hydrogen fuel storage applications will be summarized.

O-002 **Complex Metal Hydrides – Potential Hydrogen Storage Materials for Fuel Cell Applications.** M. Felderhoff, B. Bogdanovic, F. Schüth, – Max-Planck Institut für Kohlenforschung, Mülheim an der Ruhr, Germany

$NaAlH_4$ is presently one of the most advanced hydrogen storage material for the temperature range around 100 - 150°C with respect to storage capacity (approaching 5 wt.% over the two stages of dehydrogenation) and kinetics of rehydrogenation (below 10 min). These requirements for fuel cell applications are only reached if the $NaAlH_4$ is doped with different catalysts. Titanium compounds are the preferred ones. Besides Ti, some other metals (Sc, Ce) can be used as highly efficient dopants, which come close to or even exceed the efficiency of most titanium compounds as catalysts [1]. Nowadays the preferred process of doping is ball-milling of the alanate with the different catalyst compounds. A doped $NaAlH_4$ hydrogen storage material with excellent kinetics can be produced through ball-milling of NaH, Al and a catalyst (direct synthesis of doped $NaAlH_4$) under hydrogen pressure [2]. Depart from $NaAlH_4$ other light metal aluminium hydrides with high hydrogen content are described. These materials show similar thermal behaviour with a two-step decomposition pathway and structural similarity. However, most of these materials are not well described and thermodynamic data are very limited [3]. [1] B. Bogdanovic, M. Felderhoff, A. Pommerin, F. Schüth, N. Spielkamp, Adv. Mater. (2006) in press; [2] J. M. Bellosta von Colbe, M. Felderhoff, B. Bogdanovic, F. Schüth, C. Weidenthaler, Chem. Comm. (2005) 4732; [3] A. Mamatha, B. Bogdanovic, M. Felderhoff, A. Pommerin, W.Schmidt, F. Schüth, C. Weidenthaler, J. Alloys Comp. 407 (2006) 78.

O-003 **The Electrochemistry and Modelling of Hydrogen Storage Materials.** P. H. L. Notten,[1,2] P. Vermeulen,[2] P. Kalisvaart,[2] A. Ledovskikh,[2] D. Danilov,[2] – [1]Philips Research Laboratories, Eindhoven, The Netherlands; [2]Eindhoven University of Technology, Eindhoven, The Netherlands

It has been identified that hydrogen storage is one of the key drivers, enabling the future hydrogen economy. High-energy density materials will play a dominant role in future gas phase and electrochemically driven devices, such as Fuel Cells and rechargeable NiMH batteries. Significantly higher gravimetric storage capacities are, however, required to accomplish the necessary breakthroughs. It has recently been shown that more than 6.5 wt.% of hydrogen can electrochemically be absorbed and desorbed at high rates at room temperature in fluorite-based Mg-compounds [1-3]. It has been argued that, in contrast to the well-known rutile-structured Mg-alloys, these materials have a much more open crystal structure facilitating fast hydrogen transport. In this presentation the electrochemical aspects of these new materials will be reviewed. Apart from the storage capacity, one of the most important characteristics is the absorption/desorption behaviour. Both a thermodynamic and kinetic approach will be presented, allowing an accurate description of the hydrogen formation/decomposition processes in hydride-forming materials [4]. [1] P.H.L. Notten, *et al.*, *J. Power Sources*, **129** (2003) 45; [2] R.A.H. Niessen and P.H.L. Notten, *Electrochem. Solid-State Lett.*, **8** (2005) A534-A538; [3] P. Vermeulen, R.A.H. Niessen and P.H.L. Notten, *Electrochem. Comm.*, **8** (2005) 27-32; [4] A. Ledovskikh, D. Danilov, W.J.J. Rey and P.H.L. Notten, *Phys. Rev.*, **B73** (2006) 014106.

O-004 **Mobile Hydrogen Storage: A Discussion Between Science and Engineering.** S. W. Jorgensen, – General Motors R&D, Warren, MI, USA

The current, impressive, progress in hydrogen storage science is now accompanied by complementary advances in the engineering needed to package storage materials on vehicles. While the more recent goals for hydrogen storage have been based on engineered systems, a more detailed dialog is now possible. In the future this discussion between science and engineering will drive ever better understanding of what is needed to bring the important mobile portion of the hydrogen economy to reality, both in terms of scientific and engineering research. A cooperative, coordinated approach is essential to early success.

O-005 **Hydrogen in Semiconductors and Insulators.** C. G. Van de Walle, – Materials Department, University of California, Santa Barbara, CA, USA

Hydrogen exhibits a fascinating array of behaviors in semiconductors and insulators. Until a few years ago, hydrogen was thought to always act as an amphoteric impurity in semiconductors, meaning that it would always counteract the prevailing conductivity.

First-principles studies of hydrogen in ZnO [1] showed that hydrogen can also act as a *source* of conductivity. Since then we have explored a large number of materials and focused on developing a general understanding of hydrogen's behavior in a wide range of materials. Such studies are essential to support a variety of technological developments. To name one example, hydrogen is an indispensable ingredient in integrated-circuit fabrication, since it is used to passivate defects at the Si/SiO_2 interface present in every CMOS transistor. Hydrogen will likely play an equally important role in the novel dielectrics that are currently actively being pursued. Our systematic study has revealed the existence of a universal alignment for the electronic level of hydrogen in semiconductors, insulators, and even aqueous solutions [2]. The alignment allows predicting the electrical activity of hydrogen in any host material. I will review our present understanding of the behavior of hydrogen in semiconductors and insulators, and point out that the physics of hydrogen turns out to be unexpectedly connected to other important problems in materials physics and electrochemistry. I will illustrate the approach with examples for a number of technologically important materials, including InN and ZnO, and discuss connections to hydrogen in metals. I gratefully acknowledge collaborations with J. Neugebauer and S. Limpijumnong. This work was supported in part by AFOSR and the Palo Alto Research Center. [1] C. G. Van de Walle, Phys. Rev. Lett. 85, 1012 (2000); [2] C. G. Van de Walle and J. Neugebauer, Nature 423, 626 (2003).

O-006 **Density Functional Theory Calculations as a Tool for Probing Hydrogen Diffusion and Storage in Metal Hydrides.**
D. S. Sholl, – Carnegie Mellon University, Pittsburgh, PA, USA

Density Functional Theory (DFT) calculations have become an extremely useful tool to complement other approaches to describing hydrogen transport and storage in metal hydrides. I will discuss the accuracy, capabilities, and limitations of DFT calculations for metal hydrogen systems using examples involving H diffusion in elemental metals (e.g., Pd, Sc), ordered intermetallics (e.g., Laves phase AB_2 materials), and disordered alloys (e.g., binary and ternary alloys involving Pd and Cu). I will also discuss H storage in materials of interest for destabilized metal hydrides. The theoretical tools needed to connect DFT calculations with quantities of macroscopic interest such as hydrogen permeation rates through metal membranes will be emphasized.

O-007 **Global Optimization of Complex Anionic Hydride Crystal Structures.** E. H. Majzoub,[1] V. Ozolins,[2] – [1]Sandia National Laboratories, Livermore, CA, USA; [2]University of California at Los Angeles, Los Angeles, CA, USA

The search for new metal hydrides has been the primary focus of hydrogen storage research for several years. Light metals, both alkali and simple, must dominate this search in order for the hydride to possess the maximum weight fraction of hydrogen in a minimum of volume. To date, the complex ionic hydrides, such as $NaAlH_4$, have received much attention. The complex ionic hydrides, consist of hydrogen containing anions, such as XH_n with X=N,Al,B, and n=1,2,4,6, and are charge balanced by alkali metal matrices. It is well known that cohesive energy in these structures is dominated by electrostatic attraction between cations and the anionic units. The rate of finding new hydrides, with heat of formation in the 30-40 kJ/mol range, can be substantially increased if certain combinations of chemistry of the cations and anion complexes can be ruled in or out. A global optimization of crystal structure using soft sphere and electrostatic potentials between rigid anionic units and cations has been performed using Monte Carlo simulated annealing with minimization (MCM). As an aid to MCM, a rapid basin hopping scheme is used to quickly search different catchment basins for low energy states. Resulting low energy structures were relaxed via full ab-initio techniques. Structure types generated from this method, using a variety of cations and anion complexes will be discussed with their relationship to known crystal structures in this class of compounds.

O-008 **Ab Initio Study of the Hydrogenation Properties of Mg-based Binary and Ternary Compounds (Mg_2X, X=Ni,Si and $MgYNi_4$).** M. Gupta, J. Prigent, – Université Paris-Sud, Orsay, France

Extensive research effort has been devoted to the hydriding properties of Mg-based alloys. One of the crucial goal being to maintain a high massic hydrogen storage capacity while forming hydrides less stable than MgH_2. In this paper we present the results of ab initio electronic structure investigations of several Mg-based compounds using the FPLAPW method. From our total energy calculations and from the analysis of the electronic factors that control the stability of the intermetallic compounds and their hydrides, we show why Mg_2NiH_4 is stable while Mg_2Si does not absorb hydrogen. Our results are in agreement with recent experimental data on the hydrogenation of Mg_2X phases (X=Ni,Si,Ge,Sn) [1] as well as with studies of the role of Si in the destabilization of MgH_2 through the formation of Mg_2Si [2]. We have also analyzed the electronic properties of one of the Laves phase ternary compound $MgYNi_4$ recently synthesized. The lattice parameter calculated agrees with the results of Aono et al. [3], while the value quoted by Kadir et al. appears to be too large [4]. In agreement with experimental observations, we explain why $MgYNi_4H_4$ is stable. [1] R. Janot et al., Intermetallics **14** (2006) 163; [2] J.J. Vajo et al. J. Phys. Chem. B **108** (2004) 13977; [3] K. Aono et al. J. Alloys Comp. **309** (2000) L1-L4; [4] K. Kadir et al. J. Alloys Comp. **345** (2002) 141.

O-009 **A New Series of High Hydrogen Content Hydrogen-Storage Materials – a Theoretical Prediction.** P. Vajeeston,[1] P. Ravindran,[2] A. Kjekshus,[2] H. Fjellvåg,[2] – [1]Center for Materials Sciences and Nanotechnology, Department of Chemistry, University of Oslo, Oslo, Norway; [2]Department of Chemistry, University of Oslo, Oslo, Norway

Hydrogen is a clean energy carrier for the future, utilizing in principle only water as raw material for its preparation. Our research efforts on theoretical modeling have focused on metal and complex hydride materials for storage purposes. In many metal hydrides, H can be removed easily below 100°C, but such hydrides have a relatively low weight percentage of stored H (1.5 to 2.5 wt.%). On the other hand, complex hydrides can store more H (up to 18.2 wt.%), however, the problems are high operating temperatures and slow absorption/desorption kinetics. The light elements of Groups I-III of the Periodic Table, e.g., Li, Be, Na, Mg, B, and Al, form a large variety of complex hydrides which are interesting from a hydrogen storage point of view because of their light weight (the number of hydrogen atoms per matrix element being in many cases around 2). Alkali- and alkaline-earth-based complex hydrides

are expected to have a potential as viable modes for storing hydrogen at moderate temperatures and pressures. In this study we are going to present results from a structural study of the phases $MM'H_3$ (M = Li, Na, K, Rb, Cs; M' = Be, Mg, Ca, Sr, Ba). One of the motivations for this study has been to investigate the atomic arrangements, electronic structures, and bonding nature within the $MM'H_3$ series in detail in order to check the stability of these materials for hydrogen storage applications. In addition, the possible reaction pathways are also suggested for experimentalists to synthesize the predicted phases.

O-010 **Comparison of Hydrogen Adsorption in Nanoporous Materials.** R. Chahine, E. Poirier, G. Dorval-Douville, L. Lafi, P.A. Chandonia, – Hydrogen Research Institute, Université du Québec à Trois-Rivières, Trois-Rivières, Canada

We studied the hydrogen adsorption of three different types of nanoporous materials: pristine and chemically treated single wall nanotubes (SWNT); Al, Cr and Zn-based metal-organic frameworks (MOF); and high surface area activated carbon (AC). Measurements were carried out as a function of temperature in the range 77 K-300 K, and pressures up to 50 bars. The excess adsorption of the different samples ranged from 1.5 to 5 wt% at 77 K and was less than 0.5 wt% at room temperature. The total hydrogen storage capacity is larger due to the addition of the bulk phase. The Dubinin-Asthakov (DA) and Langmuir equations were used to model the adsorption isotherms and retrieve energetic and structural parameters. The experimental data was found to be consistent with the predictions of the analytical models. The isosteric heat of adsorption of the different materials calculated for zero coverage varied from about 3 kJ/mol to 6 kJ/mol for SWNTS.

O-011 **Integrated Hydrogen Storage and Delivery Using Organic Liquid-Phase Carriers.** A. C. Cooper, K. M. Campbell, G. P. Pez, – Air Products and Chemicals, Inc., Allentown, PA, USA

A cost effective hydrogen storage system is a key enabling requirement for the widespread introduction of hydrogen fuel cell and hydrogen internal combustion engine powered vehicles to the global marketplace. Our approach utilizes an ambient temperature organic liquid-phase hydrogen carrier. The liquid carrier is hydrogenated at the hydrogen production location and the resulting hydrogenated liquid is used as a two-way transportable carrier. The hydrogen is liberated at the point of use with novel, highly selective, catalytic dehydrogenation chemistry. The process is fully reversible and is conducted at much lower temperatures than have previously been possible. We have demonstrated a liquid carrier prototype, perhydro-N-ethylcarbazole, that can be dehydrogenated at 1 atmosphere hydrogen pressure and temperatures below 200 ^{o}C to yield >5.5 wt. % hydrogen. Higher capacity liquid carriers are currently in development. This integrated hydrogen storage and delivery approach offers potential advantages over other hydrogen storage technologies in development. Principally these advantages are: Minimization of new infrastructure: There are no intermediate transformation steps from delivery to storage to onboard utilization, thus eliminating the need for compression or other processing equipment. In addition, equipment used for storage and transportation of existing petroleum-based liquid fuels may be utilized for the liquid carrier. Energy-efficient storage approach: The exothermic regeneration of organic liquid carriers offboard the vehicle provides a unique opportunity to capture energy from this process. Consumer acceptance: The fueling experience for the consumer will be very similar to today's liquid fuels.

O-012 **Hydriding Kinetics Of Organic Hydrogen Getters.** G. L. Powell, – Y-12 National Security Complex, Oak Ridge, TN, USA

Organic hydrogen getters produced by Kansas City Federal Manufacturing and Technologies have proven to be a very effective means of preventing hydrogen gas accumulation in sealed containers. These getters are relatively unaffected by air and environmental gases. They can be packaged in a variety of ways to fit particular needs such as porous pellets, fine or coarse [gravel] powder, or powder loaded into molded silicone rubber. The hydrogen gettering reactions are extremely irreversible since the hydrogen gas is converted into an organic hydrocarbon. These getters are based on the palladium-catalyzed hydrogenation of triple bonds to double and then single bonds in aromatic aryl compounds using DEB (1,4 bis (phenyl ethynyl) benzene) or DPB (diphenyl butadiyne) typically mixed with 25% by weight carbon with palladium (1% by weight of carbon). The reaction mechanisms are complex involving solid state reaction with a herteogeneous catalyst leading to the many intermediates, including mixed alkyl and aryl hydrocarbons with the possibilities of many isomers. The reaction kinetics mechanisms are also strongly influenced by the form in which they are packaged and the parent organic compound. For example, the hydriding rates for pellets, powder, and gravel have a strong dependence on reaction extent (i.e., DEB or DPB reduction extent) and a kinetic order in H_2 pressure of less than unity. Silicone rubber based DEB getters hydride at a much lower (but linear) rate, have little dependence on reaction extent, have a higher kinetic order in pressure than pellets or powder, and have a lower activation energy. The kinetics of these reactions have been measured as a function of H_2 pressure, hydrogenation extent, and temperature near ambient temperature (0° to 75°C) for H_2 pressures in the 100 Pa to 0.1 Pa range. These results are presented as multi-dimensional rate models for DEB and DPB getters. The wide variations in reaction kinetics for the various getter forms are discussed in terms of the mobility of hydrogen and the mobility of the organic host. *Managed by BWXT Y-12, L.L.C for the U. S. DEPARTMENT OF ENERGY under contract DE-AC05-00OR22800

O-013 **Hydrogen Physisorption in Crystalline Microporous Materials.** A. Dailly,[1,2] S. Jorgensen,[2] – [1]Purdue University, College of Engineering, West Lafayette, IN, USA; [2]Chemical & Environmental Sciences Laboratory, General Motors Research and Development Center, Warren, MI, USA

Various crystalline microporous materials (metal organic frameworks and other high surface area compounds) have been investigated as hydrogen adsorbents in order to better assess the interaction of hydrogen with these structures. Volumetric measurements were carried out in the pressure range 1-60 bar at 77 K. All studied materials show fast kinetics and high reversibility for hydrogen adsorption, which is typical for physisorption. Experimental results give evidence that the excess hydrogen storage

capacity at saturation is not always correlated to the accessible specific surface area of the adsorbent as that is generally expected. Consideration of physical properties in addition to surface area: porosity, pore size and metal-ligand composition allows a better explanation, and a route to reach materials with high gravimetric hydrogen storage capacity.

O-014 **Pd Functionalized Multiwalled Carbon Nanotube Based Hydrogen Sensor.** M. Krishna Kumar, S. Ramaprabhu, – Alternative Energy Technology Laboratory, Department of Physics, Indian Institute of Technology Madras, Chennai, India

Gas sensor applications of carbon nanotubes (CNTs) are attractive due to large available surface area for gas adsorption in these nanostructured materials. In the present study, MWNTs have been synthesized by catalytic chemical vapor deposition (CCVD) technique. Pyrolysis of acetylene using a fixed-bed catalytic reactor over Rare earth (RE) based AB_2 alloy hydride catalyst, obtained through hydrogen decrepitation technique, has been performed to synthesize MWNTs. MWNTs have been functionalized by Pd resulting in nanostructured dispersion of Pd on CNTs. Structural, morphological and vibrational characterizations have been carried out using XRD, SEM, TEM and Raman spectroscopy. In-situ electrical resistance measurements for thin films of MWNTs obtained by spin coating samples were carried out by two probe technique in a chamber with provision to introduce known concentration of hydrogen in constant air flow. Systematic investigations of hydrogen sensing properties of Pd-MWNT ensembles with respect to their Pd loading and chemical treatment have been carried out. The experimental study reveals that the Pd-MWNTs thin films are stable after several cycles of adsorption and desorption. The change in electrical resistance due to hydrogen adsorption is reversible, with increase to saturation on exposure to hydrogen gas. The results demonstrate that chemically treated MWNTs functionalized with nanostructured Pd show the better sensing response when exposed to H_2 at room temperature.

O-015 **Observations of New Features of Hydrogen in Pd: A Phase Transition Originates from O-Site Vacancies and Possible Quantum Phenomena.** M. Kubota,[1] A. Imai,[2] S. Watanabe,[2] H. Araki,[3] A. Penzyev,[1] R. M. Mueller,[4] Y. Sakamaki,[3] S. Harada,[5] – [1]Institute for Solid State Physics, The University of Tokyo, Kashiwa, Chiba, Japan; [2]Graduate School of Science and Technology, Niigata University, Niigata, Japan; [3]Nagaoka National College of Technology, Nagaoka, Niigata, Japan; [4]Institute für Festkörperforschung, Forschungszentrum Jülich, Germany; [5]Faculty of Engineering, Niigata University, Niigata, Japan

At high concentrations hydrogen in metals sometimes behaves like a "supercritical fluid" at high temperatures while making a transition to a "solid phase" at low temperature. The PdH(D) system has the lowest temperature phase boundary between the "fluid" and "solid" states of all known MH systems. We have been seeking quantum phenomena originating in the overlap of the hydrogen wave functions contained within the metal lattice of the Pd. We discuss new features of H(D) in Pd originating from the freedom of the O-site vacancies and possible quantum many-body phenomena. Recent results from our torsional oscillator experiments and measurements of electrical resistivity and specific heat will be presented.

O-016 **Pressure Induced Phase Transformation of REH_3.** M. Tkacz, T. Palasyuk, – Institute of Physical Chemistry of Polish Academy of Sciences, Warsaw, Poland

The Rare Earth trihydrides have become increasingly interesting as model systems for many theoretical calculations [1,2] since the discovery of "switchable mirror" phenomenon [3]. Although many papers on electronic structure of the RE trihydrides appeared last decade there was very few information on high-pressure behavior of those hydrides, which could verify theoretical studies. Recently we have started with the high-pressure studies of the selected hexagonal REH_3 [4,5] and YH_3 [6]. Using the diamond anvil cell technique with the ruby pressure marker we performed energy dispersive X-ray diffraction measurements in the pressure range up to 30 GPa. For all the trihydrides the reversible hcp-fcc structural phase transition was observed for the first time. The equations of state for both hcp and fcc phases of all hydrides were determined. Lattice parameters of new cubic phases were derived. The distances of the adjacent hydrogen species have been analyzed as function of pressure suggesting possible key role of H-H interaction in the observed transformations. [1] P.J. Kelly, J.P. Dekker, R. Stumpf, Phys. Rev. Lett. 78 1997 1315; [2] R. Ahuja, B. Johansson, J.M. Wills, O. Eriksson, Appl.Phys.Lett. 71 (1997) 3497; [3] J.N. Huiberts, R.Griessen, H.H. Rector, R.J. Vijngaarden, J.P. Decker, D.G. de Groot, N.J. Koeman, Nature, 1996, 380, 231; [4] T. Palasyuk, M. Tkacz, Solid State Comm. 130 (2004) 219–221; [5] Ibid, 133 (2005) 481–486; [6] Ibid, 133 (2005) 477–480.

O-017 **Crystal Structure and H Sorption Properties of $GdMgNi_{4-x}Al_x$ (Pseudo Laves Phase). Experimental and Theoretical Approach.** J. L. Bobet, B. Chevalier, J. G. Roquefere, S. Matar, – Institut de Chimie de la Matière Condensée de Bordeaux (ICMCB), CNRS, Université Bordeaux, Pessac, France

During the past few decades, a large number of binary compounds have been studied for their hydrogen sorption properties. For example, $LaNi_5$ and ZrV_2 can store about 1.5wt.% H at room temperature and moderate pressure. On another hand, Mg can store 7.6wt.% H but at the cost of high temperature (i.e. 300°C). Then, the development of ternary alloys based on magnesium appears as an ideal alternative route. We focus here on $GdNi_4Mg$ compound crystallizing in the F -43m space group (cubic $MgCu_4Sn$ structure type, known as C15b) with a lattice parameters of 0.704 nm (close to that already reported) After H absorption, no structural change is observed and only a slight volume expansion can be noticed (e.g. 5%). The unexpected behaviour of $GdNi_4Mg$ (compared with (La or Nd)Ni_4Mg) is explained in term of crystallographic structure. For $GdNi_4Mg$, a Rietveld refinement shown that the (4a) sites weren't the only guest sites for Gd, this former being seen in both (4a) and (4c) sites. Such a mixture between Gd and Mg on 4a and 4c sites is noted as the Gd/Mg exchange ratio δ. The synthesis of substituted compounds $GdMgNi_{4-x}Al_x$ was also possible up to x = 1.2. As expected, the cell parameter increases almost linearly with the Al content. Moreover, the Gd/Mg exchange ratio δ decreases with increasing Al amount. Without aluminium, the exchange ratio is about 13% but when x = 1.2, δ is close to 0%. Furthermore it seems that $\delta = f(x)$ follows a linear law. The hydrogen sorption properties (equilibrium pressure, thermodynamic properties according to the Van't Hoff law as well as the volume expend) will be discussed and compared to those of the parent

compound $GdNi_{5-x}Al_x$ ($CaCu_5$ structure type). Moreover, both crystal structure and H sorption properties will be compared as a function of the synthesis method (solid state reaction or mechanical alloying). Finally, some calculations of DOS and chemical bonding properties using DFT-based computational methods such as ASW and FLAPW will be presented and used to get a better understanding of the relationship between structure and H sorption properties.

O-018 **Pressure-induced Phase Transition in YH_3.** J. S. de Almeida, R. Ahuja, – Condensed Matter Theory Group, Department of Physics, Uppsala University, Uppsala, Sweden

Yttrium hydrides systems are very interesting because they exhibit a reversible metal-insulator transition upon hydrogenation. At ambient conditions, YH_3 crystallizes in hexagonal structure. Ahuja *et al.*[1] predicted that YH_3 undergoes a structural phase transformation induced by pressure and that this transformation is accompanied by a metal-insulator transition. Performing high pressure experiments Winjgaarden *et al*[2] have obtained neither cubic phase nor metal-insulator transition. Palasyuk and Tkacz have found a coexistence of hexagonal and cubic phases in the pressure range 8~25 GPa[3]. Recently, the synthesization of the new phase of YH_3 at pressure above 21 GPa was reported by Machida *et al*[4]. We report a first principles calculations where the geometry optimization was taken into account. We found that the relaxation effects are important to the transition pressure and it is raised in one order of magnitude compared to early result[1]. We also find that the metal-insulator transition is driven by the structural phase transformation. [1] R. Ahuja, et al Appl. Phys. Lett. 71, (1997) 3498; [2] R. J. Winjgaarden et al., J. Alloys Compd. 308, (2000) 44; [3] T. Palasyuk and M. Tkacz, Solid State Commun. 130, (2004) 219; [4] A. Machida, et. al. Abstract presented at the workshop on crystallography at high pressure, Saskatchewn, Canada, 10-21, Aug. 2004.

O-019 **Degradation Behavior of $LaNi_{4.78}Sn_{0.22}H_x$ during Cycling to Elevated Temperature.** M. Prina,[1] P. B. Karlmann,[1] R. C. Bowman, Jr.,[1] J. W. Reiter,[2] – [1]Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA; [2]Swales Aerospace, Pasadena, CA, USA

Partial substitution of tin for nickel in the $LaNi_5$ alloy greatly enhances the stability and durability of the hydride phase during both gas phase and electrochemical cycling. A sample of the alloy $LaNi_{4.78}Sn_{0.22}$ hydride was cycled between room temperature and ~460 K for repeated hydrogen gas absorption and desorption while other samples were held at a hydrogen content of $x > 5.0$ and temperatures above 460 K to accelerate the intrinsic degradation processes. Changes in the hydrogen absorption and desorption were evaluated using gas volumetric methods. Although the Sn-substituted alloys are much more resistant to disproportionation than most other $LaNi_5$ alloys, the present test conditions did produce degradation. Effects observed included reduction in hydrogen storage capacity, decreases in the plateau pressures, increased slopes of the plateaus, and smaller hysteresis ratios. Extensive results from laboratory testing on engineering prototype as well as the flight versions of the Planck Sorption Cryocooler hydride sorbent beds containing the same alloys also showed similar degradation effects. Finally, a regeneration process that nearly completely restores the behavior of the degraded $LaNi_{4.78}Sn_{0.22}$ hydride to its initial values will be described.

O-020 **Destabilization Strategies and Kinetics Challenges in Light Metal Hydride Systems.** J. J. Vajo, T. T. Salguero, A. F. Gross, S. L. Skeith, G. L. Olson, – HRL Laboratories LLC, Malibu, CA, USA

Many light element hydrides have high gravimetric hydrogen densities but low equilibrium hydrogen pressures. Low equilibrium pressures originate from the strong ionic to polar covalent bonding typical of light s and p block elements. Without directly altering the bonding of an individual hydride, the equilibrium pressure of a mixture can be increased using mixture components that form new phases during dehydrogenation. This lowers the dehydrogenated state enthalpy, which increases the equilibrium pressure and effectively destabilizes the component hydrides. Using this strategy, we developed several destabilized systems with hydrogen capacities of 5 to 10 wt % and equilibrium pressures of 1 bar at temperatures from 25 to 225 °C. For example, dehydrogenation of $2LiBH_4 + MgH_2$ yields LiH and MgB_2 which increases the equilibrium pressure by >10x compared to pure $LiBH_4$. The strong and directional bonding in light element hydrides also means that solid-state diffusion and phase nucleation and growth have high activation barriers. Thus, the kinetics of hydrogen exchange in destabilized systems are slow. For example, temperatures of >300 °C are required for hydrogen exchange in $2LiBH_4 + MgH_2$ to occur in ~1 hr. In this talk we will describe our destabilization strategy and give several examples of destabilized systems. We will also illustrate the kinetics challenges and our approaches involving catalysis, nano-engineering, and porous scaffolds to accelerate hydrogen exchange.

O-021 **Neutron Scattering Study of the Structure, Phase Variation, and Properties of Si-Destabilized Calcium Hydrides.** H. Wu,[1,2] W. Zhou,[1,3] T. J. Udovic,[1] J. J. Rush,[1,2] T. Yildirim,[1] – [1]NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD, USA; [2]Department of Materials Science and Engineering, University of Maryland, College Park, MD, USA; [3]Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA, USA

Light alkaline-earth metal hydrides are an important family of hydrogen-storage materials because of their relatively high storage capacities (>5 wt.% H), although they are generally too stable with overly sluggish sorption kinetics for practical applications. Alloying with Group IV elements such as Si has been shown to destabilize these hydrides and accelerate the hydrogen-cycling kinetics. We will present a systematic study of the hydrogen absorption/desorption properties of various Ca-Si alloys synthesized via ball milling of CaH_2 + Si mixtures followed by evacuative hydrogen desorption. Neutron powder diffraction, neutron vibrational spectroscopy, and neutron prompt-gamma activation analysis were used to determine the crystal structure, bonding, and hydrogen concentration associated with the various novel ternary metal hydride phases formed. The ability of neutrons to pinpoint the location of hydrogen within the alloy lattices and to characterize the resulting hydrogen bonding potentials allows us to directly test the validity of related first-principles calculations, especially the claim [1] that some of the H atoms covalently bond to Si in these structures. [1] N. Ohba, M. Aoki, T. Noritake, K. Miwa, S. Towata, Phys. Rev. B 72 (2005) 075104.

O-022 **First Principles Study of the Destabilization of the Li Amide-Imide Reaction for Hydrogen Storage.** M. Gupta,[1] R. Gupta,[2] – [1]Université Paris-Sud, Orsay, France; [2]SRMP, Commissariat à l'Energie Atomique, Saclay, France

At present, there is strong interest in light weight complex hydrides since the discovery that hydrogen can be reversibly stored in sodium alanate. Recently, Li_3N has been proposed as a good candidate also for hydrogen storage with a high weight percent capacity. The chemical reactions involved are the following: $Li_3N + H_2 \rightarrow Li_2NH + LiH$ (1), and $Li_2NH + H_2 \rightarrow LiNH_2 + LiH$ (2). If both reactions were fully reversible, the weight percent capacity would be 10.2%. However, the first reaction is very exothermic (heat of reaction greater than 150 kJ), and thus requires very high temperatures for H_2 release. This reaction is therefore not useful for hydrogen storage. With the second reaction, the hydrogen storage capacity drops to 6.4% but still remains acceptable. The reaction enthalpy of this reaction is ~70 – 80 kJ which is still too high for useful hydrogen storage. We will present results of ab initio electronic structure calculations for these compounds, and show how the reaction enthalpy of the second reaction can be lowered so that hydrogen can be reversibly stored at lower temperature conditions.

O-023 **Mechanism of Hydrogen Release for the $LiBH_4/MgH_2$ System.** G. S. Walker, X. Yu, D. M. Grant, – University of Nottingham, Nottingham, UK

The dehydrogenation, under an inert atmosphere, and rehydrogenation of $LiBH_4/MgH_2$ mixtures in various ratios, produced by ball milling, were investigated by thermogravimetry coupled with mass spectrometry (TGA-MS), *in situ* x-ray diffraction (XRD) and differential scanning calorimetry. It was found that $LiBH_4/MgH_2$ mixtures rich in MgH_2 exhibited the best dehydrogenation behavior. TGA-MS (under an inert carrier gas) revealed that the hydrogen release process for all the $LiBH_4/MgH_2$ mixtures involved two steps. *In situ* XRD of the MgH_2-rich mixtures showed that the first step involved the decomposition of MgH_2 forming Mg at around 350˚C and in the second stage Mg reacted with $LiBH_4$ to form $Li_{0.184}Mg_{0.816}$ alloy at around 380~450˚C. No boron containing phases were identified until the mixture was heated to 600˚C, by which temperature boron from decomposed $LiBH_4$ had reacted with Mg from the $Li_{0.184}Mg_{0.816}$ to form MgB_2 and $Li_{0.3}Mg_{0.7}$. Interestingly the dehydrogenation of these MgH_2-rich mixtures was fully reversible and did not depend on whether a MgB_2 phase had been formed, in contrast to work reported on the $LiBH_4$-rich mixtures [1]. It can be concluded that, for the mixtures investigated, the presence of magnesium metal destabilized the $LiBH_4$, lowering the dehydrogenation temperature. The decomposition of the complex hydride led to the formation of Mg-Li alloys and that this reaction was completely reversible. [1] J. J. Vajo, S. L. Skeith, F.Mertens, J. Phys. Chem. B 109 (2005) 3719.

O-024 **Preparation of Ni-Al Alloy Catalyst at Reduced Temperature for Fuel Cell Application.** H. C. Hahm, A. P. Maganyuk, J. Han, S. P. Yoon, S. W. Nam, T.-H. Lim, – Korea Institute of Science and Technology, Seoul, Korea

Ni-Al alloys are currently used as electrode materials for molten carbonate fuel cells. In addition, the Ni-Al alloys have been applied as reforming catalysts to produce hydrogen from various fuels for fuel cells. In this study Ni-Al alloys have been produced at temperature lower than melting point of Al by using $AlCl_3$ as a mediator. Fine powders of pure Ni and Al were well mixed and heated in an inert gas atmosphere with the addition of $AlCl_3$ vapor. The reaction of Al powder and $AlCl_3$ vapor resulted in deposition of Al layers on the surface of Ni particles. With increasing heat-treatment temperature, Al can diffuse into the Ni particles, forming Ni-Al alloys. A variety of Ni-Al alloys have been produced: for example, pure Ni_3Al powders have been prepared from a powder mixture of 15wt% Al and 85wt% Ni, while mixed powders of Ni_3Al and Ni-Al solid solution were formed from mixed powders of 5wt% Al and 95wt% Ni. The effect of heat-treatment temperature on alloy formation has been thoroughly investigated.

O-025 **Electrochemical Properties of Nanocrystalline and Microcrystalline ZrV_2-Type Electrode Materials.** E. Jankowska,[1] M. Kopczyk,[1] A. Sierczynska,[1] M. Jurczyk,[2] L. Smardz,[3] – [1]Central Laboratory of Batteries and Cells, Poznan, Poland; [2]Poznan University of Technology, Poznan, Poland; [3]Polish Academy of Sciences, Poznan, Poland

In this work, we study experimentally the electrochemical properties of nanocrystalline and microcrystalline ZrV_2-type alloys. The nanocrystalline ZrV_2 and $Zr_{0.5}Ti_{0.5}V_{0.64}Mn_{0.64}Cr_{0.32}Ni_{0.8}$ alloys were synthesized by mechanical alloying followed by annealing. The electrochemical properties of nanocrystalline powders were measured and compared with those of amorphous as well as microcrystalline materials. The behaviour of MA process has been studied by X-ray diffraction. The powder mixtures milled for more than 25 h has transformed to the amorphous phase without other phase formation. The size of amorphous powder grains was of the order of 20 nm. They have a tendency to agglomerate. Formation of ordered alloys was achieved by annealing the amorphous materials in high purity argon atmosphere at 800 ^oC for 0.5 h. The electrode prepared with nanocrystalline $Zr_{0.5}Ti_{0.5}V_{0.64}Mn_{0.64}Cr_{0.32}Ni_{0.8}$ material showed better activation and higher discharge capacities. This improvement is due to a well-established diffusion path for hydrogen atoms along the numerous grain boundaries. The electrochemical results show very little difference between the nanocrystalline and microcrystalline powders, as compared with the substantial difference between these and the amorphous powder. In the annealed nanocrystalline $Zr_{0.5}Ti_{0.5}V_{0.64}Mn_{0.64}Cr_{0.32}Ni_{0.8}$ powders prepared by mechanical alloying and annealing discharging capacities up to 150 mA h g^{-1} (at 160 mA g^{-1} discharge current) have been measured.

O-026 **Performance of Polymer Electrolyte Membrane Fuel Cells with Pt/MWNTs as Oxygen Reduction Catalyst.** S. Ramaprabhu, M. M. Shaijumon, N. Rajalakshmi, A. Leela Mohana Reddy, – Alternative Energy Technology Laboratory, Department of Physics, Indian Institute of Technology Madras, Chennai, India

Fuel cells have emerged as alternatives to combustion engines due to their high environmental friendliness and low toxic emission. However, presently used Pt electrocatalyst is of high cost; hindering the possible commercialization of fuel cell technology. Better dispersion on certain supporting materials with high surface area are essential to fully utilize the electro catalytic activity of Pt

catalyst, there by reducing the catalyst loading leading without compromising on fuel cell performance[1]. MWNTs are attractive materials for catalyst support in Proton Exchange Membrane Fuel Cell (PEMFC) due to their morphology and interesting properties such as nanometer size, high accessible surface area, good electronic conductivity and high stability. Several methods have been developed to decorate CNTs with catalytic metal nanoparticles[2-3]. In the present work, aligned CNTs have been grown over alloy catalyst film coated gas diffusion layer (GDL) using water assisted chemical vapour deposition technique. Aligned CNTs have been characterized by SEM, TEM, Raman spectroscopy, TGA and XRD studies. Pt deposition over aligned nanotubes has been carried out using e-beam technique under different deposition conditions. The performance of the PEMFC with different loading of Pt over aligned nano tubes has been studied at different temperatures and results have been discussed. [1] T. S. Ahmadi, Z. L. Wang, T. C. Green, A. Henglein, and M. A. El-Sayed, *Science*, **272** (1996) 1924; [2] H. C. Choi, M. Shim, S. Bangsaruntip, and H. Dai, *J. Am. Chem. Soc.,* **124** (2002) 9058; [3] G. Che, B. B. Lakshmi, C. R. Martin, and E. R. Fisher *Langmuir,* **15** (1999) 750.

O-027 **Characterization of V-6Ni-5Co Membranes for Hydrogen Separation.** S. N. Paglieri,[1] Y. Wang,[1] T. J. Venhaus,[1] H. Oona,[1] R. E. Buxbaum,[2] K. S. Rothenberger,[3] B. H. Howard,[3] R. P. Killmeyer,[3] – [1]Los Alamos National Laboratory, Los Alamos, NM, USA; [2]REB Research and Consulting, Ferndale, MI, USA; [3]National Energy Technology Laboratory, Pittsburgh, PA, USA

V-6Ni-5Co (at.%) alloy foils were ion-milled, and 100-nm-thick palladium coatings were applied to both sides *in situ* via electron-beam-evaporation physical vapor deposition. The membranes were completely permselective for hydrogen. The hydrogen permeance of a 0.37-mm-thick Pd/V-6Ni-5Co/Pd composite membrane was 1.5E-4 mol m^{-2} s^{-1} $Pa^{-0.5}$ at 673K. This permeance is greater than that expected for pure palladium at the same conditions and for a Pd/V-10Pd/Pd composite membrane. The addition of cobalt to the V-Ni system was expected to lower the diffusivity of vanadium. Indeed, the Pd/V-6Ni-5Co/Pd membrane had excellent stability compared with palladium-coated pure vanadium membranes, with constant hydrogen flux measured for over 500 h at 673 K. Interdiffusion between the palladium surface coating and the V-6Ni-5Co foil was characterized with Rutherford backscattering spectrometry (RBS) and Auger electron spectroscopy (AES) depth profiles. After testing a membrane at 673 K for 500 h, a substantial quantity of vanadium had diffused to the surface (40 at.%), whereas essentially no palladium had diffused into the bulk V-6Ni-5Co foil according to an AES depth profile. However, at 773 K, the hydrogen flux through the composite membrane steadily decreased, reaching half of its initial value in less than 50 h.

O-028 **Amine Boranes for Chemical Hydrogen Storage.** T. Autrey, J. Linehan, W. Shaw, N. J. Hess, A. Stowe, M. Gutowski, D. Camaioni, – Pacific Northwest National Laboratory, Richland, WA, USA

Amine boranes are attractive candidates for the storage of high volumetric and gravimetric densities of hydrogen for fuel cell powered devices. The parent compound, ammonia borane (NH_3BH_3, 19wt% H_2), isoelectronic with ethane, is a solid molecular crystal under standard conditions. Ammonia borane is stable at room temperature but will release up to 2 moles of hydrogen in two discrete steps at temperatures between 100 and 160 C. Our group has been investigating the thermal and catalytic mechanisms of amine borane decomposition leading to hydrogen formation. We believe that the interactions between the hydridic BH and protic NH hydrogen are responsible for the relatively low activation barriers for hydrogen formation. In this presentation we will discuss our experimental and computational research aimed at developing a fundamental understanding of the chemical and physical properties of these hydrogen rich materials.

O-029 **Computational Studies of Materials for Chemical Hydrogen Storage.** M. Gutowski, G. Schenter, J. Li, D. Camaioni, S. Kathmann, R.A. Bachorz, – Pacific Northwest National Laboratory, Richland, WA, USA

Thermodynamics of hydrogen release from chemical hydrides will be discussed. Computational results for molecular and extended hydrogen-rich NBH_x (x=8-2) compounds will be compared with the available experimental data. The effect of solid state environment on thermodynamics of hydrogen release and uptake will be discussed. The thermodynamic stability of ammonia borane (AB), NH_3BH_3, relative to its ionic polymorphs, diammoniate of diborane (DADB ($[NH_3)_2BH_2][BH_4]$)) and its "umpolung" counterpart, DBDA ($[(BH_3)_2NH_2][NH_4]$), has been studied theoretically. Kinetic barriers for hydrogen release have been theoretically determined. A preference of the $NH_3(BH_2NH_2)_nBH_3$ oligomers to form coiled or branched forms has been theoretically analyzed. We used density functional theory for extended systems and highly-correlated electronic structure methods for clusters. Lattice energies of complex solids with unknown crystallographic structures were determined using an approximate method of Jenkins et al. New compounds, based on boron, nitrogen, and carbon, have been designed with thermodynamic properties suitable for on-board rehydrogenation of the spent material.

O-030 **Hydrolysis of $Al_{80}(CaH_2)_{20-x}Bi_x$ Alloys for Hydrogen Generation.** M.-Q. Fan, L.-X. Sun, F. Xu,[1] Y. Zhang,[1] T. Zhang,[2] – [1]Material and Thermochemistry Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, China; [2]Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, China

$Al_{80}(CaH_2)_{20-x}Bi_x$ alloys were prepared by high – energy ball milling. Hydrogen generation by hydrolysis of the alloy in pure water has been investigated. It has been found that hydrolysis reaction of the alloys become faster with increase of CaH_2 content. For the studied above system using CaH_2 as the sources of alkaline catalyst, it seems that the whole reactions can be mainly divided into two steps: one is a quickly initial step, i.e., $CaH_2 + 2H_2O \rightarrow Ca(OH)_2+2H_2$ (1); the other is a slower step, i.e., $Ca(OH)_2 + 2Al \rightarrow Ca(AlO)_2+H_2$ (2). Although the kinetics of reaction (2) is slow, the alloys show high yields of hydrogen. It appears that the addition of metal Bi can activate aluminum accentuating greatly Al corrosion resulting from the creation of numerous defects and fresh surfaces through milling process. A significant increase of the hydrogen evolution rate was observed when CaH_2 was fractionally substituted by Bi. With the augmentation of Bi content from 0 to 20%, the hydrogen evolution rate reaches to the maximum (48 $ml.min^{-1}.g^{-1}$) when Bi content is 5%. The produced hydrogen is 970 $ml.g^{-1}$ and the corresponding conversion yield of reactant is

88.1%. The power X-ray diffraction and EDX analyses demonstrated that $Al_{80}(CaH_2)_{20-x}Bi_x$ alloys are multiphase based solid solution mixtures containing dispersed grains of aluminum, CaH_2 and Bi.

O-031 **A New Portable Hydrogen Generation System: Catalytic Dissociation and Hydrolysis of Ammonia-Borane.** Q. Xu, M. Chandra, – National Institute of Advanced Industrial Science and Technology (AIST), Ikeda, Osaka, Japan

We report a new excellent catalytic system suitable for use as a portable hydrogen source from the above point of view, which is based on catalytic dissociation and hydrolysis of ammonia-borane complex (NH_3BH_3) at room temperature [1]. NH_3BH_3 dissolves in water to form a solution stable in the absence of air. The addition of a catalytic amount of suitable metal catalysts such as Pt, Rh, and Pd into the solutions with various concentrations leads to rigorous release of hydrogen gas with an H_2 to NH_3BH_3 ratio up to 3.0, corresponding to 8.9 wt% of the starting materials NH_3BH_3 and H_2O. The Pt catalysts are the most active and no significant deactivation was observed for the recycled catalysts. It is found that solid acids such as cation exchange resins and zeolites also exhibit high activities for the dissociation and hydrolysis of NH_3BH_3 to generate hydrogen with an H_2 to NH_3BH_3 ratio up to 3.0 at room temperature [2]. This new system possesses high potential to find its application to portable fuel cells. [1] M. Chandra, Q. Xu, J. Power Sources, in press (doi:10.1016/j.jpowsour.2005.05.043); [2] M. Chandra, Q. Xu, J. Power Sources, in press (doi:10.1016/j.jpowsour.2005.12.033).

ORAL PRESENTATIONS (O-032 to O-084) **Tuesday, October 3 (see schedule)**

O-032 **Catalytic Properties on the Hydrogen Desorption Process of Metallic Additives Dispersed in the MgH_2 Matrix.** R. Checchetto,[1] N. Bazzanella,[1] A. Miotello,[1] P. Mengucci,[2] – [1]Dipartimento di Fisica dell'Università di Trento, Povo, Italy; [2]Dipartimento di Fisica ed Ingegneria dei Materiali e Territorio- Università di Ancona, Ancona, Italy

Because of its high storage capacity, ~ 7.6 wt. %, magnesium is a good candidate for hydrogen storage application but the slow reaction kinetics and high dissociation temperature of MgH_2 limit its practical applications. Fast H_2 absorption and desorption kinetics can be obtained by mixing Mg with metallic additives: metal nanoclusters dispersed at the surface of Mg powders catalyse the H_2 dissociation and recombination process and favour the transfer of H atoms from and to the underlying Mg layers. The H_2 desorption process can also be accelerated when the metallic additive is dispersed in the MgH_2 matrix: we recently observed that the effective value of the activation energy for desorption is reduced from 141 kJ/mol H for pure MgH_2 to 51 kJ/mol H [1,2] with the addition of 5 at. % Nb. Structural analysis evidences the formation of NbH nanoclusters and the accelerated H_2 desorption can be explained by the large MgH_2-NbH interface area where heterogeneous nucleation of the h-Mg phase occurs and by the formation of interconnected h-Mg domains representing fast diffusion paths for the H migrating atoms [3]. In this paper we present a study on the H_2 desorption catalysis of different metallic elements (Nb, Au, Zr, Fe) dispersed in the MgH_2 matrix at atomic concentration in the 10^{-3} to 10^{-2} level. The microstructural characterization of the sample was carried out by X-rays Diffraction Spectroscopy (XRD) while the hydrogen desorption kinetics of MgH_2 samples containing different metallic additives was analysed by Thermal Desorption Spectroscopy (TDS). We discuss the catalytic properties of the metallic additives considering the chemical and physical state of the dopant element, namely the different degree of chemical affinity with hydrogen and magnesium, and its microstructure (single atom or nanosized clusters) when dispersed in the Mg matrix. [1] N. Bazzanella, R. Checchetto and A. Miotello, Appl. Phys. Lett. **85**, 5212 (2004); [2] R. Checchetto, N. Bazzanella, A. Miotello and P. Mengucci, J. Alloys Compd. **404-406**, 461 (2005); [3] R. Checchetto, N. Bazzanella, A. Miotello, C. Maurizio, F. D'Acapito, P. Mengucci, G. Barucca and G. Majini, Appl. Phys. Lett. **87**, 061904 (2005).

O-033 **Combining Electron Energy Loss Spectroscopy and Energy Dispersive Spectroscopy for Identification of Catalytic Species in Hydrogen Storage Materials.** D. D. Graham,[1] L. F. Culnane,[2] C. M. Jensen,[2] I. M. Robertson,[1] M. P. Sulic,[2] – [1]University of Illinois Urbana-Champaign, Urbana, IL, USA; [2]University of Hawaii, Honolulu, HI, USA

To meet DOE requirements for hydrogen storage in automotive applications, it is necessary for a candidate storage material to possess a high hydrogen storage capacity and be capable of rapid recharging at low pressure and temperature. Enhancing these features in complex metal hydride materials requires the use of catalysts which have been developed empirically. To improve current catalysts, a more detailed knowledge of the catalyst location and electronic structure is required. In the present study, titanium catalyzed sodium aluminum hydride has been studied using in-situ TEM heating experiments in conjunction with electron energy loss spectroscopy and x-ray energy dispersive spectroscopy. This study has revealed localized regions of catalyst within the material. Insight into the effect of these observations on reactions controlling hydrogen release and uptake will be presented.

O-034 **Hydrogen Desorption Properties of MgH_2 Nanocomposites with Nano-oxides and Special INCO Nano-and-Micro-Ni.** R. A. Varin,[1] T. Czujko,[1] E. B. Wasmund,[2] Z. S. Wronski,[3] – [1]University of Waterloo. Department of Mechanical Engineering, Waterloo, Ontario, Canada; [2]INCO Special Products, Energy Materials, Mississauga, Ontario, Canada; [3]Natural Resources Canada, CANMET's Materials Technology Laboratory, Ottawa, Ontario, Canada

The objective of this work is to study catalytic effects of 5wt.% of n-Al_2O_3 (particle 10-20nm), n-Y_2O_3 (particle 30-50nm), special n- and m-Ni (n-nano; m-micro) with a unique non-spherical morphology synthesized by INCO Limited Corporate R&D Canada and eventually the equal ratio mixtures of nano-oxides and special Ni on the hydrogen desorption properties of commercial MgH_2. The powder mixtures were mechanically milled for 20h in an argon atmosphere under strong impact mode in the magneto-mill Uni-Ball-Mill 5 yielding MgH_2-based nanocomposites. Doping with n-Al_2O_3 and n-Y_2O_3 does not have a beneficial effect on hydrogen desorption kinetics (Sieverts-type apparatus) and the onset and peak desorption temperatures measured by Differential Scanning

Calorimetry (DSC). In contrast, nanocomposites doped with special INCO Ni show hydrogen desorption onset and peak temperatures reduced by as much as 50-100℃. The lowest onset and peak desorption temperature of ~290℃ and 302℃, respectively, are observed for the MgH_2+5wt.%(m-Ni) nanocomposite. Desorption kinetics is very fast and at 275℃ and 300℃ under 1 bar H_2 pressure the MgH_2+5wt.%(m-Ni) nanocomposite desorbs about 4wt.% and 6wt.% of hydrogen in about 4000 and 1000s, respectively. The activation energy of desorption is reduced to slightly over 100 kJ/mol from about 140 kJ/mol for the as-milled MgH_2 and MgH_2 doped with nano-oxides. The relationship between catalytic effect of special INCO Ni additive and its unique morphology is discussed.

O-035 **Enhanced Hydrogen Reaction Kinetics of Nanostructured Mg-based Composites with Nanoparticle Metal Catalysts Dispersed on Supports.** Y. Yoo,[1] C.-Y. Seo,[1] R. Kondakindi,[1] M. Tuck,[2] Z. Dehouche,[3] K. Belkacemi,[3] – [1]Institute for Chemical Process and Environmental Technology, National Research Council Canada, Ottawa, Canada; [2]Department of Chemical Engineering, Dalhousie University, Halifax, Canada; [3]Department of Soil Sciences and Agri-Food Engineering, Laval University, Quebec, Canada

Magnesium hydride is considered as one of the most interesting alternatives for the reversible storage of hydrogen due to several unique advantages such as elemental abundance, economic production cost, easy handling as well as a high hydrogen storage capacity of 7.6 wt.%. However, the major problem of magnesium as a rechargeable hydrogen carrier system is its slow reaction rate and high sorption temperature. A breakthrough in hydrogen storage technology has been achieved by preparing nanocrystalline hydrides using high-energy ball milling. These new materials show very fast absorption and desorption kinetics at 300 degrees Celcius. However, desorption and absorption at lower temperatures are still too slow, limiting technical applications. To overcome this problem, metallic catalysts such as Pd, Ni, V, Ti, Mn and Fe have been added to nanocrystalline magnesium for a better better H_2-dissociation at the surface. In addition, transition metal oxides such as TiO_2, V_2O_5, CuO, Mn_2O_3, Cr_2O_3, Fe_3O_4, and Nb_2O_5 etc have been investigated as potential catalysts on the sorption behavior of nanocrystalline Mg-based systems. The composites exhibited enhanced kinetics of sorption at 300 degrees Celcius, but not improve the desorption behavior at temperatures below 250 degrees Celcius. Recently, Yoo et al. have reported the catalytic effect of proton conductive ceramics on enhancing hydrogen desorption kinetics of nanostructured magnesium hydrides [1-2]. After milling MgH_2-$Ba_3(Ca_{1+x}Nb_{2-x})O_{9-\delta}$ (BCN) composite, the nanostructured composite showed much enhanced desorption kinetics, increased desorption plateau pressure, and decreased hysteresis, $\ln(P_{abs}/P_{des})$, indicating not only ameliorate desorption kinetics but also lower temperature desorption in comparison to pure MgH_2. During the desorption process of hydrogen, protons in MgH_2 bulk lattice reach to the magnesium grain boundaries having faster proton diffusion rate and these protons diffuse out through the proton conductive ceramic catalyst as well as the decomposed hydroxide or oxide layers for consecutive recombination and desorption processes on the surface of MgH_2 particles. Therefore in this work, the hydrogen reaction kinetics of nanocrystalline Mg with nanoparticle metal catalysts such as Pd, Ni, and Pd/Ni dispesed on supports such as proton conductive ceramics and single wall carbon nanotubes (SWNTs) has been investigated. The metal catalysts of Pd, Ni, and Pd/Ni on supports of BCN and SWNTs also having catalytic effect on enhancing sorption kinetics of hydrogen storage materials were synthesized based on novel methods published in literature [3]. [1] Y. Yoo, Z. Dehouche, C.-y. Seo, I. Davidson, N. Grimard, and J. Goyette, International Partnership Hydrogen Economy hydrogen storage conference, Lucca, Italy, June 2005; [2] C.-y. Seo, Y. Yoo, and Z. Dehouche, *Proceedings of International Hydrogen Energy Congress and Exhibition*, p. 35, Istanbul, Turkey, 2005; [3] C. Bock, C. Paquet, M. Couillard, G. A. Botton, and B. R. MacDougall, J. Am. Chem. Soc.,126 (2004) 8028-8037.

O-036 **Quasielastic Neutron Scattering Investigation of the Reorientational Motion of Hydrogen in Na_3AlH_6 and $^7Li^{11}BH_4$.** M. R. Hartman,[1,2] J. J. Rush,[1] T. J. Udovic,[1] T. Yildirim,[1] – [1]NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD, USA; [2]Oregon State University, Corvallis, OR, USA

Recent research into solid-state hydrogen storage has focused heavily upon various complex metal hydrides, in particular the alanates and borohydrides. In the case of the alanates, $NaAlH_4$ has received considerable attention due to the discovery by Bogdanović and Schwickardi that the inclusion of catalytic material reduced the hydrogen desorption temperature and allowed reversibility of the reaction.[1] The desorption reaction was observed to follow a two-step desorption process, with Na_3AlH_6 appearing as an intermediate reaction product. We have utilized incoherent quasielastic neutron scattering to investigate the reorientational motions of the hydrogen associated with the $[AlH_6]^-$ octahedra. The details of these reorientational motions are presented and compared to previous NMR investigations. For the borohydrides, $LiBH_4$ is an important material because of its role in various "destabilized" hydride systems (i.e. $LiNH_2$-$LiBH_4$ and $LiBH_4$-MgH_2). To overcome the high neutron absorption associated with natural lithium and boron, we have recently synthesized $LiBH_4$ enriched in ^7Li and ^{11}B. The isotopically labeled material was subjected to incoherent quasielastic neutron scattering in both the low-temperature (T<384K) and high-temperature phases. The details of the reorientational motions of the $[BH_4]^-$ tetrahedron in both phases are presented and compared to previous NMR studies. [1] B. Bogdanović and M. Schwickardi, *J. Alloys Compd.* **253** (1997) 1-9.

O-037 **The Effect of Zero Point Vibration on $LiBH_4$.** T. J. Frankcombe, G.-J. Kroes, – University of Leiden, Leiden, The Netherlands

It is becoming commonplace to add zero point energy corrections to calculated reaction enthalpies for hydride decompositions. In this work we apply zero point vibrational contributions also to the calculation of the equilibrium lattice constants of the potential hydrogen storage material $LiBH_4$ and its decomposition products. Correctly minimising the ground state energy of the $LiBH_4$ and LiH crystals including vibrational contributions (in the quasiharmonic approximation) leads to a significantly larger unit cell than simply minimising the DFT potential energy, increasing the unit cell volume by around 10%. Thus the GGA-derived lattice constants are no longer in good agreement with the experimentally-observed values. It is expected that this is a common feature amongst

light metal hydrides, calling into question the accuracy of current GGA functionals. Cooperative effects mean that the enthalpy of dehydrogenation is not significantly affected by the lattice constant expansion, yielding the zero point energy-corrected value 59 kJ/mol H_2.

O-038 **Crystal Structure of Alanates.** B. C. Hauback, H. W. Brinks, – Physics Department, Institute for Energy Technology, Kjeller, Norway

Alanates are among the most promising metal hydrides for hydrogen storage. Synthesis of new compounds and understanding of the effect of additives and absorption/desorption processes in general are key-challenges. In all cases, detailed structural studies are important in order to improve the hydrogenation properties of the materials. Crystal structures of several alanates, including $MAlD_4$ (M=Li, Na, K), Li_3AlD_6, $Mg(AlH_4)_2$ and mixed alanates, like Na_2LiAlH_6 and K_2NaAlH_6, have been determined from high resolution powder neutron diffraction (with the PUS diffractometer at the JEEP II reactor at Kjeller, Norway) and synchrotron X-ray diffraction (at the Swiss-Norwegian Beamline at ESRF in Grenoble, France). This presentation will focus on the description of the different alanate compounds and comparison between the different structures. Financial support from the NANOMAT and RENERGI program s in the Research Council of Norway and the projects HYSTORY (FP5) and STORHY (FP6) under the Energy Programs in the European Commission is acknowledged.

O-039 **Crystal Structure of a Novel Class of Ternary Hydrides Li_4Tt_2D (*Tt*=Si and Ge).** H. Wu,[1,2] M. R. Hartman,[1,3] T. J. Udovic,[1] J. J. Rush,[1,2] W. Zhou,[1,4] R. C. Bowman, Jr.,[5] J. J. Vajo,[6] – [1]NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD, USA; [2]Department of Materials Science and Engineering, University of Maryland, College Park, MD, USA; [3]Department of Nuclear Engineering and Radiation Health Physics, Oregon State University, Corvallis, OR, USA; [4]Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA, USA; [5]Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA; [6]HRL Laboratories LLC, Malibu, CA, USA

The crystal structures of newly discovered Li_4Ge_2D and Li_4Si_2D ternary phases were solved by direct methods using neutron powder diffraction data. Both structures can be described using a *Cmmm* orthorhombic cell with all hydrogen atoms occupying Li_6-octahedral interstices. The crystal structure and the geometry of these interstices are compared with other related phases, and the stabilization of this novel class of ternary hydrides is discussed.

O-040 **Studies on Ni-MH Batteries.** J. Chen, – Institute of New Energy Material Chemistry, Nankai University, Tianjin, P. R. China

This talk addresses the issue of hydrogen storage alloys that are used as the negative electrode materials of nickel-metal hydride (Ni-MH) batteries. Hydrogen absorbing alloy electrodes were first reported in the beginning of 1970s and Ni-MH batteries using $MmNi_5$-based alloys (Mm, mischmetal) as the negative electrode materials had been commercialized in the areas of communication equipment and laptop computers in 1990. The key driving forces for the rapid growth of Ni-MH batteries are due to their environmental and energy advantages over that of nickel-cadmium (Ni-Cd) batteries, making the Ni-MH system is in high-volume production and being further developed for the applications in electric vehicles (EVs). More recently, there has been a significant shift for Ni-MH batteries by the automotive manufacturers from EVs toward hybrid EVs (HEVs), which will be promising in the short and mid-term. The charge-discharge mechanism for Ni-MH batteries involves the movement of H/H^+ between a MH electrode and a Ni electrode in an alkaline electrolyte, which is similar to the "rocking-chair" mechanism of lithium-ion batteries but clearly different from that of Ni-Cd or Pb-acid batteries. This characteristic means that the MH electrode can be widely changed or modified depending on the kind and composition of the alloys used. The AB_5, AB_3, AB_2, AB, or A_2B type alloys, where the "AB_x" designation refers to the ratio of the A type elements (La, Ce, Pr, Nd, Mm, Ti, Zr, Mg) to that of the B type elements (V, Ni, Cr, Co, Mn, Al, Fe, Sn), have been extensively studied as the active materials of MH electrodes in the aim to improve the capacity, high-rate capability, activation, and cycle life, and in the meantime to lower the cost. The structure, microstructure, chemical composition & stability, and surface state of the alloys have a great effect on the properties of both the MH electrode and the Ni-MH batteries. It is also noted that the prominent progress in the field of battery technology has made a huge achievement of Ni-MH batteries with the cylindrical and prismatic types. For example, the nominal capacity of cylindrical Ni-MH batteries with an AA size is increased from about 1000 mAh in 1990 to now nearly 3000 mAh, showing the obvious enhancement of weight/volume energy density and high-power performance. Furthermore, the hydrogen storage alloy from spent Ni-MH batteries was regenerated by chemical and physical methods, which accelerate the development of circular economy and promote the upbuilding of a conservation-minded society.

O-041 **Mg-Ti-H Thin Films with Optimal Properties for Batteries, Solar Collectors and Sensors.** D. M. Borsa, A. Baldi, M. Pasturel, H. Schreuders, B. Dam, R. Griessen, – Faculty of Sciences, Department of Physics and Astronomy, Vrije Universiteit Amsterdam, Amsterdam, The Netherlands

Notten et al. reported recently [1] that Mg-Ti-H thin films have a hydrogen storage capacity approx. 4 times larger than that of conventional NiMH-batteries. Here we show that the same Mg-Ti-H thin films exhibit also absolutely remarkable optical properties! Hydrogen absorption in Mg-Ti films triggers a fast optical transformation from a reflective to a highly absorbing black state. For example, hydrogenated $Mg_{0.80}Ti_{0.20}H_x$ thin films combine a high absorption (87% of the solar spectrum) with a low thermal emissivity (only 10%), while after removal of hydrogen $Mg_{0.80}Ti_{0.20}$ absorbs no more than 1/3 of the solar spectrum. The solar power absorption contrast is thus of the order of 3 between the hydrogenated absorbing state and the metallic state. The optical transition is fast, robust and reversible. This offers unique opportunities for smart solar collectors and optical hydrogen sensors. The hydrogenation of Mg-Ti thin films was monitored continuously optically, electrically and with x-ray diffraction. The optical transmission of $Mg_yTi_{1-y}H_x$ films increases gradually with decreasing Ti content. Structurally, however, two distinct phases can be identified: a MgH_2-like rutile

phase for low Ti contents (y=0.90) and a fluorite-like Mg-Ti-H phase otherwise (y=0.80 and y=0.70). There are no indications for phase segregation either in the fluorite or in the metallic parent alloy not even after repeated cycling at room temperature. Even hydrogen release at elevated temperatures (up to 150°C) does not induce a decomposition of the Mg-Ti hydride into Mg and TiH_2. These results point toward a rich and unexpected chemistry of Mg-Ti-H compounds. [1] R. A. H. Niessen and P. H. L. Notten, Electrochem. Solid-State Lett. 8 (2005) A53; [2] P. Vermeulen, R. A. H. Niessen, and P. H. L. Notten, Electrochem. Comm. 8 (2006) 27.

O-042 **Structural and Hydrogen Storage Properties of MgPrNi Amorphous Alloys with High Glass Formability.** Y. L. Du, Y. H. Deng, F. Xu, G. Chen, G. L. Chen, – Department of Materials Science and Engineering, Nanjing University of Science and Technology, Nanjing, P. R. China

$Mg_{63}Ni_{22}Pr_{15}$ amorphous alloys with high glass formability were prepared by a single roller melt-spinning technique at a wheel surface velocity of 5, 10, 20 and 40 m/s, respectively. The structural properties of the as-prepared samples were characterized by XRD and TEM. The glass transition and crystallization behaviors of all samples were examined with a differential scanning calorimeter. The hydrogen storage properties of $Mg_{63}Ni_{22}Pr_{15}$ amorphous alloys were investigated by pressure-composition isotherms using a conventional Sieverts'-type system. Our results indicate that Mg-based amorphous alloys with high glass formability are promising candidates for the hydrogen storage.

O-043 **Hydrogen-Induced Plastic Deformation of Rare Earth Metal Thin Films.** M. Getzlaff,[1] A. Pundt,[2] – [1]University of Düsseldorf, Institute of Applied Physics, Düsseldorf, Germany; [2]University of Göttingen, Institute of Material Physics, Göttingen, Germany

Surface modification of thin Gd films during hydrogen adsorption as well as absorption has been investigated on the nanometer scale by means of scanning tunneling microscopy. The adsorption occurs in two steps. It is initiated by surface imperfections. Starting from these nucleation centers a domain-like spreading is present which is strongly hindered at surface steps. The measurements have shown that during hydrogen loading two different types of surface pattern develop above a particular concentration: disc-like islands and ramps. These surface patterns can be well described by two plastic deformation processes in the films that lead to glide steps on the film surface. First, the emission of dislocation loops during hydride precipitation occurs. Secondly, misfit dislocations near the film-substrate interface are present. Since plastic deformation leads to stress release we suggest that a lot of thin metal films that are clamped to a substrate relax plastically after reaching a certain hydrogen-induced stress that corresponds to a critical hydrogen concentration. This conclusion is corroborated by the observation that free-standing Gd islands are deformed without structural deformation. Overall, combining the ability of preparing high-quality epitaxial thin films with the detailed analysis of the mechanical properties during hydrogen absorption may lead to a deeper fundamental understanding of hydrogen switchable thin films. It may also improve their industrial applications.

O-044 **Formation of NH_3 during the Dehydrogenation of Amide-Hydride Mixtures.** P. Chen, Z. Xiong, Y. Liu, G. Wu, J. Hu, – Physics Department, National University of Singapore, Singapore

Substantial amount of hydrogen can be desorbed from a variety of amides and hydrides mixtures under proper reaction conditions. As examples, $Mg(NH_2)_2$-2LiH releases ~5.5wt% of hydrogen at temperatures above 120°C; the exothermic reaction between $NaNH_2$ and $LiAlH_4$ produces ~ 5.0wt% of hydrogen near room temperature. It was detected that NH_3 was somehow co-produced with hydrogen in the gaseous form. The origin of NH_3 is, so far, unclear and of controversy. In this presentation, the formation of ammonia from the thermal decomposition of amides alone and from the dehydrogenation of amides-hydrides will be analyzed by both thermodynamic and kinetic approaches. By changing desorption temperature and pressure the concentration of ammonia in the gaseous products of a Li-Mg-N-H sample varies from thousands ppm to hundreds ppm. Lower down the dehydrogenation temperature could effectively reduce the ammonia content. The effects of chemical composition and additives will be discussed.

O-045 **Crystal Structure Determination and Reaction Pathway of Amide-Hydride Mixtures.** J. Rijssenbeek,[1] Y. Gao,[1] J. Hanson,[2] Q. Huang,[3] C. Jones,[3] B. Toby,[3] – [1]GE Global Research, Niskayuna, NY, USA; [2]Department of Chemistry, Brookhaven National Laboratory, Upton, NY, USA; [3]NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD, USA

Combined in-situ synchrotron X-ray diffraction and gas analysis studies were performed on mixtures of various ratios of lithium amide and magnesium hydride, which have shown promise as solid-state hydrogen storage materials. For a 2:1 ratio, the dehydrogenated product is a mixed lithium and magnesium imide, $Li_2Mg(NH)_2$, which undergoes two structural transitions at elevated temperatures. Orthorhombic α-$Li_2Mg(NH)_2$ converts to primitive cubic β-$Li_2Mg(NH)_2$ at approximately 350 °C followed by face-centered cubic γ-$Li_2Mg(NH)_2$ at around 500 °C. A fourth structural variant, δ-$Li_2Mg(NH)_2$, is observed above 300 °C under high hydrogen pressure. Disordering of the Li, Mg and cation vacancies as a function of temperature drives the structural transitions. We report the reaction pathway from in-situ X-ray diffraction studies and the crystal structures of the four structural variants of $Li_2Mg(NH)_2$ as determined by high-resolution X-ray and neutron powder diffraction. We also discuss the hydrogen storage reaction pathways for mixtures with other ratios of Li/Mg.

O-046 **Crystal Structure Investigations of Li and Mg Amide and Imide.** M. H. Sørby,[1] Y. Nakamura,[1] H. W. Brinks,[1] T. Ichikawa,[2] S. Hino,[2] H. Fujii,[2] B. C. Hauback,[1] – [1]Institute for Energy Technology, Kjeller, Norway; [2]Hiroshima University, Hiroshima, Japan

Lithium nitride (Li_3N) can reversibly store large amounts of hydrogen (9.3 wt%) under the formation of lithium hydride (LiH) and lithium amide ($LiNH_2$) via lithium imide (Li_2NH) [1]. However, impractically high temperature is needed for hydrogen desorption (> 255 ºC). Several independent investigations have shown that partial substitution of Mg for Li can lower the desorption temperature considerably (e.g. [2]). Thus, the Li-Mg-N-H system is interesting for hydrogen storage. The crystal structure of deuterated Li and Mg amide and imide have been investigated by neutron- and synchrotron powder diffraction. Both the amides are fully ordered and the metal cations are tetrahedrally coordinated by 4 amide anions. The amide anion is a rigid unit with a geometry that resembles that of the isoelectronic water molecule. The $Mg(ND_2)_2$ structure may be described as a slightly distorted fcc lattice of Mg_4 tetrahedra with amide anions in all tetrahedral interstices and 6 amide ions distributed in the periphery of the octahedral interstices. The imides have more complicated crystal structures. Similarities and differences between the imides and the amides will be discussed. Financial support from the NANOMAT program in the Research Council of Norway and the International Joint R&D project by NEDO, Japan is acknowledged. [1] P. Chen, Z. Xiong, J. Luo, J. Lin, K. L. Tan, Nature 420 (2002) 302-304; [2] W. Luo, J. Alloys Comp. 381 (2004) 284-287.

O-047 **Characterization of Titanium Based Catalysts in the Li-N-H Hydrogen Storage System by X-ray Absorption Spectroscopy.** S. Isobe, T. Ichikawa, H. Fujii, – Materials Science Center, N-BARD, Hiroshima University, Higashi-Hiroshima, Japan

Lithium-Nitrogen-Hydrogen (Li-N-H) systems have been reported as one of the attractive hydrogen storage systems [1, 2]. So far it was clarified that some catalysts, especially titanium based compounds, were significantly effective for improving the hydrogen storage kinetics in the Li-N-H system [3]. In this research, the chemical bonding states and local environmental structures of the titanium compounds in the LiH and $LiNH_2$ mixture were examined by X-ray absorption spectroscopy (XAS) measurement as the characterization of the catalysts. The results of X-ray absorption near-edge structure (XANES) indicated that the Ti atoms in the titanium compounds, which had the catalytic effect on the kinetics of the hydrogen desorption properties, had a common electronic (chemical bonding) state. Meanwhile, such common characteristics could not be found in the results of the extended X-ray absorption fine structure (EXAFS). From these results, the catalytic effect more strongly correlates with the electronic state, not the local environmental structure of the Ti atoms in the Li-N-H system. [1] P. Chen, Z. Xiong, J. Luo, J. Lin, K.L. Tan, Nature 420 (2002) 302; [2] T. Ichikawa, S. Isobe, N. Hanada, H. Fujii, J. Alloys Comp. 365 (2004) 271; [3] S. Isobe, T. Ichikawa, N. Hanada, H.Y. Leng, M. Fichtner, O. Kircher, H. Fujii, J. Alloys Comp. 404 (2005) 439.

O-048 ***Ab Initio* Investigation of Li-N-Mg-H Systems for Hydrogen Storage.** C. M. Araujo,[1] R. H. Scheicher,[1] P. Jena,[2] R. Ahuja,[1,3] – [1]Condensed Matter Theory Group, Department of Physics, Uppsala University, Uppsala, Sweden; [2]Physics Department, Virginia Commonwealth University, Richmond, VA, USA; [3]Applied Materials Physics, Department of Materials Science and Engineering, Royal Institute of Technology, Stockholm, Sweden

In this work, we provide a theoretical investigation of the thermodynamics and kinetics of various chemical reactions involved in the hydrogen absorption/desorption process in both Li_3N and $LiNH_2$ mixed with MgH_2. The latter system represents an important approach toward the achievement of suitable hydrogen storage systems for on-board applications. We have performed calculations for both the solid and gas phase. The self-consistent total energy calculations were carried out within the framework of density functional theory using the VASP plane-wave package for crystalline systems and the GAUSSIAN localized orbital package for molecular constituents. It should be highlighted that the unknown structures of the new hydrogen absorber and storage materials were extensively studied by employing systematic force minimization, Car-Parinello molecular dynamics and simulated annealing methods. Furthermore, we have also determined reaction barriers by identifying possible transition states and show that the reaction energies for molecular entities follow the same trend as their equivalent bulk systems.

O-049 **Hydrogenography: A Versatile Combinatorial Thin Film Technique to Investigate the Formation of Metal Hydrides.** B. Dam,[1] R. Gremaud,[1] A. Borgschulte,[2] D. M. Borsa,[1] Ph. Mauron,[1] C. Broedersz,[1] H. Schreuders,[1] R. Griessen,[1] – [1]Faculty of Science, Vrije Universiteit, Amsterdam, The Netherlands; [2]GKSS, Geesthacht, Germany

Hydrogenography is a combinatorial thin film technique which exploits the optical changes during exposure to hydrogen to measure the properties of hydrogenation. Sputtered thin film gradients allow us to identify the relevant parameters (enthalpy, kinetics of hydrogenation) for a large number of compositions at once. For phase identification the analysis of the optical spectra is essential. Thin films have the advantage that the grain size is automatically in the nano-range, which reduces the kinetic barriers. Nevertheless, we observe that the microstructure has a profound influence on the nucleation behaviour. Focussing on Mg-based metal hydrides we find that, depending on the microstructure, the complex Mg_2TMH_x metal hydrides nucleate within the film or at the substrate interface. It shows that the distribution of the metal hydride in a metal is not determined *solely* by the hydrogen diffusion gradient. In general, we find an extended solubility range both in the metal and the hydrogenated state. In some cases this unexpected alloying is maintained on reversible hydrogenation. As a result, the enthalpy of formation can be tuned by the compositon. Especially the stability of the fluorite Mg-based hydrides is surprising. Thin films have the advantage that one can make mixed phases in the form of (gradient) bilayers. We will show how in such mixtures the phase formation of a complex metal hydride proceeds and how additives such as Ti promotes this.

O-050 **New Insights from Raman and IR Spectroscopy into the Metal-Insulator Transition of YH_x Switchable Mirrors.** J. Schoenes, A.-M. Racu, – Institute for Physics of Condensed Matter, Technical University Braunschweig, Germany

Since the discovery of switchable mirrors in 1996 [1] elastic as well as inelastic light scattering have made important contributions to our current understanding of the electronic structure of metal hydrides. To cite only a few, we mention: gap energies, type of

transitions, crystal structures. Very recently, we discovered in a careful study of the temperature dependence of the Raman lines of $YH_{3-\delta}$ a striking broadening of one single phonon line [2]. The involved phonon corresponds to a breathing mode of Y atoms around an octahedral hydrogen site. Hydrogen vacancies in these sites will capture electrons and the formed donor states can be thermally activated. The excited electrons couple to the phonon via electron-phonon interaction and produce the observed exceptional line broadening with increasing temperature. New data extending to above room temperature corroborate the earlier fit with an activation energy of 0.1 eV. In addition, IR data will be presented showing an anomaly at the same photon energy. The results give strong support for correlated models of the electronic structure and the metal-insulator transition like that proposed by Ng et al. [3]. [1] J.N. Huiberts et al., Nature (London) 380 (1996) 231; [2] A.-M. Racu and J. Schoenes, Phys. Rev. Letters 96 (2006) 17401; [3] K.K. Ng et al. Phys. Rev. B 59 (1999) 5398

O-051 **Resistivity Changes in Cr/V 14/14 and 7/14 Superlattices during Hydrogen Uptake.** A. K. Eriksson,[1] A. Liebig,[2] S. Ólafsson,[1] B. Hjörvarsson,[2] – [1]Science Department, University of Iceland, Reykjavik, Iceland; [2]Department of Physics, Uppsala University, Uppsala, Sweden

The hydrogen concentration in superlattices such as Mo/V(001) [1] and Fe/V(001) [2] can be related to a measured change in resistivity. In Mo/V(001) the resistivity reaches a maximum at H/V~0.5 atomic ratio. Corresponding maximum is not observed in Fe/V (001) superlattices. This difference was later argued to originate from changes in the electronic band structure, resulting from the different c/a ratio within the V layers [3]. This argument seems plausible as the V is initially in a biaxial compressive (Mo) and tensile (Fe) strain state in these superlattices, resulting in a vastly different expansion coefficient of the V layers [4, 5]. Here we address this question by discussing the hydrogen induced resistivity changes in Cr/V(001) superlattices. The V layers are in a biaxial compressive strain state, as in the Fe/V(001) superlattices. By selecting appropriate thicknesses of the constituents, equivalent strain and extension of the V layers compared to Fe/V(001) are thereby accessible. Hence, the changes in the resistivity should exhibit the same lack of maximum at H/V~0.5 if the strain state is the dominating contribution to the resistivity change. The results exhibit a well profound maximum, similar to the changes observed in Mo/V(001). Therefore do not the c/a induced changes in the electronic structure appear to be a plausible explanation of these observations. These results highlight the need for a better understanding of the hydrogen induced changes of the resistivity. [1] F. Stillesjö et al. J. Phys. Condens. Matter 7 (1995) 8139; [2] G. Andersson et al. J. Phys. Condens. Matter 11 (1999) 6669; [3] V. Meded et al., Phys. Rev. B 69 (2004) 205409; [4] F. Stillesjö et al. Phys. Rev. B 54 (1996) 3079; [5] S. Olsson et al. J. Phys. Condens. Matter 13 (2001) 1685.

O-052 **Optical Properties of Hydrided Holmium Thin Films.** D. E. Azofeifa, W. E. Vargas, N. Clark, H. Solis, – Centro de Investigación en Ciencia e Ingeniería de Materiales, Universidad de Costa Rica, San José, Costa Rica

We measure the evolution of the optical transmission (300-760 nm) and the electrical resistivity on Ho films, 50 nm thick, as a function of H concentration up to 2.95 [H]/[Ho]. The Ho films are covered with a 15 nm thick Pd overcoat for hydrogenation and measurements ex situ. The films are deposited in a high vacuum chamber. Concentration is measured using a quartz crystal microbalance; all measurements are made at room temperature. From the measured transmission spectra, using an inversion method, the complex real refraction index of the Ho film is determined; from them the dielectric function, $e = e_1 + ie_2$, is calculated. Furthermore, using the inversion method, the contribution of the free electrons and the interband transitions are separated in the dielectric function. This in turn allows an estimation of the energy gap in the Holmium trihydride.

O-053 **Modelling the Binding Energy Change of Hydrogen in Metals by Interfaces Insertions in Multilayers.** S. Ólafsson, – Science Institute, University of Iceland, Reykjavik, Iceland

Hydrogen uptake in multilayers and superlattices like Mo/V and Fe/V [1,2] has shown considerable decrease of heat of solutions depending on the number of interfaces in the sample. In this work simple theoretical modeling is proposed for the effect of the density of interfaces and type of interface on binding energy reduction. This will be done for different types of interfaces. First type is the rigid interface where metal A in the multilayer A/B sample does not absorb hydrogen, effectively clamping the hydrogen absorbing layer B in a lock that hinders lattice expansion in two directions. Another type is elastic interface where metal A is also hydrogen absorbing but with lower binding energy and another characteristic lattice induced expansion than metal B. The modification of the binding energy will be calculated for simple cases according to the simple model. The effect of the substrate will be discussed and experimental approaches for measuring the binding energy of substrateless sample will be discussed. [1] Reynaldsson G, Olafsson S, Gislason HP, J. Alloys Compds. 356, 545-548, 2003; [2] Olsson S, Blixt AM, Hjorvarsson B, J. Phys.-Condensed Matter 17, 2073-2084, 2005.

O-054 **Deuterium, Tritium, and Helium Desorption from Aged Titanium Tritides.** K. L. Shanahan, J. S. Holder, – Savannah River National Laboratory, Aiken, SC, USA

Six new samples of tritium-aged bulk titanium have been examined by thermal desorption and isotope exchange chemistry. The discovery of an 'excess hydrogen capacity' in these materials, previously reported [1], has been confirmed in one of the new samples. Hydrogen 'heels' have been found in all samples and range from 0.7 to 1.0 Q/M units (Q=H+D+T). The helium release of the samples shows the more severe effects obtained from longer aging periods, i.e. higher initial He/M ratios. Several of the more aged samples were spontaneously releasing helium. The helium release and hydrogen absorption/desorption characteristics of these samples will be discussed, with focus on the newly confirmed excess hydrogen capacity, and comparison of helium release characteristics to a previous report [2]. [1] K. L. Shanahan, J. S. Holder, J. Alloys and Compounds, 404-406 (2005) 365; [2] A. M. Rhodin, V. S. Surenyants, Russ. J. Phys. Chem. 45(5) (1971) 612.

O-055 **^{3}He Retention in $LaNi_5$ and Pd tritides : Dependence on Stoichiometry, ^{3}He Distribution and Aging Effects.** S. Thiébaut,[1] M. Douilly,[1] S. Contreras,[1] B. Limacher,[1] V. Paul-Boncour,[2] B. Décamps,[2] A. Percheron-Guégan,[2] – [1]Commissariat à l'Energie Atomique, Centre d'Etudes de Valduc, Is/Tille, France; [2]Laboratoire de Chimie Métallurgique des Terres Rares, CNRS, Thiais, France

Metal tritides are commonly used for tritium storage because of safety issues, but also for their ability to retain the ^{3}He generated in their lattice, which allows to recover an almost ^{3}He-free gas.^{3}He retention has been studied at room temperature for more than 20 years in $LaNi_5$ tritide and for 12 years in Pd tritide. In this paper, ^{3}He retention measurements will be presented and results will be discussed according to the self-trapping theory [1]. For both tritides, effects of stoichiometry have been investigated by following ^{3}He retention in sub-stoichiometric, stoichiometric and replenished samples (Pd only). « Aging » effects, due to ^{3}He retention in the lattices, and attempts to determine ^{3}He distribution in $LaNi_5$ and Pd lattices, using XRD and EXAFS measurements as well as TEM observations, will also be presented. Then, very interesting differences in the evolution of thermodynamic and (micro)-structural properties between the two materials will be pointed out and discussed. At last, some results about ^{3}He retention in $LaNi_5$ samples, loaded with a D-T mixture, will be shown and differences between samples loaded with pure T_2 and D-T mixtures will be discussed, thereby confirming the effects of stoichiometry. [1] W. D. Wilson, C. L. Bisson, M. I. Baskes, Phys. Rev. B, **24** (1981) 5616.

O-056 **EELS Study of Individual Helium Bubbles in Aged $Pd_{90}Pt_{10}$.** A. Fabre,[1] D. Taverna,[2] E. Finot,[3] B. Décamps,[4] O. Stéphan,[2] M. Kociak,[2] A. Percheron-Guégan,[4] C. Colliex,[2] – [1]CEA Valduc, Is-sur-Tille, France; [2]Université Paris Sud, Orsay, France; [3]Université de Bourgogne, Dijon, France; [4]CNRS, Thiais, France

EELS has been used to investigate ^{3}He nanobubbles generated by tritium decay within a $Pd_{90}Pt_{10}$ matrix. This study was aimed at demonstrating the feasibility of measuring the internal pressure of individual bubbles enclosed in such a material. The challenge was to complete NMR experiments carried out by other authors on aged metallic tritides that brought global information about a large distribution of bubbles within the sample[1].In this study, a $Pd_{90}Pt_{10}$ sample was aged 8 months in β-phase under a tritium atmosphere before to be thinned down by jet electropolishing. Using a Scanning TEM, the K line of the 1s-2p transition of ^{3}He was analysed. The energy shift appeared to be dependent on the diameter of the studied bubble. Density of ^{3}He atoms was measured using a method only relying on the intensity of the K line[2], and was interpreted as a function of the inverse of the bubble radius, thereby retrieving theoretical results of Lucas[3]. An equation of state enabled to estimate the pressure of bubbles that appeared to be lower than the expected loop-punching pressure[1], as it will be discussed. We also mentioned a trend of bubbles to decorate defects and to get interconnected, in agreement with the theory of networks of linked-bubbles[4]. [1] G. C. Abell et al, Phys. Rev. Lett. 59, 995 (1987); [2] C. A. Walsh et al, Phil. Mag. A 80, No. 7 (2000) 1507-1543; [3] A. A. Lucas, et al, Phys. Rev. B 28 (1983) 2485; [4] D. F. Cowgill, 7th Conf. on Tritium Sci. & Tech., 2004, Baden-Baden, Germany.

O-057 **Effect of H_2S on Hydrogen Permeation of Pd-Cu/V-15Ni Composite Membrane.** J. Yang, C. Nishimura, M. Komaki, – Eco-energy Materials Group, Ecomaterials Center, National Institute for Materials Science, Tsukuba, Japan

Pd-Cu/V-15Ni composite membrane was prepared by co-sputtering in the paper. Hydrogen permeation of the composite membrane under pure H_2 and H_2+ H_2S mixed gas was studied. The composite membrane shows higher hydrogen permeability than that of Pd-Cu alloy membrane which has the same composition as the Pd-Cu overlayer of the composite membrane. A maximum hydrogen permeability was obtained as 3.72×10^{-8}mol $H_2s^{-1}m^{-1}Pa^{-1/2}$ at 573K under pure H_2 atmosphere. Effect of H_2S content on hydrogen permeability of the composite membrane was studied detailedly, and the composite membrane shows a good resistence to the poisoning of H_2S impurity. The composite membrane was characterized by microstructure observation and XRD analysis, and hydrogen permeation kinetics through the composite membrane was also analyzed.

O-058 **Enhanced Hydrogen Embrittlement of Pd-coated Niobium Metal Membrane Detected by In-situ Small Punch Test under Hydrogen Permeation.** T. Nambu,[1] H. Ezaki,[1] K. Shimizu,[2] Y. Matsumoto,[2] R. Rong,[3] H. Yukawa,[3] M. Morinaga,[3] I. Yasuda,[4] – [1]Department of Materials Science and Engineering, Suzuka National College of Technology, Japan; [2]Department of Mechanical Engineering, Oita National College of Technology, Japan; [3]Department of Materials Science and Engineering, Graduate School of Engineering, Nagoya University, Nagoya, Japan; [4]Hydrogen Business Project, Tokyo Gas Co., Ltd., Japan

The hydrogen embrittlement of pure niobium metal membrane was investigated under hydrogen permeation by using a newly developed *in-situ* small punch apparatus. In case of the palladium non-coated membrane, ductile fracture occurred at 673K in the hydrogen atmosphere of 0.005 to 0.06MPa, in agreement with the previous experiment [1]. However, once the membrane surface was coated with palladium by about 200nm in thickness, hydrogen absorption and permeation were enhanced strongly, resulting in the brittle fracture of the membrane due to the hydrogen embrittlenment. In fact, the absorption energy (i.e., SP-energy) estimated from the load-deflection curve was reduced from about 0.78J to 0.03J by the palladium coating, under the same test condition mentioned above. The boundary for the ductile-brittle transition of the palladium-coated niobium membrane was then determined from a series of the in-situ small punch tests and the PCT measurements. The measured boundary was found to be shifted greatly to the lower hydrogen content region, as compared to the boundary proposed by Gahr and Birnbaum [1]. The present results will provide us a clue to the design of niobium-based permeable membrane against the hydrogen embrittlement. [1] S. Gahr and H. K. Birnbaum, Acta Metallurgica, 26 (1978),1781-1788.

O-059 **Predicting Accurate Thermodynamic Properties of Reversible Hydrogen-Storage Destabilized Metal Hydrides and their Proper Comparison to Experiment.** D. D. Johnson, N. Zarkevich, – Department of Materials Science and Engineering, University of Illinois Urbana-Champaign, Urbana, IL, USA

Complex hydrides show promise as reversible hydrogen-storage materials when destabilized via additives because the enthalpy for H-desorption is significantly lowered, with concomitant reduction in desorption temperature. Here we predict the enthalpy of reaction *DH*(T) for destabilized hydrides using density functional theory (DFT) including electronic and vibrational free energies. From these DFT results we calculate a *van't Hoff plot* (log P versus 1/T) and obtain the quasistatic latent heat *L* for direct comparison to that assessed experimentally. We focus on the reversible reaction $2LiBH_4 + MgH_2$ « $2LiH + MgB_2 + 4H_2$ studied by Vajo et al. [J. Phys. Chem. B Lett. 109, 3719 (2005)]. We find that L assessed from the van't Hoff plot is 41.2 kJ/mol-H_2, compared to 41 kJ/mol-H_2 found in experiment, while *DH*(T) varies with temperature. We stress the importance of accounting for the R.T. phase transition and the phonon entropy, but also the rotational entropy associated with the BH_4^- units. Our results demonstrate that state-of-the-art calculations can achieve accuracy of experiment and, when comparing results from experiment and theory, agreement is found when like quantities are compared.

O-060 **Theoretical Studies of the Hydrogen Storage Properties of Magnesium-based Hydrides: Stability, H-atom Diffusivity and Hydrogen Release Temperature.** H. Jonsson, – Faculty of Science, VR-II, University of Iceland, Reykjavik, Iceland

We have calculated theoretically the stability, H-atom diffusion rate and hydrogen gas release temperature of various magnesium-based hydrides. While pure magnesium hydride has several good hydrogen storage properties, such as 7.6% hydrogen by weight, it suffers from two serious drawbacks: High H_2 gas release temperature (250 C, thermodynamically, as opposed to the target 50-100 C) and slow diffusion of H-atoms through the hydride. Recently, new hydrides with a small amount of transition metals have been synthesized (Kyoi et al, J. Alloys and Comp., 372, 213 (2004)) under high pressure conditions. We have calculated the hydrogen storage properties of these and similar hydrides containing first row transition metals. The Ti compound, for example, is predicted to contain up to 6.7% of hydrogen by weight and have chemical formula Mg_7TiH_{18}. The thermodynamic release temperature is predicted to be as low as 60 C and the H-diffusion rate increased by 16 orders of magnitude as compared with pure MgH_2 at room temperature. The addition of several other transition metals is predicted to have similar beneficial effects. But, the magnesium and the transition metal tend to separate when the hydrogen is released, making reloading difficult.

O-061 **Accelerating Development of Destabilized Metal Hydrides for Hydrogen Storage Using First Principles Calculations.** D. S. Sholl,[1,2] S. Alapati,[1] J. K. Johnson,[2,3] B. Dai,[3] – [1]Dept. of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA, USA; [2]National Energy Technology Laboratory, Pittsburgh, PA, USA; [3]Dept. of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, PA, USA

Destabilized metal hydrides have great potential for achieving reversible storage of hydrogen in practical applications. Two of the key challenges in achieving the promise of this class of materials are to select the best chemical mixtures from the enormous range of potential mixtures and to identify the kinetic effects that limit the time scale on which reaction equilibria can be reached. We describe how plane wave Density Functional Theory (DFT) calculations can be used to accelerate progress in these two topics. We have used DFT calculations to screen hundreds of potential destabilization reaction based on their reaction thermodynamics. These calculations greatly reduce the potential set of reactions that require detailed experimental study while identifying a number of promising new reaction schemes. We have also used DFT to examine potential rate-limiting steps during hydrogen uptake by materials of interest for reversible destabilized metal hydrides.

O-062 **First-Principles Studies of Phase Stability and Reaction Dynamics in Complex Metal Hydrides.** Y. Wang, Z. Ma, M.-Y. Chou, – School of Physics, Georgia Institute of Technology, Atlanta, Georgia, USA

In this presentation we will summarize our recent efforts in addressing various issues related to the stability of and reaction dynamics in complex metal hydrides. In order to better understand the catalytic role played by Ti in enhancing the reactions in sodium alanate, we present a first-principles investigation of hydrogen dissociation and adsorption on the pure Al surface as well as on the Ti doped surface elucidating a near-surface alloying mechanism. It is found that the presence of Ti promotes H adsorption on the surface. The binding between Ti and Al modifies the surface charge distribution near the adsorption site and facilitates the adsorption process. In addition, the mobility of H atom on the surface is greatly enhanced. The potential energy surface for H_2 dissociation over both pure Al and the alloy surfaces will also be discussed. To date sodium alanate $NaAlH_4$ is the only reversible complex metal hydride under practical temperature and pressure conditions that satisfies the international density targets of 5 wt.% and 70 kg/m^3. Therefore, it is desirable to increase the H wt.% by partially replacing Na with a lighter alkali metal such as Li. To study the stability of these mixed-alkali alantes, we perform first-principles calculations for the alloy systems $Na_{1-x}Li_xAlH_4$ and $Na_{3(1-x)}Li_{3x}AlH_6$ within the framework of density functional theory and pseudopotentials. The binding characteristics of these mixed-alkali alanates will be discussed.

O-063 **The Effect of Magnesium(hydride) Cluster Size on the Sorption Thermodynamics: a Quantum-Chemical Study.** R. W. P. Wagemans, J. H. van Lenthe, P. E. de Jongh, K. P. de Jong, – Utrecht University, Utrecht, The Netherlands

Magnesiumhydride is cheap and contains 7.7 wt% hydrogen, making it a very attractive hydrogen storage material. However, a fundamental barrier for bulk magnesium hydride as a hydrogen storage material is its thermodynamic stability. The large hydrogen desorption enthalpy of 75 kJ/mol H_2 dictates that in practice hydrogen can only be released at or above 300 °C. Fundamental material properties change dramatically when material dimensions shift into the nanometres regime. We theoretically investigated the thermodynamic properties of magnesium(hydride) nanoparticles, with sizes well below the ~20 nm range normally achieved by ball-milling [1]. Density Functional Theory and Hartree-Fock calculations show a profound difference in the destabilisation of magnesium versus magnesiumhydride as a function of decreasing particle size. As a result the desorption enthalpy, and hence the

temperature at which hydrogen can be desorbed, shifts to significantly lower values for particle sizes in the order of 1-2 nm and below. Furthermore intriguing results were obtained for clusters from which hydrogen had already partially been desorbed. The projected shift in thermodynamics might have important implications for hydrogen storage. Recently we experimentally succeeded in preparing systems containing magnesium with a crystallite size of 2-5 nm and below. [1] R.W.P. Wagemans, J.H. van Lenthe, P.E. de Jongh, A.J. van Dillen and K.P. de Jong, J. Am. Chem. Soc. 127 (2005) 16675.

O-064 **Interaction of Hydrogen with Defects and Their Stabilisation.** R. Kirchheim, – Institut für Materialphysik, Georg-August-Universität Göttingen, Göttingen, Germany

The interaction of hydrogen with defects like vacancies, dislocations and grain boundaries is treated in a generalized concept introduced by W. Gibbs for surface adsorption. If hydrogen segregates at the defects, their formation energy is reduced and their concentration will be altered [1]. Thus the microstructure of the absorbing matrix can be changed. Possible consequences with respect to mechanical properties, i.e. embrittlement of alloys and the properties of storage materials, namely $LaNi_5$-alloys will be discussed. For the examples of hydrogen interaction with grain boundaries [2,3] and dislocations [3] in palladium experimental results allow to calculate the reduction of the line or interfacial energy, respectively. In addition, recent reports on abundant vacancies in metals can be rationalized in a natural way. In all cases the gain in energy caused by hydrogen accumulating at the defects is counted as a decrease of the defect energy. The intriguing question will be discussed whether the defect energy may become zero or whether dislocations and grain boundaries become equilibrium defects, respectively. [1] Kirchheim, R., in Solid State Physics, eds. H. Ehrenreich and F. Spaepen, Elsevier, Amsterdam Vol. 59 (2004); [2] Kirchheim, R., *Progr. Mat. Sci.* **32,** 262 (1988); [3] Maxelon, M., Pundt, A., Pyckhout-Hintzen, W., Barker, J. and Kirchheim, R., *Acta mater.*, **49** 2625 (2001).

O-065 **Hydrogen-Induced Defects in Niobium.** J. Cizek,[1] I. Prochazka,[1] S. Danis,[1] M. Cieslar,[1] G. Brauer,[2] W. Anwand,[2] R. Kirchheim,[3] A. Pundt,[3] – [1]Faculty of Mathematics and Physics, Charles University, Prague, Czech Republic; [2]Institut für Ionenstrahlphysik und Materialforschung, Forschungszentrum Rossendorf, Germany; [3]Institut für Materialphysik, Universität Göttingen, Germany

Hydrogen loading causes formation of new defects in metals. Nature of the hydrogen-induced defects, population of these defects as a function of hydrogen concentration, and mechanism of their formation were investigated in this work. Positron annihilation spectroscopy (PAS) is a well-developed non-destructive technique with very high sensitivity to open volume defects like vacancies, vacancy clusters, dislocations etc. Type of defects as well as defect density can be determined using PAS. Thus, PAS is an ideal tool for investigations of the hydrogen-induced defects. In this work, we performed defect studies of bulk Nb specimens step-by-step loaded to various hydrogen concentrations. PAS studies were combined with X-ray diffraction and TEM investigations. The experimental data were compared with theoretical calculations of energetic stability and positron characteristics of various defect-hydrogen configurations. We have found that vacancies surrounded by hydrogen atoms are introduced into the specimens by hydrogen loading. Density of these vacancy-hydrogen complexes increases with increasing concentration of hydrogen in the specimens. The hydrogen-induced vacancies are formed even in the α-phase field, when the metal-hydrogen system is a single phase solid solution. Additional defects are introduced at higher hydrogen concentrations due to precipitation of hydride. Stability of the hydrogen-induced defects and mechanism of their formation are discussed.

O-066 **Do Diffraction Techniques Give a Reliable Measure of the Hydrogen Induced volume Changes?** G. K. Pálsson, B. Hjörvarsson, – Department of Physics, Uppsala University, Uppsala, Sweden

The hydrogen-induced expansion of materials is one of the most important physical observables, when addressing their hydrogen uptake. The local and global volume change is a measure of the H-H interaction and serves as the key for understanding, e.g., hydrogen embrittlement and self-trapping. The volume change is often determined by diffraction techniques, where the changes in the measured lattice spacing are used as a measure of the changes in volume. We will show that this presumption can be severely misleading. The design of the experiment is based on the utilization of all accessible length-scales in a scattering experiment, namely the total extension, chemical repetition and atomic distances. All these length-scales were measured utilizing a specially designed UHV based scattering chamber, allowing *in-situ* exposure to hydrogen in a wide temperature and pressure range. We will demonstrate a consistent determination of the volume changes using the changes in total extension and chemical repeat distance. The measured changes in the lattice parameter will thereafter be shown to be grossly misleading with respect to the changes in volume. We will discuss the consequences of this observation for the analysis of hydrogen-induced expansion using X-ray and neutron scattering experiments.

O-067 **Comparison of the TSSD Results Obtained by Differential Scanning Calorimetry and Neutron Diffraction.** D. Khatamian,[1] J.H. Root,[2] – [1]Atomic Energy of Canada Limited, Chalk River Laboratories, Chalk River, ON, Canada; [2]National Research Council of Canada, Chalk River Laboratories, Chalk River, ON, Canada

Due to the favourable neutronic properties, Zr alloys are used for reactor core components. The terminal solid solubility (TSS) for hydrogen in these alloys is very low – in Zr-2.5 wt.% Nb, used to fabricate pressure tubes for CANDU® power reactors, the TSS is less than 0.7 at.% H at ~300°C. The mechanical properties of the components under certain circumstances can deteriorate when the hydrogen concentration exceeds the TSS. Therefore, accurate values of the TSS are needed to assess the operating and end-of-life behaviours of these components. Differential scanning calorimetry (DSC) is used to measure the TSS of hydrogen in Zr alloys. Three definite features are marked on a typical DSC heat flow curve when the material is being heated and the hydrides are dissolving; “peak temperature”, “maximum slope temperature” and “completion temperature”. Usually, the maximum slope temperature, being about the average of the three temperatures, is interpreted as the TSS temperature for hydride dissolution

(T_{TSSD}). A set of coordinated DSC and neutron diffraction measurements have been carried out to identify the features of the heat flow signal that closely correspond to the T_{TSSD}. Neutron diffraction was chosen because hydrides generate distinctive diffraction peaks whose intensity approaches to zero at the transition temperature – an unambiguous indication of dissolution. Neutron diffraction shows that the temperature of hydride dissolution correlates closely with the DSC peak temperature.

O-068 **The Defect Structure with Superabundant Vacancies to be Formed from fcc Binary Metal Hydrides: Experiments and Simulations.** S. Harada,[1] D. Ono,[1] H. Sugimoto,[1] Y. Fukai,[2,3] – [1]Department of Physics, Chuo University, Tokyo, Japan; [2]Institute of Science and Engineering, Chuo University, Tokyo, Japan; [3]Institute of Materials Structure Science, Tsukuba, Ibaraki, Japan

The formation of superabundant vacancies (SAVs) in the presence of interstitial H in metals has attracted increasing interest in recent years as its implication for various materials properties has come to be recognized [1]. Here we address one of its basic properties, i.e. the ultimate defect hydride structure to be attained with SAVs. To this end, two different types of XRD measurements at high *p*, *T*s were performed on the fcc phase of Fe-H, Co-H, Ni-H and Pd-H systems. (1) In open-system experiments with samples placed in the H_2 environment, the same equilibrium state of composition M_3VacH_4 was attained, irrespective of *p*, *T* conditions adopted. (2) In closed-system experiments using samples of fixed H concentrations (in the Pd-H system), the equilibrium vacancy concentration was dependent on the H concentration; it stayed very small up to [H]/[Pd] ≈ 0.7, and increased steeply thereafter towards the ultimate composition Pd_3VacH_4. These characteristic features of SAV formation were successfully reproduced by Monte Carlo simulations with appropriate choice of relevant interaction parameters. [1] For a review, see, Y. Fukai, *The Metal-Hydrogen System, 2nd Ed.*, Springer, 2005, Chap.5.6.4

O-069 **Kinetics and Thermodynamics of the Aluminum Hydride Polymorphs.** J. Graetz, J. J. Reilly, – Brookhaven National Laboratory, Upton, NY, USA

Aluminum hydride (AlH_3) is a covalently bonded binary hydride that exhibits a number of interesting properties unlike any conventional metal hydride. On a volumetric basis, it contains more than twice the hydrogen of liquid H_2. It is one of only a few metal hydrides with a gravimetric hydrogen capacity that exceeds 10 wt.%. It crystallizes in seven different polymorphic structures at ambient pressure. And most surprisingly, AlH_3 forms a stable, crystalline solid at room temperature despite an equilibrium hydrogen pressure of around 5×105 bar at 298 K. In this study, polymorphs of AlH_3 were prepared by organometallic synthesis. We demonstrate that freshly synthesized, nonsolvated AlH_3 releases approximately 10 wt.% H_2 at desorption temperatures less than 100°C. The decomposition kinetics, measured by isothermal hydrogen desorption between 60° and 140°C, suggest that the rate of H_2 evolution is limited by nucleation and growth of the aluminum phase. The decomposition thermodynamics were measured using differential scanning calorimetry and ex situ x-ray diffraction. The decomposition of the less stable polymorphs (e.g. β and γ-AlH_3) occurs by an exothermic transformation to the α phase (~100°C) followed by the decomposition of α-AlH_3. A formation enthalpy of approximately -10 kJ/mol AlH3 was measured for α-AlH_3, which is in good agreement with previous experimental and calculated results.

O-070 **Crystal Structure Investigation of Alane.** H. W. Brinks,[1] A. I. Lem,[1] B. C. Hauback,[1] C. Brown,[2] C. M. Jensen,[2] – [1]Institute for Energy Technology, Kjeller, Norway; [2]University of Hawaii, Honolulu, HI, USA

AlH_3 is one of the solid compounds with the largest hydrogen content (10.1 wt%) and is therefore of interest for hydrogen storage applications. AlH_3 has been found to take at least six different crystal structures depending on the synthesis route [1]: α, α', β, γ, δ and ε. Except for α-AlH_3, which is the most stable, little is known about the crystal structures. In this work the crystal structure of AlH_3 is determined by X-ray and neutron diffraction. Furthermore, the thermal decomposition is followed by in-situ X-ray diffraction.
[1] F.M. Brower et al., J. Am. Chem. Soc. 98 (1976) 2450.

O-071 **NMR Studies of the Aluminum Hydride Phases and their Stabilities.** S.-J. Hwang,[1] R. C. Bowman, Jr.,[2] J. Graetz,[3] J. J. Reilly,[3] – [1]The Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, USA; [2]Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA; [3]Brookhaven National Laboratory, Department of Energy Science and Technology, Upton, NY, USA

Multinuclear and multidimensional solid state NMR techniques including magic-angle-spinning (MAS) and multiple-quantum (MQ) MAS experiments have been used to characterize various AlH_3 samples. At least three distinct polymorphic AlH_3 phases have been prepared by desolvating the alane etherate product from its organometallic synthesis. The most stable polymorph is denoted as α-AlH_3. MAS-NMR spectra for the ^1H and ^{27}Al nuclei have been obtained on a variety of AlH_3 samples that include the β- and γ-phases as well as the α-phase and the original etherate. While the dominant components in these NMR spectra correspond to the aluminum hydride phases, other species were identified as the materials spontaneously underwent various chemical reactions. They include Al metal, molecular hydrogen (H_2), residual solvent as well as peaks that can be assigned to Al-O species in different configurations. The occurrence and concentration of these extraneous components are dependent upon the initial AlH_3 phase composition and preparation procedures. Both the β-AlH_3 and γ-AlH_3 phases were found to generate substantial amounts of Al metal when the materials were stored at room temperature while the α-phase materials do not exhibit these changes. The roles of Al metal and H_2 gas formation on relative stabilities of the AlH_3 polymorphs will be discussed.

O-072 **Development of Complex Hydrides using Novel Techniques.** R. Zidan, K. L. Shanahan, D. L. Anton, P. Berseth, A. Jurgensen, – Savannah River National Laboratory, Aiken, SC, USA

This study developed novel hydrides for hydrogen storage through a new synthesis technique utilizing high hydrogen overpressure at elevated temperatures denoted as Molten State Processing, MSP. The MSP process was developed and used to modify and form new complex hydride compounds with desired characteristics. This synthesis technique holds the potential of fusing different known complex hydrides at elevated temperatures and pressures to form new complexes having different sorption and thermodynamic properties. The new complex hydrides produced by this method were identified through structural determination and thermodynamic characterization. Other possible high capacity hydrides are also investigated.

O-073 **Alane AlH_3 for Hydrogen Storage.** V. A. Yartys,[1] J. P. Maehlen,[1] R. V. Denys,[1] M. Fichtner,[2] Ch. Frommen,[2] B. M. Bulychev,[3] H. Emerich,[4] Y. E. Filinchuk,[4] – [1]Institute for Energy Technology, Kjeller, Norway; [2]Institute of Nanotechnology, Research Centre Karlsruhe, Germany; [3]Lomonosov Moscow State University, Moscow, Russia; [4]Swiss-Norwegian Beam Line, European Synchrotron Research Facility, Grenoble, France

Alane AlH_3 combines high gravimetric and volumetric densities of hydrogen, making the goal of building a total H storage system with efficiency exceeding 5 wt.% H reachable. AlH_3 forms several polymorphic modifications, from which we have focused our studies on α- and γ-AlH_3. A significant decrease in hydrogen packing density, by 11 %, from 2.09*LH_2 for the rhombohedral α-AlH_3 with corner-sharing AlH_6 octahedra; sp.gr. $R\bar{3}c$; a=4.44994(5); c=11.8200(2) Å to 1.85*LH_2 for the orthorhombic γ-AlH_3 with both corner- and edge-sharing AlH_6 units thus containing double bridge bonds between Al and H; sp.gr. *Pnnm*; a=5.3803(1); b=7.3572(2); c=5.77526(5) Å was found by SR XRD and is caused by a formation of rather large cavities in γ-AlH_3. This results in a decrease of its stability compared to α-AlH_3. Studies of the kinetics and mechanism of the decomposition of α-AlH_3 and γ-AlH_3 performed by *in situ* SR XRD and thermal desorption spectroscopy studies show a higher activation energy of hydrogen desorption from α-AlH_3 compared to the γ-hydride (136 kJ/mol and 92 kJ/mol, respectively). Complex, double-peak, decomposition behaviour was observed for both polymorphs. For the γ-modification, following temperature increase, three overlapping events were observed between 80 and 120 ^oC; γ→α transformation and two thermal decomposition processes, for γ- and for α-alane. Decomposition $AlH_3 \rightarrow Al + 3/2\ H_2$, which releases 10 wt.% H, because of small decomposition enthalpy and low desorption temperatures, makes AlH_3 very attractive material for the on-board hydrogen storage applications. This work has received a support from INTAS project 05-1000005-7665 “New Alane: Novel Reversible Hydrogen Storage Materials Based on the Alloys of Al”.

O-074 **H_2 Physisorption in Carbons and Metal Organic Frameworks.** C. C. Ahn, – California Institute of Technology, Pasadena, CA, USA

High surface area physisorbents are typically capable of storing 4 to 5 wt% of hydrogen at 77K. In the case of carbons, including activated carbons and aerogels, we can expect the surface excess adsorption saturation value to follow the linear behavior noted by Chahine of 1 wt% gravimetric density for every 500 m^2/gm. The saturation point generally occurs at pressures of 20 to 40 bar. In metal organic frameworks that have surface areas of ~3000m2/gm, we note, presumably due to the high molecular weight vertices of these structures, deviations from the linear behavior that is seen in carbons toward lower gravimetric density. We also note that the low-pressure isotherm behavior to 1 bar pressure, while useful for determining the Henry’s law constant, is inadequate in assessing the ultimate surface excess quantity of sorbent. The typical “heat” we measure is derived from a Henry’s law analysis, and yields a zero coverage differential enthalpy of adsorption in the range of 4 to 8 kJ/mole for most physisorbents. For practical applications, however, the isosteric enthalpy of adsorption is the more useful quantity for engineering applications as it typically shows a decrease in the heats measured as a function of gravimetric density, of importance in determining the heat transfer requirements of a storage tank.

O-075 **Hydrogen Adsorption in Metal-Organic Frameworks.** M. Hirscher, B. Panella, – Max-Planck-Institut für Metallforschung, Stuttgart, Germany

Hydrogen can be reversibly stored by adsorption on microporous materials with high specific surface areas at liquid nitrogen temperature. Recently, special attention has been given to metal-organic frameworks (MOFs), which possess the lowest densities of all known crystalline materials. These coordination polymers consist of metal oxide clusters connected by rigid aromatic linkers giving a three dimensional porous structure. We present new hydrogen adsorption measurements for MOFs, which have been prepared by large-scale synthesis methods. The results will be compared with hydrogen uptake measurements of other microporous materials, e.g., carbon nanostructures, zeolites etc. For the saturation value of hydrogen uptake an almost linear correlation with the specific surface area is found for all materials, whereas, the adsorption at lower pressures depends on the pore size or the metal ions. This will be shown by comparing various MOFs possessing different central-metal ions and organic ligands.

O-076 **Organometallic Compounds with Very Large Pore Volumes as Hydrogen Storage Materials.** M. Latroche,[1] S. Surblé,[2] C. Serre,[2] F. Millange,[2] G. Férey,[2] – [1]Laboratoire de Chimie Métallurgique des Terres Rares, CNRS, Thiais, France; [2]Institut Lavoisier, Université de Versailles, Versailles, France

This work deals with microporous materials able to store reversibly hydrogen gas. Combining targeted chemistry and computational design, different porous metal (Al, Cr) terephthalate and benzenedicarboxylate have been obtained with very large pore sizes and giant surface areas [1]. Beside the usual properties of these porous compounds, those zeotype cubic structures have potential properties for hydrogen storage. For example, MIL-101 [2] exhibits at liquid nitrogen temperature a capacity of 4.5 wt.%, one of the largest value ever reported for Metal Organic Framework (MOF) materials. Significant hydrogen upload are also observed at room temperature (about 0.4wt.%) though the reversible capacities are still to be improved. [1] G. Ferey, C. Mellot-Draznieks, C. Serre,

F. Millange, *Acc. Chem. Res.* 38 (2005) 217; [2] M. Latroche, S. Surblé, C. Serre, F. Millange, G. Férey., *Angew. Chem. Int. Ed., submitted* (2006).

O-077 **Hydrogen Storage Properties of AB3-type Compounds.** D. Sun,[1] M. Dong,[1] H. Xu,[1] G. Chen,[1] G. Cao,[2] – [1]Department of Materials Science, Fudan University, Shanghai, China; [2]Dalian Institute of Light Industry, Dalian, China

As a new hydrogen storage material, AB3 type compounds have attracted great attention recently. In this paper, various AB3 compounds were prepared by induction melting and annealing, their hydrogen storage properties in both electrochemical and solid-gas manners were determined, and discussed in terms of crystal structure and thermodynamics. Hydrogen–induced amorphrization in AB3 compound and the effects of substituted elements were addressed as well.

O-078 **Hydrogen Absorption in $Mg_3Y_2Zn_3$.** M. Sahlberg, Y. Andersson, – Department of Materials Chemistry, Uppsala University, Uppsala, Sweden

The hydrogen absorption properties of the previously reported phases $Mg_{12}YZn$ and $Mg_3Y_2Zn_3$ in the ternary Mg-Y-Zn system [1] have been investigated. The mother compounds were prepared by heating appropriate amounts of the elements at 1000°C inside a sealed tantalum tube. The samples were characterized by XRD and TEM methods. The crystal structure of $Mg_3Y_2Zn_3$ was refined from powder diffraction x-ray intensities by the Rietveld method, which showed that $Mg_3Y_2Zn_3$ crystallises in the ordered $AlMnCu_2$-type structure. It was shown by XPS and SEM/EDS that zinc had segregated to the surface. The hydrogenations were performed at temperatures up to 400°C and hydrogen pressures up to 4.5 MPa were used. $Mg_3Y_2Zn_3$ decomposes primarily into YH_2 and MgZn and secondarily into MgH_2, YH_3 and Mg_4Zn_7 or $MgZn_2$. No solid solution of hydrogen in $Mg_3Y_2Zn_3$ was observed, prior to the following reactions: (1) $Mg_3Y_2Zn_3(s) + H_2(g) \rightarrow YH_2(s) + MgZn$, (2) $YH_2(s) + H_2(g) \rightarrow YH_3(s)$, and (3) $MgZn + H_2(g) \rightarrow MgH_2(s) + Mg_4Zn_7(s)$ or $MgZn_2(s)$. The $[YH_2]/[YH_3]$-ratio is strongly dependent on the hydrogenation pressure. For hydrogen desorption in an argon atmosphere at 400°C, the previously reported Mg_3YZn_6 is obtained: $MgH_2(s) + YH_3(s) + MgZn_2(s) \rightarrow Mg3YZn_6(s) + YH_2(s) + H_2(g)$. Detailed results will be presented. [1] E. M. Padezhnova. *Russian Metallurgy (Metally).* 185-188 (1981).

O-079 **Symmetry Analysis of Hydrogen Related Structural Transformations in Laves Phase Intermetallic Compounds.** W. Sikora, J. Malinowski, H. Figiel, – Faculty of Physics and Applied Computer Science, AGH - University of Science and Technology, Krakow, Poland

The intermetallic compounds of Rare Earths and Yttrium with 3-d metal compounds easily absorb hydrogen, which enters the interstitial positions [1,2]. There are analysed all possible transformations of the parent face-centred cubic structure, with symmetry space group F d-3m leading to the structures of lower symmetry, without changes in the translation properties (corresponding the k=(0,0,0)) and selected transitions to the translation subgroup corresponding k=(0,0,1). In such structures of lower symmetry the positions of RE and 3d metal can remain the same, but the hydrogen interstitial positions split into subgroups with differentiated local symmetries and abundances. The hydrogen interstitial positions A2B2 type (96g Wyckoff sites) and AB3 type (32e Wyckoff type) are taken in to account. The cases with displacements of R and 3d metal atoms are also considered. In the present work all transformations allowed by symmetry rules are presented and discussed with the aim to analyse and understand the conditions determining phase transitions and hydrogen ordering in the Laves phase hydrides. [1] H. Figiel, A. Budziak, J. Żukrowski, G. Fischer, M.T. Kelemen, E. Dormann, J. Alloys Compds, 335, 48(2002); [2] M. Latroche, V. Paul-Boncour, A. Percheron-Guegan, F.Bourre-Vigneron, J. Andre, J.Sol. State Chem., 154, 398(2000).

O-080 **Compton Scattering Studies on the Electronic and Magnetic Structure of Metal Hydrides.** M. Yamaguchi,[1] Y. Kakeno,[1] I. Yamamoto,[1] S. Mizusaki,[2] M. Itou,[3] N. Hiraoka,[3] Y. Sakurai,[3] – [1]Yokohama National University, Yokohama, Japan; [2]Aoyama Gakuin University, Sagamihara, Japan; [3]Japan Synchrotron Radiation Research Institute, Hyogo, Japan

In this paper, we report the recent results of Compton scattering experiments for metal hydrides PdH_x, VD_x, CeH_x and NiH_x. Compton scattering is the inelastic scattering of a photon by an electron, yielding the electron momentum, which is related to the electron wave function. Experimentally, Compton scattering is suitable to metal hydrides because bulky properties can be detected with large probing depth, ambient hydrogen gas is allowable and the measurement is insensitive to lattice imperfections. The present experiment utilized a high quality x-ray source provided from synchrotron radiation and a high resolution Compton spectroscopy and the three-dimensional measurement for single crystals; as a consequence, we obtained much more advanced information on the electronic structure than previous Compton scattering experiments done in 1970-80s. The electron momentum density (EMD) of $PdH_{0.84}$, $VD_{0.64}$ or $CeH_{2.0}$ was three-dimensionally reconstructed from measured directional Compton profiles; then, the Fermi surface (FS) geometry was investigated. The FS of $PdH_{0.84}$ was determined to be the deformed electron sphere with a neck along the [111] direction like Ag metal. This agreed well with the calculated result based on the LDA-FLAPW method. [1, 2]. The difference in FS geometry between $VD_{0.64}$ and V showed that the hole surface which existed at the N-point in V completely disappears in $VD_{0.64}$. The EMD of $CeH_{2.0}$ suggested a peculiar geometry of the FS. The magnetic properties of NiH_x were investigated by the magnetic Compton scattering, which was contributed by the electrons with magnetic moments. The result indicated that the β-phase $NiH_{0.7}$ at room temperature was weakly ferromagnetic with a small magnetic moment $\mu<0.1\mu_B$ where d-like component is nearly cancelled out by the negative sp-like component. [3] In conclusion, the electronic and magnetic properties of metal hydrides have been understood by Compton scattering from the viewpoint of electron momentums. [1] S. Mizusaki, N. Hiraoka, I. Yamamoto, M. Itou, Y. Sakurai and M. Yamaguchi, J. Phys. Soc.72 (2003) 1145; [2] S. Mizusaki, T. Miyatake, N. Sato, M. Itou, I. Yamamoto, Y. Sakurai and M. Yamaguchi, J. Alloys and Comp. 404-406 (2005) 169; [3] S. Mizusaki, T. Miyatake, N. Sato, I. Yamamoto, M. Itou, Y. Sakurai and M. Yamaguchi, Jpn. J. Appl. Phys. 44 (2005) 3939.

O-081 **$LaTM_5$ Hydrides (TM = Fe, Co, Ni): Theoretical Perspectives.** J. F. Herbst, L. G. Hector, Jr., – GM R&D Center, Warren, MI, USA

Systematic theoretical results for $LaTM_5H_n$ materials with TM one of the magnetic transition metals Fe, Co, or Ni are discussed. For TM = Co, Ni the antecedent $LaCo_5$ and $LaNi_5$ intermetallics and hydrides are well known. While no La-Fe compounds exist, $LaFe_5$ hydrides are predicted to form by both Miedema's phenomenological model as well as by first-principles density functional theory (DFT) for several prototype crystal structures. Enthalpies of formation and saturation hydrogen contents derived from Miedema's model and DFT are correlated. Structure-dependent properties including site energetics, electronic densities of states, and magnetic moments obtainable only from *ab initio* work are compared for the three systems.

O-082 **Theory of Complex Hydrides.** O. M. Løvvik,[1] S. M. Opalka,[2] – [1]University of Oslo, Centre for Materials Science and Nanotechnology, Oslo, Norway; [2]United Technologies Research Center, East Hartford, CT, USA

First-principles modelling based on density functional theory is increasingly being used in combination with experiments to assess fundamental properties of materials. Examples of how this may be used in the search for complex hydrides with superior hydrogen storage properties are presented. It is demonstrated how the thermodynamic stability of known and hypothetical hydrides may be estimated from simple ground-state calculations, and how such calculations may be improved by using phonon calculations to represent the temperature dependence. The doping hypothesis of Ti additives to $NaAlH_4$ may also be tested by similar calculations, and it is explained how a careful use of reference systems for calculating the substitution enthalpy must lead us to abandon the simplest form of the hypothesis. It is finally shown how the surface most probably plays a crucial role in the hydrogenation and dehydrogenation dynamics of such materials.

O-083 **Vibrational Properties of TiH_n (n=0-8) Complexes Adsorbed on Carbon Nanostructures.** W. Zhou,[1,2] J. Iñiguez,[3] T. Yildirim,[1] – [1]NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD, USA; [2]Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA, USA; [3]Institut de Ciencia de Materials de Barcelona, Campus de la UAB, Bellaterra, Spain

According to recent theoretical studies [1-4], light transition metal coating of carbon based nano-structures provides a route towards high capacity hydrogen storage via Kubas interactions. Vibrational spectroscopies are the ideal experimental techniques to confirm these predictions regarding the metal--hydrogen bonding (of about 0.5 eV/H_2 molecule) which is expected to enable H_2 desorption at moderate temperatures. Here we report first-principles results of the vibrational spectrum of representative systems, namely, TiH_n complexes adsorbed on fullerenes and small organic molecules. The obtained distinctive features should be found in a successful experimental realization of these materials. [1] T. Yildirim and S. Ciraci, Phys. Rev. Lett. **94**, 175501 (2005); [2] Y. Zhao, Y.-H. Kim, A.C. Dillon, M.J. Heben, and S.B. Zhang, Phys. Rev. Lett. **94**, 155504 (2005); [3] T. Yildirim, J. Iñiguez, and S. Ciraci, Phys. Rev. B **72**, 153403 (2005); [4] E. Durgun, T. Yildirim, S. Ciraci, cond-mat 0609068 (2006).

O-084 **A First Principles Study of Active Species in Ti-doped Sodium Aluminum Hydride Surfaces.** J. Liu, Q. Ge, – Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, IL, USA

Density function theory slab calculations have been carried out to investigate the stability of Ti-doped $NaAlH_4$ surfaces and catalytic mechanism of Ti-doping. We found that Ti atom energetically prefers the interstitial positions and interacts with three neighboring $(AlH_4)^-$ groups in two low-index surfaces: (001) and (100), and leads to the formation of a local $TiAl_3H_x$ complex. Consequently, the hydrogen desorption energies from the $TiAl_3H_x$ complex are reduced significantly relative undoped surface. Electronic structure analysis revealed that the antibonding interaction between Ti-Al σ bonding orbitals and H s-orbital contributed to the reduction of hydrogen desorption energy. This complex could be a precursor state for the formation of $TiAl_3$ alloy that was observed experimentally and may play important roles in reversible hydrogenation/dehydrogenation from Ti-doped $NaAlH_4$. The role of the $TiAl_3H_x$ species in catalytic dehydrogenation of Ti-doped $NaAlH_4$ is further supported by both reduced hydrogen desorption energy from the neighboring AlH_4^- and easy transferring of hydrogen to the complex from the neighboring AlH_4^-. The effect of other dopants such as Sc and V was also explored.

ORAL PRESENTATIONS (O-085 to O-108) **Wednesday, October 4 (see schedule)**

O-085 **NMR to Determine Rates of Motion and Structures in Metal-Hydrides.** M. S. Conradi,[1] T. M. Ivancic,[1] M. Mendenhall,[1] C. D. Browning,[2] P. H. L. Notten,[3,4] W. P. Kalisvaart,[4] N. L. Adolphi,[5] R. C. Bowman, Jr.,[6] – [1]Washington U., Dept. of Physics, Saint Louis, MO, USA; [2]Legget and Platt, Inc., Carthage, MO, USA; [3]Philips Research Laboratory, Eindhoven, The Netherlands; [4]Eindhoven University of Technology, Eindhoven, The Netherlands; [5]New Mexico Resonance, Inc., Albuquerque, NM, USA; [6]Jet Propulsion Lab., Caltech, Pasadena, CA, USA

Measurements of nuclear magnetic resonance relaxation times allow the rates of H and D motion in metal-hydrides to be determined. A first example compares the rates of H motion in the newly developed electrode material $Mg_{65}Sc_{35}Pd_{2.4}H_x$ with x = 220 to the well-known $LaNi_5H_x$ and its Ni-substituted analogs. A second example is the so-called anomalous relaxation found at and above 800 K in several metal- hydrides. There, relaxation measurements reveal that rapid H exchange between metal and gas phases, not a new motion, is responsible for the additional relaxation. Finally, magic-angle spinning (MAS) NMR of metal-deuterides can reveal multiple inequivalent D-sites and the rate of motion between them. The examples YD_{2+x} and $ZrNiD_x$ are discussed.

O-086 **Characterization of H and D Motion in $ZrNiH_x$ and $ZrNiD_x$ by NMR Relaxation Times.** T. M. Ivancic,[1] C. D. Browning,[2] R. C. Bowman, Jr.,[3] M. S. Conradi,[1] – [1]Washington U., Dept. of Physics, Saint Louis, MO, USA; [2]Leggett and Platt, Inc., Carthage, MO, USA; [3]Jet Propulsion Lab., Caltech, Pasadena, CA, USA

Relaxation studies of the intermetallics $ZrNiH_x$ and $ZrNiD_x$ were performed using hydrogen and deuterium NMR in the beta (x = 0.85) and gamma phases (x = 2.6 and 3.0). Correlation times for atomic diffusion in the hydride were determined based on the temperature dependence of spin-lattice and spin-spin relaxation times. The hydrogen motion is shown to be thermally activated over the temperature range 300-550 K, and the activation energies for diffusion are determined. The deuterium NMR spectra exhibit incomplete line narrowing with temperature, indicating that the average electric field gradient is not zero when averaged over the deuterium atom sites of these non-cubic unit cells. The temperatures of minima in T1 and T2 for the deuterides indicate that the motion rates are similar for the D and H systems. However, the activation energies taken from the temperature dependences of the deuterides' T1 and T2 are much smaller than for the hydrides, indicating the deuteride relaxation rates have additional contributions. The spectrum of $ZrNiD_{1.87}$ reveals a coexistence of two phases, in agreement with the phase diagram.

O-087 **Effect of Inclusions in Steels on Hydrogen Diffusion and Trapping Examined by Tritium Autoradiography.** T. Otsuka,[1] H. Kawazoe,[2] K. Hashizume,[1] T. Tanabe,[1] – [1]Faculty of Engineering and Sciences, Kyushu University, Fukuoka, Japan; [2]Interdiciplinary Graduate School of Engineering and Sciences, Kyushu University, Fukuoka, Japan

Tritium autoradiography (TARG) developed in 1970s has designated various chemical species as hydrogen (H) trapping inclusions. However the inclusions are generally very small and hence the details of H trapping and its effect on H embrittlement are still unclear. In the present study, we have made pseudo-binary alloys of iron matrix with candidate inclusions (either oxide; Al_2O_3, carbide; TiC, Cr_3C_2 or sulfide; MnS: 5 mol% each and Fe: balance) by sintering and studied tritium (T) diffusion and trapping in the alloys. After H (T) loading, released T was monitored at temperatures between 263 K and 323 K by a liquid scintillation counting method. TARG was also taken for sample surfaces with specified time intervals after the loading. The apparent diffusivities of H for the alloys determined from the time sequence of the T release were less than that for sintered Fe without any inclusions. Among all, MnS showed the least diffusivity with the highest activation energy. TARGs clearly indicated strong tritium trapping in MnS at the lowest temperature. However, at RT, owing to the largest activation energy, T release from MnS was observed. In addition, T depletion in surrounding Fe matrix was observed. This indicates that MnS first attracts H in surrounding matrix and release afterward. Thus H trapping in the inculsions in steels is strongly temperature dependent and sequential TARG studies are very useful for that.

O-088 **Tunnel Splitting of Excited Optical Vibrational States of Hydrogen in α-Mn.** V. E. Antonov,[1] S. M. Bennington,[2] V. K. Fedotov,[1] A. I. Kolesnikov,[3] – [1]Institute of Solid State Physics RAS, Chernogolovka, Russia; [2]Rutherford Appleton Laboratory, Oxon, UK; [3]IPNS, Argonne National Laboratory, Argonne, IL, USA

Hydrogen atoms form an unusual sublattice in the α-$MnH_{0.07}$ high-pressure phase and occupy interstitial positions arranged in dumb-bells about 0.7 Å long [1]. This small distance results in a giant tunnel splitting of 6.4 meV of the ground state of H vibrations [1,2]. The present paper deals with tunnel splitting of the first and second excited vibrational states. An inelastic neutron scattering study of α-$MnH_{0.07}$ at $T = 20$ K revealed four peaks of about equal intensity centred at 74, 107, 130 and 190 meV and a broad band from 80 to 170 meV with a 3 times higher intensity. A study of the peaks intensity as a function of the neutron momentum transfer showed that the 74, 107 and 130 meV peaks belong to the first optical band, while the 190 meV peak to the second band. Model calculations demonstrated that the 74 and 107 meV peaks, respectively, correspond to excitations of the lower and upper levels of the split first excited state of H vibrations along the axis of the dumb-bell, the 190 meV peak corresponds to the lower level of the second excited state and the 130 meV peak together with the broad band are due to the H vibrations in the plane perpendicular to the tunnelling axis. The splitting of the first excited state therefore reaches about 33 meV, which is by an order of magnitude stronger than in any other tunnelling Me-H system. [1] V. K. Fedotov et al., J. Phys.: Condens. Matter 10 (1998) 5255; [2] V. E. Antonov et al., J. Alloys Compd. 330–332 (2002) 462.

O-089 **Nanostructured Magnesium Hydride for Pilot Tank Development.** P. de Rango,[1,2] A. Chaise,[1,2] J. Charbonnier,[1,2] D. Fruchart,[1] M. Jehan,[3] Ph. Marty,[4] S. Miraglia,[1] S. Rivoirard,[2] N. Skryabina,[1] – [1]Laboratoire de Cristallographie, CNRS, Grenoble, France; [2]CRETA, CNRS, Grenoble, France; [3]MCP Technologies, Romans sur Isère, France; [4]Laboratoire des Ecoulements Géophysiques et Industriels, Grenoble, France

The aim of the present work is a systematic investigation on MgH_2 co-milled with transition metals, in order to develop large batches of suitable materials for hydrogen storage. Systematic ball-milling operations were done using a planetary miller (Fritsch), thus leading to combine the transition metal M with MgH_2 to form richer and richer MH_x hydrides. The co-milling conditions we optimized in-lab were transferred to MCP Technologies Co, where highly reactive 1 kg batches of powder**s** were processed. A small scale MgH_2 tank was developed. Absorption and desorption cycles have been operated in many different conditions (T, P, time, cooling down, cycling…). Immediately after hydrogen absorption starts, the temperature of the bed of metal powder reaches equilibrium, which stands up to the end of the absorption process, thus slowing the H_2 absorption rate. When starting at 280°C, a relative mass of ~ 5.8 % wt is absorbed. Desorption tests have been performed starting at different temperatures. Due to the endothermic reaction, and in order to maintain a constant mass flow, a starting initial desorption temperature of 350°C is needed. Numerical simulations mapping the heat and mass transfers during the hydrogenation/dehydrogenation steps were computed using the Fluent software and a finite elements method. Comparison with experimental data allows a better understanding of the tank behavior.

O-090 **Hydrogen Uptake in Mg:C Multilayers - Interface Effects on the Binding Energy in the Hydride Layer MgH_2.** A. S. Ingason, A. K. Ericsson, S. Ólafsson, – Science Institute, University of Iceland, Reykjavik, Iceland

Hydrogen uptake in multilayers and superlattices grown from two different materials is an excellent way to study the effects of interfaces on the binding energy of hydrogen in novel nanoscale materials. Here we report on the growth of Mg:C multilayers with varying amount of Mg in between carbon layers. The structure and chemical composition of the samples is studied with X-ray diffraction, and XPS measurements. The hydrogen uptake is studied by resistance measurements, to obtain information about the kinetic and thermodynamic properties of such a system.

O-091 **Use of Super Critical Fluid Process to Deposit Nanoplot of Ni and Pd on Mg Powder Surface - Improvements of the Hydrogen Sorption Cyclability.** J.-G. Roquefere,[1] J. L. Bobet,[1] C. Aymonier,[1] F. Cansell,[1] K. Asano,[2] E. Akiba,[2] – [1]Institut de Chimie de la Matière Condensée de Bordeaux (ICMCB), CNRS, Université Bordeaux, Pessac, France; [2]National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki, Japan

Hydrogen is now one of the potential vectors of energy for the future. To overcome the problems of hydrogen storage, many works are focused towards the development of new materials. In this study, new composites materials Mg @ metal catalysts (Ni or Pd) are synthesized with an original route, the chemical fluid deposition process in supercritical fluids [1]. The two studied materials (Mg @ Ni and Mg @ Pd) show the potentiality of the CFD route in supercritical fluids to decor surfaces with a structuration from the micrometer scale down to the nanometer one. Regarding hydrogen sorption, the catalytic effect of Ni is higher than the one of palladium. The cyclability is hugely improved with “SCF materials” in comparison with ball milling ones because the catalysts stay always on the magnesium particle surface. The interaction between nanoplot and magnesium powder surface were studied mainly by XPS and the “chemical bonding” between FSC plots and Mg was estimated and the relationship between hydrogen sorption properties and the “bonding” was established. Moreover a comparison between Mg+Ni obtained by SFC method and mechanical alloying method [2] will be presented and the different behaviour was explained in term of such “bonding”. [1] F. Cansell, C. Aymonier, A. Loppinet-Serani, Current Opin. Solid State Mater. Sci., 7, **2003**, 331; [2] R. Janot, X. Darok, A. Rougier, L. Aymard, G.A. Nazri and J.-M. Tarascon, Journal of Alloys and Compounds, In Press, Corrected Proof, Available online 20 July 2005.

O-092 **Hydrogen Storage Properties of Na-Li-Mg-Al-H Complex Hydrides.** X. Tang,[1] S. M. Opalka,[1] B. L. Laube,[1] D. L. Anton,[2] R. F.-J. Wu,[3] J. R. Strickler,[3] – [1]United Technologies Research Center, East Hartford, CT, USA; [2]Savannah River National Laboratory, Aiken, SC, USA; [3]Albemarle Corporation, Baton Rouge, LA, USA

Lightweight complex hydrides have attracted attention for their high storage capacity. $NaAlH_4$ has been widely studied as a hydrogen storage material for its favorable reversible operating temperature and pressure range for automotive fuel cell applications. The increased understanding of $NaAlH_4$ has led to an expanded search for high capacity materials in mixed alkali, and akali/alkaline earth alanates. In this study, promising candidates in Na-Li-Mg-Al-H system were evaluated using a combination of experimental chemistry, atomic modeling, and thermodynamic modeling. New materials were synthesized using solid state and solution based processing methods. Their hydrogen storage properties were measured experimentally, and the test results were compared with theoretical modeling assessments.

O-093 **Tailored Nanoscale Porosity in Carbide-Derived Carbons: Optimization for High Capacity Hydrogen Storage.** J. E. Fischer, – Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA, USA

Candidate materials for on-board hydrogen storage can be divided into two broad classes: hydrogen-containing compounds (hydrides, alanates etc) which are cycled by repeated synthesis and decomposition; and cryosorbers (carbons, MOFs) which cycle by adsorption and desorption under different thermodynamic conditions. The simplest conceptual approach to cryosorbers implies that maximizing total pore volume will optimize the H_2 capacity. We have shown empirically that this is not true for carbide-derived carbon (CDC) materials. These are obtained by "burning" mineral carbides in chlorine; metals and metalloids are driven off as volatile chlorides, while the remaining carbon skeleton collapses into an amorphous sp^2-coordinated material with controllable pore size, size distribution and total pore volume. In CDC, the smallest pores (less than 1 nm diameter) provide most of the capacity while larger ones contribute only marginally except at elevated pressure. Strategies for optimizing CDC storage capacity include maximizing the volume and accessibility of small pores, enhancing the heat of adsorption by chemical modification of binding sites, and fully utilizing a distribution of pore sizes over a wide but practical pressure range. Recent progress along these lines will be described. Synthetic variables include choice of precursor carbide (in particular M/C stoichiometry and crystal structure); chlorination temperature, time and flow rates; and precursor morphology. Post-processing strategies include annealing in hydrogen to improve access to the pores, "activation" to increase the specific surface area (SSA) and "doping" to modify the binding energetics. Our experimental methods include specific surface area (SSA) from Ar, N_2 and H_2 sorption experiments, NLDFT pore size distribution (PSD) analysis, high pressure Sieverts isotherms, Raman and x-ray scattering. These are complemented by high level theory and computational modeling to identify promising materials and processes. This work is a collaboration with G. Laudisio and J. P. Singer (Penn); R. K. Dash, G. Yushin and Y. Gogotsi (Drexel); and T. Yildirim and W. Zhou (NIST). The program is supported by DOE-EERE Grant No. DE-FC36-04GO14282.

O-094 **Saturated High-Pressure Hydrofullerenes $C_{60}H_{60}$ and $C_{60}D_{60}$.** I. O. Bashkin,[1] A. V. Bazhenov,[1] T. N. Fursova,[1] A. P. Moravsky,[2] O. G. Rybchenko,[1] V. V. Shestakov,[1] Yu. M. Shulga,[3] V. E. Antonov,[1] – [1]Institute of Solid State Physics RAS, Chernogolovka, Moscow District, Russia; [2]MER Corporation, Tucson, AZ, USA; [3]Institute of Problems of Chemical Physics RAS, Chernogolovka, Moscow District, Russia

Hydrofullerenes $C_{60}H_x$ with the compositions up to $x = 36$ have been a subject of an extensive study, but synthesis of higher hydrofullerenes is still a challenge that can be accomplished with the use of high hydrogen pressure. In this work we treated the C_{60} fullerite under hydrogen pressure of 50 kbar at temperatures to 500°C and prepared stoichiometric compounds, $C_{60}H_{60}$ and $C_{60}D_{60}$, whose composition corresponds to saturation of the C-atom bonds. The recovered compounds are characterized at normal conditions by means of the X-ray diffraction and infrared optic measurements. Characteristic of the IR optic absorption spectra of $C_{60}D_{60}$ and $C_{60}H_{60}$ is a drastically reduced number of the vibrational peaks compared to $C_{60}H_{36}$, which is indicative of a high symmetry of the $C_{60}H(D)_{60}$ molecules. The X-ray diffraction patterns show that the samples contain two crystalline phases and a considerable amount of the amorphous phase. The crystalline phases have the *bcc* and *fcc* structures with the lattice parameters of a = 12.2 - 12.3 Å and a = 15.3 - 15.5 Å, respectively. The new hydrofullerenes are well soluble in toluene. A mass-spectrometric study of the compounds is under way.

O-095 **Magnesium-Carbon Nanocomposites for Hydrogen Storage?** R. W. Wagemans, T. M. Eggenhuisen, K. P. de Jong, P. E. de Jongh, – Inorganic Chemistry - Utrecht University, Utrecht, The Netherlands

For hydrogen storage in mobile applications strict requirements regarding storage density, charging times (sorption kinetics), and operating temperature and pressure (sorption thermodynamics) are set. Light-weight metal hydride systems promise to meet these goals. Kinetic limitations can be alleviated by reducing grain sizes with ball-milling, and adding catalysts. However, it remains a challenge to also meet thermodynamic requirements (reversible hydrogen desorption at 100-150 °C). Recently it has been shown that the hydrogen desorption enthalpy of a given material can be altered by reducing crystal grain sizes to 1-2 nm or below, presenting an option to lower the unfavourable high desorption temperature of 300° C for MgH_2.This has encouraged us to explore routes for the preparation of nanometer-sized metal(hydride)s, for fundamental studies, but keeping practical application in mind. For bulk systems, particle sizes down to 15-20 nm can be achieved by ball-milling, but smaller crystallite sizes (and their stabilisation upon cycling) are a challenge. We present results on a novel route for the preparation of nanosized Mg. A carbon matrix was employed to achieve small particle sizes, with intended Mg loadings up to 50 wt%. Carbon is attractive as it is light (relatively low impact on gravimetric storage density) and inert (limited oxidation of active material). Two different systems will be presented, with either 2-5 nm Mg particles, or crystallite sizes well below 2 nm.

O-096 **Neutron Spectroscopy Study of Single-Walled Carbon Nanotubes Hydrogenated under High Pressure.** A. I. Kolesnikov,[1] I. O. Bashkin,[2] V. E. Antonov,[2] D. Colognesi,[3] J. Mayers,[4] A. P. Moravsky,[5] – [1]IPNS, Argonne National Laboratory, Argonne, IL, USA; [2]Institute of Solid State Physics RAS, Chernogolovka, Moscow District, Russia; [3]Consiglio Nazionale delle Ricerche, Istituto di Fisica Applicata 'Nello Carrara', Sesto Fiorentino, Italy; [4]ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon, UK; [5]MER Corporation, Tucson, AZ, USA

New carbon nanomaterials (e.g., nanotubes, fullerenes, nanofibers) are very exciting molecular systems because of their large potential for the nano-scale technological applications and the prospects for hydrogen storage. Due to their unique crystal structures, the materials are also very attractive for the fundamental research. In the present work the single-walled carbon nanotubes (SWNT) were hydrogenated at a hydrogen pressure of 30 kbar and T = 620 K, quenched to 80 K and then studied by inelastic neutron scattering (INS) in the range of the neutron energy transfer 3 to 400 meV. INS spectra were measured first on the quenched hydrogenated sample and then on the same sample annealed at 332 and 623 K. The obtained spectra showed that the quenched sample had hydrogen covalently bound to the carbon atoms of SWNT (thus revealing that the sample was constructed of new SWNT&H "macromolecules") and molecular hydrogen on interstitial positions that exhibited nearly free rotational behavior. The larger part of H_2 molecules (~65%) left the sample after the first annealing at 332 K, but the remaining H_2 molecules (~35%) were still contained in SWNT&H. Final evolution of the H_2 molecules from the sample occurred upon the second annealing at 623 K. The covalently bound hydrogen was still observed after the second annealing. The paper will present the analysis of the SWNT&H vibrational spectra and comparison with the spectra of fullerene C_{60} hydrogenated under similar conditions.

O-097 **Sieverts Apparatus and Methodology for Accurate Determination of Hydrogen Uptake by Light-Atom Hosts.** T. Blach, E. Gray, – Nanoscale Science and Technology Centre, Griffith University, Brisbane, Australia

The most popular techniques for measuring hydrogen uptake by a solid host, the Sieverts technique and gravimetry, lose accuracy as the density of the host material decreases. The resultant loss of reliability is becoming a serious technical problem as interest in high-capacity hydrogen storage hosts based on Li, B, C, N, Mg etc. atoms rises in the pursuit of the US Department of Energy mass density criteria (6 wt% by 2010; 9 wt% by 2015). In addition to the problem of sensitivity to heavy impurity species, accurate gravimetry requires a buoyancy correction, which becomes more significant as the sample density decreases and, moreover, varies with the hydrogen content of the sample. The problem with the Sieverts method has the same origin, namely the difficulty of accurately defining and measuring the dead-volume occupied by low-density sample with an effective dimensionality between 2 and 3. The uncertainty in hydrogen concentration determined by the Sieverts method may be several tens of percent and has been in our view a likely contributor to the controversy over hydrogen uptake by nanostructured carbons. Owing to its cheapness, robustness, portability and simplicity, we focus on the Sieverts technique. We show that a simple modification of the Sieverts apparatus greatly decreases the sensitivity to the sample density and so makes the uncertainty in hydrogen content acceptable. The methodology is illustrated with measurements of hydrogen uptake by K-intercalated graphite.

O-098 **An Overview of Analytical Techniques Being Used to Characterize Today's Most Advanced Hydrogen Storage Materials.** N. T. Stetson,[1] K. J. Gross,[2] – [1]Hy-Energy LLC, Lake Orion, MI, USA; [2]Hy-Energy LLC, Newark, CA, USA

The wide variety of materials being proposed for hydrogen storage today present a number of different challenges to the researcher from an analytical characterization perspective. These include both evaluating the true performance of the materials for real-world applications as well as understanding the underlying physical mechanisms controlling the materials properties. An overview will be presented on the state-of-the-art analytical methods for characterizing the hydrogen storage properties of materials. Some challenges to measurements on particular types of materials or conditions will be discussed.

O-099 **Microstructural Changes in the Multi-Phase $Nb_{40}Ti_{30}Co_{30}$ Alloy by Rorring-Annealing Techniques and Their Hydrogen Permeability.** K. Ishikawa, S. Tokui, K. Aoki, – Kitami Institute of Technology, Kitami, Hokkaido, Japan

The present authors have demonstrated that the as-cast Nb-Ti-Co alloys, consisting of the B2-TiCo intermetallic compound and the bcc- (Nb, Ti) solid solution, show higher hydrogen permeability Φ than that of pure Pd, and large resistance to the hydrogen embrittlement. Since hydrogen flux through the alloy membrane increases inversely with decreasing its thickness, the preparation of alloy foils is one of the most important technological issues for developing high performance hydrogen permeation alloy membrane. In this paper, $Nb_{40}Ti_{30}Co_{30}$ (mol%) alloy foils are prepared using the rolling-annealing techniques, and the relation between microstructure and hydrogen permeability Φ is discussed on the basis of the experimental results.The as-cast $Nb_{40}Ti_{30}Co_{30}$ alloy consists of the primary (Nb, Ti) and the eutectic {TiCo+(Nb, Ti)} phases. The Value of Φ for this alloy is higher than that of pure Pd at 673 K, but decreases by reduction in thickness by cold rolling. The eutectic {TiCo+(Nb, Ti)} lamellar microstructure disappears and is replaced by the (Nb, Ti) precipitates embedded in the TiCo matrix by heat treatment. The value of Φ for this alloy increases with increasing annealing time, and recovers to its original value. The present work demonstrates that rolling-annealing techniques are the useful way for the preparation of the hydrogen permeation Nb-Ti-Co alloy membrane. This work was supported by New Energy and Industrial Technology Development Organization (NEDO) of Japan.

O-100 **Usable Capacity as a Criterion for Searching for Optimal Hydrogen Storage Nanomaterials.** H. Lee, W. I. Choi, J. Ihm, – School of Physics, Seoul National University, Seoul, Korea

Recently, nanostructured materials receive special attention as a novel hydrogen storage medium because of potentially large storage capacity, safety, and fast filling and delivering from the fuel tank (short molecular adsorption and desorption time). It has been reported that, through first-principles calculations, Sc-decorated fullerenes and Ti-decorated carbon nanotubes can store hydrogen up to 8.8 and 7.7 wt % in gravimetric density, respectively [1,2]. However, we show here, when the thermodynamic behavior of the gas under realistic environments is taken into account, the *usable* amount of hydrogen with these nanomaterials falls far short of the desired capacity for practical applications. The adsorption probability of hydrogen molecules on the storage material is calculated as a function of the pressure and temperature. We propose an occupation number-pressure-temperature (f-p-T) diagram (which is the counterpart of the widely-used pressure-composition isotherms (PCI) in metal hydride storage) as a criterion for comparing "thermodynamically usable" storage capacity of different nanomaterials. In practical situations, the usable capacity is found to be only one-half of the maximum storage capacity. We also report that the zero-point vibration energy calculated using the density functional theory with the generalized gradient approximation reduces the adsorption energy of H_2 molecules by as much as 25 %. [1]. Y. Zhao, *et al*. Hydrogen Storage in Novel Organometallic Buckyballs. Phys. Rev. Lett. 94, 155504 (2005); [2]. T. Yildirim & S. Ciraci, Titanium-Decorated Carbon Nanotubes as a Potential High-Capacity Hydrogen Storage Medium. Phys. Rev. Lett. 94, 175501 (2005).

O-101 **Effect of Nb Addition on the Terminal Solid Solubility of Hydrogen for Zr and Zircaloy-4.** M. Ito, K. Ko, H. Muta, M. Uno, S. Yamanaka, – Division of Sustainable Energy and Environmental Engineering, Graduate School of Engineering, Osaka University, Suita, Osaka, Japan

The integrity of Zr based alloys for fuel cladding materials has become more important because of high burnup of nuclear fuels. Hence, Nb containing Zr alloys viz., NDA, MDA, and ZIRLO have been newly introduced to improve corrosion resistance and mechanical strength. However, it was reported that Zr alloys absorb a part of evolved hydrogen by the corrosion reaction. If the total hydrogen concentration in the alloy exceeds the solubility limit, brittle Zr hydrides were formed as precipitates in the alloy, which deteriorates the material strength. Therefore, it is important to elucidate the terminal solid solubility of hydrogen (TSS) for the Zr alloys. In the present study, the TSS of Zr-Nb binary alloys with different Nb contents and Nb additive Zircaloy-4 were examined and the effects of Nb addition on the TSS were discussed. Zr-1.0Nb (Zr-1.0 wt% Nb) and Zr-2.5Nb, which were $\alpha + \beta$ biphasic specimens, and Nb additive Zircaloy-4 were prepared. Single-phase α-Zr and β-Zr specimens with different Nb contents were also prepared in order to discuss the results of the biphasic specimens. The alloys were hydrogenated by a modified UHV Sieverts' apparatus, and then the TSS of the specimens was evaluated using a differential scanning calorimeter (DSC). It was found that Nb addition led to increase TSS of Zr and Zircaloy-4 by the effect of the β-Zr precipitate which has much higher TSS. These results were further discussed from the thermodynamic point of view.

O-102 **Hydrogen Permeation and Embrittlement of Ni- and Zr-based Amorphous Alloys.** K.-B. Kim,[1] D.-Y. Lee,[1] S. Jayalakshmi,[1] E. Fleury,[1] Y.-S. Song,[2] – [1]Korea Institute of Science and Technology, Seoul, South Korea; [2]Amosense Co. Ltd, Gimpo city, Gyunggi-Do, South Korea

Amorphous alloys constitute a novel class of materials characterized by a random distribution of atoms which make them attractive for industrial applications [1]. In this paper, the hydrogen permeation and embrittlement of Ni- and Zr-based amorphous alloy will be reported. The hydrogen permeability was measured at various temperatures under a different hydrogen gas pressure. Commercialized $Pd_{60}Cu_{40}$ alloy membranes were also evaluated for the comparison. The permeated hydrogen flux increased with increasing temperature and difference in the square-roots of hydrogen pressures difference between feed side and permeate side

of the membrane. It is indicated that the diffusion of hydrogen atoms is the main factor for the hydrogen permeation in this alloy. The maximum hydrogen permeability of the Ni-based amorphous alloy was much higher than that of $Pd_{60}Cu_{40}$ membranes. Also, the susceptibility of hydrogenated amorphous alloys to hydrogen embrittlement was examined. Mechanical tests were conducted with respect to a hydrogenated hydrogen concentration. The structural changes that occur due to hydrogenation were investigated, which would be directive in understanding the phenomenon of hydrogen embrittlement. These hydrogen permeation and embrittement characteristics imply the possibility of future practical use of the amorphous alloys as the hydrogen permeable membrane. [1] A. Inoue, Acta Mater., 48(2000) 279.

O-103 **Novel Hydrides of RMn_2 Laves Phases Synthesized under Hydrogen Pressure.** S. M. Filipek,[1] V. Paul-Boncour,[2] R. S. Liu,[3] F. Bourée,[4] G. André,[4] H. D. Yang,[5] R. Wierzbicki,[1] S. Mylswamy,[3] – [1]Institute of Physical Chemistry, Polish Academy of Sci., Warsaw, Poland; [2]Laboratoire de Chim. Métall. des Terres Rares, CNRS, Thiais, France; [3]Department of Chemistry, National Taiwan University, Taipei, Taiwan ROC; [4]Laboratoire Léon Brillouin,CEA-CNRS, CEA/Saclay, Gif-sur-Yvette, France; [5]Department of Physics, National Sun Yat-Sen University, Kaoshiung, Taiwan, ROC

Recently a novel hydride YMn_2H_6 has been synthesized from C15 Laves YMn_2 [1,2] under the hydrogen pressure. According to X-ray and neutron powder diffraction experiments YMn_2H_6 crystallizes in the Fm-3m space group with *a*=6.709(1) Å at 300 K. Thus the initial C15 structure is strongly rearranged to form the structure in which the Y and half of the Mn atoms occupy statistically the 8*c* site whereas the other Mn atoms, located in 4*a* site are surrounded by 6 H atoms (24 *e*). According to our knowledge such kind of hydride has never been observed in hydrides derived from Laves phase intermetallics. We have started a systematic investigation of the synthesis of RMn_2 hydrides (where R is an heavy rare earth) under high hydrogen pressure, in order to check whether other RMn_2H_6 hydrides can be formed. We succeeded to form the same unusual structure in other RMn_2 Laves phases. Several properties of these novel hydrides are presented and discussed. It is very interesting to observe that starting from $ErMn_2$ which crystallizes in the C14 hexagonal structure, it is possible to synthesize cubic $ErMn_2H_6$ which is isostructural to YMn_2H_6 with *a*= 6.679(1) Å. [1] C.Y. Wang, V. Paul-Boncour, C.C. Kang, R.S. Liu, S. M. Filipek, M. Dorogova, I. Marchuk, T. Hirata, A. Percheron-Guégan, H.S. Sheu, L.Y. Jang, J.M. Chen and H.D. Yang, Solid State Comm. **130** (2004) 815; [2] V. Paul-Boncour, S.M. Filipek, M. Dorogova, F. Bourée, G. André, I. Marchuk, A. Percheron-Guégan, R.S. Liu, J. Solid State Chem., **178** (2005) 356.

O-104 **Deuterium Site Occupancies in $Ce_2Ni_7D_4$ and Comparison with $CeNi_3D_{2.8}$.** Y. Filinchuk,[1,2] K. Yvon,[1] – [1]Laboratory of Crystallography, University of Geneva, Switzerland; [2]Current: SNBL at ESRF, Grenoble, France

Ce_2Ni_7 and $CeNi_3$ have closely related but distinctly different crystal structures in which $CaCu_5$-type and $MgZn_2$-type slabs alternate along the hexagonal axes. Both compounds react easily with hydrogen and form so-called "interstitial" hydrides of which one has been structurally characterized ($CeNi_3D_{2.8}$ [1]). In spite of the structural differences their hydrogen equilibrium pressures at 50°C do not much differ: 0.2 bar for $Ce_2Ni_7H_x$ and 0.1 bar for $CeNi_3H_x$. In contrast to the hexagonal $La_2Ni_7D_{6.5}$ analogue [2] $Ce_2Ni_7D_4$ shows an orthorhombic distortion. A comparison with $CeNi_3D_{2.8}$ shows that in both compounds deuterium enters only the $MgZn_2$-type slabs, resulting in an anomalous expansions along the hexagonal axes (~21% for $Ce_2Ni_7D_4$, ~30% for $CeNi_3D_{2.8}$), while their basal planes remain nearly unchanged. Both deuterides dispay Ni atoms having deformed tetrahedral D atom configurations: Ni-D bond lengths and D-Ni-D bond angles range 1.52-1.95 Å and 74-127°, respectively. These findings not only provide further evidence for directional bonding effects in hydrides that are traditionally considered as "interstitial" [3], but also suggest that the thermal stability of metal hydrides having composite crystal structures can be correlated with metal-hydrogen bond formation/breaking in specific structural units. [1] V. A. Yartys et al., J. Alloys Compd. 356-357 (2003) 109; [2] V. A. Yartys et al., J. Alloys Compd. 408-412 (2006) 273; [3] Y. E. Filinchuk et al., J. Alloys Compd. 413 (2006) 106.

O-105 **Neutron Scattering Studies of Hydrogen in Carbon Materials.** C. M. Brown,[1,2] Y. Liu,[2,3] D. A. Neumann,[2] – [1]Indiana University Cyclotron Facility, Indiana University, Bloomington, IN, USA; [2]NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD, USA; [3]Department of Materials Science and Engineering, University of Maryland, College Park, MD, USA

Hydrogen adsorption on nanoporous carbons has received considerable attention since the early report of as much as 10 wt% hydrogen reversibly stored on single-walled carbon nanotubes (SWNTs) near room temperature [1] and the interest in moving to a hydrogen-based economy. The interest persists because carbon is a light element, able to be produced with very high specific surface areas (≈3000 m^2/g) and in relatively large quantities at relatively low cost. There now seems to be a consensus forming in the research community that if carbon is going to be technologically useful in storing hydrogen, methods must be developed that can enhance the binding energy of H_2 to the carbon framework while maintaining the high specific surface area. Approaches recently reported to increase the binding potential of hydrogen to carbons include decorating with metal catalysts [2] and substituting carbon for boron [3]. In this paper, we present results from inelastic neutron scattering of hydrogen adsorbed upon carbon materials synthesized with the aim of increasing the binding potential. [1] A.C. Dillon, K.M. Jones, T.A. Bekkedahl, C.H. Kiang, D.S. Bethune, M. J. Heben, Nature 386 (1997) 377; [2] T. Yildirim, S. Ciraci, Phys. Rev. Lett. 94 (2005) 175501; [3] Y-H. Kim, Y. Zhao, A. Williamson, M..J. Heben, S.B. Zhang, Phys. Rev. Lett. 96 (2006) 016102.

O-106 **NMR Investigations of Hydrogen Interaction with Metal-Containing Carbon Structures.** J. L. Herberg,[1] L. Li,[1] R. S. Maxwell,[1] T. Baumann,[1] J. Satcher,[1] C. C. Ahn,[2] R. C. Bowman, Jr.,[3] – [1]Lawrence Livermore National Laboratory, Livermore, CA, USA; [2]California Institute of Technology, Pasadena, CA, USA; [3]Jet Propulsion Laboratory, Pasadena, CA, USA

Carbon nanostructures, such as carbon nanotubes and carbon-based aerogels, have received significant attention as hydrogen storage materials due to their low molecular weight, tunable microporosity, and high specific surface areas. Any effort to optimize

the hydrogen storage properties of metal-doped carbon systems will need to be based on a more fundamental understanding of the carbon-metal, carbon-hydrogen, and metal-hydrogen interactions. NMR is an ideal method for determining the structure and dynamics of hydrogen within these materials. In the present study, the metal-carbon composites that will serve as the model systems for this work will be metal-doped carbon aerogels. These materials are ideally-suited for these NMR studies as they can be prepared reproducibly in bulk, unlike other carbon-based materials, and possess many of the essential features important to the metal-nanotube composites, namely the intimate mixing of metals and graphitic carbon on the nanometer scale. ^{1}H and ^{13}C NMR have been performed to develop a fundamental understanding of the carbon-metal, carbon-hydrogen, and metal-hydrogen interactions. In addition, we will present results on pore distribution of the carbon aerogels via xenon NMR techniques. This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory, under contract # W-7405-ENG-48.

O-107 **New Methods to Study Hydrogen Physisorption in Microporous Materials.** B. Panella, M. Hirscher, – Max-Planck-Institut für Metallforschung, Stuttgart, Germany

Physisorption is a promising method for storing hydrogen in solid materials reversibly and at 80 K. It is well known that highly porous materials are the best candidates for physical adsorption of hydrogen. A high specific surface area is a prerequisite for adsorbents to reach high storage capacities[1,2], but it is not the only criterion, which influences the hydrogen uptake. Indeed, parameters like pore size of porous carbon materials[3] or the presence of special metal-centres in metal-organic frameworks (MOFs)[4,5] and polarizing sites in zeolites[6] seem to play and important role in the adsorption of hydrogen. In order to understand the interaction between hydrogen molecules and adsorbing materials new experimental techniques working at low temperatures have to be applied. With a completely novel set-up for thermal desorption spectroscopy which works at temperatures down to 20 K, we investigated the desorption of hydrogen for different classes of microporous materials, focussing on carbon nanostructures and on MOFs. With this technique it is possible to identify the different adsorption sites for hydrogen and the corresponding desorption temperature and, for the first time, to determine quantitatively the amount of hydrogen desorbed. Another technique which is particularly suitable to study molecular adsorption is Raman spectroscopy. We will present newest results obtained using this powerful method for hydrogen adsorbed on different materials with high specific surface area. [1] M.G. Nijkamp, et al., Appl. Phys A 72 (2001) 619; [2] B. Panella, M. Hirscher, S. Roth, Carbon 43 (2005) 2209; [3] Q. Wang, J. K. Johnson. J. Chem. Phys,110 (1999) 577; [4] B. Chen et al., Angew. Chem. Int. Ed. 44 (2005) 2; [5] B. Panella, M. Hirscher, H. Pütter, U. Müller, Adv. Funct. Mater. 16 (2006) 520; [6] L.Regli et al., Phys. Chem. Chem. Phys. 7 (2005) 3197.

O-108 **Inelastic Neutron Scattering in the Study of Hydrogen Storage Materials.** A. J. Ramirez-Cuesta, – ISIS Facility, CCLRC, Rutherford Appleton Laboratory, United Kingdom

Inelastic Neutron Scattering (INS) spectroscopy is an ideal tool to study hydrogen containing materials [1]. It is also very easy to establish comparison between experimental data and theoretical calculations, allowing a straightforward comparison and interpretation of the data when DFT calculations are available [2]. The rotational spectra of molecular hydrogen, does also fall within the range of the TOSCA spectrometer at ISIS [1,3]. The importance of catalyst choice in enhancing kinetics for both hydrogen uptake/release of $NaAlH_4$ is well known but the nature of the active species and mechanism of catalytic action are not yet clear. We measured samples of the materials at different stages of hydrogenation, and using DFT calculations we identified intermediate species formed on the surface of the catalyst that indicate the formation of $(AlH_3)_n$ species [4]. The rotational energy levels of the hydrogen molecule, are very sensitive to the nature and intensity of the interaction with surfaces. The interaction with zeolites and aluminophosphates show a very unusual interaction between the hydrogen molecule and the substrate. [1] PCH Mitchell, SF Parker, AJ Ramirez-Cuesta and J Tomkinson in “Vibrational Spectroscopy with Neutrons” World Scientific, London, (2005); [2] A J Ramirez-Cuesta, Comp Phys Commun 157(2004) 226; [3] AJ Ramirez-Cuesta, PCH Mitchell, SF Parker, PA Barrett Chem Commun (2000)1257; [4] Qi Jia Fu, AJ Ramirez-Cuesta and SC Tsang, J Phys Chem B 110 (2006)711.

ORAL PRESENTATIONS (O-109 to O-157) **Thursday, October 5 (see schedule)**

O-109 **Defining the Location of Ti in the Ti-doped $NaAlH_4$ System.** M. P. Pitt,[1] P. E. Vullum,[2] M. H. Sørby,[1] M. P. Sulic,[3] H. W. Brinks,[1] C. M. Jensen,[3] B. C. Hauback,[1] – [1]Institute for Energy Technology, Kjeller, Norway; [2]Norwegian University of Science and Technology, Trondheim, Norway; [3]University of Hawaii, Honolulu, HI, USA

After almost a decade of research into the behaviour of transition metal additives in the $NaAlH_4$ system, with in the order of 150 citable experimental (20 different experimental methods) and modelling publications, there remains no simple answers to the basic but fundamental questions, a) where is the active Ti, and b) what does it do? In planetary milled samples, some 2/3rd of the added Ti is accounted for as an $Al_{0.85}Ti_{0.15}$ solid solution, however, all attempts at co-milling $NaAlH_4$ with Al-Ti type phases have resulted in poor kinetics. As it is abundantly clear both experimentally and from DFT modelling that bulk substitution is unfavourable, the powder microstructure and powder surface remain as potential locations of kinetically active Ti. We have adopted a simple but powerful geometrical technique, the measurement of crystalline mosaic (domain) size from the diffraction lineshape (high resolution X-ray synchrotron), to determine what, if any influence, Ti additives have on the microstructure. In combination with the measurement of external powder grain dimensions by TEM, we can determine if changes in diffraction lineshape due to Ti addition are the result of internal changes in the powder grain microstructure, or a surface related decrepitation of the external powder grain size. Our study follows the behaviour of Ti rich (up to 10mol%) powders under a range of temperature and pressure conditions, from wet synthesised and ball-milled powders, to hydrogen-cycled powders.

O-110 **Evolution of Ti in $TiCl_3$-doped $NaAlH_4$ – Implications for Hydrogen Storage.** C. P. Baldé,[1] H. A. Stil,[2] A. M. J. van der Eerden,[1] K. P. de Jong,[1] J. H. Bitter,[1] – [1]Utrecht University, Utrecht, The Netherlands; [2]Shell Global Solutions, Amsterdam, The Netherlands

Hydrogen release and absorption rates for NaAlH4 are improved when a Ti-precursor is added [1,2], i.e. Ti functions as a catalyst. However, the exact role and composition of the catalytic Ti species has not been elucidated so far, and has led to contradictory results. In the past years, the characteristics of the Ti have been investigated extensively, but the local structure of Ti in $NaAlH_4$ during hydrogen desorption has not been investigated. In this study, the nature of Ti in $TiCl_3$ doped $NaAlH_4$ was studied as a function of desorption temperature with advanced characterization techniques, such as extended X-ray absorption fine structure (EXAFS), and X-ray absorption near edge structure (XANES). It was observed that the local environment and geometry of Ti changed considerable as a function of the desorption temperature. In the ball-milled sample Ti resided on Al-crystallites, and functions as a nucleation centre for the growth of Al-crystallites during hydrogen desorption. The Al coordination number of Ti increased when the desorption temperature increased, and at desorption temperature ≥ 225 ºC, Ti became encapsulated with Al, and a $TiAl_3$-like alloy was formed. This encapsulation was accompanied by a deactivation of the Ti-catalyst. [1] Bodganovic B., and Schwickardi M., *J. Alloys Compd.* **1997**, *253-254,* 1-9; [2] Haiduc, A.G.; Stil, H.A.; Schwarz, M.A.; Paulus, P.; Geerlings, J.J.C.; *J. Alloys Compd.* **2005**, *393 (1-2)*, 252-263.

O-111 **Advantage of TiF_3 over $TiCl_3$ as a Dopant Precursor to Prepare Catalytically Enhanced $NaAlH_4$ System: Functional Flourine Anion.** P. Wang, L. C. Yin, X. D. Kang, H. M. Cheng, – Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang, P.R. China

TiF_3 is superior to $TiCl_3$ as a dopant precursor to prepare catalytically enhanced $NaAlH_4$ system for reversible hydrogen storage. This is evidenced by the further improved hydrogen storage performance in the TiF_3-doped $NaAlH_4$ system: higher hydrogen capacity, faster de-/hydriding rates and reduced operation temperature/pressure conditions, compared to the $TiCl_3$-doped $NaAlH_4$.[1] In particular, it was experimentally observed that the utilization of TiF_3 instead of $TiCl_3$ resulted in a substantially improved dehydriding performance at second decomposition step (from Na_3AlH_6 to NaH/Al) at moderate temperature.[1] Quite recently, this experimental finding was further supported and well explained by our first-principle computational studies. It was demonstrated that F^- and Cl^- anions differed substantially from each other with respect to the state and function in the doped hydrides. In great contrast to the case of chloride doping where Cl^- anion constitutes the "dead weight" NaCl, the fluoride doping results in a partial substitution of H^- by F^- anion in the hydride lattice and accordingly, a favorable thermodynamic adjustment of the decomposition reaction of Na_3AlH_6. The coupled computational and experimental efforts allow us to put forward a "Functional Anion" concept. This concept renews the current mechanism understanding in the catalytically enhanced sodium alanate, and more significantly it may pave a new way to pursue further improved hydrogen storage performance of complex hydrides for onboard application. [1] P. Wang, X.D. Kang, and H.M. Cheng, *ChemPhysChem* 6 (2005) 2488.

O-112 **Investigations on Hydrogen Desorption over a $LiNH_2$-$LiAlH_4$ (2/1) Mixture.** Z. T. Xiong, P. Chen, – National University of Singapore, Singapore

Solid-state reaction between $LiNH_2$ and $LiAlH_4$ with amide to hydride molar ratio 2/1 was investigated in this study. 4.55wt% of hydrogen was released at room temperature by ball milling two chemicals within a planetary mill. Simultaneously with the observation of phase transformation from tetrahedral $[AlH_4]^-$ in $LiAlH_4$ to octahedral $[AlH_6]^{3-}$ in form of Li_3AlH_6. Solid-sate ^{27}Al NMR identified new chemical shift at ~108ppm, which represented N and H coordinated Al. Together with results from XRD and FTIR existence of a new type of Li-Al-N-H compound was approved. Heating post-milled sample to 400°C resulted in the liberation of additional 5.1wt% of hydrogen. Therefore, with ~8 H atom detached the final product turn to be Li_3AlN_2, over which 4.3wt% of hydrogen was absorbed with $LiNH_2$, LiH, AlN and Li-Al-N-H compound as product.

O-113 **Hydrogen Interactions with the Ordered BCC PdCu Alloy.** S. M. Opalka,[1] Y. She,[1] W. Huang,[2] D. Wang,[3] T. B. Flanagan,[3] S. C. Emerson,[1] T. H. Vanderspurt,[1] – [1]United Technologies Research Center, East Hartford, CT, USA; [2]QuesTek Innovations LLC, Evanston, IL, USA; [3]University of Vermont, Department of Chemistry, Burlington, VT, USA

Combined experimental and modeling studies of hydrogen interactions with ordered BCC PdCu alloys are key to the development of advanced water gas shift (WGS) reactor technologies and the robust membranes they require. The WGS reaction converts CO rich feed like pre-cleaned, oxygen blown coal gas to H_2. Efficient high temperature operation of this equilibrium-controlled reaction is achieved by the separation and purification of the H_2 through sulfur-tolerant hydrogen-selective membranes. Atomic modeling was used to probe the competitive H_2 adsorption, dissociation, and solubilization on PdCu surfaces from H_2O-, CO_x- and S-laden atmospheres. These results were used to describe the surface contributions to H_2 absorption as a function of varying gas composition, temperature, and pressure conditions. Comparative experimental measurements of H solubility in BCC and FCC PdCu alloys were made with a Sievert's type apparatus. This data was assessed, along with existing experimental data and first-principles predicted finite temperature data of hypothetical end-member phases, to develop a thermodynamic description of the ternary Pd-Cu-H system encompassing the BCC PdCu phase. Ground state and lattice dynamics atomic modeling was also used to predict favorable pathways for thermally-activated hydrogen movement within the BCC lattice. The alloy H solubility and diffusivity parameters were used to model the system performance for coal gas WGS conditions.

O-114 **Towards the Design of Stable Pd-based Membranes for Hydrogen Gas Separation: a Statistical Thermodynamics Approach.** D. E. Nanu, A. J. Böttger, – Department of Materials Science and Technology, Delft University of Technology, Delft, The Netherlands

Designing stable membranes for H_2 separation is a crucial issue in the development of technologies for H_2 production. Here a statistical thermodynamics approach for designing new Pd-based membrane materials is put forward. The model is based on the cluster variation method, a proven reliable method to describe phase stabilities of interstitial solid solutions. Both the tetrahedron and the cube approximation can be used to describe the α-metal solid solutions and β-metal hydrides. The advantages and differences of both approaches are discussed. The method allows to predict the α-β phase boundaries of new, not yet developed, *ternary* alloys using effective pair potentials determined based on experimental data of known *binary* alloys. The model takes into account the volume changes during α-β transitions, and the possible order-disorder transitions. The calculations show that the strength of the effective field of the metal sublattice and the relative interaction strength between nearest-neighbor occupied and unoccupied interstitial sites determine the phase boundaries and degree of short-range order. Further, the model is used to design alloys that meet certain criteria such as, e.g., critical temperature for the α-β phase transition below operating conditions, high hydrogen solubility and permeability, minimal stress development, poisoning resistance etc. Examples of using the model in designing new membrane materials for H_2 separation separation are discussed.

O-115 **Alloy Designs for Highly Hydrogen Permeable Nb-Ti-Co Alloys with Large Resistance to Hydrogen Embrittlement.**
K. Aoki, K. Hashi, W. Luo, K. Ishikawa, – Kitami Institute of Technology, Kitami, Japan

High purity hydrogen gas is required for fuel cells. Hydrogen gas produced by steam reforming contains much CO gas that damages the Pt electrode of fuel cells, so that such gas must be purified by some methods. Pd-Ag alloys are used as hydrogen permeation alloys for purification of hydrogen gas. However, Pd is too expensive and a scarce natural resource. Then, it is strongly desired the development of low cost and high performance hydrogen permeation alloys other than Pd alloys.The usual method to attain large hydrogen permeation flux *J* is to search for alloys having high hydrogen permeability Φ. However, the coexistence of high Φ value with large resistance to the hydrogen embrittlement is generally difficult in single-phase alloys. Recently, we have proposed new alloys on the basis of the concept of the sharing of the function. An example of such alloys is the Nb-Ti-Co alloys that consist of B2-TiCo and bcc- (Nb, Ti) solid solution. In the present work, we describe alloy compositions, microstructures, structural changes induced by hydrogenation and hydrogen permeability in the Nb-Ti-Co alloys with high resistance to the hydrogen embrittlement. This work was supported by New Energy and Industrial Technology Development Organization (NEDO) of Japan.

O-116 **Performance and Degradation of Gas Gap Heat Switches in Hydride Compressor Beds.** J. W. Reiter,[1] P. B. Karlmann,[2] R. C. Bowman, Jr.,[2] M. Prina[2] – [1]Swales Aerospace, Pasadena, CA, USA; [2]Jet Propulsion Laboratory - California Institute of Technology, Pasadena, CA, USA

Hydrogen sorption cryocoolers were developed to provide ~19 K cooling to instruments aboard the Planck spacecraft that will measure the temperature anisotropy of the cosmic microwave background. Metal hydride sorbent beds are used in the compressors of these cryocoolers. A closed-cycle Gas-Gap Heat Switch (GGHS) on each sorbent bed functions as a variable vacuum dewar, allowing the reduction of nominal input power to each compressor by ~80% over its lifetime without the use of any moving parts. Hydrogen gas pressure in each GGHS is varied with an independent actuator containing ZrNi hydride. As the GGHS must attain low H_2 gas pressure in its "off" state to function reliably, any accumulation of additional gas in the GGHS can compromise the vacuum causing parasitic heat losses within the system. The effects of such accumulations have been seen during development and testing of the Planck GGHS, and were found to be a combination of outgassing from metallic components and hydrogen permeation through the walls of the high-pressure compressor bed when it was heated between 290 K and 670 K. This accumulation has been volumetrically measured over a wide range of operating temperatures and pressures on engineering models and flight versions of the hydride compressor beds to provide hydrogen accumulation rates in the GGHS. Correlations with accepted literature values are given, addressing the performance of stainless steel in terms of permeation and outgassing of hydrogen gas.

O-117 **Theoretical Prediction on Thermodynamical Stabilities of Metal Complex Hydrides.** K. Miwa,[1] N. Ohba,[1] S. Towata,[1] Y. Nakamori,[2] A. Züttel,[3] S. Orimo,[2] – [1]Toyota Central R&D Labs., Inc., Nagakute, Aichi, Japan; [2]Institute for Materials Research, Tohoku University, Sendai, Japan; [3]Physics Department, University of Fribourg, Perolles, Switzerland

Thermodynamical stabilities for the series of metal borohydrides $M(BH_4)_n$ (M = Li, Na, K, Cu, Mg, Ca, Zn, Al, Sc, Y, Zr, and Hf) have been systematically investigated by the first-principles calculations based on density functional theory. The electronic structures are found to be nonmetallic for all borohydrides considered in this study, where the ionic character is dominant for the bonding between M^{n+} cations and $[BH_4]^-$ anions. The heat of formation normalized by the number of BH_4 complexes in the formula unit, ΔH, shows a good correlation with the Pauling electronegativity of the cation, χ_P. Assuming the linear relation, the least square fitting yields $\Delta H = 252.0\chi_P - 395.4$ with an absolute mean error of 9.3 in the unit of kJ/mol BH_4. From this relation, it is expected that borohydrides with $\chi_P \geq 1.6$ are thermodynamically unstable. This study was partially supported by the New Energy and Industrial Development Organization (NEDO), International Joint Research under the "Development for Safe Utilization and Infrastructure of hydrogen" Project (2005-2006).

O-118 **Thermodynamical Stabilities of Complex Hydrides.** Y. Nakamori,[1] H.-W. Li,[1] K. Miwa,[2] S. Towata,[2] S. Orimo,[1] – [1]Institute for Materials Research, Tohoku University, Sendai, Japan; [2]Toyota Central R&D Labs., Nagakute, Japan

Thermodynamical stabilities of complex hydrides, such as $M(BH_4)_n$ and $M(NH_2)_n$ are studied theoretically and experimentally. The results of first-principles calculation revealed that the charge compensation by M^{n+} is a key feature for the stabilities of the internal bonding of BH_4 and NH_2 anions and it was expected that selecting M having larger electronegativity c_P is effective for lowering the

dehydriding temperature. In order to experimentally confirm the prediction, the series of $M(BH_4)_n$ (M=Li, Na, K, Mg, Ca, Zn, Al, Sc, Y, Zr, and Hf), where the later eight borohydrides were mechanochemically synthesized, and then the dehydriding reactions were investigated. The detected dehydriding temperature T_d correlates with c_P; T_d decrease with increasing the values of c_P, which is in agreement with the theoretical prediction. The c_P of M is a good indicator to estimate the stabilities of complex hydrides. This study was partially supported by the New Energy and Industrial Development Organization (NEDO), Development of Safe Utilization Technology and an Infrastructure for Hydrogen Use (2003-), and Iternational Joint Research Project (2005-2007).

O-119 **Dehydrogenation of $LiBH_4$ Investigated using *in-situ* Synchrotron X-ray Diffraction and MAS NMR.** L. Mosegaard,[1] B. Møller,[1] J.-E. Jørgensen,[1] Y. Cerenius,[2] J. C. Hanson,[3] F. Besenbacher,[1] H. Jørgen Jacobsen,[1] T. R. Jensen,[1] – [1]Interdisciplinary Nanoscience Center (iNANO) and Department of Chemistry, University of Aarhus, Aarhus, Denmark; [2]MAXLAB, Lund University, Lund, Sweden; [3]Department of Chemistry, Brookhaven National Laboratory, Upton, NY, USA

Lithiumborohydride, $LiBH_4$, is a potential solid-state hydrogen storage material with a high theoretical content of hydrogen, 18.5w/w%. An *in-situ* powder X-ray diffraction (PXD) study of hydrogen desorption of $LiBH_4$ and the catalytic effect of quartz was performed, at the Synchrotron NSLS, Brookhaven National Laboratory using beamline X7B and at Maxlab, Lund in Sweden using beamline I711. The phase transition of orthorhombic to hexagonal $LiBH_4$ was investigated by variable temperature solid state MAS NMR for ^1H, ^7Li and ^{11}B. The hexagonal phase of $LiBH_4$ formed at ca. 110°C has significantly higher degree of dynamical disorder evident from a decreasing line width of the NMR signals [1]. Two new unidentified phases, denoted X and Y, is observed and further characterised by PXD. Phase X is observed before the melting of $LiBH_4$ (T_{mp} = 275°C) and phase Y after the melting of phase X (T_{mp} = 310°C). A number of different experiments were performed and we argue that X and Y are two new phases of lithiumboronhydride, involved in the dehydrogenation of $LiBH_4$. It has earlier been suggested that the dehydrogenation of $LiBH_4$ can be catalysed by quartz. We have found that quartz are reacting and form nano-particles, ca. 10 nm, of Li_2SiO_3 and/or Li_4SiO_4 depending on the relative amount of SiO_2 added to $LiBH_4$. **[1]** J-Ph. Soulié et al, *J. Alloys Comp.*, 2002, **346**, 200; **[2]** Züttel et al, *J. Alloys Comp.*, 2003, **356**, 515

O-120 **Combinatorial Techniques and Results for Hydrogen Storage Discovery.** J. P. Lemmon, J.-C. Zhao, G. Rubinsztajn, J. Cui, J. T. Rijssenbeek, G. H. Soloveichik, Y. Gao, T. Raber, – General Electric Global Research, Niskayuna, NY, USA

The use of combinatorial high throughput screening is a well-established method for discovery in organic chemistry, and is now extensively utilized towards rapid synthesis and screening of biologically active molecules. In materials and inorganic chemistry the combinatorial approach has gained interest as a viable technique that allows for the rapid development of new functional materials, while improving the theoretical understanding of structure-property relationships. In this presentation, the use of combinatorial high throughput screening strategies, reactors, and analytical techniques aimed at understanding and improving materials for hydrogen storage will be described. Topics to be presented include high-throughput synthesis of new metal hydrides and rapid screening of hydrogen sorption/desorption properties using optical sensors, quartz crystal sensors and thermal imagining. Scale-up results including bulk hydrogen storage properties and mechanistic information obtained from in-situ X-ray diffraction will also be presented.

O-121 **Synthesis of New Metal Hydrides and How to Select New Potential Materials.** E. Rönnebro, – Sandia National Laboratories, Livermore, CA, USA

Anticipating a future hydrogen economy, US Department of Energy (DOE) has challenged the metal hydride community with system targets for an ideal material, including demands on 6wt% reversible hydrogen capacity at ca 100°C and 1-10atm before 2010. Since there are no materials that meet these targets, we need to discover new light-weight, high-capacity reversible hydrogen storage materials. A short review of metal hydrides and synthesis techniques will be presented, but focus will be on our work at Sandia; to screen for new complex anionic hydrides by using the hot-sintering technique under high-hydrogen pressures (<3000bar, <500°C). There are currently no theories available for predicting potential metal hydrides. In a close collaboration between experimentalists and theorists, we used our newly synthesized bialkali alanate, K_2LiAlH_6, as a role model, to explore the possibilities of using theoretical modelling as a guidance for predicting new materials.

O-122 **High Throughput Screening of a Novel Ternary Complex Hydride System.** G. J. Lewis,[1] J. W. A. Sachtler,[1] J. J. Low,[1] D. A. Lesch,[1] S. A. Faheem,[1] P. M. Dosek,[1] L. M. Knight,[1] C. M. Jensen,[2] – [1]UOP LLC, Des Plaines, IL, USA; [2]Hawaii Hydrogen Carriers, LLC, Honolulu, HI, USA

To date, no hydride meets the targets for automotive hydrogen storage and research is ongoing in many organizations to find an improved material. We are using Combinatorial Synthesis and Screening (CSS) with synthesis and testing of 48 samples in parallel to increase the rate of discovery of improved complex hydrides and dopants. In this paper we will demonstrate the application of CSS to a detailed investigation of a ternary non-alanate phase diagram. Most points on this phase diagram yield materials with theoretical hydrogen storage capacities that meet automotive targets. This system is especially interesting because binary systems along the edges of the phase diagram have yielded interesting results in the literature. By using CSS we are able to extend the exploration of this system to new complex mixtures corresponding to internal points on the ternary phase diagram that may have superior properties with respect to reversibility and desorption temperature. Hydrogen storage capacities and the structural characterization of the as-synthesized and dehydrided materials will be reported as a function of composition. More detailed characterization of the most promising materials will also be presented.

O-123 **Hydrogen Storage of Li-based Complex Hydrides Made from a Combination of Known High Capacity Hydrides.** J. Yang, A. Sudik, C. Wolverton, – Ford Research and Advanced Engineering, Dearborn, MI, USA

Solid state hydrogen storage has been identified as one of the most promising storage methods to achieve both high volumetric and gravimetric storage capacity for on-board vehicle applications. Light weight Li-containing hydrides such as $LiNH_2$[1], $LiBH_4$[2], $LiAlH_4$[3] have been studied as high capacity materials. A combination of these known complex hydrides can form new compounds. Examples include the combination of $LiBH_4$ and $LiNH_2$, forming $Li_4BN_3H_{10}$, releasing 10.5 wt.% H_2 at above 260° C[4,5], and the combination of $LiNH_2$ and MgH_2 forming $Li_2Mg(NH)_2$[6,7]. The combination of known complex hydrides can also alter the routes of chemical reactions, and correspondingly lower the reaction energy of hydrogen desorption. Examples include the combination of MgH_2 and Si[7], and $LiBH_4$ and MgH_2[8]. In this presentation, efforts at Ford in developing novel high storage capacity materials based on known high capacity Li-based complex hydrides will be discussed. As an example, we studied the formation and hydrogen storage properties of $Li_2Mg(NH)_2$ formed from $LiNH_2$ and MgH_2. We demonstrate that adequate mixing of starting materials and reducing particle size to the nanometer scale are critical to the formation and kinetics of the mixed imide $Li_2Mg(NH)_2$ compound. The initial treatment of the milled mixture under vacuum results in the decomposition of $LiNH_2$ into NH_3 and Li_2NH at approximately 300°C, resulting in irreversible capacity loss. Conversely, initial treatment under hydrogen atmosphere forms $Mg(NH_2)_2$ and LiH, which will further form $Li_2Mg(NH)_2$ upon hydrogen desorption. Recharging $Li_2Mg(NH)_2$ reversibly forms $Mg(NH_2)_2$ and LiH with a reaction enthalpy change of -41.0 kJ/mol.H_2. Based on the van't Hoff equation, a desorption temperature of about 90° C to 1 bar hydrogen is expected. However, kinetics measurements show the reaction is quite slow at temperatures below 210° C. In this presentation, our efforts in developing and incorporating effective catalysts to improve reaction kinetics of Li-based complex hydrides will also be described. [1] P. Chen, Z. Xiong, J. Luo, J. Lin and K. Tan, *Nature* 420 (2002) 302; [2]A Zuttel, P. Wenger, S. Rentsch, P. Sudan, Ph. Mauron and Ch. Emmenegger, *J. Power Sources* 118 92003) 1; [3] L. Zaluski, A. Zaluska and J.O. Strom-Olsen, *J. Alloys Compd.* 290 (1999) 71; [4] F.E. Pinkerton, G.P. Meisner, M.S. Meyer, M.P. Balogh and M.D. Kundrat, *J. Phys. Chem.* 109B (2005) 6; [5] M. Aoki, K. Miwa, T. Noritake, G. Kitahara, Y. Nakamori, S. Orimo and S. Towata, *Appl. Phys.* 80A (2005) 1409; [6] Z. Xiong, G. Wu, J. Hu and P. Chen, *Advanced Materials* 16 (2004) 1522; [7] W. Luo and S. Sickafoose, *Journal of Alloys and Compounds* 407 (2006) 274; [8] J.J Vajo, F. Mertens, C.C. Ahn, R. C. Bowman Jr. and B. Fultz, *J. Phys. Chem.* 108B (2005) 13977; [9] J.J. Vajo, S.L. Skeith and F. Mertens, *J. Phys. Chem.* 108B (2005) 13977.

O-124 **High-throughput Characterization of Hydrogen Storage Materials Using Thin Films on Micromachined Si Substrates.** A. Ludwig,[1,2] J. Cao,[1] S. Mauermann,[1] S. Groudeva-Zotova,[1] A. Savan,[1] – [1]Research Center CAESAR, Bonn, Germany; [2]University of Bochum, Germany

A new approach for the development of hydrogen storage alloys using combinatorially deposited thin films is presented. The substrates for this new screening method consist of micromachined Si cantilevers with additional layers of SiO_2 and Si_3N_4 which serve as diffusion barriers to prevent formation of silicides upon heating. A special combinatorial UHV sputter deposition system is used, where each cantilever can be coated with thin films of different chemical composition or in the form of multilayer films. The bending of up to 12 film-substrate combinations as a function of hydrogen pressure (1 to 51 bar) and substrate temperature (room temperature to 450°C) is measured in parallel, using an optical method. In addition to gas phase loading, an electrochemical apparatus was designed for the electrolytic loading of thin films with hydrogen. These cantilever-based measurement techniques were validated using Pd, Mg, Ti, and Cr thin films as reference materials. Thin films of different compositions within the system Mg-Al-B-Ti-Si will next be studied in detail by the new methods.

O-125 **Positrons in Hydrogen Storage Materials -AB_5-type Alloys and Alanates.** K. Sakaki,[1] M. T. Kuba,[2] Y. Nakamura,[1] Y. Shirai,[3] C. M. Jensen,[2] E. Akiba,[1] – [1]National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki, Japan; [2]Department of Chemistry, University of Hawaii, Honolulu, HI, USA; [3]Department of Materials Science and Engineering, Osaka University, Suita, Osaka, Japan

Vacancy and dislocation are unavoidably introduced in hydrogen storage materials to reduce the strain generated at the phase boundary consisted of solid solution and hydride phases. These lattice defects and lattice strains influence the hydrogenation properties such as reaction rate and absorption capacity in a positive and negative way. On the other hand, Ti doping to $NaAlH_4$ makes the reaction reversibly and the kinetics fast. One of our authors suggests vacancy creation by Ti doping to $NaAlH_4$. However, the role for Ti doping to $NaAlH_4$ has been not clarified yet. Positron lifetime technique is a powerful and valuable technique that can quantitatively and sensitively detect both vacancy and dislocation. Using *in-situ* positron lifetime technique by which their spectra can be measured under hydrogen pressure up to 8 MPa or in Ar atmosphere, we observed defect structures in $LaNi_5$-based alloys and $NaAlH_4$. In the case of $LaNi_{4.5}M_{0.5}$ (M=Al, Co, Ni), huge amounts of lattice defects are introduced by hydrogenation and exist in the lattice even after dehydrogenation. In the case of Sn substitution, the introduction behavior for lattice defects with hydrogenation is almost same as other $LaNi_5$ based alloys but that in dehydrogenation is significantly different though its thermal stability is not affected. The effect of substitution on their lattice defect introduction in $LaNi_5$-based alloys and that of Ti doping on defect structure in $NaAlH_4$ will be discussed.

O-126 **Dynamics of Defects in Alanates.** O. Palumbo,[1] A. Paolone,[2] R. Cantelli,[3] C. M. Jensen,[4] M. Kuba,[4] – [1]Université di Roma "La Sapienza" and Cnr-Infm, Roma, Italy; [2]Université di Roma "La Sapienza" and Cnr-Supermat, Roma, Italy; [3]Université di Roma "La Sapienza", Roma, Italy; [4]University of Hawaii, Honolulu, HI, USA

A systematic study was conducted on the dehydrogenation process of undoped and catalysed $NaAlH_4$ by means of anelastic spectroscopy. Evidence revealed the formation of a highly mobile species during decomposition, which was identified as off-stoichiometric AlH_{6-x} units in which fast local dynamics of H-vacancies occurs. The formation of such stoichiometry defects begins at temperatures much lower in Ti-doped than undoped samples, during the decomposition reaction. The catalyst atoms decrease the energy barrier to be overcome by H to break the bond, thus enhancing the kinetics of the chemical reactions and decreasing the

temperature at which the dehydrogenation processes take place. The experimental data show that at the decomposition temperatures not all of the hydrogen released by the formula units evolves out of the sample, but part of it remains in the lattice and migrates on a long-range scale within the sample. We identified in this H migrating population the species which rearranges the fast tetragonal to monoclinic phase transformation accompanying the decomposition. A partial spontaneous, thermally activated regression of decomposition was also observed by ageing experiments. A model was proposed which accounts for the role of the Ti catalyst and the mechanism of decomposition.Experiments are being carried out on the re-hydrogenation process in order to compare the mechanism of the reverse reaction.

O-127 **Point Defect Dynamics in Sodium Aluminum Hydrides.** Q. Shi,[1,2] J. Voss,[1,3] H.S. Jacobsen,[1,2] J. K. Nørskov,[3] T. Vegge,[1] – [1]Risø National Laboratory, Materials Research Department, Roskilde, Denmark; [2]University of Copenhagen, Niels Bohr Institute, Copenhagen, Denmark; [3]Technical University of Denmark, Center for Atomic-scale Materials Physics, Lyngby, Denmark

Hydrogen dynamics in $NaAlH_4$ and Na_3AlH_6 is investigated by quasi elastic neutron scattering (QENS) and DFT calculations. DFT calculations yield activation energies for vacancy mediated hydrogen diffusion between neighboring AlH_x-complexes of 0.36 and 0.88eV in $NaAlH_4$ and Na_3AlH_6, respectively. Titanium substitution at a neighboring Al-site in bulk Na_3AlH_6 lowers the barrier to 0.75eV. The QENS shows no hydrogen diffusion up to 250K in Na_3AlH_6. At 350K a few percent of the hydrogen is mobile in Na_3AlH_6 doped with 4 mol% $TiCl_3$, and at 390K 11% is mobile in undoped Na_3AlH_6. The hydrogen jump length of 2.5 Å and barriers obtained from the scattering data of 0.39 and 0.32eV for doped and undoped Na_3AlH_6, respectively, are in good agreement with the calculated values for local vacancy diffusion, *i.e.* within the AlH_5 group. Experimental elastic temperature scans and DFT calculations exclude substantial hydrogen jumps at 30-250K. Anelastic spectroscopy of $NaAlH_4$ decomposition via Na_3AlH_6 showed point defect jump rates of $5\cdot10^3 s^{-1}$ at 70K and an activation barrier of 0.126eV [1]. Although in contrast to our observations on hydrogen dynamics, our calculations yield a barrier of 0.12eV for sodium vacancy diffusion in Na_3AlH_6 and a jump rate of $4.3\cdot10^3$ jumps/s at 70K. The catalytic effect of titanium based doping on hydrogen desorption kinetics is found *not* to be related to increased macroscopic hydrogen diffusion in sodium alanates. [1] Palumbo *et al.*, J. Phys. Chem. B **109**, 1168 (2005).

O-128 **Raman Scattering and Lattice Stability of $NaAlH_4$ and Na_3AlH_6.** H. Yukawa,[1] K. Komiya,[1] R. Rong,[1] Y. Shinzato,[1] N. Morisaku,[1] R. Sekine,[2] M. Morinaga,[1] – [1]Department of Materials Science and Engineering, Graduate School of Engineering, Nagoya University, Nagoya, Japan; [2]Department of Chemistry, Faculty of Science, Shizuoka University, Japan

$NaAlH_4$, releases hydrogen to form Na_3AlH_6 through the reaction, $NaAlH_4 \rightarrow 1/3Na_3AlH_6+2/3Al+H_2$. In this study, the transition from the four-coordinated complex anion, $[AlH_4]^-$, in $NaAlH_4$ to the six-coordinated complex anion, $[AlH_6]^{3-}$, in Na_3AlH_6 was investigated experimentally by using the *in-situ* Raman spectroscopy. Also, the Raman spectrum was simulated theoretically using the Gaussian03 program. In addition, the Al-H bond energies in these alanates were calculated by the energy density analysis (EDA). It was found that the measured Raman spectrum from $NaAlH_4$ was mainly divided into three frequency regions around $1700cm^{-1}$, $800cm^{-1}$ and $500cm^{-1}$. Such characteristics of the Raman spectrum were well reproduced by the simulation. For example, the measured peaks at $1761cm^{-1}$ and $1682cm^{-1}$ corresponded to the Al-H symmetric and anti-symmetric stretching modes, respectively. In the course of decomposition of $NaAlH_4$ by heating in an argon gas atmosphere, new Raman peaks appeared at $1560\ cm^{-1}$ and $1100\ cm^{-1}$, which were attributed to the Al-H vibration modes in Na_3AlH_6. As these peaks had the lower frequencies than the corresponding peaks in $NaAlH_4$, the Al-H bond strength was supposed to be weaker in Na_3AlH_6 than in $NaAlH_4$. In fact, the Al-H bond energies estimated by the EDA were about 3.2eV for Na_3AlH_6 and about 3.6eV for $NaAlH_4$. Furthermore, a series of experiments and calculations was performed for $LiAlH_4$ and $KAlH_4$ to clarify the characteristics of alanates.

O-129 **Ultra-fast Hydrogen Sorption by Tuned Microstructure and Morphology in Sodium Alanates.** N. Eigen,[1] F. Gosch,[1] M. Dornheim,[1] T. Klassen,[2] R. Bormann,[1] – [1]GKSS Research Center, Geesthacht, Germany; [2]University of the Federal Armed Forces, Hamburg, Germany

Complex hydrides have a high potential as future hydrogen storage materials for automotive application. One of the major challenges is the fast charging. However, relatively fast kinetics could only be demonstrated in $NaAlH_4$ that was synthesised in highly complicated procedures, e.g. a chemical synthesis using high amounts of solvents and cost intensive initial components, e.g. Ti-nano clusters. This work demonstrates that extremely fast sorption kinetics in complex hydrides can be achieved by a suitable microstructure and powder morphology and that such material can be obtained even by a simple synthesis method using cost-efficient initial components. In a comprehensive study, Na-alanate was synthesised by different methods, including milling of NaH/Al with $TiCl_4$ catalyst under hydrogen and argon atmosphere as well as milling of $NaAlH_4$ with $TiCl_4$ catalyst under argon. Process conditions were optimised towards high sorption kinetics and high capacity. The influence of powder morphologies and microstructures resulting from different processes and process conditions were studied in detail. Based on these results, a cost-efficient synthesis method is proposed for $NaAlH_4$ with $TiCl_4$ exhibiting extremely fast sorption kinetics and 4,5wt.% of capacity. This synthesis method can be easily scaled up to a cost-efficient production process for large amounts of storage material.

O-130 **Synthesis and Characterisation of Transition-Metal Borohydrides.** D. Book, D. Reed, J. Matthews, V. Mann, I. R. Harris, A. Walton, – Department of Metallurgy and Materials, School of Engineering, University of Birmingham, Birmingham, UK

Metal-Borohydride compounds, such as $LiBH_4$, are promising hydrogen storage materials (able to store up to 18 wt%), but which require elevated temperatures (230 - 330°C) for hydrogen desorption and suffer from poor reversibility. The Transition-Metal Borohydride, $Zn(BH_4)_2$, has a storage capacity of 8.4 wt% and undergoes irreversible decomposition at around 85°C [1]. We have used a mechano-chemical procedure reported by Mal'tseva et al. [2], to ball-mill $NaBH_4$ and $ZnCl_2$ to produce $Zn(BH_4)_2$ and a by-product of sodium chloride. These reaction products were monitored using a combination of IR spectroscopy, XRD and SEM-EDS.

The optimum milling time was found to be about 1 hour; after longer times, the $Zn(BH_4)_2$ began to decompose leaving elemental zinc. The hydrogen sorption properties of the $Zn(BH_4)_2$-based milled samples were characterized by TGA, mass spectroscopy, and high pressure volumetric PCT and DSC measurements. Attempts were made to vary the stability of the compound using a range of substitutional and catalytic additions. [1] E. Wiberg, W. Henle, Zeitschrift fur Naturforschung, 7b, p.579-580 (1952); [2] N.N. Mal'tseva, N.S. Kedrova, L.V. Gorobinskii, L.A. Petrova, V.D. Makhaev, Russian Journal of Coordination Chemistry, 25 (4), pp.246-248, (1999).

O-131 **Transition Metal Borohydride Complexes as Reversible Hydrogen Storage Materials.** G. Severa, J. Eliseo, C. M. Jensen, – University of Hawaii, Honolulu, HI, USA

We have synthesized a family of novel transition metal borohydride complexes. These materials have been characterized by X-ray diffraction as well as ^{11}B NMR and infrared spectroscopy. The complexes undergo rapid dehydrogenation at temperatures in the 80-100 ˚C range. Unlike most other transition borohydride complexes, these materials have also been found to undergo re-hydrogenation at moderate conditions. The details of the characterization of the complexes and studies of their reversible dehydrogenation will be reported.

O-132 **Hydrogen Desorption and Absorption of the Modified $LiBH_4$.** M. Au, – Savannah River National Laboratory, Aiken, SC, USA

$LiBH_4$ has highest theoretic hydrogen content (18.5wt %) more than alanates (5.6wt %) and other conventional metal hydrides (1.2~3 wt %). Unfortunately, heating above 400°C is required to release the hydrogen. The dehydrided $LiBH_4$ can not be recharged at reasonable moderate conditions. It is found that the alkali metal borohydride catalyzed by 75% SiO_2 can be modified to release about 2.5 wt% hydrogen starting from 523K [1]. In our previous work, the $LiBH_4$ modified by several different metal oxides release 8-9 wt% hydrogen starting from 473K. After dehydrogenation, the $LiBH_4$ based materials modified by adding 25% TiO_2 was able to absorb 9 wt% hydrogen at 70 MPa and 873K. The dehydriding-rehydriding cycling shows limited reversibility at above conditions [2]. In effort to develop $LiBH_4$ based materials for reversible hydrogen storage, the new compositions and synthesis process have been explored. It is found that the hydrogen desorption behavior of the LiBH4 based materials modified by metal chlorides and alanate have been changed. The material LiBH4+0.2MgCl3+0.01TiCl3 desorbs 5.7wt% hydrogen starting from 60oC. The material also shows fair reversibility at 773K and 7MPa. This paper will present our updated results in the reducing dehydrogenation temperature, moderating rehydrogenation conditions and improving reversibility. [1] A. Zuttel, S.Rentsch, P.Fesher, P.Wenger, P.Sudan, Ph.Mauron and Ch.Emmenegger, J.Alloys Compd. 370(2004) 271; [2] M. Au and A. Jurgensen, Accepted for publication in J. Phys. Chem. B.

O-133 **Synthesis and Properties of Magnesium Boranate.** M. Fichtner,[1] Ch. Frommen,[1] A. Züttel,[2] – [1]Institute for Nanotechnology, Forschungszentrum Karlsruhe, Karlsruhe, Germany[2]Physics Department, University of Fribourg, Fribourg, Switzerland

Boranates, either in pure form or combined with a binary metal hydride in as a reactive composite, are interesting materials for hydrogen storage because of their high gravimetric hydrogen density. Whereas Li and Na boranate are rather stable hydrides and therefore, high temperatures for hydrogen desorption are necessary, magnesium boranate is less stable according to empirical models and might be interesting for applications at moderate working temperatures. $Mg(BH_4)_2$ was synthesized by means of chemical routes and by ball milling of MgB_2 under hydrogen pressures around 100 bar as well as reactive milling of $MgCl_2$ with $LiBH_4$. The structures of the intermediates and products were investigated by infrared spectroscopy and powder X ray diffraction. Thermal properties were determined in TGA-MS and high pressure-DSC measurements.

O-134 **Hydrogen Release and Reversibility in $Ca(AlH_4)_2$-based Systems.** H. Kabbour,[1] C. C. Ahn,[1] R. C. Bowman, Jr.,[2] S.-J. Hwang,[1] – [1]California Institute of Technology, Pasadena, CA, USA; [2]Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA

Hydrides properties offer the greatest promise for transportation applications and alkaline earth alanates show high levels of both gravimetric and volumetric capacity. While magnesium alanate has shown no reversible hydrogen release, calcium alanate is potentially reversible[1]. We have synthesized $Ca(AlH_4)_2$ as a precursor for further studies using the metathesis reaction [1-2] starting with mixtures of $LiAlH_4$ and $CaCl_2$ ball-milled or heated under reflux in THF. The formation of the pure phase involves the initial formation of a solvent adduct. The THF can be almost totally removed by heating the solvent adduct under vacuum. While the structure of the solvent adduct has been solved using single crystal X-ray diffractometry [2] no refinement of the pure phase has been achieved so far. However, hypothetical structures have been proposed using DFT simulations [3]. In this work, we have identified $Ca(AlH_4)_2$ using ^{27}Al NMR and FTIR measurements performed on intermediate and final products. We will discuss the kinetic and reversibility behavior of $Ca(AlH_4)_2$ based systems. [1] M. Mamatha et al, *J. Alloys Compds.*, **(2006)**, 407, 78; [2] M. Fichtner et al, *Inorg. Chem.*, **(2005)**, 44, 3479; [3] O. M. Løvvik, *Physical Review B* 71 **(2005)**, 144111.

O-135 **Role of Ammonia in the Amide-Imide Hydrogen Storage Systems.** T. Ichikawa, S. Isobe, H. Leng, H. Fujii, – Materials Science Center, N-BARD, Hiroshima University, Higashi-Hiroshima, Japan

Since Chen *et al.* reported on the hydrogen storage properties of Li_3N as a new family for hydrogen storage in 2002 [1], much attention has been paid to the amide-imide hydrogen storage systems. It is of interest that the hydrogen storage reactions related to the amide-imide systems are investigated from a viewpoint of the reaction mechanism as a model system of the solid-solid

reactions. Actually, with respect to the LiH-$Mg(NH_2)_2$ composite systems, it has been reported that ammonia molecule plays very important role to obtain the fully hydrogenated state from the mixture of Mg_3N_2 and Li_2NH [2]. Moreover, we have claimed that the hydrogen desorbing reaction of the LiH-$LiNH_2$ composite proceeds through two step processes mediated by ammonia molecule which is generated from $LiNH_2$ [3,4]. In these reactions, ammonia molecule might be transferred from the $LiNH_2$ phase to the LiH or Mg_3N_2 phase on the microscopic point of view, which plays a role as a carrier of the nitrogen element on the interface of two solid phases. As a result of the transfer, a rapid progress of the solid-solid reactions is realized, even though the disproportionation reaction takes place on both the hydrogenation and dehydrogenation processes in these amide-imide systems. [1] P. Chen, *et al.*, Nature 420 (2002) 302; [2] H.Y. Leng, *et al.* J. Phys. Chem. B, 109 (2005) 10744; [3] T. Ichikawa, *et al.*, J. Phys. Chem. B, 108 (2004) 7887; [4] S. Isobe, *et al.* J. Phys. Chem. B, 109 (2005) 14855.

O-136 **Li-Mg-N-H: Recent Investigations and Development.** W. Luo, J. Wang, K. Gross, S. Sickafoose, P. Crooker, K. Stewart, – Sandia National Laboratories, Livermore, CA, USA

One of the problems related to the employment of hydrogen-based fuel cells for vehicular transportation is “on board” storage. Hydrogen storage in solids has long been recognized as one of the most practical approaches for this purpose. The capacity of existing storage materials is markedly below that needed for vehicular use. Lithium nitride/imide/hydride system, reported by Chen [1], opens up a new avenue for hydrogen storage on-board application due to its high capacity, 11.5wt%. The sorption temperature and pressure of this system, however, are not satisfactory and modifications are necessary for on-board storage. Partial substitution of lithium by magnesium in the nitride/imide/hydride system improves sorption features significantly [2]. The plateau pressure of this new system is about 30 bars at 200°C with H capacity of 5.2 wt% [2]. Although this material is in its early stage of development, without considering composition optimization, very small capacity loss was observed during sorption cycling during 250 cycles at 200°C. Recent material development, reaction mechanism study results and engineering property measurement will be reported. Some other related issues, such as material synthesis and side reactions, will be discussed. Funding provided by the Department of Energy, Office of Energy Efficiency and Renewable Energy under the Hydrogen Storage Grand Challenge, Center of Excellence within DOE's National Hydrogen Storage Project. [1] P. Chen, Z. Xiong, J. Luo, J. Lin and K.L. Tan, Nature, 420 (2002) 302; [2] W. Luo, J. Alloys Compds, 381 (2004) 284-287.

O-137 **Synthesis and Characterization of Amide–Borohydrides: New Complex Light Hydrides for Potential Hydrogen Storage.** P. A. Chater,[1] P. A. Anderson,[1] A. Walton,[2] V. S. J. Mann,[2] D. Book,[2] W. I. F. David,[3,4] S. R. Johnson,[4] P. P. Edwards,[4] – [1]School of Chemistry, University of Birmingham, Birmingham, UK; [2]Dept. of Metallurgy and materials, School of Engineering, University of Birmingham, Birmingham, UK; [3]ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon., UK; [4]Inorganic Chemistry Laboratory, University of Oxford, Oxford, UK

The reactions xNaNH$_2$ + (1–x)NaBH$_4$ and xLiNH$_2$ + (1–x)LiBH$_4$ have been investigated and new phases identified. A new hydride of nominal composition $Na_2BH_4NH_2$ has been identified as a primitive cubic structure which appears to be disordered and thermodynamically unstable at room temperature. The lithium amide–borohydride system forms a eutectic which is dominated by a body centred cubic structure of ideal formula $Li_4BH_4(NH_2)_3$. $Li_4BH_4(NH_2)_3$, despite being constituted mainly of—and with striking structural similarities to—$LiNH_2$, has a completely different decomposition pathway from the pure amide, favouring H_2 evolution over that of ammonia. TGA–MS data confirms that ammonia is only a minor desorption product and shows that phase purity is important in reducing ammonia release. We hypothesize that $LiBH_4$ plays a similar role to LiH in the $LiNH_2$–LiH system where the normal ammonia releasing reaction of $LiNH_2$ is suppressed in favour of hydrogen release. $Li_4BH_4(NH_2)_3$ has the added benefit that BH_4^- ions are located near to NH_2^- ions at a structural level, eliminating the need for thorough mixing or ball milling as in the $LiNH_2$–LiH system. TGA–MS experiments with 2$LiNH_2$ + $LiAlH_4$, which also releases hydrogen, offer further evidence that the role of LiH in promoting hydrogen desorption from $LiNH_2$ is not unique. A careful choice of mixed complex hydrides may provide a means to tune the dehydrogenation and rehydrogenation reactions to make viable storage materials.

O-138 **Ultrasmall-Angle X-ray Scattering (USAXS) Studies on High Energy Milled $NaAlH_4$.** T. A. Dobbins,[1] V. Kamineni,[1] J. Ilavsky,[2] – [1]Louisiana Tech University, Ruston, LA, USA; [2]Advanced Photon Source, Argonne National Laboratory, Argonne, IL, USA

This research entails the study of particle morphological and powder surface area changes during high energy ball milling. Powder surface area is an indicator of hydride particle damage accumulation (i.e. crack formation in and fracture of the particle). Sodium alanate powders were high energy milled both with and without transition metal salt (i.e. $TiCl_3$, $ZrCl_4$, and $NbCl_4$) dopant additions. The variation in particle size and powder surface area with milling time was tracked. Subsequently, the powders were compacted (pelletized) and exposed to dehydrogenation/hydrogenation excursions in order to study changes in surface area occurring during the hydrogen release and uptake reactions. This work attempts to establish a link among damage accumulation in complex metal hydrides and kinetic performance of those powders. These studies also attempt to reveal chemical contributions (due to transition metal salt additions) to hydride particle fracture.

O-139 **First-Principles Studies of Thermodynamic and Structural Properties of the Li-Mg-N-H System.** A. R. Akbarzadeh,[1] V. Ozolins,[1] C. Wolverton,[2] – [1]Department of Materials Science and Engineering, University of California, Los Angeles, CA, USA; [2]Ford Research and Advanced Engineering, Dearborn, MI, USA

Amides have emerged as promising hydrogen storage materials after Chen et al. [1] reported reversible H_2 extraction from Li_2NH above 200 ^{o}C. Recently, Nakamori et al. [2] have reported a significant decrease of dehydriding temperature in $LiNH_2$ upon adding Mg. These authors predict that $Mg(NH_2)_2$ could store up to 9.1 wt. % H_2 according to the following reaction: $3Mg(NH_2)_2 + 12LiH \leftrightarrow$

$4Li_3N + Mg_3N_2 + 12H_2$. Using first-principles density functional calculations we investigate the thermodynamics, structural properties and lattice dynamics of known crystalline compounds in the Li-Mg-N-H system. From the calculated thermodynamic functions - reaction enthalpies, vibrational energies and entropies – we investigate the phase diagram of this system as a function of temperature and hydrogen pressure and predict the thermodynamically favored sequence of decomposition reactions. We also report results of extensive searches for stable crystal structures of hypothetical ordered Li-Mg amides and imides. This project is supported by DOE grants DE-FC36-04GO14013 and DE-FG02-05ER46253. [1] P. Chen et al., Nature, **420** (2002) 302; [2] Y. Nakamori et al., J. Alloys Comp., **404-406** (2005) 396

O-140 **Reaction Kinetics of Doped Light Weight Hydrides and Reactive Hydride Composites.** M. Dornheim, G. Barkhordarian, N. Eigen, U. Boesenberg, A. Borgschulte, X. Qi, C. Keller, O. Metz, T. Klassen, R. Bormann, – GKSS-Research Centre, Geesthacht, Germany

Compared to conventional room temperature hydrides light weight metal hydrides have a much higher gravimetric hydrogen storage density. However, so far light metal hydrides have not been considered competitive because of thermodynamic or kinetic limitations. Light weight hydrides exhibited rather sluggish sorption kinetics. Filling a tank could take several hours. Moreover, the hydrogen desorption temperature is rather high for most light weight metal and complex hydrides. A breakthrough in hydrogen storage technology was achieved by preparing nanocrystalline hydrides using high-energy ball milling as well as the discovery of suitable catalysts/dopants. This enabled the preparation of novel light weight materials for hydrogen storage with much higher gravimetric hydrogen storage densities. Some of these new materials show very fast ab- and desorption kinetics within few minutes. However there are still a lot of hydrides like the borohydrides with very high gravimetric hydrogen storage densities, which cannot be reversibly hydrogenated under moderate conditions. This demonstrates the demand for novel approaches to enhance the kinetics of light weight hydrides. One very exciting, successful and promising novel approach is the concept of the Reactive Hydride Composites (RHC). Such systems show reduced total reaction enthalpies as well as significantly improved ab- and desorption kinetics compared to the pure hydrides. Furthermore, in RHC reversibility is demonstrated for hydrides, which have been considered as irreversible using moderate hydrogen pressures and temperatures. In this talk, we present recent detailed results on the sorption behaviour of doped nanocrystalline light weight hydrides and the newly discovered Reactive Hydride Composites.

O-141 **The Effect of Mixed Metal Oxide Materials on the Hydrogen Sorption Properties of Milled MgH_2.** D. L. Croston, D. M. Grant, G. S. Walker, – The University of Nottingham, Nottingham, UK

MgH_2 is considered to be one of the most promising options for a solid state hydrogen storage material. However, for practical use it is still essential to find a convenient means of overcoming its slow kinetics and high stability. In this investigation, oxide materials based on Al_2O_3, SiO_2, TiO_2 and ZrO_2, including mixed metal oxides, have been prepared from alkoxide precursors via a sol-gel route. To our knowledge, there are no prior studies of the effect of mixed oxides on the H_2 sorption properties of MgH_2, nor of how these properties are affected by oxide preparation and calcination temperature. The physical nature of the prepared materials was characterised by XRD, SEM, and N_2 physisorption. The hydrogenation and dehydrogenation behaviour was investigated by TGA with mass spectrometry and cycling experiments in a gravimetric analyser. MgH_2 ball milled with the oxide samples resulted in dehydrogenation onset temperatures as low as 250°C, which is over 100°C lower than for milled MgH_2 with no additives. In cycling experiments at 300°C, between pressures of 1×10^{-2} bar H_2 and 6 bar H_2, desorption of the full H_2 capacity (3.5 wt. %) was found to occur in 10 minutes, with full absorption taking 15 minutes. These rates were significantly quicker than for milled MgH_2 with no additives, which took over 100 minutes to desorb 3.5 wt % H_2 under the same conditions. The desorption and absorption rates remained constant over 10 cycles, with no observable decrease in capacity.

O-142 **A Series of Hydrogen Rich $[Mg_{\sim.9}TM_{\sim.1}]H_2$ (TM = Ti, Zr, Hf, V, Nb and Ta) Hydrides with an FCC Structure was Found to Have Significantly Better Desorption Kinetics than MgH_2.** T. Sato,[1] D. Kyoi,[2] N. Kitamura,[2] T. Sakai,[2] D. Noréus,[1] – [1]Stockholm University, Stockholm, Sweden; [2]National Institute of Advanced Industrial Science and Technology, Osaka, Japan

Meta-stable new ternary TM doped Mg based hydrides (TM = Ti, Zr, Hf, V, Nb and Ta) adopt an FCC metal atom lattice with a ≈ 4.8 Å. The hydrides are produced in an anvil cell at 4-8 GPa and 600 ºC. The FCC unit cell corresponds to an assumed high pressure phase of MgH_2 with the CaF_2 structure type found by density-functional total energy calculations [1]. Ordering of the TM atoms in the lattice lead to a superstructure cell and a doubling of the FCC unit cell all axis. The metal atom structure is related to the Ca_7Ge structure type. Electron microscopy and electron diffraction patterns confirm structural investigation from powder X-ray diffraction pattern using synchrotron radiation. Hydrogen atoms were found in the two tetrahedral sites. The new hydrides decompose into Mg and TM-hydrides upon heating, releasing hydrogen at significant lower temperature (60-150 ºC) than MgH_2. [1] P. Vajeeston, P. Ravindran, A. Kjekshus, H. Fjellvåg, Phys. Rev. Lett. **89** (2002) 175506.

O-143 **Structural and Hydriding Properties of New Mg-Li-Ni Alloys.** T. Kohno,[1,2] M. Matsuoc,[3] S. Orimo,[3] – [1]Corporate Research & Development Center, Toshiba Corporation, Kawasakai, Kanagawa, Japan; [2]Graduate School of Environmental Studies, Tohoku University, Sendai, Japan; [3]Institute for Materials Research, Tohoku University, Sendai, Japan

Structural and hydriding properties of Mg-based alloys have been extensively studied from the viewpoint of developing advanced hydrogen storage materials. For example, (pseudo-)binary compounds such as Mg(-Y)Ni_2 with C15*b*-type [1] and Mg(-Ca)Ni_2 with C15-type [2] Laves phase structures, and also ternary compounds such as RMg_2Ni_9 with $ThNi_3$-type [3] and new series of La-Mg-Ni (La_2MgNi_9, $La_5Mg_2Ni_{23}$ and La_3MgNi_{14}) with super-lattice structures [4] were successfully reported so far. Besides the long range ordering of the crystalline alloys, amorphous MgNi alloy and its Al-substitutions with a short range ordering related to CsCl-type cubic structure have been investigated [5]. In this study, we focus on the new (pseudo-)binary and ternary alloys, Mg-Li-Ni, in order

to increase gravimetric hydrogen densities of the Mg-based alloys. The structural and hydriding properties of the alloys will be presented in detail. [1] K. Aono S. Orimo, H. Fujii, *J Alloys Comp.* 309 (2000) L1; [2] N. Terashita, K. Kobayashi, T. Sasai, E. Akiba, *J Alloys Comp.* 327 (2001) 275; [3] K. Kadir, T. Sakai, I. Uehara, *J Alloys Comp.* 302 (2000) 112; [4] T. Kohno, H. Yoshida, F. Kawashima, T. Inaba, I. Sakai, M. Yamamoto, M. Kanda. *J Alloys Comp.* 311 (2000) L5; [5] S. Orimo, H. Fujii, *Appl Phys* A 72 (2001) 167.

O-144 **The Mechanisms and the Kinetics of Hydride Formation.** J. Bloch,[1] I. A. Chernov,[2] E. A. Evard,[3] I. E. Gabis,[3] – [1]Nuclear Research Center – Negev, Beer Sheva, Israel; [2]Institute of Applied Mathematical Research of Karelian Research Center of RAS, Petrozavodsk, Russia; [3]V. A. Fock Institute of Physics, St. Petersburg State University, St. Petersburg, Russia

The aim of our research was to discover the mechanisms of hydride formation. We chose MgH_2 and UH_3 as examples. As we have been sure that Avrami-Erofeev's approach has very limited use, we looked for a solution in the form of physically valid models. The experiment of uranium hydriding is described in detail in [1]. Magnesium hydriding was done isothermally with pressures 100-500 bar at 300-400^{0}C and 0.7-1 bar at 250^{0}C. Hydrogen diffusion in the metal lattice was assumed to be "fast" due to small sizes of the particles of the powder. On the contrary, significantly slower diffusion in the ion-covalent hydrides was considered as an important factor that influences on hydrogen sorption together with the adsorption rate. Hydriding mechanisms essentially depend on hydrogen pressure. If the pressure is low, one or a few nuclei of the hydride phase appear and little-by-little fill the entire volume of the particle. Higher pressure provides many nuclei which grow and form the complete hydride skin. Mathematical models considered all these processes, including nucleation, skin appearance and growth and hydrogen sorption by the metal phase. We checked the adequacy of the models by how well they approximated the experimental data. This result is satisfactory. The approximation provided rate evaluations of the processes considered in the models. [1] J. Bloch, J. Alloys Compds. 361 (2003) 130.

O-145 **Synthesis of Hydrogen Storage Materials by Ball-milling and Cold Rolling Techniques.** J. Huot, – Université du Québec à Trois-Rivières, Trois-Rivières, Québec, Canada

In the development of metal hydrides for commercial applications, a special attention should be devoted to the ways of production. For commercial success, the synthesis process should be inexpensive and easily scalable. Therefore, it is important to put some effort on the elaboration of new and more efficient means of producing metal hydrides. It has recently been shown that cold rolling could produce nanocrystalline alloys and composites[1]. In this talk, we will present results on cold rolled and ball milled Mg-Pd. The laminated sample is much easier to activate and has a better resistance to air exposure before activation. It is well known that due to its high ductility, magnesium is very difficult to ball mill. By using cold rolled magnesium we show that magnesium could then be milled without important agglomeration of the materials. Therefore, a combination cold rolling-milling could be used to process ductile materials. The crystal structure of cold rolled and ball milled materials were studied in-situ by neutron diffraction. [1] T.T. Ueda, M. Tsukahara, Y. Kamiya et al., J. Alloys Compds. 386 (2004) 253.

O-146 **Nuclear Magnetic Resonance Studies of Ball-Milled Hydrides.** A. V. Skripov, – Institute of Metal Physics, Urals Branch of the Academy of Sciences, Ekaterinburg, Russia

Nanostructured hydrides prepared by ball milling show a number of interesting properties. In particular, the ball milling is known to accelerate the hydrogen absorption/desorption in some hydrogen-storage materials. In the present work, the proton nuclear magnetic resonance (NMR) is applied to study the behavior of hydrogen in two classes of ball-milled systems: Mg-based hydrides and Laves-phase hydrides.The ball milling of Mg with some additives (such as transition-metal oxides) strongly improves the hydriding kinetics. In order to clarify the nature of these changes, we have measured the proton spin-lattice relaxation rates R_1 and the proton NMR spectra in nanocrystalline MgH_2-based systems prepared by ball milling of Mg with different additives in hydrogen atmosphere. For all the nanocrystalline samples studied, the measured proton spin-lattice rates are much higher than in a bulk MgH_2. While no effects of H jump motion at the NMR frequency scale have been found up to 420 K (this means that H jump rates remain below 10^5 s^{-1}), the observed R_1 enhancement can be attributed to the interaction between proton spins and paramagnetic centers. It should be stressed that such paramagnetic centers appear to be related to the special structure of a ball-milled system; they do not originate from the ball material. For Laves-phase hydrides where H mobility is known to be extremely high, our NMR measurements have revealed strong effects of ball milling on the hydrogen jump rates.

O-147 **Ageing of $NaAlH_4$ Doped with either $TiCl_3$ or Ti_{13}·6THF by Ball Milling.** A. Léon,[1] J. Rothe,[2] M. Fichtner,[1] – [1]Forschungszentrum Karlsruhe, Institut für Nanotechnologie, Karlsruhe, Germany; [2]FZK Karlsruhe, Institut für Nuclear Entsorgung, Karlsruhe, Germany

Complex aluminum hydrides became particularly attractive for hydrogen storage since it was shown that dehydrogenation and hydrogenation cycling was feasible by using appropriate catalysts. However, among the alanates, only the doped sodium alanate fulfils at the moment some of the requirements for mobile applications. That is why research on the fundamental aspect of the transformation mechanism is of valuable interest to improve both the reversible amount of hydrogen and the reaction rates. From recent investigations of the local structure around Ti using X-ray absorption spectroscopy, the decrease of the reaction rate and the hydrogen storage capacity with the number of cycles has been correlated with the formation of a small entity between Al and Ti during cycling, regardless of the nature of the precursor used. Important insights into the reaction have been obtained concerning the evolution of the local atomic structure around the Ti atoms in Ti doped sodium alanate. In this work, we investigated the evolution of this environment with respect to ageing. Isothermal kinetic measurements and X-ray absorption spectroscopy have been performed on Ti-doped sodium alanate samples stored in the glove box for several months to one year. Preliminary data

analysis indicates that the valence state of Ti as well as the local structure around Ti does not evolve with time. Moreover, kinetic measurements performed on these aged samples shows no significant change compared to the initial state.

O-148 **Effect of Mechanochemical Treatment and Catalyst Addition on the Decomposition of $LiAlH_4$.** S. Doppiu, L. Schultz, O. Gutfleisch, – IFW Dresden, Institute for Metallic Materials, Dresden, Germany

Complex hydrides such us alanates and borohydrides received in the last years large attention as attractive materials for hydrogen storage applications. The high hydrogen content and, in some cases, the relatively low decomposition temperatures make them promising candidates for on-board storage. The hydrogen release of these compounds is characterized by a sequence of decomposition steps often including the melting of the hydride. The understanding of the steps involved during the decomposition and the influence of structural modification and catalyst addition is fundamental to achieve improved thermodynamic and kinetic properties. In this study, the effect of mechanical activation on the decomposition of $LiAlH_4$ and $LiAlH_4$ doped with $TiCl_3$ as a function of milling time is presented. The mechanochemical treatment was performed in an especially constructed vial allowing *in-situ* monitoring of the temperature and pressure (<150 bar). Structural changes and the degree of hydride decomposition were analyzed by x-ray powder diffraction analysis using the Rietveld method. The behavior under heating was studied by DSC under different atmospheres (Ar, H_2) and different pressures (<150 bar) and by TG-DTA analysis. The influence of the catalyst addition on the decomposition of the hydride increasing milling time has been analyzed. Most importantly, the enthalpy related to the different reaction steps involved in the decomposition has been derived.

O-149 **Synthesis, Structure and Stability of Mixed Alanates.** S. Sartori, M. S. Sørby, A. Fossdal, H. W. Brinks, B. C. Hauback, – Physics Department, Institute for Energy Technology, Kjeller, Norway

Mixed hexa-alanates with different combinations of Li, Na, K, Mg and Ca, including Na_2LiAlH_6, K_2NaAlH_6 and K_2LiAlH_6, have been synthesized by ball milling. In addition, reactive milling under high and low hydrogen pressure of combinations of alkaline, earth-alkaline elements and aluminium has been carried out to follow the thermodynamic stability and reversibility of the obtained mixed hexa-alanates. Reactive hydride milling allowed an efficient evaluation of these new solid-state materials as candidates for hydrogen storage. Structural properties of the mixed hydrides were characterized by X-ray powder diffraction (including synchrotron radiation experiments at ESRF) and neutron diffraction (PUS-instrument at the JEEP II reactor, IFE). The determination of thermodynamic properties and equilibrium conditions of the mixed alanates were investigated with a Sievert's apparatus. Financial support from the project STORHY under the FP6 Energy Program in the European Commission is acknowledged.

O-150 **A Thermodynamic Database for Metal-Hydrogen Systems.** U. R. Kattner, – National Institute of Standards and Technology, Metallurgy Division, Gaithersburg, MD, USA

The thermodynamic properties of metal-hydrogen systems are key to assessing the suitability of particular systems for hydrogen storage. Thermodynamic modeling using the Calphad method provides a way to incorporate results from experimental investigations and *ab-initio* calculations into an overall temperature-pressure-composition framework. The calculations provide temperature and pressure of the hydriding reaction as well as heats of reaction and reaction sequences. A comprehensive thermodynamic database with Gibbs energy functions for the phases in metal-hydrogen systems and relevant metal-metal systems has been assembled from published data evaluations and newly generated thermodynamic descriptions. The initial focus in the construction of the database is on ternary and quaternary hydride systems with light elements.

O-151 **Results of an Investigation on Some Novel Complex Hydrogen Storage Materials.** K. J. Gross,[1] N. T. Stetson,[2] – [1]Hy-Energy LLC, Newark, CA, USA; [2]Hy-Energy LLC, Lake Orion, MI, USA

For the successful emergence of the Hydrogen Economy development of improved hydrogen storage methods is considered critical. Developing new hydrogen storage methods with significantly enhanced properties over the traditional storage methods present tremendous challenges. These advanced hydrogen storage methods will be based on novel materials with superior properties. New materials of complex metal hydrides/amides show promise of having high hydrogen storage capacity and being reversible. Results of investigations on the reversible storage capacity, thermodynamics and kinetics of these exciting new materials will be presented.

O-152 **Synthesis and Dehydrogenation of $M(AlH_4)_2$(M=Mg, Ca).** K. Komiya,[1] N. Morisaku,[1] Y. Shinzato,[1] S. Orimo,[1] Y. Ohki,[2] K. Tatsumi,[2] H. Yukawa,[1] M. Morinaga,[1] – [1]Department of Materials Science and Engineering, Graduate School of Engineering, Nagoya University, Chikusa-Ku, Nagoya, Japan; [2]Department of Chemistry, Graduated School of Science and Research Center for Materials Science, Nagoya University, Chikusa-Ku, Nagoya, Japan

$Mg(AlH_4)_2$ was synthesized by a metathesis reaction of $MgCl_2$ and $NaAlH_4$. It was decomposed in the two-steps reactions, in agreement with the previous report [1]. The first reaction is characteristic of the decomposition to form MgH_2, and the second reaction is the further decomposition of this MgH_2 into some aluminum alloy phases. The decomposition temperature of the first reaction could be reduced remarkably when it was mixed with 1-5mol% $TiCl_3$. For example, in case of $Mg(AlH_4)_2$ mixed with 5mol% $TiCl_3$ by ball-milling for 3 hours, a large portion of hydrogen was released during milling at ambient temperature. The decomposition temperature of the first reaction decreased with increasing content of $TiCl_3$ in the specimen. However, the re-hydrogenation reaction scarcely occurred even in the pre-decomposed $TiCl_3$-containing specimen. For example, only 0.5mass% of hydrogen was absorbed in the 1mol% $TiCl_3$-doped specimen by exposing it for a long time to the hydrogen atmosphere of 30MPa at 353K. This result indicates that $Mg(AlH_4)_2$ is too unstable to progress the re-hydrogenation reaction smoothly. So, $Ca(AlH_4)_2$ was chosen next,

because this seems more stable than $Mg(AlH_4)_2$, judging from the phase stability diagram of complex hydrides proposed by us [2]. $Ca(AlH_4)_2$ was synthesized and its decomposition and re-hydrogenation reactions were investigated in a fundamental manner. [1] M.Fichtner et al, J.Alloys Compd. 365-357(2003) 418; [2] M.Yoshino et al, J.Alloys Compd. 404-406(2005) 185.

O-153 **Hydrogen Isotope Scrambling and Thermodynamic Studies on Doped Sodium Alanate.** G. Streukens, J. M. Bellosta von Colbe, W. Schmidt, M. Felderhoff, B. Bogdanovic, F. Schüth, – Max-Planck-Institut für Kohlenforschung, Mülheim a. d. Ruhr, Germany

Doping $NaAlH_4$ with Titanium brings about a two-step reversible chemical system with extremely enhanced de- and rehydrogenation rates. While the effect of Ti on the kinetics is well documented, this does not hold for mechanism and thermodynamics of the system. Hydrogen isotope scrambling experiments on Ti-doped $NaAlH_4$ show that titanium facilitates the dissociation of hydrogen at the surface of $NaAlH_4$ and diffusion of hydrogen into the bulk of the alanate. Kinetics studies indicate that the rate-limiting step of the charging/discharging process is the mass transfer in the solid. Titanium facilitates dissociation of hydrogen and activates it for exchange with the solid. However, dissociation of hydrogen cannot be the only effect of the titanium. We propose that there is another effect of the titanium that is associated with the mass transfer of the solid in the bulk of the alanate.[1] In order to study the thermodynamics of the system, pressure-concentration isotherms have been recorded for $NaAlH_4$ with different doping levels of titanium. Our studies have shown, that the titanium doping also significantly alters the thermodynamics of the system, which is demonstrated by the change of the dissociation pressure with doping level. An explanation will be given in terms of additional energetic contributions due to reactions associated with the presence of titanium.[2] [1] J. Bellosta von Colbe, W. Schmidt, M. Felderhoff, B.Bogdanovic, F. Schüth, Angew. Chem., in press; [2] G. Streukens, B. Bogdanovic, M. Felderhoff, F. Schüth, Phys. Chem. Chem. Phys., submitted.

O-154 **Isotope Effect on the Metamagnetic Transitions in $Y_{1-x}R_xFe_2(H,D)_{4.3}$ Compounds (R=Tb, Er, Lu).** T. Leblond,[1] V. Paul-Boncour,[1] M. Guillot,[2] O. Isnard,[3] A. Percheron-Guégan,[1] – [1]LCMTR, CNRS,Thiais, France; [2]LCMI, CNRS-MPI, Grenoble, France; [3]ILL, Grenoble, France

RFe_2 Laves phases compounds absorb hydrogen or deuterium up to 5 H(D)/mol [1]. The YFe_2D_x deuterides are ferromagnetic with an increase of the mean Fe moment and a decrease of T_C for $x \leq 3.5$ D/mol. For x=4.2, the monoclinic compound is ferromagnetic at low temperature then undergoes a sharp first-order magnetovolumic transition towards an antiferromagnetic structure at 84 K. Thanks to complementary methods, this transition has been attributed to an itinerant electron metamagnetic behaviour (IEM) of one of the Fe sites surrounded by about 5 D atoms. Surprisingly this transition is very sensitive to the H for D substitution, which increases the mean Fe moment at 4.2 K and shifts the transition temperature to 130 K (50 %) [2, 3]. Since the cell volume of the hydride is 0.78 % larger than the deuteride, this giant isotope effect has been related to the strong dependency of the IEM behaviour on the volume [3]. In order to better understand the interplay between magnetic and elastic energies on this magnetovolumic transition, we have undertaken the study of $Y_{1-x}R_xFe_2(H,D)_{4.3}$ compounds. Tb and Er for Y substitutions introduce both volume changes and internal molecular field of the magnetic rare earth whereas Lu decreases the volume. The large isotope effect on the metamagnetic transition is confirmed for all the compounds. Although the cell volume has a dominant effect, the influence of the magnetic rare earth has also to be taken into account. The influence of these different parameters on the first order metamagnetic transition, in particular its sensitivity to the large (H,D) isotope effect, will be presented. [1] V. Paul-Boncour, S. M. Filipek, A. Percheron-Guégan, I. Marchuck, J. Pielaszek, J. Alloys Compds., **317-318** (2001) 83; [2] V. Paul-Boncour, M. Guillot, G. André, F. Bourée, G. Wiesinger, A. Percheron-Guégan, J. Alloys Compds., **404-406** (2005) 355; [3] V. Paul-Boncour, M. Guillot, G. Wiesinger, G. André, Phys. Rev. B, **72** (2005) 174430.

O-155 **5*f* Magnetism Studied in Complex Intermetallic U-based Hydrides.** L. Havela,[1] K. Miliyanchuk,[1] A. V. Kolomiets,[2] L. C. J. Pereira,[3] A. P. Gonçalves,[3] E. Šantavá,[4] – [1]Faculty of Mathematics and Physics, Charles University, Prague, Czech Republic; [2]European Commission, Joint Research Centre, Institute for Transuranium Elements, Karlsruhe, Germany; [3]Departamento do Quimica, Instituto Technólogico e Nuclear, Sacavém, Portugal; [4]Institute of Physics, Academy of Sciences of the Czech Republic, Prague, Czech Republic

Narrow-band magnetism of uranium intermetallic compounds is very sensitive to external variables as pressure and to doping. The reason is the varying overlap of the 5*f* wave functions modifying the width of the 5*f* band and varying hybridization with other components. Hydrogen absorption and the concommitant volume expansion are a very convenient probe into a system, as a basic U coordination can remain practically unchanged. We have been studying several groups of U ternary intermetallics and checked for hydrogen absoroption for pressures up to 150 bar. From equiatomic compounds of the UTX type, the Néel temperature T_N = 19 K for UNiAl is enhanced to 99 K for $UNiAlH_{2.3}$. Smaller enhancement of the Curie temperature T_C and ordered moment μ_s was found for ferromagnet $UCoSnH_{1.4}$ (T_C = 102 K). The reason for exceptional situation in $URuSnH_{1.4}$ with both T_C and μ_s decreasing can be seen in structure details. Even larger variability was found in the family of U_2T_2X compounds and their hydrides. In U_2Co_2Sn, which has a non magnetic ground state but is located in the vicinity of the verge of magnetism and exhibits non-Fermi liquid features, a small amount of dissolved hydrogen (α-hydride) induces weak ferromagnetism, whereas $U_2Co_2SnH_{1.4}$ (β-hydride) with largely expanded unit-cell volume (by 8.1 %) is antiferromagnet (AF). In compounds with the AF ground state (U_2Ni_2Sn, U_2Ni_2In) the hydrogen absorption increases markedly the respective T_N values. These findings seem indicative of prominent role of lattice expansion as the ingredient boosting the magnetism in U intermetallics. But a more quantitative study performed on other group, $UTSiH_x$, using magnetization studies at high pressure indicates that the increase of ordering temperatures due to hydrogenation is actually much smaller than expected on the basis of the pressure variations of T_N of the respective hydrides and their bulk moduli. Consequently, we have to consider effects of hydrogen absorption on the 5*f*-ligand

hybridization, rather than a pure expansion, as a more general framework of understanding the tendencies of the 5*f* magnetism in the hydrides.

O-156 **Hydriding Kinetics of $Ho_{1-x}Mm_xCo_2$-H System.** G. Srinivas,[1] V. Sankaranarayanan,[2] S. Ramaprabhu,[3] – [1]Alternative Energy Technology Laboratory and Low Temperature laboratory, Department of Physics, Indian Institute of Technology Madras, Chennai, India; [2]Low Temperature Laboratory, Department of Physics, Indian Institute of Technology Madras, Chennai, India; [3]Alternative Energy Technology Laboratory, Department of Physics, Indian Institute of Technology Madras, Chennai, India

The Laves phase AB_2-type alloys have drawn much attention as hydrogen storage material because of their high storage capacity and rapid kinetics of hydrogenation at low temperatures. Their hydrogen absorption-desorption properties could be modified through substitution with foreign atoms. The kinetics of metal hydrides have been investigated extensively in order to map the reaction mechanisms of hydrogen absorption and desorption and to identify possible rate limiting steps to ultimately take steps toward improving the kinetics. In addition, at a given temperature, the working pressure P of hydrogen is most pronounced when it is not too high relative to the equilibrium pressure P_{eq} of the hydride. In this present study, we present temperature and pressure dependence of hydriding reaction kinetics of Laves phase AB_2-type $Ho_{1-x}Mm_xCo_2$ (x = 0, 0.1, 0.2, 0.3 and 0.4 and Mm = misch metal) alloys. The reaction rate constant and order of reaction were obtained from fit of the Johnson-Mehl-Avrami model to the experimental data. The experimental data is correlated as a function of pressure, temperature and hydride composition. The dependence of the rate constants, on the temperature is discussed under constant initial hydrogen pressures. The results of pressure dependence of the reaction rate have been analyzed and discussed. The extent of reaction rate depends more strongly on the system pressure and temperature than on the hydride composition.

O-157 **Hydrogen Effect on the Structural Stability of an Amorphous Metal.** P.-R. Cha,[1] N.-Y. Park,[1] Y.-C. Kim,[2] H.-K. Seok,[2] K.-B. Kim,[2] – [1]School of Advanced Materials Engineering, Kookmin University, Seoul, Korea; [2]Advanced Metals Research Center, Korean Institute of Science and Technology, Seoul, Korea

Hydrogen is getting important gradually in our life with developing hydrogen fuel cells. If the hydrogen fuel cells are realized, there will occur so many materials problems induced by hydrogen, especially, related to the hydrogen embrittlement. The behavior of hydrogen in the metals and their hydrogen embrittlement have been intensively studied for last several decades but their mechanism is not still clear, especially, for amorphous metals. Using molecular dynamics simulations, with a realistic many-body embedded-atom potential, and a novel method to characterize local order, we study the structural stabilities of amorphous nickel with different hydrogen content. We find the nonlinear increase of atomic volume of amorphous Ni with increasing hydrogen concentration while crystalline Ni shows linear increase. We also find crystallization of amorphous Ni at room temperature above a critical hydrogen concentration (the crystallization temperature (T_x) of pure amorphous Ni is around 575 K) and the decrease of its T_x with increasing hydrogen concentration. We call the above enhanced crystallization of amorphous nickel hydrogen-induced crystallization (HIC) and discuss its mechanism.

ORAL PRESENTATIONS (O-158 to O-175) **Friday, October 6 (see schedule)**

O-158 **Relationship Between Microstructure and Hydrogenation Properties of $Ti_{0.85}Zr_{0.15}Mn_{1.5}V_{0.5}$ Alloy.** F. Cuevas,[1] B. Villeroy,[1] P. Olier,[2] M. Latroche,[1] – [1]LCMTR-CNRS, Thiais, France; [2]LTMEX-CEA, Saclay, Gif-sur-Yvette, France

$TiMn_2$-type C14 Laves phase alloys have attracted much attention as hydrogen storage materials due to their good capacity (~ 1.0 H/M atoms), easy activation and fast kinetics at normal conditions [1]. For room temperature applications, Zr and V substituting $TiMn_2$ alloys have been developed: Zr increases hydride stability and V reduces the plateau hysteresis [2]. However, as a drawback for applications, significant sloping plateau occurs in these alloys [3]. This can be explained by the difficulty to override compositional inhomogeneity in $(Ti,Zr)(Mn,V)_2$-substituted alloys. In this work, we study the relationship between alloy microstructure and hydrogenation properties of $Ti_{0.85}Zr_{0.15}Mn_{1.5}V_{0.5}$ alloy. Using four different elaboration methods, namely as-cast, high-temperature annealed, ball-milled and low-temperature annealed ball-milled alloys, distinct microstructures were obtained. Low-temperature annealing of ball-milled alloys appears to be the most efficient route for getting flat plateaux. In all cases but for sluggish ball-milled alloys, reactions times of a few seconds are obtained at room temperature. These results will be explained in terms of the microstructural alloy properties. [1] O. Bernauer, J. Töpler, D. Noréus, R. Hempelmann, D. Richter, Int. J. Hydrogen Energy, 14 (1989) 187–200; [2] B. H. Liu, D. M. Kim, K. Y. Lee, J. Y. Lee, J. Alloys Compd., 240 (1996) 214–218; [3]Y. Moriwaki, T. Gamo, T. Iwaki, J. Less-Common Met., 172-174 (1991) 1028–1035.

O-159 **Synthesis and Properties of Hydrides Under High Hydrogen Pressure.** S. Mitrokhin, V. Verbetsky, – Chemistry Department Lomonosov Moscow State University, Moscow, Russia

An extensive review of works on synthesis and properties of intermetallic hydrides under gaseous pressure over 200 atm is given. Transformations of metallic matrix taking place at these conditions are considered. Our own recent results of investigations of hydrogen interaction with various types of intermetallic compounds are presented and discussed.

O-160 **High-pressure Synthesis of Novel Hydride in Mg-TM Systems (TM = Ti, V, Zr, Nb, Hf, Ta).** M. Okada, Y. Goto, R. Kataoka, Y. Yambe, A. Kamegawa, H. Takamura, – Department of Materials Science, Tohoku University, Sendai, Miyagi, Japan

High-pressure synthesis has been widely used for exploration of novel materials. In this study, new Mg-based hydrides have been prepared under GPa-order by using a cubic-anvil-type apparatus. For Mg-TM-H (TM = Zr, Nb and Hf) systems, novel hydrides of $MgTM_2H_y$ with monoclinic-type structure were synthesized at 923 K under ≥2 GPa (TM = Zr and Hf) or ≥3 GPa (TM = Nb). Their lattice parameters were a = 5.816, b = 3.3569, c = 8.519 Å, b = 103.06˚, a = 5.70, b = 3.2888, c = 7.927 Å, b = 103.06˚, and a = 5.782, b = 3.317, c = 8.507 Å, b = 103.06˚, for TM = Zr, Nb and Hf, respectively. From fusion analysis, it was found that hydrogen contents of novel compounds were 2.99, 2.76 and 1.66 mass%, respectively. For Mg-TM-H (TM = Nb and Ta) systems, novel hydrides of Mg_7TMH_y were synthesized under 3 GPa or higher. These novel compounds exhibited FCC-type structure with a = 9.5526 and 9.5376 Å, respectively. From fusion analysis, it was found that hydrogen contents of Mg_7NbH_y were 5.78 mass%. Moreover, this novel hydride was observed to dehydrogenate with exothermic reaction at 595 K. In this study for these novel hydrides, their crystal structures, thermal stabilities and hydrogen contents were investigated, as well as the influence of applied pressure.

O-161 **Thermophysical and Thermochemical Properties of Metal Hydrides MH_X (M=Ti, Y, and Zr).** S. Yamanaka, M. Ito, H. Muta, M. Uno, – Division of Sustainable Energy and Environmental Engineering, Graduate School of Engineering, Osaka University, Suita, Osaka, Japan

Metal hydrides, such as Ti, Y, and Zr hydrides, are attractive and promising material as the U-Zr hydride fuel, neutron moderator, and reflector in nuclear plants. From the aspect of the integrity of structural materials, the several properties of hydrided metals have been extensively studied for a long time. However, the properties of the hydride itself have been scarcely studied due to the difficulty in production of bulk specimen, whereas the influence of the precipitated hydrides has been watched with keen notice. It is essential to study the thermophysical and thermochemical properties of single-phase metal hydrides in order to use them in practice. In the present study, the single-phase bulk Ti, Y, and Zr hydrides were successfully produced without any defects, and their properties viz., the lattice parameter, elastic modulus, Vickers hardness, thermal expansion coefficient, thermal conductivity, and electrical conductivity were investigated. It was found that although Ti, Y, and Zr are adjacent in the periodic table and their metals and hydrides have same crystal structures, they have respectively unique thermophysical and thermochemical properties. For example, the thermal and electrical conductivities of Ti and Zr hydrides are as same as those of the metals, whereas those of Y hydride are quite higher than those of the metal. The other results will be reported and the differences in the properties between the hydrides will be discussed.

O-162 **The Effect of Surface State on the Kinetics of Cerium-Hydride Formation.** H. Bach, J. S. Bridgewater, T. J. Venhaus, S. S. Paglieri, T. H. Allen, J. R. Wermer, H. Oona, – Los Alamos National Laboratory, Los Alamos, NM, USA

The effect of surface oxidation on the hydriding kinetics of cerium foils and ingots were examined at temperatures of 298-1000 K. Cerium samples were dosed with oxygen and the state of the surface oxide was studied during thermal activation using X-ray photoelectron spectroscopy (XPS). The dependence of hydrogen absorption and desorption kinetics on the surface state of the metal will be discussed.

O-163 **Effects of Carbide Intermediate Layers on High Temperature Durability of Pd Coating Prepared on Nb and Ta.** Y. Hatano, K. Ishiyama, T. Nozaki, H. Homma, – Hydrogen Isotope Research Center, University of Toyama, Toyama, Japan

Group 5 metals and their alloys are candidate materials of hydrogen separation membranes. The surfaces of thease materials are generally coated by Pd to prevent poisoning by impurities in hydrogen gas. Pd, however, reacts with the substrate materials at high temperatures and loses the coating effect. In the present study, the intermediate layers of carbides were prepared between Pd and Nb or Ta, and their effects on durability of Pd layer were examined as a way to solve such problem. Pd layer (100 nm) were prepared on disk-type specimens of Nb and Ta with or without carburization. These specimens were heated in vacuum at temperatures from 573 to 973 K for 1 h and exposed to air at room temperautre. Then, the resistance against poisoning was examined by measuring hydrogen absorption rate at 573 K. The Nb specimen without carbide layer showed significant reduction in H_2 absorption rate even after heating at 573 K due to degradation of coating effect, and the extent of degradation increased with heating temperature. The specimen with Nb_2C lintermediate layer showed noticeably higher hydrogen absorption rate at any heat-treatment conditions. The preparation of NbC layer led to further improvement in high temperature durability of Pd layer and slight reduction in initial hydrogen absorption rate. The reaction rate of Ta with Pd was much smaller than that of Nb, but significant improvement in the durability of Pd layer was observed at 973 K by prepartion of Ta_2C layer.

O-164 **Hydrogen Absorption in Palladium Clusters: Does the Structure Matter?** M. Suleiman,[1] D. Fritsch,[2] C. Borchers,[1] R. Kirchheim,[1] A. Pundt,[1] – [1]Institute of Material Physics, University of Göttingen, Germany; [2]GKSS Research Centre Geestacht, Germany

Palladium nano-sized clusters have distinct hydrogen uptake characteristics as comparred to bulk palladium. These are not only due to the different physical properties of the small-size system, but it is also affected by the type of the stabiliser [1] and the different structure of the clusters [2]. The effect of the lattice structure of the clusters on the H uptake is a fundamental question. In this work pressure-lattice parameter isotherms obtained by in situ X-ray diffraction measurements, using synchrotron radiation, for different Pd-clusters (3.0 nm, 3.6 nm, 4.8nm, 5.2 nm and 6.0 nm) will be presented. We will show that the differences in the isotherms are not due to the different cluster sizes but rather to different lattice structures. This will be proven by showing the hydrogen absorption behaviour of 3.0 nm Pd clusters in two different lattice structures. First, icosahedral Pd clusters obtained by an electrochemical method and stabilized in tetraoctylammonium bromide. Second, cubic Pd clusters obtained by a chemical method and stabilized in Teflon AF matrix [3]. The effect of the different lattice structure of both samples on the H uptake will be discussed.

[1] M. Suleiman, J. Faupel, C. Borchers, H.-U Krebs, R. Kirchheim and A. Pundt JALCOM 404-406(2005)523; [2] M. Suleiman, N. M. Jisrawi, O. Dankert, M. T. Reetz, C. Baehtz, R. Kirchheim and A. Pundt ALCOM 356-357 (2003) 644; [3] D. Fritsch, unpublished results.

O-165 **A New Example for a Hydrogen Induced Insulating State in the La-Ni-Mg-H System.** J. N. Chotard,[1] Y. Filinchuk,[1] N. Clayton,[2] K. Yvon,[1] – [1]Laboratory of Crystallography University of Geneva, Geneva, Switzerland; [2]University of Geneva, Geneva, Switzerland

Following our discovery of a hydrogen-induced insulating phase in the $LaMg_2Ni$-H system [1] we have investigated the closely related La_2MgNi_2-H system. Hydrogenation of tetragonal La_2MgNi_2 at 10 bar and 100°C leads to a complex metal hydride of composition $La_2MgNi_2H_8$ having monoclinic symmetry. In contrast to $LaMg_2NiH_7$ which displays tetradedral $[NiH_4]^{4-}$ complexes which are isolated one from another, $La_2MgNi_2H_8$ displays two types of polyanionic hydrido complexes having novel geometries. The complexes are ordered and represent the first case of a mixed polyanionic metal hydride system in the literature. The Ni-H distances vary from 1.43 to 1.91Å. Some hydrogen atoms are coordinated by La and Mg atoms only in octahedral $[La_4Mg_2]$-type or tetrahedral $[La_2Mg_2]$-type configurations. The hydride does not desorb hydrogen below 190°C and 1.10^{-1} mbar pressure and segregates into LaH_3 and other unidentified phases above 300°C. Electrical resistivity measurements on powder samples confirm the hydride to be non-metallic. [1] K. Yvon, G. Renaudin, C. M. Wei, and M.Y. Chou, Phys. Rev. Lett. **94** (2005) 066403

O-166 **Toyota's Vision of the Development of Hydrogen Storage Materials for Vehicular Applications.** K. Hirose, D. Mori, – Toyota Motor Corporation, Toyota, Aichi, Japan

The Fuel Cell Vehicle has high potential to reduce both energy consumption and carbon dioxide emissions. However, the low density of hydrogen gas limits its cruising range. Hydrogen storage is the key technology towards the hydrogen society. Currently high-pressure tank and liquid hydrogen tank are used for the road test but both technologies do not meet the requirements of future fuel cell vehicles. My presentation shows the latest results of our own development such as 70MPa high pressure tank and hybrid tank system (metal hydride + high pressure) as well as the current status of conventional technologies such as cryo storage and other systems. Then I would like to discuss the future target and milestone of the hydrogen storage materials and systems for the future hydrogen powered vehicles.

O-167 **Design, Fabrication and Testing of $NaAlH_4$ Based Hydrogen Storage Systems.** D. A. Mosher,[1] S. Arsenault,[1] X. Tang,[1] D. L. Anton,[2] – [1]United Technologies Research Center, East Hartford, CT, USA; [2]Savannah River National Laboratory, Aiken, SC, USA

To complement the vigorous search for novel hydrogen storage materials, efforts focused on system implementation of candidate compounds are important parallel activities to identify new or reprioritized system challenges and assess overall performance. The current presentation will discuss the design, fabrication and testing of on-board rechargeable storage systems based on the complex hydride $NaAlH_4$. Emphasis will be placed on the system elements affected by the different material characteristics compared with conventional metal hydrides such as $LaNi_5$. Design aspects will include reaction kinetics modeling, finite element analysis and heat exchanger optimization for a second generation pre-prototype. Fabrication challenges associated with material processing at scaled-up quantities and powder loading methods that are compatible with composite pressure vessel manufacture will be addressed. Testing facilities and techniques to evaluate a full scale vessel containing nearly 20 kg of $NaAlH_4$ also will be covered.

O-168 **The Planck Sorption Cooler: Using Metal Hydrides to Produce 20 K.** D. Pearson, R. C. Bowman, Jr., M. Prina, P. Wilson, – Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA

The Jet Propulsion Laboratory has built and delivered two continuous closed cycle hydrogen Joule-Thomson (JT) cryocoolers for the ESA Planck mission, which will measure the anisotropy in the cosmic microwave background. The metal hydride compressor consists of six sorbent beds containing $LaNi_{4.78}Sn_{0.22}$ alloy and a low pressure storage bed of the same material. Each sorbent bed contains a separate gas-gap heat switch that couples or isolates the bed with radiators during the compressor operating cycle. $ZrNiH_x$ hydride is used in this heat switch. The Planck compressor produces hydrogen gas at a pressure of 48 Bar by heating the hydride to ~450 K. This gas passes through a cryogenic cold end consisting of a tube-in-tube heat exchanger, three pre-cooling stages to bring the gas to nominally 52 K, a JT value to expand the gas into the two-phase regime at ~20 K, and two liquid – vapor heat exchangers that must remove 190 and 646 mW of heat respectively. Gas evaporated from the liquid phase is recovered by three hydride beds at ~0.3 Bar and 270 K. Each cooler was designed to provide 1 W cooling at ~20 K for a total input power of 470 W, excluding electronics. The performance of these coolers is mainly a function of the compressor interface and final pre-cooling stage temperatures. We present results from the testing of these two coolers for the input power, cooling power, temperature, and temperature fluctuations over the flight allowable ranges for these interfaces.

O-169 **Evaluation of Zr_2Fe (SAES St198) and Zr_3Fe for Hydrogen Gettering.** J. I. Abes,[1] S. N. Paglieri,[1] J. R. Wermer,[1] H. Oona,[1] D. Chandra,[2] M. I. Edwards,[3] M. R. Cortez,[1] M. Coleman,[2] – [1]Los Alamos National Laboratory, Los Alamos, NM, USA; [2]The University of Nevada, Reno, NV, USA; [3]Indiana University, Bloomington, IN, USA

Pressure-composition-temperature (PCT) hydriding experiments were conducted with Zr_2Fe getter (St198™, SAES Getters Sp.A., Milan, Italy) and Zr_3Fe in an automated Sieverts'-type apparatus. Repeated hydriding-dehydriding cycles were conducted to determine the suitability of these materials for long-term use in a system used to capture tritium from tritiated waste gas. For each

material, PCT curves were measured at temperatures between 100-500ºC after activation at 500ºC for 1 h under vacuum. One cycle consisted of a PCT curve measurement at 300ºC followed by dehydriding under active vacuum at temperatures from 600-900ºC for 8-24 h. Zr_2Fe showed a significant decrease in hydrogen capacity between the first PCT taken directly after activation and subsequent PCT curves measured after dehydriding under vacuum at 600-900ºC. Possibilities for the changes in this material that cause this reduction in capacity, including phase transformation, will be discussed. After 30 PCT cycles at 300ºC with dehydriding at 700ºC for 8 h, only a small decrease in capacity was observed (0.2 H/M). Dehydriding temperatures above 650ºC are required to maintain the hydrogen capacity and dehydriding at 800 or 900ºC resulted in only marginal increases in capacity. Zr_3Fe showed a capacity for hydrogen absorption comparable to that of Zr_2Fe, but without a significant decrease in hydrogen capacity between the first and second PCT curves.

O-170 **The Energy Efficiency of On-board Hydrogen Storage.** J. O. Jensen, A. P. Vestbø, Q. Li, N. J. Bjerrum, – Department of Chemistry, Technical University of Denmark, Lyngby, Denmark

For decades researchers worldwide have been striving towards development of suitable techniques for hydrogen storage in order to use hydrogen for energy storage. Hydrogen storage in interstitial metal hydrides is well known as a very compact and safe technology, but in most cases less than 2 weight percent hydrogen is stored. A hydrogen powered vehicle then needs several hundreds kilos of hydride in order to obtain a reasonable driving range. For this reason the research has to a large extent been focused on the hydrogen storage capacity in terms of weight percent. Several light materials with high hydrogen content have been suggested, like $NaBH_4$ (for reaction with water), methanol, ammonia and pure light metals or their binary hydrides. These materials are indeed able to release high amounts of hydrogen, but they are not practically reversible and must be regenerated or synthesized elsewhere. Regeneration or charging of these systems is energy consuming, and in some cases liberation of hydrogen is also energy consuming. The aim of this presentation is to review the energy efficiency of a broad range of hydrogen storage systems from compressed and liquid hydrogen over reversible metal hydrides to irreversible systems. Distinction is made between energy losses during regeneration and during hydrogen liberation. In the latter case the energy may have to be provided by part of the released hydrogen, and the true storage density is then equivalently smaller.

O-171 **Hydrogen Concentration Fluctuations in the α and β Phases of the Gd(0001)/W(110) – H system: STM Observations.** H. Realpe,[1,2] Y. Manassen,[2] N. Shamir,[3] M. H. Mintz,[1,3] – [1]Department of Nuclear Engineering, Ben Gurion University of the Negev, Beer Sheva, Israel; [2]Department of Physics, Ben Gurion University of the Negev, Beer Sheva, Israel; [3]Nuclear Research Center – Negev, Beer Sheva, Israel

STM Observations of Gd(0001) islands grown on a W(110) substrate and exposed to low doses of hydrogen were performed. Two types of hydrogen – induced time-dependent effects were displayed in the STM images. One effect was a periodic appearance – disappearance of certain Gd islands which was attributed to time-dependent periodic variations of the dissolved H at the Gd/W interfaces of the corresponding islands. Hence, a non-uniform fluctuating H distribution seems to exist for the α – phase (solid solution) region of this system. The other type of effect was observed for the β - phase hydride that nucleated within the α – phase Gd islands. These hydride precipitates displayed time – dependent fluctuations in their shape and size and did not follow a regular monotonic growth process. Both effects may be associated with the misfit strains experienced at the Gd/W interface.

O-172 **Crystal Structure and Magnetic Properties of Hydrides Under Very High Pressures.** I. Goncharenko,[1] O. Makarova,[2] – [1]Laboratoire Léon Brillouin, C.E.A.-C.N.R.S., Gif-sur-Yvette, France; [2]RRC "Kurchatov Institute", Moscow, Russia

We describe recent progress in neutron and X-ray diffraction studies of magnetic and structural properties of hydrides. By combining the two diffraction probes, we were able to characterise magnetic, hydrogen and metal sublattices under pressures up to 10-50 GPa. The magnetic Laves hydrides RMn_2H_x exhibit many intricate phenomena under pressure, namely a pressure induced magnetic collapse in the Mn-sublattice, hydrogen segregation, transitions from short-range to long-range ordered magnetic states, and structural transitions [1-3]. We report new pressure data on the hexagonal C14 hydrides (R=Tb, Y), metastable under ambient conditions, and discuss a general picture of magneto-structural phenomena in the Laves hydrides. Most of published high-pressure data concern interstitial hydrides. Recently, “light” covalent and ionic hydrides attracted much of attention. Experiments under pressure allow to test rigidity of the Me-H bonds and therefore provide crucial information on exact type of Me-H bonding in these hydrides, which is crucial for potential applications. We present new data on crystal structures of light hydrides under pressure and evidence for new pressure-induced phases. [1] I. Goncharenko, P. Cadavez-Peres, I. Mirebea and O.L. Makarova, Europhys. Lett. 54 (2001) 807; [2] I. Goncharenko, P. Cadavez-Peres, I. Mirebeau, O.L. Makarova, T. Le Bihan, and M. Mezouar, Phys. Rev. B 68 (2003) 214418; [3] O. Makarova, I. Goncharenko, T. Le Bihan, Solid State Comm. 132 (2004) 329.

O-173 **Raman and Visible Absorption Study of YH_3 at High Pressure.** T. Kume,[1] H. Ohura,[1] H. Shimizu,[1] A. Ohmura,[2] A. Machida,[2] T. Watanuki,[2] K. Aoki,[2] K. Takemura,[3] – [1]Gifu University, Gifu, Japan; [2]Synchrotron Radiation Center, Japan Atomic Energy Agency, Hyogo, Japan; [3]National Institute for Materials Science, Tsukuba, Japan

A great deal of attention to the hydrides of yttrium and some other rare earth metals has been paid from aspects of fundamental physics and practical applications as switchable mirrors[1]. Recently, various experimental studies have been performed for YH_3 under high pressures above 20 GPa by means of x-ray diffraction [2], infrared [3] and visible absorption [4], and a phase transition from hexagonal to cubic structure was observed above 10 GPa [2]. Very recently, an insulator-metal transition with band gap closing was suggested to occur around 23 GPa by the IR experiments [3]. In this work, we performed Raman and visible optical absorption experiments under high pressures above 20 GPa for better understanding the role of proton for the hexagonal-cubic transition and the gap closing. The experiments at high pressures were carried out by a diamond anvil cell (DAC). For the preparing

of YH_3 sample in the sample chamber of DAC, the sample chamber, in which a Y thin foil was located in advance, was filled with fluid hydrogen using gas loading apparatus at NIMS. The Raman and visible absorption spectra were detected as a function of pressure. On the basis of the spectral changes, the mechanism of hexagonal to cubic transition will be discussed. [1] J.N. Huiberts *et al*., Nature **380**, 231 (1996); [2] T. Palasyuk and M. Tkacz, Solid State Commun. **133**, 477 (2005); [3] A. Ohmura *et al*., submitted; [4] R. J. Wijngaarden *et al*., J. Alloys and Comp. **308**, 44 (2000).

O-174 **Pressure-Induced Structural Phase Transition in Metal Dihydrides.** W. Luo, R. Ahuja, – Uppsala University, Uppsala, Sweden

Alkaline earth hydrides CaH_2, SrH_2, BaH_2 and rare earth dihydrides EuH_2 and YbH_2 crystallize in an orthorhombic structure (Co_2Si-type) having a Pnma space group at ambient conditions. Under high pressure, it was shown experimentally that CaH_2, SrH_2, and YbH_2 transform to a hexagonal Ni_2In type structure with $P6_3/mmc$ space group. In this work, we have performed fully relaxed *ab initio* electronic structure calculations using projector augmented wave method as implemented in VASP program in conjunction with generalized gradient approximation (GGA). Our calculations well reproduced the structural phase transitions in these dihydrides as observed in the experiments. Further, we have also looked into the desorption of hydrogen in high pressure phases and compared it with ambient pressure phases.

O-175 **Hydriding Combustion Synthesis of TiFe.** I. Saita,[1] M. Sato,[1] H. Uesugi,[2] T. Akiyama,[1] – [1]Hokkaido University, Sapporo, Hokkaido, Japan; [2]Waseda University, Shinjuku-ku, Tokyo, Japan

Titanium iron (TiFe) is one of the most attractive metal hydrides because of the abundance and low cost of raw materials and the moderate conditions for hydrogen storage/release. However, it has not been practically used in spite of the tremendous efforts to reduce the time- and energy-consuming activation treatment. Aiming to improve the initial activity of TiFe, we applied Hydriding Combustion Synthesis (HCS) to the TiFe production. The HCS has attractive advantages for the direct production of metal hydride; time and energy saving, highly hydrogenated high purity product, large surface area, and activation-free product [1]. In the experiments, the reaction of hydriding titanium ($Ti + H_2 = TiH_2 + 144$ KJ) was utilized as the igniter for the HCS of TiFe because the adiabatic flame temperature of this reaction is 1800 K, which is enough high for melting both iron and titanium. The raw material of Ti and Fe powders mixed with 1:1 molar ratio was covered with additional Ti powders from above and placed in hydrogen atmosphere. After the Ti powders were ignited by electrically heated carbon filament, the TiFe synthesis reaction ($Ti + Fe + H_2 = TiFeH_2 + 64$ kJ) occurred successfully. As expected, the HCSed TiFe,stored hydrogen about 2.0 mass%, had improved initial activity for hydrogen storage with less activation treatment than current ingot product. [1] Akiyama T, Isogai H, Yagi J., J. Alloys and Compounds, 252, L1-L4 (1997).

POSTER SESSION I (P-176 to P-244) **Monday, October 2 – (8:00 PM – 10:30 PM)**

P-176 **Investigation on the Microstructure and Electrochemical Performances of As-cast and Quenched $La_{0.7}Mg_{0.3}Ni_{2.55-x}Co_{0.45}M_x$ (M = Cu, Al, Mn; x = 0-0.4) Electrode Alloys.** Y.-H. Zhang,[1,2] B.-W. Li,[2] H.-P. Ren,[2] Y. Cai,[2] X.-P, Dong,[1] X.-L. Wang,[1] – [1]Department of Functional Material Research, Central Iron and Steel Research Institute, Beijing, China; [2]School of Material, Inner Mongolia University of Science and Technology, Baotou, China

A new La-Mg-Ni system ($PuNi_3$-type) electrode alloy with high discharge capacity was investigated. $La_{0.7}Mg_{0.3}Ni_{2.55-x}Co_{0.45}M_x$ (M = Cu, Al, Mn; x = 0, 0.1, 0.2, 0.3, 0.4) electrode alloys were prepared by casting and rapid quenching. The effects of element substitution and rapid quenching on the microstructures and electrochemical performances of the alloys were investigated. The results obtained by XRD, SEM and TEM show that the alloys have a multiphase structure, including the (La, Mg)Ni_3 phase, the $LaNi_5$ phase and the $LaNi_2$ phase. The rapid quenching has an imperceptible influence on the phase compositions of the alloys, but changes the phase abundance of the alloys, and it can significantly improve the composition homogeneity of the alloys and markedly decrease the grain size of the alloys. The substitution of Cu for Ni can promote the formation of an amorphous phase in the as-quenched alloy, and a reversal result produced by the substitution of Al for Ni. The electrochemical measurement indicates that the element substitution decreases the discharge capacity of the alloys, whereas it obviously improved the cycle stability of the alloys. The positive influence of three kinds of substitution elements on the cycle life of the alloys is in the sequence Al > Cu> Mn, and negative influence on the discharge capacity in the sequence Al > Mn > Cu. The rapid quenching significantly enhances the cycle stability of the alloys, but it decreases the discharge capacity of the alloys.

P-177 **Effects of Cr Addition on the Microstructures and Electrochemical Performances of La-Mg-Ni System ($PuNi_3$-type) Hydrogen Storage Alloy.** X.-L. Wang,[1] Y.-H. Zhang,[1,2] X.-P. Dong,[1] G.-Q. Wang,[1] S.-H. Guo,[1] J.-Y. Ren,[2] – [1]Department of Functional Material Research, Central Iron and Steel Research Institute, Beijing, China; [2]School of Material, Inner Mongolia University of Science and Technology, Baotou, China

In order to improve the electrochemical cycle stability of La-Mg-Ni system ($PuNi_3$-type) hydrogen storage alloy, a trace of Cr was added in the alloy and $La_2Mg(Ni_{0.85}Co_{0.15})_9Cr_x$ (x = 0, 0.1, 0.2, 0.3, 0.4) hydrogen storage alloys were prepared by casting and rapid quenching. The electrochemical performances and microstructures of the as-cast and quenched alloys were determined and measured. The effects of Cr addition on the microstructures and electrochemical performances of the as-cast and quenched alloys were investigated in detail. The obtained results show that Cr addition has an inappreciable influence on the phase composition of the as-cast and quenched alloys, but change the phase abundance of the alloys obviously. The Cr addition obviously enhances the cycle stability of the as-cast and quenched alloys, but it decreases the discharge capacity. When Cr content increased from 0 to

0.4, the discharge capacity of the as-cast alloy decreased from 396.3 mAh/g to 355.6 mAh/g, and the cycle life increased from 72 cycles to 97 cycles. For the as-quenched (30 m/s) alloys, the discharge capacity decreased from 364.2 mAh/g to 334.2 mAh/g, and the cycle life increased from 100 cycles to 131 cycles. The Cr addition (x = 0.1) increases the activation capability and discharge voltage of the as-cast and quenched alloys.

P-178 **Multicomponent Alloys as a Source of Hydrogen for Fuel Cells.** D. V. Schur, A. F. Savenko, S. Yu. Zaginaichenko, K. A. Meleshevich, – Institute for Problems of Materials Science of NAS of Ukraine, Kiev, Ukraine

The hydrogen storage in metal hydrides is the urgent problem of hydrogen power engineering. The hydrogen use in transport, for fuel cells, in laboratory-scale and test units and for another purposes are the especially topical problems of today. The demand for metal hydrides as high-capacitive, safe and convenient in service sources of hydrogen have stimulated the investigation of hydrogen capacity of multicomponent alloys. The present work presents the investigation of alloy of AB5 type based on the commercial cerium ligature on addition of LaNi5 and V. The test specimens were produced both by mechanochemical method and by remelting in the electric arc furnace in the argon medium. The alloy composition was selected so that the equilibrium pressure of hydrogen over metal hydride was provided in the range from 0.5 to 10.0 MPa at room temperature. The developed multicomponent systems are characterised by high compactness, relatively low working temperature at the hydrogen supply under predetermined pressure and by good dynamics of process.

P-179 **The Effects of the Substitution of Ti and La for Zr in $ZrMn_{0.7}V_{0.2}Co_{0.1}Ni_{1.2}$ Hydrogen Storage Alloys on the Phase Structure and Electrochemical Properties.** J. C. Sun, S. Li, S. J. Ji, – Institute of Materials and Technology, Dalian Maritime University, Dalian, China

In this paper, phase structure and electrochemical properties of the overstoichiometric hydrogen storage electrode alloys $Zr_{1-x}Ti_x(Mn_{0.7}V_{0.2}Co_{0.1}Ni_{1.2})$ have been investigated. The results showed that when the Ti content increased, the content of the C15 Laves phase decreased while that of the C14 Laves phase increased. At same time, the Zr_7M_{10} phase and TiNi phase decomposed totally, which demonstrated high Ti content inhibited the appearance of second phase in the alloys. When x = 0. 2, the storage hydrogen electrode alloy $Zr_{0.8}Ti_{0.2}(Mn_{0.7}V_{0.2}Co_{0.1}Ni_{1.2})$ possessed the maximum discharge capacity 354mAh/ g, and preserved 91 % of total capacity at current 300mA/ g. In addition, due to doping La, the alloy $Zr_{0.75}Ti_{0.2}La_{0.05}Mn_{0.7}V_{0.2}Co_{0.1}Ni_{1.2}$ reached the maximum capacity 372mAh/ g after 4 cycles, and preserved 93 % of the maximum capacity after 30 cycles.

P-180 **The Effect of Cooling Rate on the Electrochemical Properties of Low Co-containing $Ml(NiCoMnAl)_5$ Alloy.** Y.-M. Du,[1] Y.-Q. Lei,[1] L.-X. Chen,[1] G.-L. Lu,[2] H.-G. Pan,[1] Q.-D. Wang,[1] – [1]Department of Materials and Engineering, Zhejiang University, Hangzhou, China; [2]Central Laboratory, Zhejiang University, Hangzhou, China

The crystal structure and electrochemical properties of $MlNi_{4.0}Co_{0.3}Mn_{0.4}Al_{0.3}$ (Ml: La-rich mishmetal) alloy prepared by both vacuum induction melting and melt-spinning at different cooling rates were comparatively studied by XRD, EDS and different electrochemical methods. The results show that all the as prepared alloys have a single $CaCu_5$ type structure, but the increase of cooling rate of the alloys leads to an increase in both crystallizability and composition homogeneity, and leads to a noticeable decrease in cell volume expansion rate ($\Delta V/V$) on hydriding. With the increase of cooling rate, the cycling stability of the alloys is greatly improved, but their initial discharge capacity and high-rate dischargeablity (HRD) are lowered somewhat. It is found that the improvement in cycling stability of the alloys is closely related to their lower cell volume expansion on hydriding and more uniform composition, and the decrease of HRD of the alloys is mainly attributed to the decrease of electro-catalytic activity for change-transfer reaction and the lowering of the diffusion rate of hydrogen in the alloy bulk.

P-181 **Effect of Rare Earth on Hydrogenation for Mm-based AB_5-type Alloy.** D. Endo,[1] K. Sakaki,[2] E. Akiba,[2] – [1]GS-YUASA Corporation, Kyoto, Japan; [2]National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki, Japan

Misch metal (Mm) based hydrogen storage alloys are applied to the negative electrode of the Ni-MH battery for consumer and HEV uses. Because it is known that the lattice volume has a linear relationship with the hydrogen equilibrium pressure, there has been few studies on a chemical effect of the element for the hydrogenation properties especially for the equilibrium pressure. In this study the effect of species of rare earth elements for the hydrogenation has been investigated. $(La\text{-}Pr\text{-}Nd\text{-}M)(Ni_{3.55}Co_{0.75}Al_{0.3}Mn_{0.4})$ (M : rare earths) AB_5-type alloys that had the same lattice parameters were prepared. Using in-situ XRD measurement with Rietveld analysis, changes of lattice parameters and lattice strain were calculated from their diffraction profiles during hydrogenation. Ce containing alloy $(La_{0.34}Ce_{0.47}Pr_{0.05}Nd_{0.14}\text{-}Ni_{3.55}Co_{0.75}Al_{0.3}Mn_{0.4})$ showed higher equilibrium hydrogen pressure (0.11 MPa) than the others (0.08 MPa) and the lattice expansion from the solid solution to the hydride phases was 11% which is larger than the others (average 7 %). The isotropic strain in the hydride phase of Ce containing alloy was 0.9 % at H/M = 0.4 but that of the other alloys ranged 0.3 – 0.9 % at the same hydrogen content. It can be concluded that Ce has a chemical effect for the hydrogenation properties in lattice expansion, equilibrium pressure and strain in the lattice if they are compared for the alloys with the same lattice volume.

P-182 **Synthesis of Mg-Ni-Ca Metal Hydride by Mechanical Alloying.** E. Y. Lee, K. S. Jung, K. S. Lee, – Division of Advanced Materials Science & Engineering, Hanyang University, Seoul, South Korea

Mixtures of Mg-Ni-Ca were ball–milled to synthesize an amorphous phase or a composite phase by changing the composition of the mixtures. $(Mg_{0.5}Ca_{0.5})Ni_2$ yielded the composite of Mg_2Ni and $CaNi_5$, while other compositions produced the amorphous phase. Among the amorphous alloys, $MgNi_{0.95}Ca_{0.05}$ alloy had the highest initial discharge capacity 460 mAh/g and retained 58 % after 10

cycles, but $(Mg_{0.5}Ca_{0.5})Ni_2$ alloy had the best cycle life retaining 60 % of the initial discharge capacity of 210 mAh/g after 30 cycles. XPS (X-ray Photoelectron Spectroscopy) analysis revealed Mg spectra of the amorphous $MgNi_{0.95}Ca_{0.05}$ alloy was shifted to lower binding energy because Mg reacted with OH^- of the electrolyte. However, Mg spectra of the composite $(Mg_{0.5}Ca_{0.5})Ni_2$ alloy did not show any changes of binding energy during cycle test. These results indicate that the amorphous phase had the highest discharge capacity and the composite formation improved the cycle life.Keywords : Metal hydride, Calcium, Amorphous, Composite, Electrode properties

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P-183 **Structural Analysis and Hydrogen Storage Properties of La-Mg-Ni System Alloys.** T. Kohno,[1] M. Yamamoto,[1] H. Yoshida,[2] M. Kanda,[2] – [1]Corporate Research & Development Center, Toshiba Corporation, Kawasakai, Kanagawa, Japan; [2]Japan Science and Technology Corporation, Chiyoda-ku, Tokyo, Japan

The capacity of Nickel-Metal Hydride battery (MH) using $LaNi_5$ type alloy is approaching its limits, because the improvements to increase the capacity have already realized high utilization of the theoretical capacity of this alloy. For increasing the discharge capacity of the negative electrode of MH battery, La-Mg-Ni alloy is one of the most promising systems. We studied La-Mg-Ni_X (X=3-3.5) system alloy, and discovered the new ternary system alloys: La_2MgNi_9, $La_5Mg_2Ni_{23}$, La_3MgNi_{14}. In this work, the hydrogen storage properties of these La-Mg-Ni system alloys, La_2MgNi_9, $La_5Mg_2Ni_{23}$, La_3MgNi_{14}, were investigated. As a result, the negative electrode of the $La_5Mg_2Ni_{23}$ system alloy showed a large discharge capacity (410 mAh/g), 1.3 times larger than that of $LaNi_5$ type alloy. The structural analysis of these new hydrogen storage alloys was also performed by using HRTEM. As a result, these ternary system alloys were found to be mainly composed of stacked RNi_5 ($CaCu_5$ type) and R_2Ni_4 (Laves type) structure subunits in a superstructure arrangement. $La_5Mg_2Ni_{23}$ alloy is composed of the primitive cell of three $LaNi_5$ units and the primitive cell of two $LaMgNi_4$ units.

P-184 **Effect of Al and Ce Substitution of the Electrochemical Properties of Amorphous MgNi-based Alloy Electrodes.** H. Yuan, Y. Feng, L. Jiao, Y. Wang, – Institute of New Energy Materials Chemistry, Nankai University, Tianjin, China

Mg-based hydrogen storage alloys $Mg_{0.9}Al_{0.1-x}Ce_xNi$(x=0.00, 0.01, 0.02, 0.025, 0.075) were successfully prepared by means of mechanical alloying (MA).The structure and the electrochemical characteristic of these Mg-based electrodes were also studied. The result of X-ray diffraction (XRD) shows that the main phase of the alloys has amorphous structures. The charge-discharge cycle tests indicate that these alloys have good electrochemistry active characteristics. And the cycle performance of $Mg_{0.9}Al_{0.1-x}Ce_xNi$(x=0.00, 0.01, 0.02, 0.025) are better than MgNi alloys. Among these alloys, the $Mg_{0.9}Al_{0.08}Ce_{0.02}Ni$ has the best cycle stability and its highest discharge capacity was 435.1mAhg^{-1}. The Ce added content should not over 0.025 (alloy element mass ratio) in order to obtain good cycle stability. The cyclic voltammograms (CV), electrochemical impedance spectroscopy (EIS) and anticorruptionm test (Potentiodynamic polarization curves) were also studied. These tests indicated that the appropriate substitution of Al and Ce can improve the anticorrosion behavior in alkali solution.

P-185 **A Novel Hydrogen Storage Alloy CoSi as Anode Material for Ni-MH Battery.** L. Jiao, G. He, H. Yuan, Y. Wang, – Institute of New Energy Materials Chemistry, Nankai University, Tianjin, China

A series of storage alloys CoSi was prepared by means of mechanical alloying (MA) at different ball milling time and investigated as an anode material in aqueous KOH solution. The experimental results demonstrated that the CoSi particles prepared show excellent electrochemical reversibility and considerably high charge-discharge capacity. CoSi milled 5h had the highest initial discharge capacity of 405 mAh/g and still kept 263.1mAh/g which is 65% of initial discharge capacity after 50 cycles at current density 25 mA/g, while the CoSi milled 40h showed the best cycling stability, and the capacity is no declination after 50 charge-discharge cycles which kept about 220 mAh/g. The comparison of the XRD patterns between the fresh alloy and the alloy after 50 cycles indicated that charge-discharge process changed the structure of the alloy from amorphous to crystal.

P-186 **Characterization of Initial Activation Behavior for Hydrogen Storage Alloys by Acoustic Emission Technique.** H. Inoue, R. Tsuzuki, S. Nohara, C. Iwakura, – Osaka Prefecture University, Sakai, Japan

Acoustic emission (AE) method is a technique for detecting elastic waves generated by the cracking of materials. The AE method has several advantages as follows; 1) a simple and economic system, 2) a nondestructive technique, 3) a realtime analysis with high sensitivity. In this study, we used the AE technique for analyzing the cracking of hydrogen storage alloys, negative electrode materials for Ni-MH batteries, during charge-discharge processes and the difference in initial activation behavior among the alloys was characterized. The elastic waves generated by the cracking etc. were detected by the AE transducer and transformed into AE signals. The AE signals were amplified and stored in the automatic AE monitoring system. The stored data were exhibited in forms of time history of the AE signals, power spectrum and an AE waveform, respectively. The power spectrum and AE waveform show the distribution of frequency for the AE signals and the lifetime of the AE signals, respectively. We obtained the following results from the analysis of the time histories of the AE signals, power spectra and AE waveforms in charge processes for two kinds of alloy particles. $MmNi_{3.6}Mn_{0.4}Al_{0.3}Co_{0.7}$ alloy particles with sizes of 106-125 mm cracked frequently in the former half of the first charging, followed by hydrogen evolution. The AE signals decreased steadily with repeating the charge-discharge cycle. $TiCr_{0.3}V_{1.8}Ni_{0.3}$ alloy particles with sizes of 75-106 mm exhibited AE signals due to hydrogen evolution at the beginning of the first charge process and then they were replaced with the AE signals due to the cracking of the alloy. In both cases, the decrease in particle size led to the decrease in number and intensity of AE signals due to the cracking.

P-187 **Electrochemical Properties of $La_{0.7-x}Ti_xMg_{0.3}Ni_{2.45}Mn_{0.1}Co_{0.75}Al_{0.2}$ (x=0-0.1) Hydrogen Storage Electrode Alloys.** H. Pan, Y. Yue, M. Gao, Y. Lei, – Department of Materials Science and Engineering, Zhejiang University, Hangzhou, P. R. China

In this paper, the structure and electrochemical properties of the $La_{0.7-x}Ti_xMg_{0.3}Ni_{2.45}Mn_{0.1}Co_{0.75}Al_{0.2}$ (x=0, 0.02, 0.04, 0.06, 0.08, 0.1) hydrogen storage alloys have been studied systematically. X-ray powder diffraction (XRD) analysis shows that all the alloys mainly consist of a $(La,Mg)Ni_3$ phase and a $LaNi_5$ phase. The cell volumes of these two phases decrease with increasing x. Electrochemical studies indicate that the maximum discharge capacity decreases from 366.6 mAh/g (x=0) to 329.7 mAh/g (x=0.1). The high rate dischargeability (HRD) first increases and then decreases with increasing x. Electrochemical impedance spectroscopy (EIS), linear polarization, anodic polarization and potential-step measurements showed that the exchange current density I_0 and the limiting current density I_L first decrease and then increase, the hydrogen diffusion coefficient D always increases with x increasing from 0 to 0.1.

P-188 **Electrochemical Properties of Vanadium Electrode under Different Temperatures.** J. Liang, Y. Chen, M. Tao, C. Wu, – School of Materials Science and Engineering, Sichuan University, Chengdu, China

The electrochemical properties of V electrode under 293K to 353 were studied in this paper. It was found that V electrode showed a high discharge capacity of 979mAh/g at 293K, but its discharge plateau potential was as low as –0.4V *vs* Hg/HgO reference electrode. With the increase of the testing temperature, the discharge capacity had little change, but the discharge plateau potential and high-rate dischargeability were improved. The discharge plateau potential was up to -0.65V *vs* Hg/HgO reference electrode at 353K. The increase of the discharge plateau potential might be due to the enhanced electrochemical reaction rate at the electrode-electrolyte interface at the elevated temperatures.

P-189 **Low-Temperature Discharge Performances of $Mm(NiMnAl)_{5-x}Co_x$ Hydrogen Storage Alloy.** M. Tao, Y. Chen, C. Wu, C. Fu, M. Tu, – School of Materials Science and Engineering, Sichuan University, Chengdu, China

The effects of Co on the discharging capacity, hydride stability and hydrogen diffusion coefficient of $Mm(NiMnAl)_{5-x}Co_x$ ($0.2<x<0.8$) hydrogen storage alloys at -40□ were investigated. The results manifested that with the increase of Co content in the alloy, the crystal unit cell volume and hydride decomposing enthalpy increase, the discharging capacity and hydrogen diffusion coefficient decrease. The hydrogen diffusion coefficient is a dominant factor influencing the discharging properties of hydrogen storage alloy at -40□.

P-190 **Electrochemical Reaction of $LiAlH_4$ in THF Solution.** H. Senoh, T. Kiyobayashi, C. Lu, K. Tatsumi, N. Kuriyama, – National Institute of Advanced Industrial Science and Technology (AIST), Ikeda, Japan

Metal hydrides are one of the most hopeful candidates as electrochemical storage media. Rechargeable nickel-metal hydride battery with high power and long cycle life has brought about drastic developments of battery applications to such as a hybrid electric vehicle [1]. The potential of sodium borohydride as an anodic material appeared in fuel cell [2]. In the case of another complex hydride, 'Hydride bath' with $LiAlH_4$ [3] has been applied to the electrodeposition of Al in nonaqueous systems. Anodic oxidation of $LiAlH_4$ itself is, however, yet to be investigated. In this paper, we present electrochemical reaction of $LiAlH_4$ in THF solution at room temperature. The oxidation potential of AlH_4^- anion is *ca.* 0.5 V vs. Li^+/Li, which is in good agreement with that calculated from the thermodynamic data of $LiAlH_4$. During anodic polarization, the AlH_4^- anion is oxidized to generate H_2 gas and the limiting current is over 10 mA/cm^2 on a Pt electrode. Overpotential against logarithmic current density is linear, suggesting that the oxidation reaction of AlH_4^- anion proceeds through the charge-transfer step. The system may lead to a novel electrochemical system with high voltage and high power density. [1] T. Sakai, M. Matsuoka, C. Iwakura, Handbook on the Physics and Chemistry of Rare Earths, 21 (1995) 133; [2] M. E. Indig, R. N. Snyder, J. Electrochem. Soc., 109 (1962) 1104; [3] D. E. Couch, A, Brenner, J. Electrochem. Soc., 99 (1952) 234.

P-191 **The Hydrogen Desorption Kinetics of $Mg_{0.9-x}Ti_{0.1}Pd_xNi$ (x = 0.04, 0.06, 0.08 and 0.1) Electrode Alloys.** Q. F. Tian,[1] Y. Zhang,[1] L. X. Sun,[1] F. Xu,[1] H. T. Yuan,[2] – [1]Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, China; [2]Institute of New Energy Material Chemistry, Nankai University, Tianjin, China

The $Mg_{0.9-x}Ti_{0.1}Pd_xNi$ (x = 0.04, 0.06, 0.08, 0.1) hydrogen storage alloys were prepared by mechanical alloying. The hydrogen desorption kinetics of the electrode alloys were studied by potentiostatic discharge experiments. Experimental results shown that the three-dimensional diffusion dominated the hydrogen desorption process of electrode alloys. The rate constants of hydrogen desorption reaction increased with temperature. The activation energies of the desorption were calculated according to the Arrenius equation. The values were 49.11, 45.99, 42.50 and 40.66 $kJ\cdot mol^{-1}$ for x = 0.04, 0.06, 0.08 and 0.1 of $Mg_{0.9-x}Ti_{0.1}Pd_xNi$ electrode alloys, respectively. The limiting currents were determined by anodic polarization experiments and its variation with Pd content agreed well with those of hydrogen desorption activation energies.

P-192 **Electrochemical Investigations on Mg-based Alloys using a Cavity Microelectrode.** N. Katif, M. Mohamedi, L. Roue, – INRS-Energie, Matériaux et Télécommunications, Varennes, Québec, Canada

Electrochemical investigations on metal hydrides for Ni-MH batteries are usually performed with composite electrode which consists in a pellet made from a mixture of powder active material, graphite and Teflon binder compacted on a porous current collector. This electrode design is well-adapted for slow experiments such as galvanostatic charge/discharge cycling tests. However, for faster electrochemical investigations such as cyclic voltammetry experiments, its large dimensions (typically, one cm diameter and a few fractions of a mm thickness) induce both large ohmic drop and capacitive current. This leads to distorted and no well-resolved electrochemical responses, even at the usual scan rate of 5-500 mV/s. The use of a cavity microelectrode where the cavity

(typically, 20-50 µm diameter) is filled up with pure metal hydride grains allows to minimize such drawbacks. The present contribution illustrates the advantages of the cavity microelectrode for the electrochemical characterization of Mg-based alloy powders elaborated by high-energy ball milling.

P-193 **Stacking Structures and Electrode Performances of Rare Earth-Mg-Ni -based Alloys for Nickel-Metal Hydride Battery.** T. Ozaki,[1] Y. Kitano,[1] S. Tanase,[1] T. Sakai,[1] M. Kanemoto,[2] T. Kakeya,[2] M. Kuzuhara,[2] M. Watada,[2] – [1]National Institute of Advanced Industrial Science and Technology (AIST), Ikeda, Osaka, Japan; [2]GS Yuasa Corporation, Kyoto, Japan

Rare earth-Mg-Ni-based alloys with stacking structures consisting of AB_5 unit ($CaCu_5$-type structure) and A_2B_4 unit (Laves structure) have received attention as negative electrode materials for advanced nickel-metal hydride (Ni-MH) battery. These alloy materials are very attractive because of high hydrogen storage capacity, low cobalt content and moderate plateau pressure, but have some difficulty to control the phase abundance and electrode performances. In this paper, relationship among composition, phase abundance, and electrochemical properties was investigated. Structural analysis was done using synchrotron X-ray diffraction patterns. In alloys such as $La_{0.8}Mg_{0.2}Ni_{3.4-x}Co_{0.3}(Mn,Al)_x$, phase abundance was drastically changed with increasing amount of Mn and Al. In the range of $0.1<x<0.2$, hexagonal Pr_5Co_{19}-type (5:19H) or rhombohedral 1:4R phases were dominant. The Rietveld analysis suggested that Mg occupy La sites in A_2B_4 unit, and Al have tendency to occupy Ni sites between A_2B_4 unit and AB_5 unit or between AB_5 units in these types of phases. The developed alloys showed higher discharge capacity by 20% than the conventional one at a 0.2 C discharge rate. [1] K. Kadir, T. Sakai, I. Uehara, *J. Alloys Compds.*, **257** (1997)115; **287** (1999)264; [2] J. Chen, N. Kuriyama, H.T. Takashita, H. Tanaka, T. Sakai, and M. Haruta, *Electrochem. Solid State Lett.*, **3**(6) (2000)249; [3] T. Kohno, H. Yoshida, F. Kawashima, T. Inaba, I. Sakai, M. Yamamoto, and M. Kanda, *J. Alloys Compds.*, **311**, L5 (2000).

P-194 **Investigation on High-Pressure Thermal Driven Hydride Hydrogen Compressors.** X. H. Wang, R. G. Chen, L. X. Chen, S. Q. Li, C. P. Chen, Q. D. Wang, – Department of Materials Science and Engineering, Zhejiang University, Hangzhou, China

It is well-known that metal hydrides can be used to compress hydrogen. In the present study, AB_5 type and AB_2 type multicomponent hydrogen storage alloys have been studied for the purpose of high-pressure hydrogen compression and several alloys with favorable hydrogen storage properties have been selected. Some techniques to improve the heat and mass transfer of the metal hydride bed were investigated and several types of metal hydride high-pressure compressors were designed and built with the hydrogen capacity from 20 L to 80 Nm^3 and product hydrogen pressure in the range of 5-40MPa. These metal hydride hydrogen compressors are integrated with the functions of hydrogen combination and hydrogen purification. The product hydrogen purity reaches 99.9999% when the raw hydrogen of 98% purity is used. These hydride compressors are competent for hydrogen refueling for the on-board hydrogen storage units of fuel cell vehicles, including high-pressure hydrogen tanks and metal hydride hydrogen storage units.

P-195 **Accuracy in Hydrogen Sorption Measurements.** D. P. Broom, C. Filiou, P. Moretto, – Institute for Energy, Petten, The Netherlands

The accuracy of sorption measurements performed on potential hydrogen storage materials has been the subject of much controversy in recent years, particularly in the case of sorption by carbon nanostructures. As the technological interest in the solid state storage of hydrogen increases, it is of increasing importance to investigate the methods used to determine the sorption properties and hence the storage capacities of new and existing materials. In this paper, we briefly review the different techniques available and recent literature on the topic, discuss the possible sources of errors and present some comparative measurements on some AB_5 hydrogen-absorbing intermetallics. Equilibrium pressure-composition isotherm data measured on two $LaNi_{5-x}Al_x$ samples using commercial gravimetric and volumetric instrumentation were found to be in good agreement with each other.

P-196 **Closed Loop Cycling Device for Hydride Forming Materials Characterization.** M. S. Grinberg,[1] A. Talagañis,[2] P. Arneodo Larochette,[2] A. Baruj,[2] F. J. Castro,[2] G. Meyer,[2] – [1]Fac. Ingeniería, U. Nac. Cuyo, Mendoza, Argentina; [2]Centro Atómico Bariloche, CNEA and CONICET, S. C. Bariloche, Argentina

For most practical applications, hydride forming materials should stand a large number of hydrogen absorption/desorption cycles during their lifetime. So, the study of the change of technological properties of materials under cycling is a necessary test before industrial application. Cycling devices are usually based on open loop configurations involving a high purity hydrogen source and an exhaust system. The main drawbacks of such configurations are an important hydrogen waste and a potential concern with gas purity. Here we present a novel, fully automated, device designed to perform cycling tests in a closed loop configuration. The equipment allows us to detect variations in the storage capacity of the material and in the hydrogen absorption/desorption kinetics. The setup involves three parts: a) a reactor where the sample to be studied is loaded, b) an intermediate volume and c) a hydrogen supply/sink. These parts are connected to each other via electrically actuated valves. The main novelty of our device consists in the use of LaNi5 as the hydrogen supply/sink when is heated/cooled during cycling. The LaNi5 is mixed with 15% Cu powder in order to improve the thermal transference, reducing the time of an absorption/desorption cycle. In this way, gas economy and gas purity are insured. The available cycling pressure range is 5 - 55 bar, with a minimum cycle time of 4 min. The temperature of the reactor can be set between room temperature and 300 deg C.

P-197 **Grain Size Refinements in Al-Mg and Cu-Mg Alloys by Hydrogen Heat-treatment.** A. Kamegawa, T. Funayama, H. Takamura, M. Okada, – Department of Materials Science, Tohoku University, Sendai, Miyagi, Japan

Among a number of grain size refinement technique, the author group has investigated hydrogen heat-treatment of so-called Hydrogenation- Disproportionation- Desorption- Recombination (HDDR) process applied to the alloys which contain some amounts of elements with strong affinity with hydrogen such as Mg, even though the alloys are mostly consist of the elements with weak affinity with hydrogen. We chose Al-(3-7.8)mass%Mg and Cu-3 mass%Mg to research the possibility of occurrence of HDDR phenomena and their effects on the evolution of the microstructure in the Al-Mg and Cu-Mg alloys. Upon hydrogenation of the Al-Mg alloys, a disproportionation reaction occurred in forming of MgH_2 embedded Al matrix phase. In the subsequent hydrogen-desorption of the alloys MgH_2 was decomposed and Mg was resolved into Al matrix phase, in resulting in the original solid solution alloys. This means that the HDDR phenomena take place in the Al-Mg alloys. It is found that the grain size of the alloys turned into an order of 10nm after HDDR treatments such as heat-treatment at 350°C under hydrogen pressure of 7.5MPa for 72h, in following by the hydrogen desorption at 350°C for 4h in vacuum. The grain size of the HDDR-treated alloys increased with decreasing Mg content. It is found that the Cu-Mg alloys also exhibit HDDR phenomena and the grain size was refined into the order of 100nm. The mechanical properties of the treated alloys were also investigated by nano-indentation method.

P-198 **V-Ti-Cr-Fe Hydrogen Storage Alloys Prepared by V-Fe Master Alloy.** Y. Yan, Y. Chen, H. Liang, X. Zhou, C. Wu, M. Tao, – School of Materials Science and Engineering, Sichuan University, Chengdu, P. R. China

V-based alloys having high hydrogen capacity arouse popular concerns, but their application is difficult mainly due to the high cost of pure metal vanadium. V-Fe master alloy is a cheap vanadium source to prepare low-cost V-based alloys.In this paper, the hydrogen storage properties and microstructure of V(30~55at%)-Ti(18~35at%)-Cr(16□25at%)-Fe(6~10at%) alloys prepared with V-Fe master alloy were studied by PCT measurement, XRD and SEM. Two phases, Laves phase and BCC phase, appear in all these alloys due to the existence of Si from V-Fe master alloy. All these alloys show good activation properties, which absorb hydrogen directly at room temperature without any pretreatment and reach their maximum capacities within 5min. The alloys show high absorption capacities higher than 3.4wt% at room temperature under 3MPa hydrogen pressure and desorption capacities exceeding 2.2wt% at 353K.

P-199 **An Overview of Hazardous Materials Regulations and their Impact on Developers of Hydrogen Storage Materials and Systems.** N. T. Stetson, K. J. Gross, – Hy-Energy LLC, Newark, CA, USA

Currently there is a tremendous push to develop commercial technologies for the emerging Hydrogen Economy, and new advanced materials and systems for hydrogen storage are now at the forefront of this effort. With the increased visibility and funding, new groups are joining the effort, new collaborations are being established and there is more sharing of samples and partitioning of work efforts. The increased visibility has also led to more scrutiny of the activities and procedures of researchers. Therefore it is critical, both in terms of actual safety and the perception of safety, that researchers are aware of hazardous materials regulations and how they impact the safe and legal transport of samples and systems. This paper presents an overview of hazardous materials regulations that directly relate to the transport, storage and use of materials and systems for hydrogen storage. Also provided are references to useful resources on these regulations and their compliance.

P-200 **Experimental and Theoretical Investigation of the Cycle Durability Against CO and Degradation Mechanism of the $LaNi_5$ Hydrogen Storage Alloy.** S. Han,[1] H. Tanaka,[1] X. B. Zhang,[1] N. Kuriyama,[1] N. Taoka,[2] K. Aihara,[2] Q. Xu,[1] – [1]National Institute of Advanced Industrial Science and Technology (AIST), Ikeda, Osaka, Japan; [2]New Material Center (NMC), Osaka Science and Technology Center (OSTEC), Nishi-Ku, Osaka, Japan

From both the experimental and theoretical aspects we have investigated the cycle durability against CO and degradation mechanism of the $LaNi_5$ hydrogen storage alloy with CO-containing H_2. Temperature-programmed desorption (TPD) measurements on the original alloy and the corresponding one after hydrogen absorption-desorption cycles exhibit that: (1) the molecular CO can be adsorbed on the clean alloy surface, and thus decrease the hydrogen storage ability of the alloy; (2) with the increase of the cycle number the partial decomposition of the CO and the subsequent adsorption of C atom and O atom on the surface is deleterious to the hydrogen storage competence of alloy; (3) the alloy after a large number of hydrogen absorption-desorption cycles with pure hydrogen exhibits lower cycle durability against CO than the un-pretreated one. From the results of first-principle calculations, it is found that the adsorption of the molecular CO prefers the on-top and bridging sites on the Ni atoms. Moreover, the latter one is more stable than the former one.

P-201 **Change in the Rate of Hydrogen Absorption and Work Function of Pd by Irradiation of Ions(N^+, Cr^+, Ag^+ and Xe^+).** R. Morimoto,[1] H. Abe,[2] H. Uchida,[1] – [1]Department of Applied Science, Graduate School of Engineering, Tokai University Kita-Kaname, Hiratuka, Kanagawa Japan; [2]Department of Radiation Effect Group, Japan Atomic Energy Agency Watanuki Takasaki, Gunma, Japan

In previous studies, the induction of vacancy in Pd was found effective to increase the rate of hydrogen absorption rate. In this study, we investigated the effects of ion irradiation on the rate of electrochemical hydrogen absorption of Pd using N^+, Cr^+, Ag^+, and Xe^+ ions in the range of acceleration energy from 30 keV to 350 keV, and ion densities up to a dose of 1 x 10^{17} cm^{-2}. The ion irradiation is known to induce vacancy type defects in a metal. The ion irradiation was carried out using a facility, TIARA (Takasaki Ion Accelerators for Advanced Radiation Application) in JAEA (Japan Atomic Energy Agency). The rate of hydrogen absorption was measured electrochemically at room temperature. In previous studies, we reported the remarkable enhancement of the initial activation rate of $LaNi_{2.5}Co_{2.5}$ alloy in the H_2 gas phase and in alkaline electrochemical process by the pretreatment of the surface of these alloy with the alkaline hydroxide solution such as KOH, NaOH and LiOH. As a result, the work function of the alloy became higher, and this resulted in the increasing initial hydriding rate. After these irradiated samples had been treated with KOH, the

measurement of work function was made. With the increasing surface concentration of K atoms and vacancy concentration, the work function became decreased from 0.1eV to 0.8eV. In this report, the reaction mechanisms are discussed.

P-203 **Extreme Surface as the Gateway for Hydrogen Uptake - Roles of Mg-Surface in Synthesizing Sodium Borohydride from Borax.** S. Suda,[1] N. Morigasaki,[2] S. Hara,[2] – [1]MERIT (ICHST), Tateshina, Chino, Japan; [2]ICHST, Tateshina, Chino, Japan

In a regeneration process for producing sodium borohydride (ABH, $NaBH_4$), the Mg-surface acts important roles for transferring hydrogen to H in MgH_2 and then to H in SBH. The reaction mechanism during SBH formation will be reported based on the recent experimental works.

P-204 **Transmission Electron Microscopy Characterization of $NaAlH_4$ and Ti-doped $NaAlH_4$.** P. E. Vullum,[1] M. P. Pitt,[2] B. C. Hauback,[2] J. Walmsley,[1] R. Holmestad,[1] – [1]Department of Physics, Norwegian University of Science and Technology, Trondheim, Norway; [2]Institute for Energy Technology, Kjeller, Norway

Adding transition metals such as Ti to $NaAlH_4$ have enabled the alanate to both absorb and desorb hydrogen at moderate temperatures (120–140°C). In addition, the kinetics of hydrogen reabsorption are increased by several orders of magnitude. Since the discovery of adding Ti as a catalyst to make $NaAlH_4$ a potential hydrogen storage material, no experimental effort has succeeded to locate the active Ti, and the physical role played by Ti in enhancing hydrogen absorption/desorption kinetics is still an unsolved matter of controversy. Transmission electron microscopy (TEM) is a versatile tool to characterize materials with resolution down to the atomic scale. However, two problems have limited the use of TEM in the context of alanates: a) The alanate is highly unstable under the electron beam, and b) it is a challenge to transport the alanate into the microscope without exposing the sample to O_2 or H_2O. We have carefully explored the possibilities and limitations by using TEM to characterize $NaAlH_4$ and Ti doped $NaAlH_4$. Grain sizes, microstructure and morphology for $NaAlH_4$, exposed to different kind of milling conditions, hydrogen cycling and Ti enrichment (up to 10 mol%), have been determined. In addition, the location of Ti, and especially the active Ti, has been in focus for the TEM characterization.

P-205 **Hydrogen Generation From Hydrolysis of Sodium Borohydride Using Hydrogenphosphate-Stabilized Nickel(0) Nanoclusters as Catalyst.** Ö. Metin, S. Özkar, – Department of Chemistry, Middle East Technical University, Ankara, Turkey

The development of new storage materials will facilitate the use of hydrogen as a major energy carrier in near future. In hydrogen economy, chemical hydrides have been tested as hydrogen storage materials for supplying hydrogen under mild conditions. Among these chemical hydrides, sodium borohydride, $NaBH_4$, appears to be a promising hydrogen storage material as it provides a safe and practical mean of producing hydrogen and has a hydrogen content of 10.7 % by weight. However, hydrolysis of sodium borohydride requires a catalyst for the generation of hydrogen at a useful rate. All of the prior catalysts tested for the hydrolysis of sodium borohydride with one exception are heterogeneous and, therefore, have limited activity because of the surface area. Here, we report for the first time the synthesis and use of water-dispersible hydrogenphosphate-stabilized nickel(0) nanoclusters as catalyst in the hydrolysis of sodium borohydride. Kinetics of this nickel(0) nanoclusters catalyzed hydrolysis of sodium borohydride was studied as well. The reaction was found to be first order in catalyst concentration and zero order in substrate concentration. The hydrogenphosphate-stabilized nickel(0) nanoclusters catalyst provides a lower activation energy (Ea = 46,6 kJ/mol) than bulk nickel (Ea= 71 kJ/mol) for the hydrolysis of sodium borohydride.

P-206 **Effect of Surface Contaminations on the Reaction Rate of the $TiCr_{1.4}Mn_{0.6}$.** I. Tajima, Y. Takada, H. Uchida, – Course of Applied Physics, Graduate School of Engineering, Tokai University, Kitakaname, Hiratsuka, Kanagawa, Japan

As well known, Ti-Cr alloys absorb hydrogen at low temperatures below 273K, and these alloys are applied to metal hydride freezers without CFC or ammonia gas. In practical use, hydrogen storage alloys tend to be exposed to low vacuum or air. Therefore, the surface becomes contaminated by O_2, H_2O and the surface is covered with oxide or hydroxide layers. This problem becomes more serious at low temperatures because the dissociation of hydrogen molecules on the metal surface is inhibited. In this study, the surface of the $TiCr_{1.4}Mn_{0.6}$ was exposed to air from 30 minutes to 50 hours in low vacua and the initial rate of hydrogen absorbing was measured with respect to the pressure and temperature dependences. The influence of surface contaminations on the kinetic properties of hydrogen absorption by the $TiCr_{1.4}Mn_{0.6}$ to reported.

P-207 **The Plutonium Hydriding Reaction: The Role of Air Formed Oxide in Controlling Reaction Initiation.** G. W. McGillivray, I. M. Findlay, – Atomic Weapons Establishment, Aldermaston, Reading, United Kingdom

The safe, long term storage of massive plutonium can be compromised by the metal's susceptibility to hydriding attack[1]. Furthermore, it has been shown that once formed, hydride can act to catalyse O_2 oxidation of the metal[2][3], leading to the generation of easily dispersible oxide and hydride powders. A predictive model of long-term hydriding behaviour is required, and a necessary precursor of such a model is a quantificationof reaction initiation as a function of relevant parameters. Mechanistically, the initiation of the plutonium / hydrogen reaction is controlled by an ever present oxide overlayer which controls the diffusion of hydrogen species from the gas / oxide interface to the oxide / metal interface. This process is analogous to that which governs hydriding initiation in the uranium / hydrogen system[4]. In the case of plutonium, an added complication is that the composition of the oxide varies as a function of the storage environment. The air formed oxide has a duplex structure comprising a PuO_2 overlayer and athinner Pu_2O_3 layer at the oxide / metal interface. As the position of the intra-oxide interface within the overall oxide structure can changeas a function of temperature and storage atmosphere, it is necessary to have an understanding of the hydrogen transport properties of both $PuO_2$and Pu_2O_3 as individual compounds before a true understanding of the behaviour of the duplex

oxide can be gleaned. Data will be presented which will show the variation of hydriding initiation time as a function of hydrogen pressure in the range 0 - 1 bar,for both oxide structures. Additionally, temperature dependence data will be used to determine the activation energy of reaction initiation for both oxide structures. [1] J. M. Haschke & J. C. Martz, "Plutonium Storage" in "Encyclopaedia of Environmental Analysis and Remediation" John Wiley and Sons, pp. 3740-3755; [2] J. M. Haschke & T. H. Allen, J. Alloys Comp., 320, 2001, 58-71; [3] J. M. Haschke & J. C. Martz, J. Alloys Comp., 266, 1998, 81-89; [4] J. Bloch, F. Simca, M. Kroup, A. Stern, D. Shmariahu, & M. H. Mintz, J. Less Comm. Met., 103, 1984, 163; Copyright must be acknowledged in the published full text in the following form © British Crown Copyright 2006 / MOD Published with the permission of the controller of Her Britannic Majesty's Stationary Office.

P-208 **Hydrogen Sorption Kinetics of the Composites 85%Mg-15%$Mg_2Ni_{1-x}Co_x$ Obtained by Ball Milling.** M. Khrussanova,[1] E. Grigorova,[1] Ts. Mandzhukova,[1] M. Khristov,[1] J. L. Bobet,[2] P. Peshev,[1] – [1]Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria; [2]Institut de Chimie de la Matiere Condensee de Bordeaux, ICMCB CNRS, Pessac, France

Magnesium based composites containing different additives, obtained by ball milling are found to possess promising absorption-desorption characteristics as hydrogen storage materials. The positive effect is due to the presence of additives like metals, oxides or intermetallics as well as to the process of mechanical alloying. The subject of the present study are the absorption-desorption properties of the nanocomposites 85%Mg-15%$Mg_2Ni_{1-x}Co_x$ prepared by ball milling in inert atmosphere. Hydriding proceeded at T= 573, 473, 423, 373K and P = 1 MPa and dehydriding, at 573 K and P = 0.15 MPa. A significant improvement of the hydriding kinetics of all composites was established, the hydrogen absorption rate beeing 1.36 wt.% H/min, 1.33 wt.% H/min and 1.04 wt.% H/min, respectively. The samples absorption capacity at 573 K and P = 1MPa was 4.9 wt.%- 6.6 wt.% and remained high even at low hydriding temperatures. During cycling at 573 K and P = 1MPa, the composite 85%Mg-15%$Mg_2Ni_{0.8}Co_{0.2}$ preserved the value of its absorption capacity after 70 absorption-desorption cycles. The promising absorption-desorption characteristics of the nanocomposites investigated are explained by the catalytic effect of the intermetallic $Mg_2Ni_{1-x}Co_x$, the presence of Ni and Co superparamagnetic particles on the sample surface and the process of mechanical alloying.

P-209 **Hydrogen Absorption Kinetics in the Catalysed MgH_2 with Niobium Oxide.** N. Hanada, T. Ichikawa, H. Fujii, – Materials Science Center, N-BARD, Hiroshima University, Higashi-Hiroshima, Japan

The kinetics of hydrogen sorption has been investigated on the MgH_2 composite doped with 1 mol% Nb_2O_5 as a catalyst by ball milling [1,2]. The composite after dehydrogenation at 200 ℃ absorbed gaseous hydrogen of ~4.5 mass% even at room temperature under 1 MPa hydrogen pressure within 15 sec and finally its capacity reached more than 5 mass%. At 150 and 250 ℃, hydrogen gas of more than 5.0 mass% is absorbed within 30 sec and its capacity reached up to 5.7 mass%. Especially, it is of interest that the reaction speed of hydrogen absorption at the initial reaction stage in the time scale within 10 sec decreases with increasing temperature. Generally, the kinetics of hydrogen absorption is controlled by a thermally activated process, where the speed of the reactions increases with increasing temperature. As the reason of this phenomenon, there are two possibilities to be considerable. One is due to the appearance of the reverse reaction. The other is due to the variation of surface coverage of hydrogen atoms on the Mg surface with temperature. On the contrary, in the longer reaction time scale than several hours, the absorption speed increases with increasing temperature. It might correspond to the diffusion process of hydrogen atom in an inner part of Mg metal itself. [1] N. Hanada, T. Ichikawa and H. Fujii, J. Alloys Comp. 404-406, 716-719 (2005); [2] N. Hanada, T. Ichikawa, S. Hino and H. Fujii, J. Alloys Comp. (in press).

P-210 **Effects of O_2 and H_2O Preadsorptions in H_2 Reactivity with the Cr Surface.** S. Kato, M. Terashima, R. Yamakawa, H. Uchida, – Tokai University, Hiratsuka-City, Japan

Ti-Cr based alloys are well known as a low temperature type of hydrogen storage alloy, and are applied to MH freezer systems. However, information about the surface features of Ti-Cr based alloys and its compositional element Cr with respect to the H_2 reactivity is lacking, especially for the H_2 reactivity on the Cr surface at low temperature and pressure. As well, recently, there have been reports that Cr oxide is one of the most effective catalysts for nano-crystalline Mg based systems [1]. In our group, the surface property of Cr has been focused on, and we reported about the reactivities of H_2, O_2 and H_2O with the clean Cr surface at 298 K and also for H_2 at 77 K [2]. In the present study, we aimed at investigating quantitatively the effects of O_2 and H_2O preadsorption layers in H_2 reactivity with the Cr surface prepared under ultra high vacuum condition. The reaction probability of H_2 was measured volumetrically at 298 K and pressures raging from 10^{-8} to 10^{-2} Pa. The reaction probability of H_2 on the hydroxidized Cr surface was found higher compared to the one on the oxidized surface. [1] W. Oelerich, T. Klassen, R. Bormann, J. Alloys Comp. 315 (2001) 237; [2] S. Kato, R. Suzuki, Y. Kawamoto, H. Uchida, J. Alloys Comp. 413 (2006) 214.

P-211 **H_2 Reactivity on the Surfaces of In and Sn.** M. Terashima,[1] R. Yamakawa,[1] H. Uchida,[1] S. Kato,[1] M. Sato,[1] Y. Matsumura,[1] H. H. Uchida,[2] V. A. Yartys,[3] J. P. Maehlen,[3] – [1]Course of Applied Science, Graduate Scool of Engineering, Tokai University, Hiratsuka, Kanagawa, Japan; [2]Department of Human Development, Environmental and Resources, School of Humanities and Culture, Tokai University, Kita-Kaname, Hiratsuka, Kanagawa, Japan; [3]Institute for Energy Technology, Kjeller, Norway

We reported quantitative studies on the reactivities of H_2, O_2 and H_2O gases with the surfaces of rare earths (La, Ce, Tb, Dy) and hydrogen storage alloys ($LaNi_5$, $LaNi_{4.5}Al_{0.5}$, $LaNi_{2.5}Co_{2.5}$) prepared under UHV condition [1,2]. Normally, non-transition elements such as In and Sn do not from hydrides. However, Sn substitution for Ni in $LaNi_5$ yields an improvement in the kinetics and cyclic properties both for thermal and electrochemical processes [3]. Presently only little information is available for the surface features of the In and Sn. In this study, the reactivities of H_2, O_2 and H_2O gases with the In and Sn surfaces were measured volumetrically at

pressures ranging from 10^{-8} to 10^{-2} Pa at 298K. At the initial stage, the reactivity of H_2 with a clean surface of In or Sn exhibited r_{H2}~10^{-2}. In contrast, the reactivities of H_2 with the surface precovered by O_2 or H_2O were higher than that of clean surface. [1] H. Uchida, *et al.*, J.Less-Common Met., 231 (1995) 684-688; [2] M. Hadano *et al.*, J.Alloys Comp., 293-295 (1999) 403; [3] B. V. Rantnakumar, *et al.*, J. Electrochem. Soc., 143 (8) (1996) 2578.

P-212 **A Study on the Hydrogen Absorption Characteristic of the $TbFe_2$ Alloy.** T. Onodera,[1] H. Uchida,[1] T. Haraki,[2] – [1]Course of Applied Science, Graduate School of Engineering, Tokai University, Hiratsuka, Kanagawa, Japan; [2]Technical Service Coordination Office, Tokai University, Hiratsuka, Kanagawa, Japan

We have investigated thin films of giant-magnetostrictive alloys (GMA) such as $TbFe_2$. For the preparation of films, we use powder samples of GMA. The powder sample is used for thin film formations by flash evaporation or by sputtering using a sputter target. The powder sample can be produced by cyclic hydriding and dehydriding (CHD) reactions of GMA bulk samples [1-3]. In this study, we investigated hydrogen absorption characteristics of $TbFe_2$. The alloy sample used was prepared by arc melting using Tb (99.9 %) and Fe (99.9 %). The structure and the chemical composition of the alloy were examined by XRD and EDX, respectively. The sample surface was observed using SEM. The equilibrium hydrogen pressure of the $TbFe_2$-H system, and the reaction rate were measured using a Sieverts' type apparatus. [1] H. Uchida, Y Matsumura, H.H Uchida and H. Kaneko, *Journal of Magnetism and Magnetic Materials* 239 (2002) 540; [2] T. Yamaki, M. Sekine, T. Haraki, H. Uchida and Y. Matsumura, *Surface and Coatings Technology* 169 (2003) 616; [3] M. Wada, H. Uchida and H. Kaneko, *J. Alloys and Compounds* 258 (1997) 42.

P-213 **Low Temperature Decomposition of AlH_3.** J. Johnson, W.-M. Zhou, – Brookhaven National Laboratory, Upton, NY, USA

Aluminum hydride, AlH_3, is potentially an attractive storage material for automotive applications due to the large amount of hydrogen that can be contained in a relatively small, lightweight package. AlH_3 contains 10 % H by weight and has a theoretical H density of 148 g/L. Thermodynamically, AlH_3 is unstable at ambient pressure and should readily decompose to H_2 and Al at room temperature. However, room temperature decomposition occurs slowly with freshly prepared powders and large crystallites of AlH_3 (prepared by Dow Chem. Co.) do not decompose at temperatures below 80 C. In this study, we investigate the low temperature (< 80 C) decomposition of AlH_3. The purpose of this study is to better understand the slow release of hydrogen at temperatures from 20 to 40 C to determine the shelf life and the allowable time-period a vehicle may be parked without running the engine or fuel cell. Experimental studies suggest that AlH_3 can be stabilized by the application of various coatings (oxide or polymer) or destabilized by the addition of dopants (e.g. $LiAlH_4$). In this poster we propose a number of methods to limit the room temperature decomposition while maintaining the rapid kinetics at 80-100 C.

P-214 **Dehydrogenation Kinetics of Alkali Metal Alanates Catalyzed with $TiAl_3$ Ultrafine Powder.** J.-H. Shim,[1] G.-J. Lee,[2] K. S. Lee,[2] Y. W. Cho,[1] – [1]Nano-Materials Research Center, Korea Institute of Science and Technology, Seoul, Republic of Korea; [2]Division of Materials Science and Engineering, Hanyang University, Seoul, Republic of Korea

Alkali metal alanates (aluminum hydrides) have gained much attention as lightweight hydrogen storage materials due to its inherent high capacity of hydrogen. Since it was shown that the addition of titanium chloride and organometallic Ti can dramatically improve the dehydrogenation and rehydrogenation kinetics of $NaAlH_4$, there has been great interest in catalysts. The catalytic role of Ti in alanates is, however, still poorly understood, although various attempts to understand what form of Ti resides in alanates have been made so far. In this study, we investigated how Ti resides in alanates by mixing $TiCl_3$ and alkali metal alanates. It was found that alkali metal chlorides and $L1_2$-$TiAl_3$ formed as primary phases by the reaction between $TiCl_3$ and alanates. A small amount of TiH_2 was also observed. We synthesized ultrafine $TiAl_3$ powders of about 100 nm using a mechanochemical reaction. The addition of this $TiAl_3$ catalyst into $NaAlH_4$ and Li_3AlH_6 brought about the decrease in the dehydrogenation starting temperatures. It also significantly improved the dehydrogenation kinetics of $NaAlH_4$ and Li_3AlH_6. Alanates catalyzed with $TiAl_3$ released more hydrogen during dehydrogenation than alanates with $TiCl_3$ catalyst. Therefore, it is favorable to use ultrafine $TiAl_3$ catalyst instead of $TiCl_3$ in terms of hydrogen storage capacity. It is expected that this ultrafine $TiAl_3$ catalyst can be applied to other alanates in order to minimize the loss in hydrogen storage capacity.

P-215 **Hydrogenation Properties of Mg_2Ni-(5mass%)Nb Composites by Mechanical Alloying.** S. Seok,[1] K. B. Kim,[2] T.-W. Hong,[1] – [1]Department of Materials Science and Engineering/ReSEM, Chungju National University, Chungju, Korea; [2]Advanced Metals Research Center, Division of Materials, Korea Institute of Science and Technology, Seoul, Korea

Mg-based alloys are most promising hydrogen storage materials because of their lightweight, high specific storage capacity. However, the formation of hydride at high temperature, the deterioration effect, the hydriding and dehydriding kinetics have problem. Recently, it has been reported that addition of a transitional metal also produces a catalytic effect on hydrogen absorption properties. In this study, in order to improve the absorption/desorption kinetic properties of Mg-Ni alloys, we add to 3d-transitional metal Niobium. Mg_2Ni alloys were prepared by mechanical alloying using the planetary ball mill for 72hrs at hydrogen atmosphere. Then, Mg_2Ni synthesized add to 5mass%Nb. Morphologies of composites synthesized were observed by SEM. Also, particles synthesized were characterized by XRD, TEM and TG/DSC. The hydrogenation behaviors were evaluated by using an sievert's type automatic PCT apparatus.

P-216 **Reactivities of H_2, O_2 and H_2O with a Clean Surface of Yttrium.** R. Yamakawa,[1] M. Terashima,[1] H. Uchida,[2] S. Kato,[2] M. Sato,[2] Y. Matsumura,[2] H. H. Uchida,[3] V. A. Yartys,[4] J. P. Maehlen,[4] – [1]Course of Applied Science, Graduate School of Engineering, Tokai University, Hiratsuka, Kangawa, Japan; [2]Department of Applied Science, School of Engineering, Tokai

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So far we have made systematic studies on the reactivity of H_2 with rare earths (La, Ce, Tb, Dy) at 298K under ultra high vacuum condition [1,2]. Y has similar chemical characteristics to those of rare earths as well known. However there are few works about the reactivity of H_2 on Y with a clean surface. In this study, we investigated the quantitative reactivities of H_2, O_2 and H_2O with a clean surface of Y, and the effect of O_2 or H_2O preadsorption on the H_2 reactivity under ultra high vacuum condition. A clean surface of Y exhibited the highest reactivity in the reaction probability r=1 for H_2, O_2 and H_2O. [1] M.Hadano, N.Urushihara, T.Inoue, H.Uchida, J. Alloys Comp. 293-295 (1999) 403; [2] H.Uchida, S.Kato, J. Alloys Comp. 408-412 (2006) 319.

P-217 **Hydrogen Absorption Characteristics of YNiIn.** M. Sato,[1] A. Furumoto,[1] S. Kato,[1] H. Uchida,[1] Y. Matsumura,[1] H. H. Uchida,[2] J. P. Maehlen,[3] V. A. Yartys,[3] – [1]Course of Science, Graduate School of Engineering, Tokai University, Hiratuka, Kanagawa, Japan; [2]Department of Human Development, Environmental and Resources,School of Humanities and Culture, Tokai University, Hiratuka, Kanagawa, Japan; [3]Institute for Energy Technology, Kjeller, Norway

The crystal structures of the RENiIn deuterides (RE=La,Ce,Nd) are characterised by the presence of anomalously short D…D separations in the range 1.56-1.64 Å depending on the rare earth element. At low hydrogen content, hydrogen atoms occupy every second of the tetrahedral RE_3Ni sites. Increase of hydrogen content leads to the double occupancy of the trigonal bipyramidal RE_3Ni_2 sites with the limiting overall composition $RENiInH_{1.33}$. As a result, a violation of the Switendick criteria (rule of 2.1 Å) has been shown to take place. The present work aims at extending further knowledge concerning the properties and mechanism of hydrogen bonding in the corresponding systems. This work was devoted to studies of the hydrogen interaction focusing on the chemically related intermetallic compound YNiIn. The formation of nearly single phase YNiIn with ZrNiAl-type structures was confirmed by powder X-ray diffraction. P-C-T relations were determined using a high pressure volumetric Sieverts' apparatus. The thermal stability of the hydrides was determined by means of the thermal desorption spectroscopy technique. The P-C-T curves for YNiIn-H system show the presence of clear plateau regions in the range of H content 0.66<H/YNiIn<1.33, which indicates the formation of a hydrogen pair in the hydride phase. The partial molar enthalpy and entropy calculated for the formation of the $YNiInH_{1.33}$ are -11.1 kJ $(mol_H)^{-1}$ and -51.9 J$(K{\cdot}mol_H)^{-1}$, respectively.

P-218 **Hydrogen Storage Properties of Mg/Cu and Mg/Pd Laminate Composites and Metallographic Structure.** N. Takeichi,[1] K. Tanaka,[1] H. Tanaka,[1] N. Kuriyama,[1] T. T. Ueda,[2] Y. Kamaya,[2] M. Tsukahara,[2] H. Miyamura,[3] S. Kikuchi,[3] – [1]National Institute of Advanced Industrial Science and Technology (AIST), Ikeda, Japan; [2]IMRA Material R&D Co.Ltd., Kariya, Japan; [3]University of Shiga Prefecture, Hikone, Japan

Mg can absorb a large amount of hydrogen up to 7.6 mass%. Many Mg-based materials have been investigated to improve their kinetics of hydrogenation and dehydrogenation at elevated temperature. Recently, a co-author Ueda reported that Mg-based laminate composites prepared by repetition rolling absorb and desorb hydrogen reversibly at 473K. In this study, we investigated the mechanism of hydrogen absorption and desorption of Mg/Cu and Mg/Pd composites at 473K. *In-situ* XRD results suggest that the reaction mechanism of Mg/Cu composite is as follows. In activation process at 573 K, Mg_2Cu is formed at the interface between Mg and Cu by interdiffusion. This Mg_2Cu absorbs and desorbs hydrogen reversibly through the disproportionation and recombination process. In Mg/Pd composite, Mg_6Pd is formed during initial activation process. This Mg_6Pd also can store hydrogen reversibly through the disproportionation and recombination process. TEM observations revealed that the as-rolled Mg-based laminate composite had the sub-micrometer-ordered laminate structure. After initial activation and dehydrogenation process, the samples have kept the sub-micrometer-ordered laminate structure. The nano-structure of Mg-based laminates leads to lower hydrogen desorption temperature and better kinetics, which would contribute to achieve high capacity hydrogen storage materials. NEDO supported this work under "Development of fundamental technologies in the safe utilization of hydrogen".

P-219 **Hydriding Properties of Nano-Structured FeTi Alloys Prepared by Mechanical Grinding.** H. Hattori,[1] K. Oishi,[1] H. Uchida,[1] Y. Miyamoto,[2] T. Haraki,[2] M. Abe,[3] T. Kokaji,[3] S. Uchida,[4] – [1]Department of Applied Science, Graduate School of Engineering, Tokai University, Kitakaname, Hiratuka, Kanagawa, Japan; [2]Technical Service Coordination Office, Tokai University, Kitakaname, Hiratuka, Kanagawa, Japan; [3]Nasu Denki Tekko Co., Arasuna, Koutou-ku, Tokyo, Japan; [4] Tokyo Metropolitan Industrial Research Institute, Nisigaoka, Kita-ku, Tokyo, Japan

The FeTi alloy is a hydrogen storage alloy with a hydrogen storage capacity 1.8wt.% and has a relatively low cost compared with other alloys. However, the intermetallic FeTi dose not absorb hydrogen under normal conditions because of the presence of very stable oxide layers covering the alloy surface. In order to activate the alloy, the alloy needs a high temperature (over 720 K) and a high hydrogen pressure (6.5MPa). We reported the formation of nanostructured layers on a polycrystalline FeTi surface by mechanical grinding(MG). and the nano-structured surface exhibits a high initial activation compared with an untreated polycrystalline alloy. This study aims at the investigation of the mechanism of the H_2 absorption kinetics of the n-FeTi alloy.

P-220 **Degradation Mechanism on Hydrogen Sorption Cycle of the Hydrogen Storage Alloys and Influence of CO.** H. Tanaka,[1] N. Kuriyama,[1] Q. Xu,[1] N. Taoka,[2] K. Aihara,[2] – [1]National Institute of Advanced Industrial Science and Technology (AIST), Ikeda, Osaka, Japan; [2]New Material Center (NMC), Osaka Science and Technology Center (OSTEC), Nishi-Ku, Osaka, Japan

Hydrogen sorption cycle durability of Ti-Cr- and V-based solid solutions with BCC-type structure and a Ca-Mg-Ni-based Laves phase alloy as investigated under H_2 gases with CO (1, 10 and 100 ppm) till 1,000th cycle. As for all the alloys, the higher the CO concentration is, the more remarkably the capacity decreased in progress of hydrogen sorption cycle. Cycle capacity of the alloys

hardly decreased and microstructure was not also affected so much at an H_2 atmosphere with CO less than 1 ppm. With more than 100 ppm, the capacity decreases immediately although the microstructure was not damaged. On the other hand, the equilibrium capacity hardly decreased in spite of CO concentration. The tendency of degradation during cycle progress of the Laves phase alloy was similar to that of BCC alloys. As a result, it was suggested that a small amount of CO absorbing on the surface of the alloys could be released by heat in hydrogenation. And, it suggested that a large amount of CO made the alloy surface "suffocate" and made heat of hydrogenation small, which led to rapid decrease of capacity. This work has been funded through "WE-NET" and "Development for Safe Utilization and Infrastructure of Hydrogen" programs administrated by NEDO. [1] H. Tanaka, S. Ichikawa, H. Senoh, N. Kuriyama, N. Naka, K. Aihara, H. Itoh and T. Tsukahara, Mater. Sci. Forum, 475-479 (2005) 2481-2484; [2] H. Tanaka, et al., http://www.tech.nedo.go.jp/WWWROOT/HOKOKUSYO/DOWNLOAD/10000576299.pdf, NEDO report (2005).

P-221 **Hydrogenation Properties of Mg-based Composites Prepared by Reactive Mechanical Alloying.** F. Li, Z. Huang, L. Jiang, J. Du, – General Research Institute for Nonferrous Metal, Beijing, P. R. China

A nanocrystalline composite of Mg-$LaNi_3$-Cu have been prepared by reactive mechanical alloying of Mg, Cu and $LaNi_3$ powders after 60h ball-milling under a hydrogen atmosphere. This composite desorbed 1.06mass.% of hydrogen at 533K under a hydrogen pressure of 0.1MPa.$MgCu_2$ dramatically promotes the hydrogen desorption. [1]L.Schlapbach, A.Züttel, Nature 2001; 414: 353.

P-222 **Structural Characterization and Hydrogen Absorption Kinetics of $Ce_xZr_{1-x}O_2$ Solid Solutions Produced by Mechanical Milling.** D. B. Domanski,[1] M. L. Rodríguez,[2] J. J. Andrade Gamboa,[3,4] F. C. Gennari,[5,6] – [1]Universidad Tecnológica Nacional, Facultad Regional de Córdoba, Córdoba, Argentina; [2]Universidad Nacional del Sur (PLAPIQUI), Bahía Blanca, Argentina; [3]Centro Atómico Bariloche- CNEA, Bariloche, Argentina; [4]Centro Regional Universitario Bariloche (Univ. Nacional del Comahue), Bariloche, Argentina; [5]Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Bariloche, Argentina; [6]Instituto Balseiro (Univ. Nacional de Cuyo), Bariloche, Argentina

Ceria based solid solutions ($Ce_xZr_{1-x}O_2$, CZ) have been widely used as catalysts in different industrial processes. In these materials some key properties, such as redox behavior, thermal stability and reactivity with hydrogen are associated with the material characteristics (phases and its structure, particle size, surface area) and are dependent of the synthesis method selected. In this work the mechanical milling process has been used successfully for the production of two different $Ce_xZr_{1-x}O_2$ solid solutions (x=0.8 and 0.5, CZ80 and CZ50, respectively) at room temperature and air atmosphere. The evolution of Zr incorporation into CeO_2 structure during milling and crystallite size reduction to the nanometric range were determined using X-ray diffraction (XRD) and transmission electron microscopy (TEM). Hydrogen absorption kinetics of Pd supported on CZ80 and bare CZ80 were determined using volumetric equipment. For Pd/CZ80 both total hydrogen uptake and absorption rate were dependent of the temperature in the range of 25 to 80 ºC. No hydrogen reduction occurs up to this temperature for CZ80. At higher temperatures (250-400 ºC), hydrogen reduction of CZ80 starts and the kinetic can be fitted with a zero order model. In this case the apparent activation energy is 17 $kJ.mol^{-1}$, suggesting a reaction mechanism controlled by a non-activated process.

P-223 **Application of Pressure Programmed Absorption and Desorption to Characterize Hydriding and Dehydriding Kinetics.** V. Fuster, F. J. Castro, G. Urretavizcaya, – Centro Atómico Bariloche, S. C. de Bariloche, Río Negro, Argentina

Hydriding and dehydriding kinetics is an important aspect of the reaction of hydrogen with different hydride forming materials. In particular, it is a key factor in several applications of hydrogen from an energetic point of view. We present here the use of a recently developed technique to characterize hydrogen absorption and desorption kinetics: pressure programmed absorption and desorption (PPAD) [1]. The technique is based on an isothermal pressure-ramped measurement of the hydriding and dehydriding rate, and its principal advantages are the absence of an initial blind period, the short time required to complete an experimental run, and the possibility to perform consecutive hydrogen absorption and desorption cycles. To illustrate this, we present here the results obtained in the characterization by PPAD of the Pd-H, $LaNi_5$-H, and Mg-H systems. [1] G. Urretavizcaya, V. Fuster and F. J. Castro, Rev. Sci. Instrum. 76 (2005) 073902.

P-224 **Models For The Initiation Of Hydride Attack Sites On Uranium.** J. Glascott, – AWE, Aldermaston, UK

The attack of uranium by hydrogen generally occurs in a localised manner initially. The rate at which hydride attack sites are initiated increases with increase of hydrogen pressure or temperature[1]. However, common gaseous impurities in the hydrogen atmosphere[2] or the presence of thick surface oxide films[3,4,5] can reduce the rate of attack of the metal. Also, hydride precipitation may occur beneath and not at the oxide-metal interface[6]. Any hydride initiation mechanism must explain all of these observations. Mathematical models of some possible mechanisms of hydride site initiation have been derived and are considered in the light of the above. It is concluded that the temperature, gas pressure, gas composition and the characteristics of the oxide film are important in that they determine the extent of diffusion of hydrogen through the oxide film and to the metal. However, hydride precipitation in the metal is dependent on this hydrogen flow together metallurgical factors. [1] J. Glascott, Discovery – Science & Technology Journal of AWE, Issue 6 (2003); [2] J. Bloch, D. Brami & A. Kremner, J. Less Common Met., 139, 371 (1988); [3] L.W. Owen & R.A. Scudamore, Corr. Sci., 6, 461 (1966); [4] R. Harker, (Accepted for publication, J. Alloys & Compounds, 2006); [5] T. Scott, G. Allen, I. Findlay & J. Glascott (Unpublished work); [6] J.F. Bingert, R.J. Hanrahan, R.D. Field & P.O. Dickerson, J. Alloys & Compounds, 365, 138 (2004).

P-225 **Hydrogenation Properties of Mg_2Cu Prepared by Mechanical Alloying.** M. Tanaka, – Kansai University, Suita, Osaka, Japan

There are following two reports about the condition of equilibrium dissociation pressure in the reaction expressed by (1) $2Mg_2Cu + 3H_2 = 3MgH_2 + MgCu_2$ (1) 1[1] 3.3MPa, 573K (Mg_2Cu was prepared by melting method.) 2[2] 3.3MPa, 473K (Mg_2Cu was prepared by repetitive rolling and annealing.) We thought this discrepancy is referred from the difference in microstructures, so we tried to synthesize Mg_2Cu by mechanical alloying (MA), which produces many grain boundaries, and the sample was measured hydrogenation properties. Starting materials were Mg powder and Cu powder. Mg were mixed with Cu in a molar ratio of 2 to 1, and these powders were sealed in a vial in a glove box. MA was performed in planetary ball mill at a rotation speed of 300rpm. An XRD technique was applied for identification of the constituent phases in the samples milled for various periods ranging from 0 to 28.8ks. Hydrogenation properties were measured by DSC measurement. After MA for 28.8ks., we could obtain Mg_2Cu contained a little Cu. From DSC measurement, sample prepared by MA could absorb/desorb hydrogen reversibly, and activation energy for milled Mg_2Cu was 323.77 kJ/mol as a result that DSC measurement was operated in various heating rates. We will discuss a comparison of hydrogenation properties between samples prepared by melting and mechanochemical methods. [1] J. J. Reilly and R. H. Wiswall, Inorg. Chem., 6 (1967) 2220; [2] T. T. Ueda et al., 15th World Hydrogen Energy Conference (2004) 28B-05.

P-226 **A Chemical Route to Improve the Hydrogen Sorption Kinetics of MgH_2.** A. Walton,[1] J. W. Prendergast,[2] P. A. Anderson,[2] V. S. J. Mann,[1] I. R. Harris,[1] D. Book,[1] S. R. Johnson,[3] P. P. Edwards,[3] – [1]Department of Metallurgy and Materials, University of Birmingham, Birmingham, UK; [2]School of Chemistry, University of Birmingham, Birmingham, UK; [3]Inorganic Chemistry Laboratory, University of Oxford, Oxford, UK

Magnesium is known to absorb large quantities of hydrogen (7.6wt%). However, the hydrogen desorption temperature is too high (300℃) and the kinetics of hydrogen sorption are too slow for a practical storage material. It has been shown that by high velocity ball milling MgH_2, a material can be produced with a nanocrystalline microstructure and faster hydrogen sorption kinetics. However, this process is very energy intensive. Work carried out at the University of Birmingham has demonstrated that by mixing MgH_2 or Mg metal with $LiBH_4$ in a 1:0.1 molar ratio and then heating the material at 300˚C in either vacuum or inert gas, it is possible to produce a (non-milled) magnesium hydride-based material with improved hydrogen storage kinetics [1]. In this work, the possible mechanism for the improved hydrogen sorption kinetics of $LiBH_4$-treated Mg metal and MgH_2 powders, is investigated further. Pressure Composition Isotherms and DSC measurements have been carried out, in order to calculate the effect of $LiBH_4$ treatment on the enthalpy of formation of MgH_2. Detailed electron microscopy has been performed to investigate the characteristics of the mixed material over the first 6 hydrogen absorption/desorption cycles on both powdered and solid Mg/MgH_2 samples mixed with $LiBH_4$. The thermal decomposition of the mixed material has been assessed using thermogravimetric analysis and mass spectrometry. [1] S. R. Johnson et al. Chem.Commun. (2005) p.2823.

P-227 **Mechanical Milling of Magnesium at Cryogenic Temperatures for Hydrogen Storage Applications.** D. T. Reed, A. Walton, V. S. J. Mann, D. Book, I. T. H. Chang, I. R. Harris, – Department of Metallurgy and Materials, School of Engineering, University of Birmingham, Birmingham, UK

With a high gravimetric storage capacity (7.6wt%), magnesium is of interest for hydrogen storage. However, the desorption temperature is too high (~300˚C), and the kinetics of hydrogen sorption need to be greatly improved. The kinetics can be improved by reducing grain and particle size, by mechanical milling MgH_2. Due its high ductility, it is not possible to directly mechanically mill metallic magnesium. However, this should be possible if the magnesium granules are cooled below their brittle-ductile transition temperature. A SPEX 6750 freezer mill was used to mechanically mill magnesium granules at 77K. This resulted in a decrease in particle size from ~1mm to ~10µm. DSC measurements show an increase in strain energy in the cryomilled powders, indicating some plastic deformation. The shape and size distribution of the particles also suggests that the predominant mechanism is brittle intergranular fracture (BIF type II), which corresponds to what would be expected from the fracture map of magnesium. Compared with the starting material, the TGA measurements showed that the hydrogen storage capacity and sorption kinetics improved significantly after the cryomilling treatment.

P-228 **Thermodynamics and Kinetics of the Ce-La-Hydrogen/Deuterium System.** J. S. Bridgewater, S. N. Paglieri, J. R. Wermer, H. Oona, D. E. Dooley, S. Richmond, – Los Alamos National Laboratory, Los Alamos, NM, USA

The H(D) pressure-composition-temperature (PCT) isotherms of the Ce-La (1-10 at.%) system were determined. Hydrogen/deuterium equilibrium pressures were measured as a function of hydrogen concentration in the pressure range of $1x10^{-2}$ to $1x10^{5}$ Pa and temperatures between 298 and 1000 K. The absorption and desorption kinetics were also investigated. The thermodynamics of the Ce-La-H(D) system are compared with the known thermodynamics of the Ce-H(D) system.

P-229 **Dehydrogenation Kinetics of Ti-doped $NaAlH_4$ - Influence of Ti Precursors and Preparation Methods.** M. Onkawa,[1] H. Takeshita,[2] M. Adachi,[2] T. Kiyobayashi,[3] – [1]Graduate School of Engineering, Kansai University, Osaka, Japan; [2]Kansai University, Osaka, Japan; [3]National Institute of Advanced Industrial Science and Technology, Osaka, Japan

Following the breakthrough by Bogdanović *et al.*[1] that a few mole fraction of a certain Ti species significantly enhances kinetics of the thermal dehydrogenation of $NaAlH_4$ and renders the rehydrogenation possible, many researchers have studied Ti doped $NaAlH_4$. However, the mechanism how the catalysts work is not yet fully understood. There are mainly two hypotheses about the state and role of Ti precursors; Ti works just as a catalyst on the surface of alanates [1] or Ti alters the thermodynamic properties of alatnates [2]. As these hypotheses are based on materials whose Ti doping methods and precursors are different, we focus on their influence in the present study. We investigated the dehydrogenation kinetics of Ti doped alanate prepared by different Ti precursors and doping methods. For the first cycle of dehydrogenaion the kinetics depends on the dopant and doping method. But when we cycled the dehydrogenation and hydrogenantion several times, the kinetics properties converge with showing similar values of the

rate constants. [1] B. Bogdanović and M. Schwickardi, *J. Alloys Compd.*, **253-254** (1997), 1-9; [2] D. Sun, T. Kiyobayashi, H.T. Takeshita, N. Kuriyama and C.M. Jensen, *J. Alloys Compd.*, **337** (2002), L8-L11.

P-230 **Thermal Decomposition of Alane AlH_3 Studied by *in situ* Synchrotron X-ray Diffraction and Thermal Desorption Spectroscopy.** J. P. Maehlen,[1] V. A. Yartys,[1] R. V. Denys,[1] M. Fichtner,[2] Ch. Frommen,[2] B. M. Bulychev,[3] P. Pattison,[4] H. Emerich,[4] – [1]Institute for Energy Technology, Kjeller, Norway; [2]Institute of Nanotechnology, Research Centre Karlsruhe, Germany; [3]Lomonosov Moscow State University, Moscow, Russia; [4]Swiss-Norwegian Beam Line, European Synchrotron Research Facility, Grenoble, France

Low operating pressures, combined with high gravimetric and volumetric efficiencies, fast kinetics of hydrogen release at ambient temperatures and low heat of decomposition, are the most important features of alane AlH_3 as H storage material. This work was focused on studies of the thermal decomposition of alane by application of SR XRD and TDS. Two polymorphs were studied, α- and γ-AlH_3. The *in situ* diffraction pattern showed that a linear increase of the unit cell dimensions of α-AlH_3 takes place in an interval from RT to ~400 K. The volume expansion is along [100] and can be attributed to the elongations of the bridge bonds Al-H-Al aligned along [1 -1 ½], Δd/d ~ 0.17 %. The decomposition of alane leads to the formation of a non-crystalline (probably amorphous) Al. At a temperature of about 410 K aluminium starts to crystallise and first appears in the SR diffraction pattern; the peaks from AlH_3 become weaker with a gradual change in relative amount of both constituents, until a transformation is completed at about 420 K. The *in situ* data agree well with the TDS measurements. Activation energy of hydrogen desorption from γ-hydride, 92 kJ/mol, is lower compared to α-AlH_3, 136 kJ/mol. A double-peak decomposition behaviour was observed for both polymorphs. For the γ-modification two events overlap; γ→α transformation and a thermal decomposition process $AlH_3 \rightarrow Al + 3/2\ H_2$.

P-231 **Hydrogen Penetration of Fusion Materials.** N. M. Vlasov, I. I. Fedik, – Scientific Research Institute Industrial Association "Luch", Podolsk, Moscow Region, Russia

Fusion materials of the first wall interact with plasma. The plasma comprises hydrogen isotopes. The hydrogen atoms penetrate into the material and cause mechanical property degradation. Hydrogen penetration of the material depends on the level and character of internal stress distribution. The main types of the latter are the temperature and residual ones and fields of structural defects as well.The kinetics of hydrogen atom diffusion is described by an equation of parabolic type under corresponding initial and boundary conditions. The process of simulating the hydrogen penetration of a hollow cylinder with internal stresses is considered as an example. The choice of such a simulative system is connected with the following reasons. Firstly, hollow cylinders with thin walls are used to study the hydrogen penetration of fusion materials experimentally. Such a dependence permits obtaining an exact analytic solution of diffusion kinetics problem in view of internal stresses. Analytic dependences of hydrogen penetration of a hollow cylinder are given.A possibility of controlling the hydrogen penetration of fusion materials by changing the stress field is discussed.

P-232 **Hydrogen Permeable Ta-Ti-Ni Duplex Phase Alloys with High Resistance to Hydrogen Embrittlement.** W. Luo, K. Ishikawa, K. Aoki, – Kitami Institute of Technology, Kitami, Hokkaido, Japan

Hydrogen gas produced by steam reforming of hydrocarbons contains much CO gas, which damages the Pt electrode of fuel cells, so that such gas must be purified by some methods. Pd-Ag alloys are mainly used for a hydrogen permeation membrane to purify hydrogen gas. However, Pd is too expensive and rare resources. Then, it is eagerly desired to develop low cost and high performance hydrogen permeation alloys. Bcc-metals such as V, Nb and Ta show much higher hydrogen permeability *F* than that of Pd-Ag alloys, but suffer from the severe hydrogen embrittlement. In addition to high *F*, high strength and high resistance to the hydrogen embrittlement are essential for the hydrogen permeation membrane. However, the coexistence of high *F* with high large resistance to the hydrogen embrittlement is generally impossible in single-phase alloys. Recently, the present authors have proposed new alloys on the basis of the concept of duplex phases. An example of such alloys is the Ta-Ti-Ni system that consists of B2-TiNi and bcc-(Ta, Ti) solid solution. The former absorbs a little hydrogen and show high resistance to the hydrogen embrittlement, while the latter permeate much amount of hydrogen. In this work, microstructures, structural changes induced by hydrogenation and hydrogen permeation properties of the Ta-Ti-Ni alloys are investigated in order to develop new high permeation alloys. This work was supported by New Energy and Industrial Technology Development Organization (NEDO) of Japan.

P-233 **Hydrogen Elasticity Phenomenon in Metal-Hydrogen Systems.** Z. Glukhova, A. Redko, V. Goltsov, – Donetsk National Technical University, Donetsk, Ukraine

Hydrogen-elasticity phenomenon in metal-hydrogen systems and its thermodynamic description for non-isothermal and isothermal conditions are generalized in [1]. Coupled nonlinear equations that describe the interrelated evolution of hydrogen-concentration fields, temperature fields, and strain (stress) fields are written and discussed. The equations of isothermal hydrogen elasticity are used in this work for mathematical simulation of mechanical and diffusive effects caused by the phenomenon of hydrogen elasticity. Results of digital computing for changes of hydrogen concentration and stress distribution versus time during dissolution of hydrogen concentration inhomogeneities are given and discussed. [1] V.A. Goltsov, A.L. Redko, Zh.L. Glukhova, The Physics of Metals and Metallography, Vol 95, No 1,2003, pp. 17-22.

P-234 **Anharmonicity of Optical Hydrogen Vibrations in RhH.** V. E. Antonov,[1] T. E. Antonova,[1] V. K. Fedotov,[1] B. A. Gnesin,[1] A. S. Ivanov,[2] A. I. Kolesnikov,[3] – [1]Institute of Solid State Physics RAS, Chernogolovka, Russia; [2]Institut Laue-Langevin, Grenoble, France; [3]IPNS, Argonne National Laboratory, Argonne, IL, USA

Similar to monohydrides of Pd and Ni, rhodium monohydride is formed under high hydrogen pressure via an isomorphous transition accompanied by an increase in the lattice parameter of the *fcc* metal lattice. Hydrogen atoms occupy every octahedral interstitial position in this lattice. Our earlier studies of plate-like PdH and NiH samples with a strong (001)[100] texture by inelastic neutron scattering (INS) showed that, despite the cubic symmetry of the hydrogen positions, optical H vibrations polarised along the <100> axes in the second and third vibrational band were significantly anharmonic. In the present paper, in order to investigate the anharmonicity and anisotropy of the vibrational spectrum of RhH, the sample was also made of a textured foil. The INS investigation of this RhH sample showed that its first (fundamental) band of optical H vibrations consisted of an intense peak at 74 meV with a shoulder extending towards higher energies. The band demonstrated no anisotropy in agreement with the symmetry requirements to fundamental optical vibrations. Surprisingly, the second and third bands appeared strongly anharmonic and significant hardening of all vibrational modes, whatever polarisation they have, occurred at energies exceeding 150 meV. This distinguishes RhH from PdH and NiH, which have a mostly harmonic H potential well and anharmonicity is only observed for hydrogen vibrations along the <100> axes.

P-235 **Solubility and Diffusion of Hydrogen in NiTiCu Shape-Memory Alloys.** G. Mazzolai, – University of Perugia, Department of Physics, Perugia, Italy

The solubility limit in the α-phase and the chemical diffusion coefficient D_c of hydrogen have been determined in NiTiCu shape-memory alloys by absorption techniques. The measurements of the solubility were made between 700-1150 K with hydrogen gas pressures ranging between zero and 1.072 bar and hydrogen to metal atomic ratios from zero to 0.02. The diffusion coefficient was obtained by fitting the isothermal pressure vs time curves, obtained during H_2 gas absorption, to a P(t) relationship derived from the second Fick's diffusion equation, solved for the bar shaped samples of the present experiments [1]. The activation energies and the pre-exponential factors of the diffusion coefficient were deduced from Arrhenius type of plots. [1] P. G. Shewmon, Diffusion in solids, ed. Mc Graw Hill, N.Y. 1963, p. 18.

P-236 **Microstructure and Hydrogen Permeability of Nb-Ti-Ni Alloys after Rolling and Annealing Treatments.** S. Tokui, K. Ishikawa, K. Aoki, – Kitami Institute of Technology, Kitami Hokkaido, Japan

Much high purity hydrogen gas may be used as fuel of fuel cells in the near future. Hydrogen permeation alloys are effectively used for separation and purification of hydrogen gas including impure substance. Pd-based alloys are commercially used for hydrogen purification, but Pd is too expensive and a rare resource. Therefore, non-Pd based hydrogen permeation alloys are strongly desired. Recently, the present authors have reported high hydrogen permeability (Φ) and large resistance to the hydrogen embrittlement in the as-cast Nb-Ti-Ni multiphase alloys. These alloys consist of the primary (Nb, Ti) solid solution and the eutectic {TiNi+(Nb, Ti)} phases, and show higher Φ than that of pure Pd at 673K. Furthermore, these alloys show more than 70 % of rolling reduction ratio at room temperature. In this paper, microstructure and hydrogen permeability of Nb-Ti-Ni alloys are investigated before and after rolling-annealing treatments. Furthermore, the relation between microstructure and the value of Φ is discussed. The value of Φ for the $Nb_{40}Ti_{30}Ni_{30}$ alloy decreases with increasing the rolling reduction ratio. The value of Φ for the cold rolled alloy recovers to the original value by annealing at 1373 K. The present work indicates strong possibility for the developing of the high Φ alloy membrane by microstructural control of the Nb-Ti-Ni alloys using the rolling-annealing techniques. This work was supported by New Energy and Industrial Technology Organization (NEDO) of Japan.

P-237 **Rates of Hydrogen Motion in Substituted $LaNi_5H_x$ from NMR.** M. P. Mendenhall,[1] R. C. Bowman, Jr.,[2] M. S. Conradi,[1] T. M. Ivancic[1] – [1]Washington U., Dept. of Physics, Saint Louis, MO, USA; [2]Jet Propulsion Lab., Caltech, Pasadena, CA, USA

Partial substitution of other elements for Ni in $LaNi_5H_x$ alters the thermodynamics (e.g., equilibrium hydrogen pressure and storage capacity) of the hydride phases. In particular, substitution by Sn, Ge, or Si has been observed to greatly enhance the stability under repeated cycling. Proton NMR is used here to measure the rates of H hopping motion in $LaNi_{4.6}M_{0.4}H_x$ for M = Sn, Ge, and Si as well as unsubstituted $LaNi_5H_x$. Relaxation times T2*, T2 (Hahn echo), T2 (CPMG), T1, and T1rho were determined from 130 to 375 K. The 3 substituents all result in at most small increases in the average rate of motion at a given temperature but a broader distribution of rates across the many inequivalent sites. In these materials, T2* is severely limited by sample magnetism; broad minima in T1 are observed near 300 K. At the highest temperatures, spin-echo T2 values are limited by H-diffusion through field gradients arising from material magnetic susceptibility. The present results in substituted materials will be compared to previously published results in $LaNi_5H_x$.

P-238 **Crystal Structure of the Deuteride $LaCu_5D_{3.2}$ Studied by Neutron Powder Diffraction.** M. Latroche,[1] R. C. Bowman, Jr.,[2] – [1]LCMTR, UPR209, CNRS, Thiais, France; [2]Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA

Among the AB_5 family (A: rare earths, B: transition metals), most of the crystal structures of hydride forming compounds have been determined. Usually the parent $CaCu_5$-type structure (*P*6/*mmm* s.g.) is preserved upon hydrogenation but superstructures related to deuterium ordering may appears. For example, the compound $LaNi_5H_x$ exhibits a structural transformation due to a progressive ordering of the hydrogen atoms within the b phase [1]. This induces a symmetry reduction and the appearance of superstructure lines leading to a doubling of the **c**-axis with a new description in space group $P6_3mc$ and seven different deuterium interstitial sites.In the present work, the crystal structure of $LaCu_5D_{3.2}$ is investigated by neutron diffraction. Analysis of the diffraction pattern shows that the initial $CaCu_5$-type cell is not preserved upon deuteration. The pattern can be indexed in a new ortho-hexagonal cell (*Pmma* s.g.; $\boldsymbol{a}'=2.\boldsymbol{a}$, $\boldsymbol{b}'=\boldsymbol{c}$, $\boldsymbol{c}'=2\boldsymbol{a}+\boldsymbol{b}$). Eight different sites are occupied by deuterium. 2.1 D atoms are found in tetrahedral positions (La2Cu2 sites) and 1.6 D are in octahedral positions (La2Cu4 sites). The deuterium ordering is responsible for the symmetry lowering observed for the $LaCu_5$ compound upon hydrogenation. Finally, the impact of this structure on the unusual diffusion

properties previously observed [2] for $LaCu_5H_{3.4}$ during NMR studies will be described. [1] C. Lartigue *et al.*, *J. Less-Common Met.,* **129** (1987) 65; [2] F.E. Spada *et al.*, *J. Less-Common Met.,* **129** (1987) 261.

P-239 **Hydrogen Induced Insulating State in $LaMg_2Pd$.** J.-P. Rapin,[1] K. Yvon,[1] N. Clayton,[2] Z. Ma,[3] M.-Y. Chou,[3] – [1]Laboratoire de Cristallographie, Université de Genève, Genève, Switzerland; [2]Département de Physique, Université de Genève, Genève, Switzerland; [3]School of Physics, Georgia Institute of Technology, Atlanta, GA, USA

Hydrogenation of $LaMg_2Pd$ at 373K and 10 bar leads to a new quaternary metal hydride of composition $LaMg_2PdH_7$. In contrast to the previously investigated nickel analogue $LaMg_2NiH_7$ which has monoclinic symmetry and displays two symmetry independent tetrahedral $[NiH_4]^{4-}$ complexes [1], it has orthorhombic symmetry (space group $P2_12_12_1$) and contains one tetrahedral $[PdH_4]^{4-}$ complex. The Pd-D bond distances range from 1.71 to 1.78 Å and the D-Pd-D bond angles from 97.5 to 122.0°. Three additional D atoms occupy La_2Mg_2-type interstices with tetrahedral configurations. At 543K and 30 bar the hydride decomposes into LaH_3 and unidentified phases. Electric resistance measurements on powders confirm the non-metallic behaviour of the deuteride. Electronic calculations were carried out using the Vienna *ab-initio* simulation package based on density functional theory and the projector augmented wave method with plane waves. The fundamental gap is found to be direct and about 0.66 eV using the generalized gradient approximation. With the self-energy correction, the actual quasiparticle gap is therefore expected to be larger than 1.0 eV. The occupied states are identified to be associated with H-*s* and Pd-*d* orbitals. [1] K. Yvon, G. Renaudin, C. M. Wei, and M.Y. Chou, Phys. Rev. Lett. 94 (2005) 066403.

P-240 **Hydrogen-related Defects in Sodium Alanate.** A. Peles, C. G. Van de Walle, – Materials Department, University of California, Santa Barbara, CA, USA

Titanium-doped sodium alanate has attracted much recent attention as a viable hydrogen storage material. The addition of a very small amount of Ti dramatically alters dehydrogenation reaction dynamics and allows reversible sorption of hydrogen [1]. In order to understand the fundamental factors that control (de)hydrogenation processes as well as hydrogen-promoted mass transport we investigate the electronic structure and structural properties in the presence of native defects. Our study is based on density functional theory with plane-wave basis sets and projector-augmented-wave potentials. Our detailed investigations identify hydrogen vacancies and interstitials as the predominant defect species, with low formation energies, that play an important role in the (de)hydrogenation processes. The calculated low energy barriers for propagation of these defects imply high mobility. Interestingly, both vacancies and interstitials cause large rearrangements of the surrounding crystal lattice, and they are always charged; their formation energy therefore depends on the Fermi level. Our study indicates that addition of titanium has the important effect of shifting the Fermi level; this Ti-induced shift lowers the formation energies and hence increases concentrations of the relevant hydrogen-related defects. This mechanism provides an explanation for the observed improvement in kinetics of the (de)hydrogenation reactions. [1] Bogdanovic et al. J. Alloys Compd. 253, 1 (1997).

P-241 **X-ray Diffraction Investigation on The Hexagonal-Fcc Transition Process in Yttrium Trihydride at Pressures of 11-21 GPa.** A. Machida,[1] A. Ohmura,[1] T. Watanuki,[1] K. Aoki,[1] K. Takemura,[2] – [1]Synchrotron Radiation Research Center, Japan Atomic Energy Agency, Hyogo, Japan; [2]Advanced Materials Laboratory, National Institute for Materials Science, Tsukuba, Japan

The structural transition of yttrium trihydride, YH_3, has been investigated by x-ray diffraction experiments at high pressure and room temperature. The hexagonal metal lattice transformed gradually to the fcc lattice for a wide intermediate region from 11 to 21 GPa in agreement with the previous report [1]. The transition process was measured precisely under hydrostatic condition: the YH_3 was compressed in helium pressure medium with a diamond anvil cell (DAC) and the powder diffraction patterns were collected using brilliant synchrotron radiation lights at BL22XU beamline, SPring-8. The observed reflection peaks allowed peak fitting to determine accurately the peak positions and intensities, and revealed that the diffraction patterns of the intermediate state were not interpreted in terms of the coexistence phases with the hexagonal and fcc structures as discussed previously [1]. The reflection peaks, which originated from the low-pressure hexagonal structure, disappeared gradually and several peaks, which were not indexed with the high-pressure fcc structure, appeared as the pressure increased beyond 11 GPa. Eventually, they merged into the reflection peaks well indexed with the fcc structure at about 21 GPa. The hexagonal-fcc transition process will be discussed on the basis of the further analysis of the x-ray data. [1] T. Palasyuk and M. Tkacz, Solid State Commun. 133 (2005) 477.

P-242 **Synthesis of CaMg-based bcc Alloys and their Hydrogenation Properties.** T. Nobuki,[1] T. Kuji,[2] – [1]School of High Technology for Human Welfare, Tokai University, Numazu, Shizuoka, Japan; [2]Course of Materials Science and Chemistry, Unified Graduate School, Tokai University, Numazu, Shizuoka, Japan

We have demonstrated in our previous report that the excess energy created during mechanical alloying (MA) yielded alloying of couples with negative mixing enthalpy and the new ternary bcc phase was formed. It was noticed that the important issue there was the structural correlation between the Laves and bcc structures. The aim of this study is to synthesize $CaMg_2$ based bcc alloys in structural relation to the Laves phase structure with additive bcc elements (V, Fe, Mo), and to clarify the above issue on the structure and hydrogenation. The parent materials used in this study were $CaMg_2$ and metal element powders. The MA was performed under Ar gas atmosphere and the rotation speed is 710 rpm. The ratio of powder to ball weight is 1:40. The results are summarized as follows: 1) With increasing of the MA time, the lattice parameter of bcc alloy increased. 2) After 60 hours of MA, single bcc phase was formed. 3) The TEM observation showed that the alloy made after 60 hours of MA was composed of nano-structured bcc grains without the deviation from nominal composition. 4) The TDS was used to measure the hydride properties of the synthesized bcc alloys. The result showed that 3 weight % of hydrogen was absorbed. 5) Although the phase segregation

occurred after hydrogen released. This reason can be explained by electronegativity argument of alloy element relative to hydrogen. This result could encourage us to have a chance of new alloy phases with stale during hydrogenation.

P-243 **Hydrogen Absorption of TiFe Alloy Synthesized by Ball Milling and Post Annealing.** M. Abe,[1] T. Kuji,[2] – [1]Nasu Denki-Tekko Co., Tokyo, Japan; [2]Course in Materials Science and Chemistry, Unified Graduate School, Tokai University, Numazu-city, Japan

The TiFe alloy is a promising candidate as a high capacity (1.8wt%H_2) hydrogen storage alloy. However, it is well known that the TiFe alloy has the difficulty to be activated for hydrogenation. Repeating absorption/desorption process under a high temperature (>773K) and a high H_2 pressure (> 6.5MPa) is necessary. In recent years, the nano-structural or amorphous alloys synthesized by mechanical alloying (MA) have been extensively studied. MA has been proposed as one of the attractive methods to improve activation of TiFe to absorb the hydrogen. However, the alloying efficiency of MA is in general really low, i.e., long duration and high energy to synthesize alloys. In this study, TiFe alloy was synthesized by short period of ball milling and post annealing at relatively low temperature. The alloying process will be discussed from the thermodynamic point of view. TiFe alloys were fabricated from elemental mixture of Fe and Ti and mixture of Fe and TiH_2. It is demonstrated that the synthesized TiFe alloy powders were able to absorb hydrogen rapidly at room temperature even without any initial activation treatments.

P-244 **Effects of Phase Transformation on Heat Transfer Behavior of Hafnium Hydrides.** B. Tsuchiya,[1] M. Teshigawara,[2] K. Konashi,[1] S. Nagata,[1] T. Shikama,[1] – [1]Institute for Materials Research, Tohoku Univ., Sendai, Japan; [2]Tokai Research Establishment, Japan Atomic Energy Agency, Hitachi-naka, Japan

An application of hafnium hydrides (HfH_x) as control rods in fast neutron flux in fast reactor has been recently proposed. Because Hf has significantly a high neutron absorption and capture cross sections with thermal neutrons and dose not generate some fission product gases such as ^4He by the nuclear reaction. Also, the hydrides play a role as fast neutron moderators to gain much thermal neutron. Therefore it will be expected that the HfH_x control rod can efficiently absorb much fast neutrons and has an advantage of much longer life-time than boron carbide (B_4C) one which has been recently utilized. In order to design the hydride control rod assembly, it is extremely important to understand changes of physical, chemical and mechanical properties for the hydrides relative to hydrogen distribution. In the present study, thermal diffusivities of hafnium hydrides with different hydrogen concentrations and phases have been measured within the temperature range from room temperature to 550 K by means of a laser flash method. The thermal diffusivities at low temperatures below 373 K drastically changed due to the phase transformation with increasing hydrogen concentration, while those at high temperatures above 373 K hardly changed with the hydrogen concentration. Moreover, the thermal conductivities have been evaluated with the experimental result of the thermal diffusivity and the reference data of the specific heat and the density and their temperature.

POSTER SESSION II (P-245 to P-313) **Tuesday, October 3 – (8:00 PM – 10:30 PM)**

P-245 **Synthesis and Structural Studies of $LiMg(AlD_4)_3$.** H. Grove,[1] H. W. Brinks,[1] R. H. Heyn,[2] X. Tang,[3] S. M. Opalka,[3] B. C. Hauback,[1] – [1]Physics Department, Institute for Energy Technology, Kjeller, Norway; [2]SINTEF Materials and Chemistry, Oslo, Norway; [3]United Technologies Research Center, East Hartford, CT, USA

Alanates are among the most promising reversible hydrogen storage materials. Since Bogdanovic et al. in 1997 discovered that $NaAlH_4$ with Ti-based additives are reversible at reasonable temperatures [1], synthesis of new alanates and understanding of the effect of the additives have been in focus. The mixed alanate $LiMg(AlH_4)_3$ contains 9.73 wt% hydrogen. $LiMg(AlH_4)_3$ desorbs hydrogen in a three step reaction: $LiMg(AlH_4)_3 \rightarrow LiMgAlH_6 + 2Al + 3\,H_2$ at about 120 ºC; $LiMgAlH_6 \rightarrow Al + LiH + MgH_2 + 3/2H_2$ at about 170 ºC; MgH_2 decomposes to Mg at about 220ºC. $LiMg(AlD_4)_3$ can be synthesised by ball milling $LiAlD_4$ and $MgCl_2$ in ratio 3:1; $3LiAlH_4 + MgCl_2 \rightarrow LiMg(AlH_4)_3 + 2LiCl$ [2-4]. The product was recrystallised using diethylether and toluene [2-3]. The structure of $LiMg(AlD_4)_3$ has been determined using synchrotron X-ray and neutron powder diffraction. The compound crystallises in a monoclinic lattice; the space group is $P2_1/c$ with cell dimensions a = 8.3602(1) Å, b = 8.7285(1) Å, c = 14.2826(2) Å and β = 124.8234(5)°. The structure consists of AlD_4^- tetrahedra, connected to each other through hexa-coordinated Li-ions or Mg-ions. The structure can be described as distorted hexagonal close-packing, hcp, of the AlD_4^- tetrahedra with 1/3 of the octahedral sites occupied by Mg-ions and 1/3 of the octahedral sites occupied by Li-ions. Financial support from the NANOMAT-program in the Research Council of Norway is acknowledged. [1] B. Bogdanovic et al., J. Alloys Compd. 253-4 (1997) 1; [2] B.M. Bulychev et al., Koord. Khim. 4 (1978) 374; [3] M. Mamatha et al., J. of Alloys Compd. 407 (2006) 78; [4] M. Mamatha et al., J. of Alloys Compd. 416 (2006) 303.

P-246 **Unit Cell Expansion in Laves Phase Type Compounds Caused by Interstitial Hydrogen.** H. Figiel, S. Osuchowski, A. Paja, – Faculty of Physics and Applied Computer Science, AGH - University of Science and Technology, Krakow, Poland

The Laves phase type compounds of yttrium and Rare Earths with manganese (RMn_2) easily absorb hydrogen which locates in the interstitial sites. It is well known that as a function of hydrogen concentration the lattice expands and the volume increases up to about 30%. The increase of the unit cell volume is a nonlinear function of hydrogen content. To explain this behavior Hirata [1] proposed a model in which he related the hydrogen induced volume changes to the changes of the bulk modulus with hydrogen concentration. This is due to entering hydrogen into A2B2 type interstitials. His model describes properly the initial volume increase but does not reflect the changes at higher concentrations. For the hydrides investigated (R = Y, Gd, Er, Dy, Tb, Ho) at x ≈ 3 the volume of AB3 interstitials becomes large enough for entering of hydrogen. According to this observation we extend this

model by assumption that starting from concentrations x ≈ 3 the expansion due to entering the AB3 type interstitial positions takes place. The excess volume due to hydrogen in AB3 interstitials is calculated using the same formula as for A2B2 interstitials at lower concentrations, which explains the observed volume jump for x > 3. We show that the calculated volume expansion fits very well to the experimental data for RMn_2 (R = Y, Gd, Dy, Tb, Ho). [1] T. Hirata, M. Dorogova, S. M. Filipek, Phys. Stat. Sol. (a), **201** (2004)1458.

P-247 **Improving Rechargeable Hydrogen Storage Capacity of BCC Alloy by Eliminating Internal Defects.** K. Kubo, K. Hashi, H. Arashima, H. Itoh, T. Kabutomori, K. Ohnishi, – Muroran Research Laboratory, The Japan Steel Works, Ltd., Muroran, Hokkaido, Japan

In fuel cell powered automobiles, hydrogen is required to be stored in materials that have a hydrogen storage density of over 4 mass%; further, these materials should be capable of supplying hydrogen by using the waste heat from a fuel cell, which is at a temperature of 373 K, in order to match the mileage of gasoline-powered vehicles. A Ti-Cr-V alloy, which exhibits a BCC structure and forms a solid solution, is a promising candidate for onboard hydrogen storage materials. Although it has a large hydrogen storage capacity of over 3.9 mass%, the rechargeable hydrogen capacity is limited to approximately 2.6 mass%. In this study, the effects of fine pulverization of the alloy on PCT characteristics were investigated. From the PCT measurements of the finely pulverized samples, a plateau in the absorption curve was observed to begin at a hydrogen content of 0.5 mass%; further, a rechargeable hydrogen storage capacity of 3.3 mass% was obtained. This was greater than that obtained from the sample that was not finely pulverized, i.e., 2.5 mass%. The increase in the rechargeable hydrogen capacity during absorption is attributed to the precipitation of the γ-hydride phase ($MH_{\sim 2}$) directly from the metal phase (α phase). The precipitation of the β phase ($MH_{\sim 0.5}$), which should be formed in low hydrogen content, is suppressed as a result of a possible reduction in the internal defects such as dislocations, vacancies, and grain boundaries by fine pulverization and annealing of the alloy.

P-248 **Pressure-induced Structural Change from hcp to fcc-like Metal Lattice in Scandium Trihydride.** A. Ohmura,[1] A. Machida,[1] T. Watanuki,[1] K. Aoki,[1] S. Nakano,[2] K. Takemura,[2] – [1]Japan Atomic Energy Agency, Sayo, Hyogo, Japan; [2]National Institute for Material Science, Tsukuba, Ibaraki, Japan

Pressure-induced structural change from hcp to fcc-like metal lattice was investigated for scandium hydride, ScH_x, by x-ray diffraction measurement up to 60 GPa at room temperature. Hydride was prepared in a diamond anvil cell (DAC) by compressing the metal foil with fluid hydrogen. The metal foil reacted with fluid hydrogen to form ScH_2 with an fcc metal lattice at about 4 GPa. Up to 5 GPa, fcc ScH_2 changed for the most part to ScH_3 with a hexagonal metal lattice, which persisted to about 25 GPa together with unreacted ScH_2. On further compression, the hcp lattice began to transform towards an fcc-like lattice. The transition completed at about 46 GPa. The successive change in diffraction pattern during the transition was quite similar to that observed for YH_x [1]: the transient state was not explained by the coexistence phase of ScH_2 and ScH_3 but able to be interpreted in terms of the gradual change in the sequential stacking of the metal layers. There were two characteristic features of the diffraction patterns measured for the intermediate state between 25 and 46 GPa: the splitting of the hcp 101 reflection peak to the fcc 111 and 200 peaks and the continuous conversion from the hcp 110 to the fcc 220 peak. These experimental results provided insights into the microscopic transition process. [1] T. Palasyuk and M. Tkacz, Solid State Commun. **133** (2005) 477.

P-249 **A Structural Correlation between Laves Compound and BCC Phase in $TiCr_2$ Using Electron and Ion Irradiation.** H. Abe,[1,2] T. Kuji,[2] – [1]Radiation Effect Group, Quantum Beam Science Directorate, Japan Atomic Energy Agency, Takasaki, Gunma, Japan; [2]Course of Materials Science and Chemistry, Unified Graduate School, Tokai University, Numazu, Shizuoka, Japan

According to the binary Ti-Cr phase diagram, $TiCr_2$ is stable in the Laves structure at RT but it transforms to bcc at higher temperatures. In this study, the structural correlation of $TiCr_2$ Laves compound to the bcc phase will be discussed. It has been already known that the transformation of the $TiCr_2$ Laves compound to bcc structure takes place by large excess energy created during mechanical grinding. However, this transformation has not been well understood quantitatively. In this study, it will be demonstrated that the transformation occurs by the electron and the ion irradiation because the energy introduced during irradiation can be precisely estimated. The significance of the mechanism for this transformation from the Laves phases to bcc will be discussed with the model on the basis of the dynamic reconstruction within displacement cascades. The reflecting this transformation on the hydrogen solubility will be also discussed.

P-250 **Lattice Location of Hydrogen in β-V_2H.** E. Yagi,[1,2] T. Hayashi,[2] S. Koike,[3] T. Yoshida,[2] N. Higami,[2] K. Hirabayashi,[2] A. Takebayashi,[2] K. Ogiwara,[1] – [1]RIKEN(The Inst. Phys. Chem. Res.), Wako, Japan; [2]Sch. Sci. Eng. Waseda Univ., Tokyo, Japan; [3]Fac. Sci., Tokyo Univ. Sci., Tokyo, Japan

The lattice location of hydrogen in β-V_2H phase was investigated by the nuclear reaction channelling method with a ^{11}B beam of about 2 MeV. Hydrogen was detected by measuring a particles emitted as a result of a nuclear reaction $^{1}H(^{11}B, a)aa$. Two types of b-V_2H single crystals with different crystal structures, i.e., tetragonal and monoclinic structures, were prepared. The tetragonal V_2H was prepared by hydrogen charging and cooling from an a phase under tensile stress of about 1 kg/mm^2 along the [001] direction, while the monoclinic $V_2H_{1.1}$ was prepared without stress. It was observed that, in the tetragonal V_2H, hydrogen atoms are located at octahedral sites with a principal axis along the z-axis (O_z-site), whereas, in the monoclinic $V_2H_{1.1,}$ most of hydrogen atoms are located at O_z sites and about 20% of them are at O_x and O_y sites. This result suggests that the stress-induced site change from *T* to *O* sites takes place.

P-251 **Developments in Advanced Borohydride Materials for Hydrogen Storage.** J. R. Eliseo, C. M. Jensen, – Department of Chemistry, University of Hawaii, Honolulu, HI, USA

Researchers are challenged to develop economical, environmentally-friendly, lightweight hydrogen storage materials with high hydrogen capacities. Zinc borohydride ($Zn(BH_4)_2$) is an appealing hydrogen storage material with a low decomposition temperature (about 85˚C) and a high theoretical weight capacity (8.5% H_2). However, there have been many safety concerns about the desorption of diborane in addition to hydrogen. Here we have synthesized zinc borohydride and its alkali metal derivatives by mechanochemical activation and studied their thermal decomposition.

P-252 **Dehydrogenation Reaction of $Mg(NH_2)_2$ with LiH studied by *in situ* Synchrotron Powder X-ray Diffraction.** Y. Nakamura,[1] S. Hino,[2] T. Ichikawa,[2] H. Fujii,[2] H. W. Brinks,[1] B. C. Hauback,[1] – [1]Physics Department, Institute for Energy Technology, Kjeller, Norway; [2]Materials Science Center, N-BARD, Hiroshima University, Higashi-Hiroshima, Japan

Amides of alkali or alkali-earth metals, e.g. $LiNH_2$, $Mg(NH_2)_2$, $Ca(NH_2)_2$, react with metal hydrides to release hydrogen [1]. Among several combinations, reactions of $Mg(NH_2)_2$ with LiH have an advantage of providing a reasonably high hydrogen desorption pressure as well as a high capacity in wt% [2-5]. However, the reaction mechanism is still not clear. In this work, a dehydrogenation reaction of $Mg(NH_2)_2$ with LiH in a 3:8 ratio has been investigated using *in situ* synchrotron powder X-ray diffraction at the Swiss-Norwegian Beamline at ESRF and powder neutron diffraction at the JEEP II reactor, IFE. With increasing temperature, the intensities for $Mg(NH_2)_2$ and LiH decreased while a pattern for a new phase appeared. This reaction proceeded between 150˚C and 210˚C, which corresponds to the main peak of hydrogen emission observed in the thermal desorption measurement [3]. The phase development at elevated temperature will be presented. Financial support from the NANOMAT program in the Research Council of Norway and the International Joint R&D project by NEDO, Japan is acknowledged. [1] P. Chen et al., Nature 420 (2002) 302; [2] Z. Xiong et al., Adv. Mater., 16 (2004) 1522; [3] H. Leng et al., J. Alloys Compd., 404-406 (2005) 443; [4] T. Ichikawa et al., J. Alloys Compd., 400 (2005) 245; [5] W. Luo et al., J. Alloys Compd., 407 (2006) 274.

P-253 **Synthesis and Structural Properties of Sr-Alanates.** S. Ronneteg, Y. Nakamura, H. W. Brinks, B. C. Hauback, – Physics Department, Institute for Energy Technology, Kjeller, Norway

One of the most promising group of materials with respect to hydrogen storage is the complex hydrides, especially the so-called alanates (hydroaluminates) based on group I and II elements in the periodic table. This work focuses on strontium compounds. Dymova *et al*. [1] synthesized different kinds of strontium alanates monitoring the mechanochemical activation of mixtures of AlH_3 and SrH_2. Both $Sr(AlH_4)_2$, $SrAlH_5$ and $Sr_2(AlH_6)_3$ were observed. Furthermore, two other ternary Sr-Al-H compounds have earlier been reported, $SrAl_2H_2$ [2] and Sr_2AlH_7 [3] generated from hydrogenation of $SrAl_2$. In this study we have instead used ball milling of a mixture of $LiAlD_4$ and $SrCl_2$ in a ratio of 2:1 to form strontium alanate (and LiCl). The resulting compound has been investigated by powder X-ray, neutron diffraction and with a Sievert's apparatus. Financial support from the NANOMAT-program in the Research Council of Norway is acknowledged. [1] T.N. Dymova *et al*, Russ. J. Coord. Chem. 26 (2000) 531. [2] F. Gingl *et al*, J. Alloys Comp. 306 (2000) 127; [3] Q.A. Zhang *et al*, J. Alloys Comp. 394 (2005) 308.

P-254 **Neutron Diffraction Study of Thermal Decomposition of the Clathrate D_2O-D_2 Phase.** V. E. Antonov,[1] O. I. Barkalov,[1] A. I. Beskrovnyi,[2] V. S. Efimchenko,[1] V. K. Fedotov,[1] S. N. Klyamkin,[3] – [1]Institute of Solid State Physics RAS, Chernogolovka, Russia; [2]Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Russia; [3]Moscow State University, Chemical Faculty, Moscow, Russia

A real-time neutron diffraction (ND) experiment earlier demonstrated [1] that the hydrogen content of the high-pressure clathrate D_2O-D_2 phase sII with the starting D_2/D_2O ratio $x = 48/136$ gradually decreased to $x = 32/136$ on heating at ambient pressure from 40 to about 160 K. In the present paper, a sample of the sII phase prepared by thermobaric quenching procedure was repeatedly measured by ND at 90 K after successive runs of rapid heating to a chosen temperature (145, 195, 220 and, finally, 250 K), annealing at that temperature for 15 min and rapid cooling back to 90 K. The initial sample with $x \approx 32/136$ was prepared from powdered D_2O ice and D_2 gas at $P = 1.7$ kbar at $T = 253$ K. In agreement with earlier results for $x = 32/136$ [1], our initial sample had an sII structure with two D_2 molecules in each "large" cage (position 8b) and one D_2 molecule in each "small" cage (16c) of the cubic unit cell formed by 136 D_2O molecules. The annealing at 145 K did not change the ND pattern. After annealing at 195 K, the occupancy of the small cages decreased to about 0.5 D_2 molecules. After 220 K, about half of the sample transformed to mixture of low-density amorphous ice (lda) with crystalline cubic ice Ic and hexagonal ice Ih. After 250 K, the sample consisted of lda, Ih and a smaller fraction of Ic. [1] K. A. Lokshin et al., Phys. Rev. Lett. 93 (2004) 125503.

P-255 **A Comparison of the Evolution During Mechanical Milling of Both a $MmNi_5$-Ni and a Mm-Ni Mixture: Stages of Milling and Microstructural Characterization.** M. R. Esquivel, G. Meyer, – Centro Atómico Bariloche-Comisión Nacional de Energía Atómica-Consejo Nacional de Investigaciones Científicas y Técnicas, S. C. Bariloche, Argentina

Many of the advantages attributed to materials synthesized by mechanical milling oriented to interaction with hydrogen are related to the introduction of defects and strain on microstructure which enhances the alloy-H interaction. To asses this argument, a study of the evolution during mechanical milling of both Mm-Ni and $MmNi_5$-Ni mixtures is presented. Milling was performed under Ar using a Uni-Ball Mill II apparatus. Experimental set-up includes sample extraction at different milling time in a glove box. Both stages detected during milling and comparison of the microstructure for finally obtained $MmNi_5$ compound was done. Strain and crystallite size of Ni and $MmNi_5$ in both mixtures are correlated to milling time. These parameters were studied by X-ray diffraction technique (XRD). Particle size and morphology obtained in each case are related to the presence of four typical stages developed during

milling: Initial, Intermediate, Final and Completion. This study was performed by combined energy dispersive spectroscopy (EDS) and scanning electron microscopy (SEM) techniques. Complete formation of $MmNi_5$ was obtained at 40 h by direct mechanical milling. Formation of $MmNi_5$ was detected after only 2 h of milling the Mm-Ni mixture at milling times as low as 2 h in a low energy ball mill by heating resultant mixture at temperatures lower than 600 ºC. It was attributed to the energy supplied by mechanical milling to the system. Optimal milling time was found for each mixture studied.

P-256 **Nanocrystalline Silicon for Hydrogen Storage.** D. Neiner, C. Chervin, M. Blessent, S. M. Kauzlarich, H. W. Chiu, – University of California Davis, Davis, CA, USA

Hydrogen constitutes the primary candidate for a clean, efficient and environmental friendly fuel. Early studies on bulk silicon revealed hydrogen emission upon annealing. The surface to volume ratio for a nanomaterial increases as its size decreases. This makes nanocrystalline silicon a serious candidate for hydrogen storage. Preparation of hydrogen capped silicon nanoparticles have been attempted by both solid state and solution reaction routes. The precursors are NaSi and Mg_2Si and as hydrogen sources ammonium halides have been used. The X-ray powder patterns of the resulted materials correspond to nc-Si. SEM/TEM images indicate that these materials are on the nanometer scale.

P-257 **Thermal Analysis on the M-B-H Systems.** T. Nakagawa,[1] T. Ichikawa,[2] N. Hanada,[2] H. Fujii,[2] – [1]Graduate School of Advanced Sciences of Matter, Hiroshima University, Higashi-Hiroshima, Japan; [2]Natural Science Center for Basic Research and Development, Hiroshima University, Higashi-Hiroshima, Japan

It has been reported that the reaction between MgH_2 and $LiBH_4$, [$MgH_2 + 2LiBH_4 \leftrightarrow MgB_2 + 2LiH + 4H_2$] (reaction (1)), exhibits superior hydrogen storage properties with a higher hydrogen capacity than 10 mass% [1]. This system shows quite characteristic features. Actually, the above reaction proceeds only under a suitable hydrogen pressure, while an inert gas atmosphere leads to another hydrogen desorption reaction pathway expressed by [$MgH_2 + 2LiBH_4 \rightarrow Mg + 2B + 2LiH + 4H_2$] (reaction (2)). However, the mechanism of these reactions is not clear yet. Therefore, in order to clarify this reaction mechanism, we performed the thermal analyses on the MgH_2, $LiBH_4$ and MgH_2-$2LiBH_4$ products under different atmospheric conditions by using a pressurized differential scanning calorimetry (p-DSC, H_2 0.5MPa or Ar flow) and a thermogravimetry/differential thermal analysis (TG-DTA, He flow). The results indicated that the dehydrogenation of MgH_2 and the melting of $LiBH_4$ took place before the reaction (1) or (2) progresses under both inert gas and hydrogen atmospheres with increasing temperature. In addition, the melted $LiBH_4$ did not decompose into LiH, B and H_2 below 450 ℃ under 1 MPa H_2, while the $LiBH_4$ decomposed into them even below 450 ℃ under an inert gas atmosphere. From these results, it is deduced that the above mentioned reaction (1) is a solid-liquid reaction between the solid Mg phase and melted $LiBH_4$ phase. [1] J. J. Vajo, S. L. Skeith, J. Phys. Chem. B 109 (2005)3719.

P-258 **Structure of Amorphous $CeFe_2D_x$ Observed by X-ray and Neutron Diffraction.** K. Itoh,[1] K. Aoki,[2] K. Mori,[1] M. Sugiyama,[1] T. Fukunaga,[1] – [1]Research Reactor Institute, Kyoto University, Kumatori-cho, Sennan-gun, Osaka, Japan; [2]Department of Materials Science, Faculty of Engineering,Kitami Institute of Technology, Kitami, Japan

A great deal of interest has been given to hydrogen-induced amorphization (HIA), i.e. the transformation from a crystalline to an amorphous phase by hydrogen absorption [1, 2]. HIA has been observed in a large number of intermetallic compounds [1]. However, the mechanism of HIA is poorly understood. Structural information of the atomic rearrangement induced by hydrogen absorption is needed to understand the mechanism of HIA. Our recent X-ray and neutron diffraction studies on amorphous $TbFe_2D_{3.0}$ [3] have shown that the concentration fluctuations between metal atoms occur and the deuterium atoms occupy tetrahedral sites consisting mainly of rare-earth metal atoms. In this work, we investigated the structures of amorphous $CeFe_2D_x$ by X-ray and neutron diffraction techniques and compared with the results of amorphous $TbFe_2D_{3.0}$. Moreover, the reverse Monte Carlo modeling method was employed to clarify the characteristics of the atomic arrangement of amorphous $CeFe_2D_x$. [1] K. Aoki, T. Yamamoto and T. Masumoto, Scripta Metall.,21(1987) 27; [2] X. G. Li, A. Chiba, K. Aoki and T. Masumoto, Intermetallics, 5 (1997) 387; [3] K. Itoh, K. Kanda, K. Aoki and T. Fukunaga, J. Alloys Comp.348 (2002) 167.

P-259 **Structural Stability of Zr_7Ni_{10} Changing to Tetragonal via Formation of Intermediate Phase.** H. T. Takeshita, T. Kishida, S. Inaoka, – Kansai University, Suita, Japan

Zr_7Ni_{10} originally has an orthorhombic structure of *Cmca* in space group and is reported to change to a tetragonal one of *I*4/*mmm* by hydrogenation followed by dehydrogenation [1] and rapid cooling of melt[2]. If the tetragonal structure of Zr_7Ni_{10} is found to be metastable, hydrogenation followed by dehydrogenation can be a method to prepare metastable materials. In the present study, these two structures were experimentally and theoretically examined in order to obtain the information about their relative stability. Mechanical grinding of Zr_7Ni_{10} with the orthorhombic structure for a long period resulted in the formation of an amorphous phase. When it was heated up to 873K, two exothermic peaks, corresponding to crystallization and precipitation of Laves phase due to contamination, respectively, were observed. The structure of Zr_7Ni_{10} was changed from amorphous to tetragonal, and finally to orthorhombic during the heat treatment. Thus it was found that the formation of tetragonal structure was achieved via the formation of hydrides, liquid and amorphous phases. The XRD profiles of the hydrides showed significant heterogeneous deformation of metal lattice, which implies that formation of tetragonal structure requires loss of long-period structure. On the other hand, there was little difference between orthorhombic and tetragonal for stability. [1] H. T. Takeshita et al., J. Alloys Compd., 360 (2003), 250-255; [2] H. T. Takeshita et al., J. Alloys Compd., 376 (2004), 268-274.

P-260 **The Crystal Structure of $NbVCoD_{2.5}$, Synthesized at High Gas Pressure.** V. P. Glazkov,[1] V. A. Somenkov,[1] S. A. Lushnikov,[2] V. N. Verbetsky,[2] – [1]Russian Research Center "Kurchatov Institute", Moscow, Russia; [2]Moscow Lomonosov M.V. State University, Moscow, Russia

At a high pressure of hydrogen (up to 2 kbar) synthesis intermetallic deuterides NbVCo with structure of hexagonal Laves phase carried out. By thermodesorption it is established, that the maximal deuterium contents corresponds to $NbVCoD_{2.5}$. With the help of neutron and x-ray diffraction positions of atoms of metal and deuterium and their parameters are determined. It is shown, that atoms V and Co are statistically distributed mainly in sublattices (2a, 6h), and deuterium atoms take basically positions 24l and 12k, typical for hydrogen in hexagonal Laves phases. Blocking of neighboring position is demonstrated. The work has been supported by RFBR under the grants 06-02-17062, 06-03-33114.

P-261 **A High-Resolution Neutron Scattering Study of the Deuterium-Driven Metal-Insulator Phase Transition in KC_8D_x Graphite Intercalation Compound.** A. Lovell,[1] N. T. Skipper,[1] S. M. Bennington,[2] R. I. Smith,[2] – [1]UCL, London, UK; [2]ISIS-RAL, Chilton, Oxon., UK

Stage-1 graphite intercalation compound KC_8 is known to chemisorb deuterium or hydrogen at room temperature, driving a change of staging to a ternary stage-2 compound at concentrations of D greater than 0.1 up to ~0.67 per KC_8 unit. The dissociated deuterium has been seen to undergo a metal to non-metal transition to form the filling in a triple layer of atomic planes between every other pair of graphene sheets; no potassium remains in the alternate gallery spaces. Thus the new arrangement has layer order C-C-K-D-K-C, where the deuterium is electro-negatively charged and the potassium positively charged. This study charted the transition between 300 and 315 K in the D-saturated sample with time-resolved high-resolution neutron scattering to investigate the structural changes and charge transfer in unprecedented detail. [1] S. A. Solin and H. Zabel, Adv. Physics 37 (1988) 87-254; [2] T. Enoki, S. Miyajima, M. Sano, H. Inokuchi, J. Mater. Res. 5 (1990) 435; [3] S. Miyajima, T. Chiba, T. Enoki, H. Inokuchi, M. Sano, Phys. Rev. B, 37 (1988) 3246.

P-262 **Hydriding Properties of Mischmetal-based AB_3 System.** A. Leela Mohana Reddy, N. Mani, S. Ramaprabhu, – Indian Institute of Technology Madras, Chennai, India

The hydriding properties of intermetallic compounds RM_n (R = rare earth or Zirconium, Titanium, M = transition elements and n = 1, 2, 5) have been studied elaborately in search of better hydrogen storage materials. Hence, in the present work, Mischmetal (Mm) based AB_3 alloys ($MmNi_3$, $MmFe_{1.5}Ni_{1.5}$ and MmFeNiCo) are prepared and its single phase formation has been confirmed by powder X - ray diffractograms. The hydrogen absorption isotherms of Mm based AB_3 alloy using low and high pressure hydrogen absorption / desorption facilities in the temperature and pressure ranges $30 \leq T/^{\circ}C \leq 200$ and $0.001 \leq P/bar \leq 30$ have been obtained. Besides, the thermodynamics of dissolved hydrogen have been calculated from the P-C isotherms and the results are discussed. The kinetics of hydrogen absorption at 50°C, 100°C, and 150°C has been studied for these alloys and the results are discussed. The activation energies (E_a) of alloy hydrides have been obtained from the kinetics of hydrogen absorption. The powder X – ray diffractograms of the alloy hydrides have been performed in order to find the volume expansion in the lattice upon hydrogenation. The different phases identified by both kinetic and X-ray studies of hydrides have been correlated to those seen in the hydrogen absorption isotherms. Further, metal to semiconductor transition upon hydrogenation of this alloy has been studied from electrical resistivity measurements in the temperature range 80 K to 300 K and the results have been discussed.

P-263 **Neutron Vibrational Spectroscopy of the Pr_2Fe_{17}-based Hydrides.** T. J. Udovic,[1] C. M. Brown,[1] E. Mamontov,[1] J. J. Rush,[1] O. Isnard,[2,3] W. Zhou[1,4] – [1]NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD, USA; [2]Laboratoire de Cristallographie, CNRS, Grenoble, France; [3]Institut Universitaire de France, Paris, France; [4]Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA, USA

Neutron vibrational spectroscopy measurements of $Pr_2Fe_{17}H_x$ and $Pr_2Fe_{17}D_x$ ($x \leq 5$) reveal dynamic features consistent with the interstitial hydrogen locations previously assigned by neutron diffraction. In particular, for $Pr_2Fe_{17}H_3$, two peaks centered at ≈85.4 meV and 106.0 meV correspond to the normal-mode vibrational energies of hydrogen in octahedral (*o*) sites comprised of a near-square planar arrangement of four Fe atoms and two apical Pr atoms. Based on first-principles calculations, the lower energy is assigned to the *c*-directed H_o vibration in the Fe-defined plane. The higher energy is assigned to the H_o vibration along the Pr-H_o-Pr axis and to the other orthogonal H_o vibration in the Fe-defined plane. For $Pr_2Fe_{17}H_4$ and $Pr_2Fe_{17}H_5$, the lower-energy H_o mode softens considerably by ≈6 meV and 10 meV, respectively. This is in part due to the *c*-axis expansion to accommodate the additional hydrogen occupying the neighboring distorted tetrahedral (*t*) sites comprised of two Fe atoms and two Pr atoms. For $Pr_2Fe_{17}H_5$, in addition to slightly softened H_o basal-plane modes centered at ≈104.7 meV, there is extra scattering intensity evident near ≈112 meV and 123.7 meV due to two of the H_t normal modes. The analogous $Pr_2Fe_{17}D_5$ spectrum suggests that the third H_t normal mode is located near 104 meV, obscured by the 104.7 meV H_o peak. A comparison of $Pr_2Fe_{17}H_x$ and $Pr_2Fe_{17}D_x$ vibrational energies indicates that the *o*-site bonding potential is largely harmonic, whereas the *t*-site bonding potential is more anharmonic.

P-264 **Interrelation of Structural Characteristics and Hydrogenation / Dehydrogenation Behaviour in V–Ti–Zr b.c.c. Alloys.** M. V. Lototsky,[1] V. A. Yartys,[1] R. V. Denys,[1] I. Yu. Zavaliy,[2] J. P. Maehlen,[1] – [1]Institute for Energy Technology, Kjeller, Norway; [2]Physico-Mechanical Institute of NAS Ukraine, Lviv, Ukraine

Quaternary V-based BCC alloys modified by Ti, Zr and transition metals Cr, Mn, Fe, Co, Ni have significant potential in thermally managed applications of metal hydrides [1]. Small variations of the composition of the alloys lead to dramatic changes in their hydrogenation behaviour and in thermodynamic characteristics of the M–H interaction. This work is focused on studies of the

interrelation of composition, structure and hydrogen sorption properties of the BCC V–Ti–Zr alloys characterised by a range of Ti/V ratios reaching 0.23. The non-hydrogenated and hydrogenated samples were studied using SEM, XRD, *in situ* SR-XRD in H_2 atmosphere (following transformations β→(α+β)→α), and *in situ* PND in D_2 atmosphere (following the process ε→(α'+ε)→α'→α). H_2/D_2 sorption properties were studied using PCT and vacuum TDS. For the $V_{82.5}Ti_{10}Zr_{7.5}D_x$ deuteride D_2 desorption isotherms at T=90 °C were built using both volumetric measurements and PND data. The correlation of the determined structural parameters of the alloys and corresponding hydrides at different H/M contents and the hydrogenation/ dehydrogenation behaviours are discussed. Emphasis is on the influence of Ti/V ratio on the width and thermodynamic parameters of the second plateau (including slope and hysteresis), as well as characteristics of the inverse isotopic effect. [1] M.V.Lototsky, V.A.Yartys, I.Yu.Zavaliy, JALCOM 404–406 (2005) 421–426.

P-265 **Hydrogen Ordering and Relaxation of Internal Stress Fields in α-$YH_{1/6}$ AND α-$ScH_{1/6}$.** J. Garces,[1] J. L. Gervasoni,[1,2] P. Vajda,[3] – [1]Centro Atómico Bariloche, S. C. de Bariloche, Rio Negro, Argentina; [2]CONICET, S. C. Bariloche, Rio Negro, Argentina; [3]Laboratoire des Solides Irradies, CNRS- CEA, Ecole Polytechnique, Palaiseau, France

In this work we study some aspects related to hydrogen ordering in the α*-YH_x and α*-ScH_x solid solution in order to contribute to the understanding of basic questions such as the formation of H chains in Sc, Y, and several hcp lanthanides (for a review, see e.g. ref.[1]). After relaxing the internal positions of all atoms in the cell we study the character of the bands, the density of states, the charge density, and the Fermi surface in each system. We use the FLAPW method, as implemented in the Wien2k code [2]. In a previous work [3], we calculate both the optimal structure of H-H pairs in Y and total energies as well as electronic structures for different ratios H/Y, in order to find the driving forces that determine the formation of these chains. In the present work we use the results obtained in [3], for a giving composition YH_x, extending it to the same concentration of hydrogen in Sc. The results and their comparison with known experimental data are encouraging. [1] P. Vajda, "Hydrogen in rare earth metals, including RH_{2+x} phases" in Handbook on the Physics and Chemistry of Rare Earths, (ed. by K.A. Gschneidner), vol. 20, ch. 137 (Elsevier 1995); [2] P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka and J. Luitz, WIEN2K, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties (K. Schwarz, Techn. Universitat Wien, Austria),2001. ISBN3-9501031-1-2; [3] J. Garces, J. L. Gervasoni and P. Vajda, Journal of Alloys and Compounds 404-406, pp. 126 130 (2005).

P-266 **Hydrogen Storage Properties and Structure of $La_{1-x}Mg_x(Ni_{1-y}[Mn,Al]_y)_3$ Intermetallics.** R. V. Denys,[1,2] V. A. Yartys,[1] M. Sato,[3] R. G. Delaplane,[4] A. B. Riabov,[2] – [1]Institute for Energy Technology, Kjeller, Norway; [2]Physico-Mechanical Institute of the National Academy of Sciences of Ukraine, L'viv, Ukraine; [3]Department of Applied Science, School of Engineering, Tokai University, Hiratsuka, Kanagawa, Japan; [4]The Studsvik Neutron Research Laboratory, Uppsala University, Nyköping, Sweden

'Hybrid' RNi_3 structures are built of slabs of $CaCu_5$- and $MgZn_2$-type units (RNi_5+2*RNi_2 = 3*RNi_3). Different affinities of these slabs to hydrogen result in unusual anisotropic structural behaviour of RNi_3 on hydrogenation [1]. This work focuses on studies of the influence of Mg, Mn and Al on structure and hydrogen storage properties of the $La_{1-x}Mg_x(Ni_{1-y}[Mn,Al]_y)_3$ intermetallics belonging to the homogeneity area of the $PuNi_3/CeNi_3$ type structures. In $LaNi_3D_3$ a preferential H insertion into the RNi_2 slabs takes place, together with a huge uniaxial expansion (60%) and rebuilding of the metal sublattice. Mg causes a complete alteration of the hydrogenation behaviour of $LaNi_3$. $La_{0.67}Mg_{0.33}Ni_3D_4$ isotropically expands on its formation preserving the metal sublattice without major modifications. Mg substitution leads to a substantial increase of the reversible hydrogenation capacity and stability against hydrogenation-induced amorphisation. The difference in the behaviours is attributed to an ordered substitution of La by Mg in the $MgZn_2$-type slabs. Replacement of Ni by Mn or Al leads to the change of the crystal structures from $PuNi_3$ to the $CeNi_3$ type in the $LaNi_{3-y}Mn_y$ and $LaNi_{3-y}Al_y$ alloys. An ordered substitution of Ni by Mn and Al inside the RNi_5 slabs takes place. Both Mn and Al decrease the stability of $LaNi_3$ against amorphisation during hydrogen absorption. [1] V.A. Yartys et al., JALCOM, 408-412 (2006) 273.

P-267 **Mg – Mm – Ni Eutectic Alloy: Structure, Hydrogen Sorption Properties and Performance in Hydrogen Storage Unit.** B. P. Tarasov,[1] D. N. Borisov,[1,2] P. V. Fursikov,[1,3] V. N. Fokin,[1] S. N. Klyamkin,[4] M. V. Lototsky,[2] V. A. Yartys,[2] A. Schrøder Pedersen,[3] – [1]Institute of Problems of Chemical Physics of RAS, Chernogolovka, Russia; [2]Institute for Energy Technology, Kjeller, Norway; [3]Materials Research Department, Risø National Laboratory, Roskilde, Denmark; [4]Moscow State University, Moscow, Russia

Eutectic alloy Mg72Ni20Ln8 (wt.%; Ln = mischmetal) consists of three phases: Mg-Mg_2Ni-Ln_2Mg_{17}. Its hydrogenation results in the formation of LnH_3, MgH_2 and Mg_2NiH_4. Further hydrogenation↔dehydrogenation proceeds by the reactions: Mg_2Ni↔Mg_2NiH_4, Mg↔MgH_2, and LnH_{2+x}↔LnH_{3-y}. After several cycles of H uptake-release, the material can reversibly store up to 5.5 wt.% H. This work is devoted to the elucidation of the processes taking place during interaction of the alloy with hydrogen, and to the demonstration of the efficiency of H storage system based on this material. Both initial and hydrogenated alloy were characterised by optical microscopy, SEM, EDX, and XRD (including *in-situ* measurements during decomposition of the hydride). Hydrogen sorption performances were studied using Sieverts technique and TDS. Presence of easy-hydrogenated phases (Mg_2Ni, LnH_{2+x}) in combination with fine microstructure results in very fast H absorption-desorption allowing to create dynamically efficient H storage unit based on this material. The developed prototype has H_2 storage capacity of 270 l. It is characterised by a short charge time (at 10 bar H_2 and 250 °C 90 % capacity was reached in less than 10 min) and fast discharge rate (at 2 bar H_2 and 350 °C 90 % H_2 were released in less than 30 min). Supported by Nordisk Energiforskning (NORSTORE 46-02), Russian Foundation for Basic Research (Grant 05-08-18130) and Federal Agency for Science and Innovations (Lot 2005-EE.22.2/001).

P-268 **The Effect of Solidification Rate on Microstructural Evolution and Hydrogen Storage Properties of the Melt-Spun Mg-20Ni-8Mm Alloy.** Y. Wu,[1] J. K. Solberg,[1] V. A Yartys,[1,2] – [1]Department of Materials Technology, Norwegian University of Science and Technology, Trondheim, Norway; [2]Institute for Energy Technology, Kjeller, Norway

Magnesium-based alloys have been considered as the most promising candidates for hydrogen storage system due to their low specific weight, high hydrogen storage capacity and rich natural resources. Mechanical alloying and rapid solidification methods have been applied to produce microcrystalline, nanocrystalline and amorphous microstructures to improve the hydrogenation characteristics. In the present studies, microcrystalline/nanocrystalline/ amorphous Mg-20Ni-8Mm (wt.%) (Mm=Ce, La-rich Mischmetal) materials were prepared by rapid solidification, and their microstructures and hydrogen storage properties were compared with those of a conventionally prepared polycrystalline alloy. The microstructural evolution under various cooling rates in the melt-spun ribbons was focused so as to obtain the maximum hydrogen absorption capacity and excellent hydrogenation kinetics. The melt-spun ribbons were obtained by a single roller melt-spinning technique (graphite, stainless steel and copper quenching discs, respectively, with a diameter of 200 mm) in an argon atmosphere of 200 mbar. The microstructure of the specimens was examined by X-ray diffractometry (XRD), transmission electron microscopy (TEM) and scanning electron microscopy (SEM) with an energy-dispersive X-ray spectrometry (EDS). Hydrogen absorption and desorption kinetics as well as pressure-composition-isotherms was measured by a PCT equipment. The as-cast masteralloy has a typical dendrite microstructure, which consists of mainly Mg_2Ni with a size of 2-80 mm and a minor Mischmetal-rich Mg-containing phase (probably $Mg_{12}Ce$ and Mg_9La) in a matrix of Mg. The effect of solidification rate on microstructure and hydrogen storage properties of the melt-spun ribbons is being studied. It is expected that the present work will be helpful for clarifying the effect of solidification rate on microstructural evolution and hydrogen storage properties of the melt-spun Mg-based alloy, and to attain an optimal microstructure with large hydrogen storage capacities.

P-269 **Zr_2Fe and Zr_3Fe Hydrides for Nuclear Materials.** D. Chandra,[1] J. R. Wermer,[2] M. Coleman,[3] S. N. Paglieri,[2] J. I. Abes,[2] T. J. Udovic,[4] A. Payzant,[5] – [1]University of Nevada, Reno, NV, USA; [2]Los Alamos National Laboratory, Los Alamos, NM, USA; [3]Altair Technologies, Reno, NV, USA; [4]NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD, USA; [5]Oak Ridge National Laboratory, HTML, Oak Ridge, TN, USA

Nuclear materials processing requires gettering materials for removal of residual amounts of tritium from nitrogen gas streams. One of the most commonly used getters is the commercial ST198 (SAES) alloy. We have performed x-ray diffraction studies on Zr_2Fe, $ZrFe_2$ hydrides and the commercial alloy ST198. The major phase of this alloy is Zr_2Fe with some other minor phases. Buttons of alloy composition Zr_2Fe, and Zr_3Fe were prepared in our laboratories and thermodynamic and in-situ crystal studies were performed. Disproportionation was observed at elevated temperatures and was responsible for the reduced capacity for hydrogen and its isotopes. High temperature x-ray diffraction studies under N_2/H_2 environment showed that alloy did not react with nitrogen to form zirconium nitrides up to ~923K. The Zr_2Fe hydrides were stable up to 623K, but this temperature Zr_3Fe hydrides have been observed during hydriding of Zr_2Fe. Neutron scattering studies have also shown that Zr_2Fe begins to transform to Zr_3Fe by simple annealing; suggesting that phase stability of Zr_3Fe at around ambient temperatures. Results of neutron scattering, in-situ x-ray diffraction, isotherms of Zr_3Fe and Zr_2Fe at different temperatures, and issues with the Zr-Fe phase diagram will be presented [1, 2, 3]. [1] Yartys V.A., Fjellvag H., Hauback B.C., Riabov A.B., J. Alloys Compds. 274 (1998) 217; [2] Arias D, Abriata J.C., in Massalski et al. (Ed.), 2nd ed., Binary Alloys Phase Diagrams, Vol. 2, ASM International, USA (1990) 1798; [3] Chatain, S, Gueneau, C, Chatillon, C, J. Nuclear Materials 344 (2005) 218. **Program Sponsored by Los Alamos National Laboratory.*

P-270 **Iron Contamination in Ball Milled BCC Alloys.** J. Charbonnier,[1,2] D. Fruchart,[1] J. Huot,[3] S. Miraglia,[1] P. de Rango,[1,2] N. Skryabina,[1] – [1]Laboratoire de Cristallographie, CNRS, Grenoble, France; [2]CRETA, CNRS, Grenoble, France; [3]Institut de Recherche sur l'Hydrogène, Université du Québec à Trois-Rivières, Trois-Rivières, Canada

Ball milling technique is extensively used for the synthesis of nanocrystalline metal hydrides. However, high energy milling produces contamination from milling tools that could be significant. In this paper we show that for BCC alloys the iron contamination is highly dependent on the nature of the alloy. Two BCC systems were studied: Ti-V-Cr and Ti-V-Mn alloys. For both systems, extensive milling produced a mixture of BCC and FCC phases. However, iron contamination is one order of magnitude higher in the Ti-V-Cr system compare to the Ti-V-Mn. Powder diffraction patterns do not show the presence of metallic iron. Therefore, the iron contamination formed a solid solution with the bcc and fcc phases. However, the situation is a little more complex since the thermomagnetic traces clearly evidence two magnetic ordering temperatures, at ~ 200 and ~ 750℃, respectively. Therefore, if the iron contamination formed a solid solution with the BCC and FCC phases, iron-rich nano-particles (or poorly crystallised) remain still present. Upon a short time annealing, these particles react rapidly with the rest of the powder to form some iron rich phase. Comparison with arc melted samples Ti-V-Cr-Fe and Ti-V-Mn-Fe will be shown. The mechanism of this contamination will be discussed as well as the impact on hydrogen storage characteristics.

P-271 **Destabilization Behavior and Phase Compositions for LiH-Ge.** R. C. Bowman, Jr.,[1] S.-J. Hwang,[2] C. C. Ahn,[2] J. J. Vajo,[3] M. R. Hartman,[4] T. J. Udovic,[4] J. J. Rush,[4] – [1]Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA; [2]California Institute of Technology, Pasadena, CA, USA; [3]HRL Laboratories, Malibu, CA, USA; [4]National Institute of Standards and Technology, Gaithersburg, MD, USA

Destabilizing hydrogen rich but strongly bound hydrides such as LiH via alloying with elements (i.e., Si) can improve substantially their potential as hydrogen storage materials in fuel cell powered vehicles. A reversible hydrogen storage capacity of ~5.0 wt.% was previously measured with LiH–Si producing a large increase in the equilibrium pressure compared to LiH for temperatures below 800 K. Similar behavior has also been found for the LiH+Ge system. Volumetric measurements of the hydrogen absorption and

desorption isotherms that have been obtained for a ball milled mixture of 4.4LiH+Ge powder reveal increased pressures expected from the destabilization effect. The phase compositions at the various stages of reaction have been examined by solid state nuclear magnetic resonance, powder x-ray diffraction, and neutron scattering methods. The initial mixtures of LiH and Ge were found to convert into various known Li-Ge intermetallic phases as hydrogen is desorbed. The distributions of the germanide and hydride phases for various stages of reaction are discussed within the context of destabilization processes involving intermediate phases that alter observed thermodynamic parameters. Consistent with the Li-Si-H system at an analogous Li/Si ratio of 4.4, there is no formation of a separate Li-Ge-H ternary phase. Prompt gamma activation analysis has been employed to provide a quantitative measure of the hydrogen contents of the LiH-Ge samples at different levels of dehydrogenation.

P-272 **Thin Film Combinatorial Approach to Storage Materials with Direct Real-Time Compositional Monitoring.** E. Engstrom, C. Friesen, – Materials Science & Engineering, Arizona State University, Tempe, AZ, USA

Combinatorial materials synthesis is able to greatly increase the rate of compositionally dependent storage density and reversibility optimization in hydrogen storage applications. A thin film combinatorial approach was utilized to produce compositionally varied films of Li, Mg, B, Na and Al alloys. Film composition was confirmed with Auger depth profiling. A Pd capping layer was used as both a barrier to oxidation and as a catalyst for the dissociation and uptake of hydrogen from the gas phase. Samples were reacted in a high-vacuum chamber allowing the introduction of partial pressures of hydrogen gas. A temperature-controlled stage and a quartz crystal microbalance were also incorporated in the chamber. The microbalance is sensitive to 0.4 ng/cm^2 allowing for sub-percentage sensitivity to compositional changes. Storage density, reversibility, thermodynamic, and kinetic properties of the various alloy compositions examined will be presented.

P-273 **Theoretical Study of Hydrogenation of Metalfullerides.** S. Yu. Zaginaichenko,[1] D. V. Schur,[1] Z. A. Matysina,[2] – [1]Institute for Problems of Materials Science of NAS of Ukraine, Kiev, Ukraine; [2]Dnepropetrovsk State University, Dnepropetrovsk, Ukraine

The statistical theory of process of phase transformations, realized as the result of hydrogenation of platinum fullerides $C_{60}Pt$, $C_{70}Pt$ has been developed. The theory provides an explanation and substantiation for formation of phases of hydrofulleride $C_{60}PtH_x$ and then of fullerite $C_{60}H_x$ with a rise in temperature. The atomic configurational model of crystals has been used in calculation without considering possible processes in subsystems of interstitial atoms of hydrogen and platinum. The free energies dependences of respective $C_{60}Pt$, $C_{60}PtH_x$, $C_{60}H_x$ phases on temperature, composition, order parameters in fullerenes subsystem, energetic constants have been defined. The evaluation of energetic constants has been performed with the use of experimental data on temperature and concentration ranges of realization of each phase. The plots of free energies of these phases have been constructed as a function of concentration for different temperatures. The phase diagram has been constructed by intersection points of these plots and with the use of method of total tangent lines to them. This diagram defines the temperature and concentration regions of all phases realization and corresponds to experimental data of phases existence of chemical reaction with increased temperature. The hydrogen solubility in the $C_{60}PtH_x$, $C_{60}H_x$ phases has been calculated, it is determined by the equilibrium concentration of hydrogen atoms in relation to the temperature.

P-274 **Development of a High Pressure Microbalance for Hydrogen Storage Materials.** A. P. Vestbø, J. O. Jensen, N. J. Bjerrum, – Technical University of Denmark, Lyngby, Denmark

Pressure-composition isotherms (PCI's) help to determine thermodynamic properties related to hydrogen uptake of materials. PCI's are normally obtained volumetrically in a Sieverts type apparatus or gravimetrically in a microbalance. A common problem with the gravimetric technique is that the sample is momentarily exposed to air when transferring it to the system often causing unwanted changes such as oxidation and reaction with moisture in the air. In this study, a high pressure microbalance was built from scratch inside a glove box with inert atmosphere. The system consists of an electromagnetic microbalance, pressure resistant casing for up to 100 bar hydrogen, a flow system for hydrogen and inert gas, heating elements for temperature control, and software for controlling the system. The system was calibrated with regard to buoyancy and thermal convection. The precision of the mass measurements was ±20 µg and proved to be independent of pressure and temperature. In this presentation the system is described in detail.

P-275 **Influence of Hydrogen on Nano-mechanical Properties of Oxidized Fuel Cladding.** H. Muta, M. Ito, M. Uno, S. Yamanaka, – Division of Sustainable Energy and Environmental Engineering, Graduate School of Engineering, Osaka University, Suita, Osaka, Japan

Zirconium based fuel cladding tube becomes brittle due to rapid β-α transformation under loss-of-coolant accident (LOCA) conditions. Accumulated hydrogen in fuel cladding also affects the fracture behavior. Hence it is considered to be important to study the influence of hydrogen on claddings under LOCA condition. The high-temperature oxidized fuel cladding has inhomogeneous structure called as the Widmann-Stätten structure, composed by the needle-like α-zirconium grains (α' phase) and the matrix (α phase). In this study, the nanoindentation tests on the high-temperature oxidized cladding were performed and the influence of hydrogen on mechanical properties of each phase was discussed. Hydrogenated and non-hydrogenated Zircaloy-4 cladding tubes were oxidized by steam with the temperature of 1273 ~ 1473 K followed by quenching. The nano-indentation was performed for polished surface of these samples. It was found that the hydrogenation led to increase the elastic modulus for both α' and matrix α phases. On the other hand there was no significant difference in hardness between the samples with and without hydrogen. Since the hardness number can be related to the yield stress or the ultimate tensile strength, the stress for fracture is

considered to be unchanged by hydrogen. The increased elastic modulus by the hydrogen addition implies the small strain for fracture of claddings, indicating the degradation of the cladding.

P-276 **Study of the Extended Domain Range in $Mg_{17}Al_{12}$ Intermetallic Phase and their Hydrogen Storage Properties.** J.-C. Crivello,[1] T. Nobuki,[1] S. Kato,[2] T. Kuji,[3] – [1]School of High Technology for Human Welfare, Tokai University, Japan; [2]Course of Applied Science, Graduate School of Engineering, Tokai University, Japan; [3]Courses of Materials Science and Chemistry Unified Graduate School, Tokai University, Japan

In order to modulate the thermodynamic properties of the (Mg-Al)-H_2 system, the extended homogeneity range of the intermetallic phase $Mg_{17}Al_{12}$ has been studied, particularly in higher Al-rich domain. Because alloying needed a long time to synthesize these binary compounds, the bulk mechanical alloying (BMA) method was used, reducing drastically the process time. XRD and DSC measurements were used to analyze the phase's homogeneity with the influence of the temperature. The hydrogenation properties are presented at 350°C. The Pressure-Composition isotherm (PCT) curves show plateaux corresponding to the hydride formation and decomposition. This family of compounds present a capacity of absorption of about 3 wt% at 30 bars with a slow speed of reaction. Conservation or decomposition of the Mg-Al phases initially in presence has been carefully checked after hydrogenation cycling and heat treatments.

P-277 **Investigation of $ZrMn_{2+X}$-H_2 by Means of Calorimetric Method.** E. Yu. Anikina, V. N. Verbetsky, – Moscow State University, Moscow, Russia

It is well known, that intermetallic compounds (IMC) $ZrMn_{2+X}$ with C 14 Laves phase structure have wide homogeneity range. In the present work hydrogen interaction with IMC $ZrMn_2$ and $ZrMn_{2.7}$was studied in the temperature range from 100 to 305°C for $ZrMn_2$ and from 75 to 180°C for $ZrMn_{2.7}$ and hydrogen pressure up to 60 atm. The twin-cell differential heat-conducting calorimeter Tian-Calvet type, connectied with the apparatus for gas dose feeding, was applied for these measurements. The dependences of partial molar enthalpy for hydride decomposition and equilibrium hydrogen pressure on hydrogen concentration C ($C=[H]/[AB_2]$) in $ZrMn_{2+X}$ and reaction temperature were obtained. Analysing the plots of hydrogen desorption isotherms versus C, obtained for $ZrMn_2$ and $ZrMn_{2.7}$, it can be concluded that plateau slopping for $ZrMn_{2.7}$-H_2 system is greater, than for $ZrMn_2$-H_2. It has been established that in the $ZrMn_2$-H_2 and $ZrMn_{2.7}$-H_2 systems the partial molar enthalpies of hydrogen desorption changed with the temperature of experiment and hydrogen concentrations in these systems. It should be marked that we did not observe trapping-effect on the plots of ΔH versus C in the system $ZrMn_{2.7}$-H_2, that is, possibly, connected with the absence of the tetrahedral interstitial A_3B sites in the metallic matrix.

P-278 **Kinetics and Thermodynamics of Metal-Hydride Formation Measured Optically by Hydrogenography.** R. Gremaud,[1] A. Borgschulte,[2] C. Broedersz,[1] D. M. Borsa,[1] H. Schreuders,[1] B. Dam,[1] R. Griessen,[1] – [1]Vrije Universiteit, Amsterdam, The Netherlands; [2]GKSS-Research Center Geesthacht GmbH, Geesthacht, Germany

Hydrogenography is a novel technique that exploits the optical changes induced by hydrogen absorption in metal thin films [1-2]. We show that this technique can also be used to measure and tune the kinetics and thermodynamics of hydrogen-metal systems. As a model system, we produce Mg_xNi_{1-x} thin films with a compositional gradient by co-sputtering. By increasing gradually the H_2 pressure and measuring the associated changes in optical transmission, we determine simultaneously the equilibrium pressures of all compositions x. With this technique we easily discriminate between Ni-doped MgH_2 and the complex Mg_2NiH_4. From measurements at various temperatures, the enthalpy of formation ΔH of each composition x is obtained. ΔH of stoïchiometric Mg_2NiH_4 is in good agreement with literature [3]. Moreover, we find that a Ni excess/deficiency destabilizes Mg_2NiH_4. Complementary to the equilibrium measurements, we record the hydrogenation kinetics. The pressure dependence of the kinetics gives us a second method to extrapolate the equilibrium pressure. This indirect procedure is especially valuable for systems such as alanates whose hydride phase nucleation is slow. Having tested the validity of our method on the archetypal Mg_2NiH_4 we move to the Mg-Ti-H system, which is promising for application in batteries and solar collectors [4-5]. Using hydrogenography we determine the thermodynamics of the $Mg_xTi_{1-x}H_y$ phases including the fluorite-type hydride which is reversibly formed in films. [1] A. Borgschulte et al., Appl. Phys. Lett. 85 (2004) 4884; [2] R. Gremaud et al., accepted in Appl. Phys. A (2006); [3] W. Lohstroh et al, Phys. Rev. B 70 (2004) 165411; [4] R. A. H. Niessen and P. H. L. Notten, Electrochem. Solid-State Lett. 8 (2005) A534; [5] D. Borsa et al., submitted to Appl. Phys. Lett. (2006).

P-279 **Structural and Thermodynamic Characteristics of LaNiIn Intermetallic Hydrides Modified by Cu and Al.** M. Sato,[1,2] R. V. Denys,[3,4] A. B. Riabov,[3] J. P. Maehlen,[2] M. Stange,[2] R. G. Delaplane,[4] V. A. Yartys,[2] S. Kato,[1] H. Uchida,[1] Y. Matsumura,[1] H. H. Uchida,[5] – [1]School of Engineering, Tokai University, Kanagawa, Japan; [2]Institute for Energy Technology, Kjeller, Norway; [3]Physico-Mechanical Institute, NAS of Ukraine, Lviv, Ukraine; [4]The Studsvik Neutron Research Laboratory, Studsvik, Sweden; [5]School of Humanities and Culture, Tokai University, Kanagawa, Japan

$RENiInD_{1.33}$ hydrides (RE=La, Ce, Nd) are characterised by the shortest known separation of the hydrogen atoms in the structures of metal hydrides (1.56-1.60 Å). Studying the effect of substitutions of RE, Ni and In, by chemically similar elements will assist in better understanding of the mechanism to form corresponding hydrides. It may consequently help in the optimisation of the materials with high volumetric density of hydrogen. The present work focuses on studies of the influence of substitution, by Cu for Ni or by Al for In, in the LaNiIn-based hydrides on their structure and thermodynamics. The substitutions by Cu for Ni and by Al for In sensitively affect the P-C-T relationships, stability of the hydrides, slope of the isotherms, hysteresis effect between hydrogen absorption / desorption processes and critical temperatures of the β-γ transition. The relative partial molar thermodynamic properties for the studied systems are: ΔH_H=-34.6 ± 2.1 kJ$(mol_H)^{-1}$, ΔS_H=-70.7 ± 3.6 J$(K\cdot mol_H)^{-1}$ for LaNiIn-H; ΔH_H=-34.1 ± 0.5

$kJ(mol_H)^{-1}$, ΔS_H=-74.9 ± 1.0 $J(K\cdot mol_H)^{-1}$ for $LaNi_{0.95}Cu_{0.05}In$-H; ΔH_H=-33.2 ± 0.8 $kJ(mol_H)^{-1}$, ΔS_H=-68.3 ± 1.2 $J(K\cdot mol_H)^{-1}$ for $LaNiIn_{0.98}Al_{0.02}$-H. The paper will present a detailed data concerning an influence of Cu and Al on the crystal structure of the deuterides formed with a focus on the materials with short D…D separations.

P-280 **Hydrogen Desorption from Pure Titanium with Different Concentration Levels of Hydrogen.** Y. Furuya,[1] A. Takasaki,[2] K. Mizuno,[3] T. Yoshiie,[4] – [1] Faculty of Education, Nagasaki University, Nagasaki, Japan; [2]School of Engineering., Shibaura Institute of Technology, Toyosu, Tokyo, Japan; [3]Interdisciplinary Faculty of Science and Engineering, Shimane University, Matsue, Japan; [4]Research Reactor Institute, Kyoto University, Kumatori, Osaka, Japan

Hydrogen evolution behaviors from pure titanium platelet samples, for which hydrogen has been thermally charged under a gas phase of 0.1MPa hydrogen, were investigated by means of thermal desorption spectroscopy (TDS). The hydrogen concentration levels in the samples were varied from extremely low to high as to form the hydride, by controlling the charging times (2-20h) and temperatures (398-773K). Evolution peaks of hydrogen from the samples varied depending upon the concentration levels of hydrogen. At lower hydrogen concentration of 0.2 to 0.4 at%, evolution peaks were observed between 1000 K and 1150K, and, with increasing the hydrogen concentration level, two peaks at 850K and 900-950K were observed in addition. The peak at lower temperature dominated only for the samples with higher hydrogen concentration, while the higher one for the ones with lower hydrogen concentration. In the initial stage of hydrogen dissolution in the samples, four evolution peaks would be characterized in TDS spectra. The hydride formation has occurred suddenly at the charging temperature more than about 680K and at the hydrogen concentration level more than about 15-16 at%, resulting in the concentration of hydrogen more than 50 at%, in which the sample evolved a large amount of hydrogen with an evolution peak from 550K to 900K. The composition of hydride was estimated to be TiH_x (x: 1-1.9). The hydride formed in the sample was examined by the diffraction-enhanced X-ray imaging technique.

P-281 **Phase Transitions in Nanoscale Niobium Hydrides.** V. P. Glazkov, I. F. Kokin, V. A. Somenkov, – RRC "Kurchatov Institute", Moscow, Russia

By methods of neutron and x-ray diffraction it is established, that at ball milling crystal niobium deuterides with concentration $NbD_{0.7}$-$NbD_{1.84}$ phase transition takes place. Transition is expressed in disappearance on diffraction patterns of superstructural peaks of type (½½0), occurrence of peaks (100), strong distortion of a cell (c⁄a ~1.07) and widening of peaks. It is similar to transition found out earlier in niobium hydride by means of X-rays at high pressures. The work has been supported by RFBR under the grants 06-02-17062, 06-03-33114, 06-02-17515.

P-282 ***Ab Initio* Calculation of Dynamical Properties for Borates (MBH_4 ; M=Li, Na, K).** D. Y. Kim,[1] R. H. Scheicher,[1] C. M. Araujo,[1] P. Jena,[2] R. Ahuja,[1,3] – [1]Condensed Matter Theory Group, Department of Physics, Uppsala University, Uppsala, Sweden; [2]Physics Department, Virginia Commonwealth University, Richmond, VA, USA; [3]Applied Material Physics, Department of Materials Science and Engineering, Royal Institute of Technology, Stockholm, Sweden

A systematic density functional theory based study of the phonon density of states (PDOS) has been carried out for selected phases of $LiBH_4$, $NaBH_4$ and KBH_4. The PDOS obtained with the direct method, which gives information on the dynamical stability of each structure, was compared with experimental results and calculations of molecular vibrations for BH_4^-. Furthermore, the change of stretching and bending modes with pressure between B and H showed the stability of the structural entity. The effect of zero-point vibrations on the calculated lattice parameters was large enough to be significant, as it can be expected for light element compounds. The importance of these findings for applications of the above materials in hydrogen storage will be discussed.

P-283 ***Ab Initio* Study of 3d- and 4d-Transition Metal Doped $NaAlH_4$.** A. Blomqvist,[1] C. M. Araujo,[1] P. Jena,[2] R. Ahuja,[1,3] – [1]Condensed Matter Theory Group, Department of Physics, Uppsala University, Uppsala, Sweden; [2]Department of Physics, Virginia Commonwealth University, Richmond, VA, USA; [3]Applied Materials Physics, Department of Materials Science and Engineering, Royal Institute of Technology, Stockholm, Sweden

Sodium alanate ($NaAlH_4$) has been considered as a potential hydrogen storage material mainly due to its high hydrogen content (5.6wt%). However the desorption kinetics are slow and it is not a reversible process, hence limiting its practical application in hydrogen storage. It has been shown that such limitations can be overcome by doping $NaAlH_4$ with Ti.[1] In this work we have performed a systematic theoretical investigation of 3d- and 4d-transition metal (TM) doped $NaAlH_4$. Self-cosistent total energy calculations were carried out within the framework of density functional theory using the PAW method. In sodium alanate the H and Al atoms form a very stable tetrahedral structure $(AlH_4)^-$. In the doped systems a stretching of the Al-H bonds was observed, implying that the strength of the chemical bond between these atoms is diminished. This would suggest that the TMs help to destabilize the Al-H bonds. This weakening of the bonds were further established by calculating the energy cost to remove one hydrogen atom from the intrinsic and doped systems. Bond lengths and lattice parameters were studied in order to understand the impurity effects on the crystal structure. From the doped systems we have observed a tendency to form TM-Al alloys by analyzing the bond length between these atoms. [1] B. Bogdanovic and M. Schwickardi, J Alloys Compd. 253, 1 (1997).

P-284 **Phase Boundary Study of the Pd-H(D) Systems by Means of Electrical Resistivity Measurements.** H. Araki,[1] Y. Sakamaki,[1] S. Harada,[2] M. Kubota,[3] – [1]Nagaoka National College of Technology, Nagaoka, Niigata, Japan; [2]Faculty of Engineering, Niigata University, Niigata, Japan; [3]Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba, Japan

Electrical resistivity measurements have been performed on PdH(D)x at high hydrogen concentrations in the range $0.6 < x < 0.92$. The samples were prepared by hydrogen loading using electolysis at low temperatures. A broad peak in the electrical resistivity

was used to investigate the variations of phase boundaries with hydrogen concentration in the high hydrogen concentration region. The plotted heating curves showed a broad peak which we believe originates in a new phase of the system. The peak temperature increased with the increase in hydrogen concentration *x*.

P-285 **Hydrogen Absorption Capacity of AB_5-type Alloys at Elevated Pressures.** T. A. Zotov, V. N. Verbetsky, S. V. Mitrokhin, E. A. Movlaev, – Chemistry Department, Lomonosov Moscow State University, Moscow, Russia

A new installation for high pressure investigations of hydrogen interaction with alloys is presented. The installation is designed for high pressure measurements of PC-isotherms at pressures up to 3000 bar in the temperature range -30 – 100°C. The latest results of such measurements for typical representatives of AB_5-type alloys will be presented and discussed. For YNi_5 and YCo_5 PC-isoterms at temperatures -20 – 80°C were measured. The maximum absorption capacity corresponded to compositions $YNi_5H_{5.9}$ and $YCo_5H_{3.3}$.

P-286 **Hydrogen Bonding in the LnT_3H_x Intermetallic Hydrides (Ln=Er,Ho, T=Ni,Co) Hydrides.** R. Castañeda,[1] A. Aburto,[2] E. Orgaz,[1] – [1]Departamento de Física y Química Teórica, Facultad de Química, UNAM, Mexico; [2]Departamento de Física, Facultad de Ciencias, UNAM, Mexico

In a recent work, Filinchuk et al. [1-3] investigated the directional metal-hydrogen bonding in $LnNi_3$ (Ln=Er,Ho) and $ErCo_3$ derived hydrides. Quantum mechanical solid-state computations of the electronic structure were performed in order to investigate the bonding properties, density of states, electronic and magnetic properties of these series of compounds. We employed a mixed approach (i) solid state computations using the state-of-the-art DFT-based linearized-augmented plane waves method and (ii) molecular computations of the electronic structure of representative molecular clusters. This approach has been proved to be useful to investigate the electronic structure of hydrides [4]. The $LnTi_3$ (Ln=Er, Ho, T=Ni, Co) intermetallics as well as the b_1-LnT_3H_x phases were fully investigated. [1] Y. E. Filinchuk, K. Yvon. J. Alloys Compds., 404-406 (2005) 89; [2] Y. E. Filinchuk, D. Sheptyakov, K. Yvon. J. Alloys Compds., in press (2006); [3] Y. E. Filinchuk, K. Yvon. J. Solid State Chem., 179 (2006) 1037; [4] E. Orgaz, J. Hernández-Trujillo, Int. J. Quantum Chem. 94, 150 (2003).

P-287 **Electronic Structure of $RNiSnH_x$ (R=La, Ce, Pr, Nd) Hydrides.** A. Aburto,[1] E. Orgaz,[2] R. Castañeda,[2] – [1]Departamento de Física, Facultad de Ciencias, UNAM, Mexico; [2]Departamento de Física y Química Teórica, Facultad de Química, UNAM, Mexico

Rare-earth elements based intermetallics are of particular fundamental interest. The interplay between the chemical composition, crystal structure and the consequent complex magnetic and electric behavior yield a wide field of investigation. This is the case of RNiSn (R=La, Ce, Pr, Nd) intermetallic compounds and their corresponding hydrides [1,2]. In this work we report our results of the electronic structure of these series of compounds by investigating the band structure, density of states and chemical bonding characteristics. We performed band structure calculations of these series of compounds by means of a DFT-based linearized-augmented plane waves method. [1] M. Stange, V. Paul-Boncour, M. Latroche, A. Percheron-Guégan, O. Isnard, V.A. Yartys, J. Alloys and Compounds 404, 144 (2005); [2] B. Chevalier, M. Pasturel, J-L. Bobet, R. Decourt, J. Etourneau, J. Sánchez Marcos, J. Rodriguez Fernández, J. Alloys Compds 383, 4 (2004).

P-288 **How does $TiCl_3$ Catalyst in $LiNH_2$+LiH Mixture Change During the Dehydrogenation·Rehydrogenation?** R. Iida,[1] N. Takeichi,[2] T. Kiyobayashi,[2] H. Takeshita,[3] L. Cheng,[2] Z. Shu,[2] – [1]Graduate School of Kansai University, Suita, Osaka, Japan; [2]National Institute of Advanced Industrial Science and Technology, Ikeda, Osaka, Japan; [3]Kansai University, Suita, Osaka, Japan

The $LiNH_2$+LiH mixture is considered to store 6.5 wt% of hydrogen theoretically [1]. It is reported that the dehydrogenation properties are improved by catalysts such as $TiCl_3$ [2].usually added to the $LiNH_2$+LiH mixture by ball milling. However, how the catalyst in the mixture work has not been clarified. We can imagine that the Ti precursor reacts with the mixture during the milling and/or during the dehydrogenation-rehydrogenation with forming other species from the precursor. And it might work first as the catalyst. So I examined a change of $TiCl_3$ during the dehydrogenation and rehydrogenation by XRD. Sample of LiH, $LiNH_2$ added $TiCl_3$ respectively and the sample of $LiNH_2$+LiH mixture added as the molar ratio at $LiNH_2$: LiH : $TiCl_3$ = 1 : 4.4 : 1 were milled to measured by ex-situ and in-situ XRD. Because, It is necessary to add excessive amount of $TiCl_3$ to observe changes of $TiCl_3$ by XRD. After milling, $TiCl_3$ + LiH sample produces LiCl and TiH_X. The reaction seems that $3aLiH+aTiCl_3 \rightarrow 3aLiCl+aTiH_X+a((3-X)/2)H_2$.The reaction has progressed further after heated. And, $TiCl_3$ peak disappeared and Ti compounds peak did not appear excluding Ti hydride peaks of low intensities. $LiNH_2$ + $TiCl_3$ sample does not change so much though it is milled and heated. I will also report that changing of $TiCl_3$ in the mixture during dehydrogenation-rehydrogenation by in-situ XRD. [1]P. Chen, *et al.*, *Nature*, 420, (2002), 302-304; [2]H. Leng, *et al.*, *J. Phys. Chem. B,* 108, (2004), 8763-8765.

P-289 **Nanostructured Mg – Mm – Ni Hydrogen Storage Alloy: Structure – Properties Relationship.** S. Løken,[1,2] J. K. Solberg,[2] J. P. Maehlen,[1] R. V. Denys,[1] M. V. Lototsky,[1] V. A. Yartys,[1,2] B. P. Tarasov,[3] – [1]Institute for Energy Technology, Kjeller, Norway; [2]Norwegian University of Science and Technology, Trondheim, Norway; [3]Institute of Problems of Chemical Physics of RAS, Chernogolovka, Russia

Kinetics of H uptake / release in Mg can be improved by its alloying with Ni and RE, as well as by reducing the grain size of Mg alloy. Both these approaches were applied in present work, for the alloy 72 wt.% Mg – 20 wt.% Ni – 8 wt.% Mm (ternary eutectic Mg – Mg_2Ni – $MmMg_{12}$). The alloy was processed by Equal Channel Angular Pressing (ECAP) technique [1]. In ECAP the sample is subjected to plastic strain by pressing through a die with an angle of 90°. ECAP treatment resulted in fine microstructure compared to the rather heterogeneous as cast material. Hydrogenated and non-hydrogenated samples were investigated using SEM and

XRD. Hydrogenation properties were studied by TDS and PCT. Hydrogenated sample consists of MgH_2, Mg_2NiH_4 and MmH_{2+x} and exhibits maximum H storage capacity of ~5.5 wt.%. To initiate the first hydrogenation, the alloy needs to be activated at ~300℃. However, already after one hydrogenation cycle its H absorption becomes quite fast: 4.5 wt.% H is absorbed in just 15 minutes. Vacuum TDS (heating rate 0.5℃/min) shows that desorption starts at low temperature, ~135℃, with a peak at ~210℃. The alloy was also subjected to High Energy Ball Milling (HEBM) in Ar or H_2 to yield further refinement of the microstructure. ~1 wt.% Nb_2O_5 was added to facilitate H exchange. The H sorption characteristics of the alloy treated by ECAP and HEBM are compared with the ones for the as cast material. [1] V.M. Segal, Materials Science and Engineering A271 (1999) 322-333.

P-290 **The Hydrogen Effect on the Electronic Structure of R_2Fe_{17} Intermetallic Compounds (*R* = Y, Nd, Sm).** S. Mizusaki, N. Kawamura, T. Taniguchi, Y. Nagata, – College of Science and Engineering, Aoyama Gakuin University, Sagamihara, Japan

The insertion of interstitial hydrogen into the crystal lattice of a compound generally induces dramatic changes in its electronic and magnetic properties, such as electronic and magnetic ordering and metal-insulator transitions. It is very important to understand how electronic structural changes take place in the course of hydrogenation, and hence it must be necessary to study these effects for different hydrogen concentrations and various metallic host lattices. The *R*-Fe intermetallic compounds (*R* = rare-earth metal) have been studied from the viewpoint of hydrogen effect [1], [2]. Hydrogenation provides further insight into the magnetic structure, which gives important information on the *R*-Fe coupling in the hydrides. However it is still unclear that the insertion hydrogen affects the electronic structure of the $R_xR'_{1-x}$ – Fe compounds (*R'* = rare-earth metal). In the present study, we investigated the hydrogen effect on the electronic and magnetic properties of the $(Y, Nd, Sm)_2Fe_{17}$ by means of pressure-composition-isotherm measurement, magnetic susceptibility measurements, and iron^{57} Mössbauer spectroscopy and discussed the influence of interstitial hydrogen on the basic electronic structure of the compounds. [1] V. Paul-Boncour, M. Guillot, G. Wiesinger, and G. André, Phys. Rev. B 72, (2005) 174430; [2] Qi-nian Qi, Hong Sun, R. Skomski, and J. M. D. Coey, Phys. Rev. B 45, (1992) 12278.

P-291 **Specific Heat of $RMn_2(HD)_x$.** L. Kolwicz-Chodak,[1] Z. Tarnawski,[1] H. Figiel,[1] L. Havela,[2] K. Miliyanchuk,[2] E. Šantavá,[3] N.-T. H. Kim-Ngan,[4] – [1]Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, Krakow, Poland; [2]Department of Electronic Structures, Charles University, Prague, Czech Republic; [3]Institute of Physics, Academy of Sciences of the Czech Republic, Prague, Czech Republic; [4]Institute of Physics, Pedagogical University, Krakow, Poland

Specific heat (SH) measurements on $RMn_2(H,D)_x$ powders (R = Y, Nd, Ho and Er; x = 0 - 4.3) have been performed in the temperature range 50 - 320 K by means of a quasi-adiabatic method. Detailed investigations in a wider temperature range (2 - 400 K) and in magnetic fields (0 – 9 T) have been performed on a few selected compounds using the Quantum Design PPMS equipment by a relaxation method. The hydrogenation leads to a dramatic increase of the Néel temperature (T_N), the anomaly of SH at T_N is more pronounced, and an excessive specific heat appears in the whole temperature range of 50 - 300 K. The magnetic ordering temperature appears as a single SH peak in the pure samples (x=0), whereas double SH peaks were always observed for the hydrides. Under the applied magnetic field of 9 T, the SH upturns below 5 K was suppressed, whereas no visible influence on the double SH peak was found. Moreover, magnetic susceptibility was studied in detail in the temperature range of the phase transitions.

P-292 **Hydrogen Ordering Induced Resistivity Anomalies in the Superstoichiometric Light Rare-Earth Dihydrides.** N. Z. Namoradze,[1] I. G. Ratishvili,[2] – [1]Institute of Cybernetics, Tbilisi, Republic of Georgia; [2]E.Andronikashvili Institute of Physics, Tbilisi, Republic of Georgia

The rare-earth superstoichiometric dihydrides are known to reveal some anomalies in the temperature dependence of electric resistivity within the concentration range of β-phase, where the ordering of octa-hydrogens is established [1]. To describe the contribution of the octa-hydrogen ordering subsystem in the total resistivity of the dihydride a modified version of the theory of binary alloys electric resistivity [2] is applied. For some RH_{2+c} systems this part of electric resistivity is determined in a wide range of temperatures and concentrations. It is shown that in a number of RH_{2+c} systems the development of ordering processes by different scenario [3] can be determined by characteristic anomalies in the electric resistivity concentration and temperature dependences. [1] P.Vajda. in *Handbook on the Physics and Chemistry of Rare Earths*. v. **20**, p. 207 (1995); [2] M.A.Krivoglaz, A.A.Smirnov. "*The Theory of Order-Disorder in Alloys*". Elsevier, New York,1964; [3] I.G.Ratishvili, P.Vajda. J. Alloys Comp., **253-254**, 171-174 (1997).

P-293 **High Throughput Screening of Complex Hydrides for Hydrogen Storage.** J. W. A. Sachtler,[1] G. J. Lewis,[1] J. J. Low,[1] D. A. Lesch,[1] S. A. Faheem,[1] P. M. Dosek,[1] L. M. Knight,[1] C. M. Jensen,[2] – [1]UOP LLC, Des Plaines, IL, USA; [2]Hawaii Hydrogen Carriers, LLC, Honolulu, HI, USA

To date, no hydride meets the targets for automotive hydrogen storage and research is ongoing in many organizations to find an improved material. We are using Combinatorial Synthesis and Screening (CSS) to increase the rate of discovery of improved complex hydrides and dopants. In the first stage of the work, we use medium-throughput techniques to synthesize and test 8 samples in parallel. The second stage expands this to 48 samples at a time. Samples are prepared by ball milling mixtures of hydrides and dopants similar to the reported method of preparing Ti doped $NaAlH_4$. In this poster we will present results from our medium throughput CSS experiments covering ternary reaction mixtures selected from the NaH, LiH, KH, MgH_2, and CaH_2 –Al system, focusing on the rehydriding reaction rather than the initial decomposition of alanates. XRD results show the samples examined after a final re-hydriding cycle often consist of both alanates and aluminum hexahydride species, along with some unconverted Al. The samples that showed the best reversibility contained mixed-metal aluminum hexahydrides, prompting us to synthesize and test these as pure phases. Finally, we will show early results obtained with our high-throughput 48-reactor system.

P-294 **Hydrogen Behavior and its Effect on Optical Absorption of Tungsten Oxide Films.** S. Nagata,[1] A. Inouye,[2] K. Takano,[2] S. Yamamoto,[2] B. Tsuchiya,[1] K. Toh,[1] T. Shikama,[1] – [1]Institute for Materials Research, Tohoku University, Sendai, Japan; [2]Japan Atomic Energy Agency, Takasaki, Japan

It is known that optical absorption of a tungsten oxide film is drastically changed when the surface covered with catalyst layer as exposed by hydrogen gas. However, the role of the hydrogen on the gasochromic characteristics was not clearly understood. In this paper, the correlation between the hydrogen behavior and the optical absorption was studied for tungsten oxides with different composition and structure to clarify the gasochrmic mechanism in the tungsten oxide. The tungsten films were prepared by reactive R.F magnetron sputtering with various oxygen gas pressures for substrate temperatures between 300 and 830 K. The crystal structure and elemental composition were examined by the X-ray diffraction and Rutherford backscattering experiments. Hydrogen was introduced to the oxide film by dissociation of H_2 gas at a thin layer of Pt formed on the oxide surface, or by keV hydrogen ion implantation. The hydrogen concentration in the film was measured by the Elastic Recoil Detection Analysis technique, and the optical absorption of the film was measured in visible wavelengths. The gasochromic characteristic was sensitively affected by the sample preparation condition. Oxide films with highly oriented structure showed the quick response of the transmittance when the film was exposed by the 1% H_2 gas. On the other hand, the H concentration depth profile in the oxides did not depend on small differences of the composition and the structure.

P-295 **Magneto-Structural Phenomena in the Hexagonal Hydrides RMn_2Hx (R=Tb, Y).** O. L. Makarova,[1] I. N. Goncharenko,[1,2] A. V. Tsvyashenko,[3] F. Bourée,[2] – [1]Russian Recearch Center "Kurchatov Institute", Moscow, Russia; [2]Laboratoire Leon Brillouin, CEA/Saclay, France; [3]Vereshagin Institute of High Pressures Physics, Troitsk, Russia

The RMn_2 compounds exhibit very unusual coupling between the magnetic and structural (hydrogen) sublattices. Different correlations between structural and magnetic ordering parameters had been observed in the cubic (C15) and hexagonal (C14) Laves phases [1], and the origin of this difference is not yet understood. Recent progress in synthesis of the RMn_2 compounds R=Y, Dy, Gd, Tb, Ho (which usually exist only in the cubic C15 modification) in the C14 structure [2] gives an opportunity to test directly the influence of the topology on the magneto-structural coupling by studying hydrides having exactly the same chemical composition but different (C14 or C15) structures. Here we present new results on the crystal and magnetic structures of the hexagonal C14 hydrides RMn_2H_x (R=Y, Tb; $2.8<x<4.6$) and compare them with those of the cubic C15 hydrides.

P-296 **Photoelectrochemical Study of Hydrogen in Oxide Films of Zr-based Alloys for Fuel Cladding Materials of Light Water Reactor.** M. Uno, K. Takahashi, T. Nakayama, S. Yamanaka, – Division of Sustainable Energy and Environmental Engineering, Graduate School of Engineering, Osaka University, Suita, Osaka, Japan

Hydrogen plays an important roll in the degradation of Zr based cladding materials for light water reactors. Since the cladding absorbs hydrogen through the oxide films formed on its surface during the irradiation the chemical states of hydrogen in the oxide film should be clarified. The chemical states of hydrogen in oxides films of 1%NbZr alloy, 2.5%NbZr alloy and Nb added Zry-4 produced by the absorption of hydrogen and oxidation in air were studied by photoelectrochemical (PEC) measurements and electrochemical impedance spectroscopy (EIS) measurements. Obtained data were compared with those for Zr and Zry-2 and discussed with the estimation by the DV-Xa molecular orbital method. From the PEC measurements, it is found that the Nb added Zr alloy oxide films with hydrogen have the band gap energy of about 5 eV which is nearly the same as that of pure Zirconium dioxide. In addition they have two sub-band gap energies of around 4.5 eV and 3.5 eV arising from hydrogen and niobium, respectively. This can be explained by the formation of new electron levels in the original band gap of pure Zirconium dioxide by the addition of niobium and hydrogen. DV-Xa calculation supports this change in the band structure by the H and Nb addition. The calculation also suggests the low bonding force between hydrogen and the other atoms in the oxides.

P-297 **A Neutron Powder Diffraction Study of the Transition Metal (Ti, Cr) Substitution Effect on $Mg_{2-x}Ti_xNi_{1-y}Cr_y$ (x=0, 0.1; y=0, 0.1) Deuterides.** X. L. Wang,[1] J. P. Tu,[1] X. S. Jiao,[2] K. Sun,[2] – [1]Department of Materials Science and Engineering, Zhejiang University, Hangzhou, China; [2]China Institute of Atomic Energy, China

$Mg_{2-x}Ti_xNi_{1-y}Cr_y$ (x= 0, 0.1; y= 0, 0.1) alloys were prepared by powder-sintering at 823 K for 72 h under vacuum with subsequent mechanically smashing into powder less than 100 mesh. XRD results showed single phase as Mg_2Ni for the samples with Ti / Cr substitution. In addition, Ti / Cr substitution showed few effects on the lattice parameters calculated through structure refinement and profile matching. After hydriding, neutron powder diffraction was used to investigate the hydrogen location in the deuterides. The effects of transition metal (Ti, Cr) substitution on the deuterium atom location and content in Mg-Ni deuterides were discussed.

P-298 **Hydrogenation of R_7Rh_3 Series of Intermetallic Alloys under Large Range of Hydrogen/Deuterium Pressure.** S. M. Filipek,[1] T. Tsutaoka,[2] R. Sato,[1] I. Marchuk,[1] – [1]Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland; [2]Phys Laboratory, Fac. of School Educ., Hiroshima University, Hiroshima, Japan

Intermetallic compounds R_7M_3 (where R = rare earth metal; M = eight group metal) which crystallize in Th_7Fe_3 type hexagonal structure with the space group *P6₃mc* are actually intensively investigated [1] due to their interesting electronic and magnetic properties. We have started a systematic investigation of these intermetallics within a large range of hydrogen pressure, in order to check the possibility of hydrides formation, stability of these hydrides and the influence of hydrogen on the properties of parent materials. For series of R_7Rh_3 compounds it was found that treatment by hydrogen even at moderate pressures leads to formation of hydrides with nearly H/M = 2. The hydrides retained their parent symmetry but large lattice expansion has been observed.

Hydrides were stable when kept long time at normal conditions after release of hydrogen pressure. Heat treatment at 100ºC up to 500 MPa(H_2) did not cause amorphisation neither decomposition. The structural properties of new hydrides are determined and reported. The influence of hydrogen on magnetic properties is presented and discussed. [1] T. Tsutaoka, Y. Nakamori, T. Tokunaga, H. Kadomatsu, Y. Itoh, J. Alloys and Comp.270 (1998), 53-57.

P-299 **Research & Development at the SRNL Hydrogen Technology Research Laboratory.** J. S. Holder, – Savannah River National Laboratory, Aiken, SC, USA

In the past twenty years, metal hydride materials have been used at the Savannah River Site in a variety of hydrogen processing applications, including storage, pumping, compression, separation, and purification. These applications have been developed and implemented by scientists and engineers in the Savannah River National Laboratory. This work continues in the new SRNL Hydrogen Technology Research Laboratory (HTRL), a 24,000 square foot facility dedicated to hydrogen R&D. The HTRL consists of 22 lab modules designed specifically for conducting R&D on hydrogen related technologies, along with a high bay for larger scale projects, and office space for permanent staff, post-docs, interns and students in a collaborative environment. An overview of current R&D efforts and opportunities will be presented.

P-300 **Hydrogen Storage Systems for Automotive Application (EU 6th FP Project "StorHy" /"SP-Solid" Sub Project / with Contract Number: 502667).** J. Muller,[1] S. Sartori,[1] DaimlerChrysler,[2] GKSS,[3] FZK,[4] NCSR-D,[5] – [1] Institute for Energy Technology IFE, Kjeller, Norway; [2]DaimlerChrysler AG, Germany; [3]Forschungszentrum Geesthacht GKSS, Germany; [4]Forschungszentrum Karlsruhe FZK, Germany; [5]NCSR Demokritos, Greece

StorHy aims to develop safe and efficient on-board vehicle hydrogen storage systems suitable for use in hydrogen-fuelled fuel cell or internal combustion engine vehicles. The project is structured along three major Sub-projects (SP) corresponding to the three major storage technologies (compressed gas, cryo liquid and solid storage). The Sub Project "SP Solid" focuses on lightweight complex alanates as these are considered as one of the most promising materials for solid hydrogen storage. The investigations concentrate on screening the most relevant candidates (using amongst others reactive milling), and improving their hydrogen storage density as well as hydrogenation /dehydrogenation kinetics. Furthermore, up scaling of the material production process is considered aimimg at construction and testing of demonstration and tutorial tanks, which include heat management studies. The project also deals with safety experiments of alanate powders relevant to their use as hydrogen storage materials. The Sub Project "SP Solid" focuses on lightweight complex alanates as these are considered as one of the most promising materials for solid hydrogen storage. The investigations concentrate on screening the most relevant candidates (using amongst others reactive milling), and improving their hydrogen storage density as well as hydrogenation /dehydrogenation kinetics. Furthermore, up scaling of the material production process is considered aimimg at construction and testing of demonstration and tutorial tanks, which include heat management studies. Theproject also deals with safety experiments of alanate powders relevant to their use as hydrogen storage materials.

P-301 **Hydriding and Dehydriding Properties of $Mg(NH_2)_2$-LiH Systems.** M. Aoki,[1] T. Noritake,[1] Y. Nakamori,[2] S. Towata,[1] S. Orimo,[2] – [1]Toyota Central R&D Labs., Inc., Nagakute, Aichi, Japan; [2]Institute for Materials Research, Tohoku University, Sendai, Japan

We have studied the hydriding and dehydriding properties of 3 $Mg(NH_2)_2$ + 12 LiH system and reported the reversible reactions with hydrogen [1-3]. In this work, the hydriding and dehydriding properties of 3 $Mg(NH_2)_2$ + x LiH (x = 6, 8, 12) systems were investigated to discuss the effects of LiH content changes. The mixtures of 3 $Mg(NH_2)_2$ + x LiH (x = 6, 8, 12) were mechanically milled for 2 h under 1 MPa of hydrogon pressure using a planetary ball mill (Fritsch P-5). The samples were handled in a glove-box filled with purified argon. The hydriding and dehydriding properties were characterized by pressure-composition (*p-c*) isotherm and X-ray diffraction (XRD) measurements. Although 3 $Mg(NH_2)_2$ + x LiH (x = 6, 8, 12) systems showed similar *p-c* isotherms at 523 K, the amount of the desorbed hydrogen decreased with increasing LiH content. In addition, XRD profiles of 3 $Mg(NH_2)_2$ + x LiH (x = 6, 8, 12) systems were similar after the *p-c* isotherm measurement. On the other hand, the reversible hydrogen capacity at higher temperature increased with increasing LiH content. [1] Y. Nakamori, G. Kitahara, K. Miwa, S. Towata, S. Orimo, Appl. Phys. A 80 (2005) 1-3; [2] Y. Nakamori, G. Kitahara, A. Ninomiya, M. Aoki, T. Noritake, S. Towata, S. Orimo, Mater. Trans. 46 (2005) 2093-2097; [3] M. Aoki, T. Noritake, G. Kitahara, Y. Nakamori, S. Towata, S. Orimo, J. Alloys Compd. (to be submitted).

P-302 **Effect of Li Addition on Synthesis of Mg-Ti BCC Alloy by Means of Ball Milling.** K. Asano, H. Enoki, E. Akiba, – National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki, Japan

In the previous works [1], novel Mg-Ti alloys with a body centered cubic (BCC) structure have been successfully synthesized by means of ball milling. However, these Mg-Ti BCC alloys hardly absorbed hydrogen. To synthesize Mg based alloys with high capacity of hydrogen the synthesis process of Mg-Ti BCC alloy by means of ball milling has been studied [2]. The mechanical properties of Mg and Ti are significantly different. As Ti is harder than Mg, Ti acts as abrasives for Mg stuck on a milling pot and balls. The difference in the mechanical properties among raw materials is an essential factor for synthesis of Mg based alloys by means of ball milling. Metals with a hexagonal close packed (HCP) structure as Mg and Ti are deformed by anisotropic slips. It is well known that the addition of Li makes the compressive ductility of Mg larger [3]. In the present work, the effect of Li addition on the synthesis of Mg-Ti BCC alloy by means of ball milling has been investigated. [1] Akiba et al., Collected Abstracts of Int. Symp. on Metal-Hydrogen Systems (MH2002), (2002) p.115; [2] Asano et al., Collected Abstracts of the 2006 Spring Meeting of MRS, (2006); [3] Agnew et al., Acta Mater., **49** (2001) 4277.

P-303 **Mg_3La— a New Type of Mg-based Hydrogen Storage Material and the Effect of Ni Addition to It.** L. Ouyang, C. Peng, M. Zhu, – College of Mechanical and Engineering, South China University of Technology, Guangdong, Guangzhou, China

Magnesium–lanthanum (Mg-La) alloys were prepared by induction melting in an alumina crucible under protection of pure argon atmosphere. Ni was added to the Mg-La alloy to improve the dynamic properties. XRD patterns show that the as melted Mg-La and $Mg_3LaNi_{0.1}$ diffraction peaks can be excellently indexed with $D0_3$ structure (BiF_3 type, space group Fm3m). The lattice constant of Mg_3La phase is 0.7498 nm, which are determined by XRD analysis using Cohen's extrapolation method. The reversible hydrogen storage capacity reaches 2.89 wt.% for Mg_3La and 2.73 wt.% for $Mg_3LaNi_{0.1}$. The desorption of hydrogen takes palce at 274 □ for Mg_3La and at 256 □ for $Mg_3LaNi_{0.1}$. The alloys could absorb hydrogen at room temperature with rapid hydriding and dehydriding kinetics. The experimental results also showed low degree of decrepitation and high cyclic stability after tens hydriding–dehydriding cycles. The enthalpy (ΔH) and entropy (ΔS) of Mg_3La-H dehydriding reaction were -81.0kJ/mol H_2 and -0.142kJ/K-mol H_2 determined by using van't Hoff plot according to the pressure-composition-isotherms (P-C-I) curve measured at different temperature. Hydrogen absorption kinetic properties of Mg_3La and $Mg_3LaNi_{0.1}$ alloys were measured at room temperature. The experimental curves fitted best to Avrami–Erofeev equation and suggest that the hydriding of Mg_3La and $Mg_3LaNi_{0.1}$ alloy at room temperature is basically a one-dimensional diffusion-controlled nucleation and growth process.

P-304 **Effect of Alloying Substitution and Addition of Rare-earth Chlorides on Hydrogen Storage Performance of $NaAlH_4$ Complex Metal Hydride.** B. Zhou, T. Sun, L. Z. Ouyang, H. Wang, M. Zhu, – College of Mechanical Engineering, South China University of Technology, Guangzhou, China

The hydrogen storage performance of the complex metal hydride requires substantial improvement. In this work, the method of high energy ball milling was used to prepare $NaAlH_4$ and $LiAlH_4$ with rare-earth chlorides such as $LaCl_3$, $CeCl_3$, and YCl_3 as catalyst. Attempt has also been made to adding Fe, Co, Ni or Cu through high energy ball milling to partially substitute Al. XRD and SEM analysis was used to characterize the microstructure and hydrogen storage performance of the obtained complex metal hydrides. The preliminary results show that rare-earth chlorides can be well dispersed in the complex metal hydride matrix by ball milling. The hydrogen storage performance is affected by the addition of these additives. The mechanism of the effect of adding rare-earth chlorides has been discussed.

P-305 **H(D)-Lattice Interactions in Single Wall Carbon Nanotubes.** A. Paolone,[1] O. Palumbo,[2] R. Cantelli,[3] U. Dettlaff,[4] S. Roth,[4] – [1]Université "La Sapienza" and Cnr-Supermat, Rome, Italy; [2]Université "La Sapienza" and Cnr-Infm, Rome, Italy; [3]Université "La Sapienza", Rome, Italy; [4]Max Planck Institut für Festkörperforschung, Stuttgart, Germany

The anelastic spectrum of HiPco carbon nanotubes was measured in the temperature range from 1.3 to 700 K Three thermally activated relaxation processes were found, which denote the presence of mobile particles on the surface of CNT. The peak at 550 K is due either to the motion of the bundles of nanotubes or to the dynamics of molecular groups (carboxylic or hydroxylic) attached to the surface of CNT. The peak at 150 K increases in height after its exposition to a H_2 atmosphere at 80 K; therefore, it should be attributed to the motion of molecular hydrogen, and likely to the magnetoelastic coupling between the ortho-hydrogen molecules and the hexagonal CNT lattice. The presence of this process indicates that the CNT lattice does not behave neutrally and new types of interactions should be considered. The peak at 25 K is almost absent in intentionally hydrogenated samples, but grows after subsequent thermal treatments which partially remove hydrogen. On the basis of the isotope peak shift, we propose that the relaxation is due to hydrogen, and that its intensity increases with decrease of c_H as more free sites are made available for the H jumps. The species giving rise to this peak is very mobile, indicating that it can hardly be ascribed to a hydrogen molecule. Moreover classical models cannot reproduce the peak, suggesting that the motion of H is governed by a quantum tunneling.

P-306 **Reaction Steps in the Li-Mg-N-H Hydrogen Storage System.** W. Lohstroh, M. Fichtner, – Institute for Nanotechnology, Karlsruhe Research Center, Karlsruhe, Germany

Since the discovery of Chen et al. [1] that mixtures of $LiNH_2$ and LiH can reversible store 10.5 wt. % H_2, amide based systems are considered promising candidates as storage materials in a future hydrogen economy. We will present results on the reaction steps in the Li-Mg-N-H system studied by high pressure differential scanning calorimetry (HP-DSC), infrared spectrometry (FT-IR), thermal desorption spectroscopy (TDS) and x-ray diffraction (XRD). For a mixture of $2LiNH_2$-MgH_2 it was reported that the reversible hydrogen ab- and desorption takes place between $Mg(NH_2)_2$ (+LiH) in the hydrogenated state and a new LiMgNH phase in the desorbed state [2]. We show that during the first desorption of ball milled $2LiNH_2$-MgH_2 first an exothermic phase transition takes place (T_1 » 210 °C) where $Mg(NH_2)_2$ is formed, followed by an endothermic hydrogen desorption (T_2 » 250 °C). HP-DSC experiments at various H_2- pressures show that the initial decomposition comprises several steps and their transition temperature crucially depends on the applied hydrogen pressure. The addition of 2mol% $TiCl_3$ in the initial $2LiNH_2$-MgH_2 mixture does not affect the exothermic phase transition but the hydrogen release shifts to lower temperatures. Adding 2mol% $TiCl_3$ after cycling the material has no effect on the desorption properties. [1] P. Chen, Z T. Xiong et al., Nature **420** (2002) 302; [2] W. Luo and S. Sickafoose, J. Alloys Comp. **407** (2006) 274.

P-307 **Correlation Between Lattice Parameter and Hydrogen Properties of Mg-based BCC Alloys.** H. Shao, K. Asano, M. Shibuya, E. Akiba, – National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki, Japan

One of the authors reported that an optimum lattice parameter of hydrogen storage alloys with BCC structure working at room temperature is about 0.303 nm because the BCC systems such as V metal, Ti-Cr-V alloys and Mg-V-TM alloys with this value of lattice parameter absorb and desorb hydrogen at room temperature. In the present work, we confirmed this hypothesis for the

$Mg_{60}Ni_5Co_{32-x}M_x$ (M=none, B, Al, Cu, Pd, V, Ti, Cr) BCC alloys synthesized by the ball milling method. $Mg_{60}Ni_5Co_{32-x}M_x$ (M=none, B, Al, Cu, Pd, V, Ti, Cr) alloys were synthesized by ball milling of 200h under 0.1 MPa argon. The BCC structure was confirmed by electron diffraction. TEM observation shows that these alloys consisted of particle with several nm in diameter. The Mg-based BCC alloys studied absorbed hydrogen without any activation process at 373 K. During the hydrogenation and dehydrogenation, the BCC structure was kept, but the lattice parameter of the BCC structure changed. There was an optimum lattice parameter of the BCC structure at 0.306 nm. $Mg_{60}Ni_5Co_{32}B_3$ with lattice parameter of 0.306 nm showed a hydrogen absorption content of 2.05 wt % at 373 K. It was found that the BCC alloy with lattice parameter larger than 0.315 nm did not absorb hydrogen at 373 K and under hydrogen pressure of 6 MPa.

P-308 **Energy Density Analysis of the Chemical Bond Between Atoms in Pervoskite-type Hydrides.** Y. Shinzato,[1] H. Yukawa,[1] M. Morinaga,[1] T. Baba,[2] H. Nakai,[2] – [1]Department of Materials Science and Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Japan; [2]Department of Chemistry, School of Science and Engineering, Waseda University, Okubo, Shinjuku-ku, Tokyo, Japan

Energy density analysis (EDA) [1] was first applied to pervoskite-type hydrides, $AMgH_3$(A=Na,K,Rb). The EDA is a method to partition the total energy of system into atomic energy densities.The calculated atomic energy density for hydrogen in these hydrides changed in the order, $KMgH_3<RbMgH_3<NaMgH_3$, whereas the atomic energy density for magnesium changed in the reverse way, $NaMgH_3<RbMgH_3<KMgH_3$. On the other hand, the atomic energy density for A (A=Na,K,Rb) scarcely deviated from the energy in an isolated atomic state. This indicates that the chemical interaction between magnesium and hydrogen atoms is most dominant in the pervoskite-type hydrides. The average bond energy between magnesium and its first-nearest-neighbor hydrogen atoms was estimated to be about 1.6eV for $NaMgH_3$, 1.7eV for $RbMgH_3$ and 1.8eV for $KMgH_3$. This order of the bond energy, $NaMgH_3<RbMgH_3<KMgH_3$, was consistent with the order of the measured heat of hydride formation. Also, the bond energy changed in the completely reverse way as the atomic energy density for hydrogen. Thus, the higher hydride stability seems to be associated with the lower atomic energy density for hydrogen. [1] H.Nakai, Chem. Phys.Lett., 363(2002), 73-79.

P-309 **Reactive Hydride Composites (RHC) for Hydrogen Storage.** G. Barkhordarian, T. Klassen, A. Borgschulte, M. Dornheim, U. Bösenberg, R. Bormann, – Institute for Materials Research, GKSS Research Centre, Geesthacht, Germany

Light weight metal hydrides are promising candidates for hydrogen storage materials due to their high gravimetric hydrogen density and safety. Apart from these, additional factors are required for metal hydride hydrogen storage system such as reversibility, low reaction enthalpy and low desorption temperature. Up to now, no system could be found which fullfills all the needed requirements. By a novel approach, composites of hydrides are used, instead of single compounds to tune the above mentioned parameters. By choosing appropriate reactants, it is found that the reaction enthalpy and desorption temperature can be reduced. In addition, compounds which can hardly be synthesized from the elements, can be reversibly cycled in such a reactive hydride composite (RHC) at moderate temperatures and pressures. Structural, thermodynamic and kinetic properties of various high capacity (up to 11wt.%) RHCs based on borohydrides will be discussed. The calculated desorption temperatures are in the range of 150-170℃, though the measured desorption temperatures are higher yet, due to kinetic constrains. In this respect, the impact of suitable catalysts on the sorption kinetics is investigated.

P-310 **Kinetic and Thermodynamic Properties of NH_3 Emission from the Li-N-H Hydrogen Storage System Examined by Spectroscopic Methods.** S. Hino,[1] T. Ichikawa,[2] K. Tokoyoda,[3] K. Okamoto,[3] N. Ogita,[4] M. Udagawa,[4] H. Fujii,[2] – [1]Graduate School of Advanced Sciences of Matter, Hiroshima University, Higashi-Hiroshima, Japan; [2]N-BARD, Hiroshima University, Higashi-Hiroshima, Japan; [3]R&D Center, Taiheiyo Cement Corporation, Sakura, Japan; [4]Faculty of Integrated Arts & Sciences, Hiroshima University, Higashi-Hiroshima, Japan

The H_2 desorption reaction of the Li-N-H system, which is described by $LiNH_2 + LiH \rightarrow Li_2NH + H_2$, has been clarified to be composed of two elementary steps mediated by NH_3: $2LiNH_2 \rightarrow Li_2NH + NH_3$, $LiH + NH_3 \rightarrow LiNH_2 + H_2$.[1] It is indicated that a quite small amount of NH_3 could be emitted from this reaction system. Actually, the knowledge of the emitted NH_3 partial pressure is a crucial issue for developing the metal-N-H system because the contamination with a trace of NH_3 (>10 ppm) in H_2 gas causes a noticeable decrease in performance of the fuel cells.[2] In a non-equilibrium experimental condition like in a thermal desorption mass spectroscopy measurement, the NH_3 emission originates in a kinetic reason, while in an equilibrium condition, it should come from a thermodynamic one. Since a practical application to the H_2 storage tank is available as a closed system, we should consider both the contributions with respect to the NH_3 emission. In fact, we estimated the NH_3 partial pressure in desorbed gas from the mixture of $LiNH_2$+LiH (doped with 1mol%TiO_2) in the closed system by Raman spectroscopy, indicating ~0.1% NH_3/H_2 was emitted in the temperature range of 300~400 ℃.[3] In this work, more multidirectional examinations from both kinetic and thermodynamic aspects by infrared and Raman spectroscopies are focused on. [1] T. Ichikawa et al., J. Phys. Chem. B 108 (2004) 8763; [2] N. Rajalakshmi et al., Fuel Cells 3 (2003) 177; [3] S. Hino et al., Chem Comm. (2005) 3038.

P-311 **Mechanochemical Synthesis and Thermal Decomposition of Complex Metal Hydrides.** Y. W. Cho,[1] Y. Kim,[2] K. B. Yoon,[2] E. Jeon,[1] E.-K. Lee,[1] J.-H. Shim,[1] – [1]Nano-Materials Research Center, Korea Institute of Science and Technology, Seoul, Republic of Korea; [2]Department of Chemistry and Center for Microcrystal Assembly, Sogang University, Seoul, Republic of Korea

$Mg(AlH_4)_2$ (9.3% H_2)and $Zn(BH_4)_2$ (8.5% H_2) seem to be promising hydrogen storage materials as they have very high theoretical hydrogen content. $Mg(AlH_4)_2$ was first synthesized in solvent in 1950s, but its precise thermal decomposition behavior was difficult to analyze because it always contained some amount of solvent adduct. On the other hand, the thermal stability of $Zn(BH_4)_2$ so low that even slight heating to remove solvent adduct easily provoke decomposition. In this study, we have synthesized solvent-free

$Mg(AlH_4)_2$ and $Zn(BH_4)_2$ using mechanochemical reactions between $NaAlH_4$ and $MgCl_2$, and $NaBH_4$ and $ZnCl_2$, respectively. Their thermal decomposition behavior has been investigated using DSC, TG/MS, and XRD. We also have performed ab-initio and thermodynamic calculations on the decomposition reactions of $Mg(AlH_4)_2$, and the results agreed quite well with those of experiments. For the first time, it was unambiguously confirmed that the first decomposition reaction step of $Mg(AlH_4)_2$ is exothermic. It was also confirmed that $Zn(BH_4)_2$ decomposed into Zn and gaseous B_2H_6 with H_2 rather than a solid mixture of Zn and B with H_2.

P-312 **The Hydrogen Storage Properties and Microstructure of Ti-doped Sodium Aluminum Hydride Prepared by Ball-Milling.** X. Z. Xiao, L. X. Chen, X. H. Wang, Q. D. Wang, C. P. Chen, – Department of Materials Science and Engineering, Zhejiang University, Hangzhou, P. R. China

Recently, Ti-doped $NaAlH_4$ complex hydride is attracting much attention for its potential application in the hydrogen-powered fuel-cell vehicles because of its high hydrogen storage capacity. However, the nature of Ti in hydriding-dehydriding process is still an enigma. In order to improve the reversible hydrogen capacity further and understand the catalytic mechanism of hydrogenation-dehydrogenation reaction, we prepared Ti-doped $NaAlH_4$ complex by hydrogenating the ball-milled composites NaH/Al + x mol% Ti (x= 0, 4, 6, 10), and then investigated their hydrogen storage properties and microstructures. It is found that hydrogen is a better atmosphere than argon for the ball-milling composites. The reversible hydrogen storage capacities of the composites with x=10 prepared by ball-milling for 12 h under hydrogen and argon atmosphere are 4.01 wt.% and 3.81 wt.% respectively. As the milling-time (t) increases from 6 h to 24 h, the hydrogen absorption capacity increases first and then decreases, and reaches a highest capacity of 4.21 wt.% at t=12. With the increase of Ti content, the hydrogen storage property is enhanced obviously. The results show that the catalytic mechanism of Ti-doped $NaAlH_4$ may be attributed to the active $TiH_{1.924}$ and TiAl particles, which concentrate on the surface of $NaAlH_4$ (NaH/Al) composition, and act as the catalytic active sites for the complex hydride and play an important catalytic role in reversible hydriding-dehydriding process.

P-313 **Hydriding and Dehydriding Properties of Ca-Si-X.** M. Miyoshi,[1] K. Kinoshita,[1] M. Aoki,[2] N. Ohba,[2] K. Miwa,[2] T. Noritake,[2] S. Towata,[2] – [1]Toyota Industries Corporation, Obu, Aichi, Japan; [2]Toyota Central R&D Labs., Inc., Nagakute, Aichi, Japan

We have already reported that CaSi reversibly absorbs and desorbs hydrogen[(1-3)]. The maximum hydrogen content and the enthalpy of hydride formation of CaSi were 1.9wt%($CaSiH_{1.3}$) and -62kJ/molH_2, respectively. However, the hydrogen content of 1.9wt% for CaSi is rather low for practical use as a hydrogen storage material. We have investigated the validity for the substitution for Ca or Si. To select the substituent X, the stability of Ca-Si-X hydride has been theoretically studied using first-principles calculations with the ultrasoft pseudopotential method based on density functional theory. As a result, it has been predicted that the hydrogen content is improved for X=Al, Ge, Mg etc. Encouraged by this prediction, we have conducted the experiment to investigate the hydriding and dehydriding properties of Ca-Si-X. The sample has been prepared by the high frequency induction melting of Ca(purity 99.5%), Si(purity 99.999%up) and X. Hydriding and dehydriding properties of Ca-Si-X have been characterized by X-ray diffraction analysis and pressure-composition isotherm measurements. [1] M.Aoki et al, Appl. Phys. Lett,85(2004),387; [2] M.Aoki et al,J. Alloys Compd, 404-406(2005)402-403; [3] N.Ohba et al, Phys. Rev. B 72, 075104(2005).

POSTER SESSION III (P-314 to P-381) **Wednesday, October 4 – (8:00 PM – 10:30 PM)**

P-314 **Materials Designing of Metal Borohydrides: Selection of Metals and Formation of Intermediate Compounds.** S. Orimo,[1] H.-W. Li,[1] Y. Nakamori,[1] K. Miwa,[2] N. Ohba,[2] S. Towata,[2] A. Züttel,[3] – [1]Institute for Materials Research, Tohoku University, Sendai, Japan; [2]Toyota Central R&D Labs., Inc., Nagakute, Aichi, Japan; [3]Physics Department, University of Fribourg, Perolles, Switzerland

Metal borohydrides (M-B-H) are potential candidates for advanced hydrogen storage materials. The charge compensation by the cation M^{n+} is a key feature for the stabilities of the internal bonding of $[BH_4]^-$ anions. Then, it is expected that selecting another M with a larger electronegativity c_P is effective to lower the dehydriding temperatures, i.e. the stability of the complex hydride. Another key feature on the hydrides is the possible formation of appropriate intermediate compounds, as it is the case in alanates (M-Al-H) and amides/imides (M-N-H), for the promotion of the dehydriding and rehydriding reactions. The paper presents the results of experimental studies on the intrinsic thermal stabilities depending on wide variations of M (M = alkali-, alkaline-earth-, and transition-metals) and also on the formation of the intermediate compound in lithium borohydride. This study is partially supported by the New Energy and Industrial Development Organization (NEDO), International Joint Research under the "Development for Safe Utilization and Infrastructure of hydrogen" Project (2005-2007).

P-315 **Perovskite-type Hydrides: Formation Abilities, Structural Analyses and Hydriding Properties.** K. Ikeda,[1] S. Kato,[1] Y. Nakamori,[1] A. Kitano,[2] H. Yukawa,[3] M. Morinaga,[3] S. Orimo,[1] – [1]Institute for Materials Research, Tohoku University, Sendai, Japan; [2]Japan Synchrotron Radiation Research Institute, Hyogo, Japan; [3]Graduate School of Engineering, Nagoya University, Nagoya, Japan

Compounds with perovskite structure are typically expressed as ABX_3, where A and B are cations and X is an anion. Many kinds of the perovskite-type oxides ABO_3 have been extensively investigated in detail, and also known to provide various material functions, such as ionic conductivities, catalysis effects and so on. In addition, some ternary hydrides exhibit the perovskite structures expressed as ABH_3. So far, we have reported that the formation abilities of the perovskite-type hydrides were reasonably explained

from the viewpoint of the geometric restrictions on ions, using Goldschmidt tolerance factors [1]. Also, the reversible dehydriding and rehydriding properties were confirmed for the perovskite-type hydride, $NaMgH_3$ [2]. In the paper, hydriding properties of the perovskite-type hydrides such as $NaMgH_3$- and $CaNiH_3$-related systems, depending on their electronic and atomistic structures, will be presented in detail. This study was partially supported by the Research Fellowships of the Japan Society for the Promotion of Science for Young Scientists. [1] K. Ikeda, Y. Nakamori, S. Orimo, *Acta Mater.*, **53** (2005) 3453; [2] K. Ikeda, Y. Kogure, Y. Nakamori, S. Orimo, *Scripta Mater.*, **53** (2005) 319.

P-316 **Synthesis and Hydriding Properties of Mg-based Laves Phase Alloys.** N. Terashita,[1] E. Akiba,[2] – [1]Japan Metals & Chemicals Co., Ltd. (JMC), Nishiokitama-gun, Yamagata, Japan[2]National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki, Japan

We have developed a novel Mg-based alloy $(Mg_{0.67}Ca_{0.33})Ni_2$ with the C15-type Laves structure which can reversibly absorb and desorb hydrogen at room temperature [1]. Recently we have developed a novel melting technique using helium gas as the atmospheric gas inside of the furnace to prepare Mg-based alloys to develop the alloy having a larger hydrogen capacity and cycle durability than $(Mg_{0.67}Ca_{0.33})Ni_2$. We have investigated the effect of substitution of R for Mg in $MgNi_2$ and its hydriding properties. We prepared various compositions of $(Mg_{1-x}M_x)Ni_2$ in which M=La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Yb, Y, Sr, Ba, Li, Si, Zr and x=0.3. The alloys were synthesized by levitation melting under 0.1MPa helium atmosphere. The chemical compositions were analyzed using a conventional ICP analyzer. The crystal structure, morphology and chemical compositions of each phase were characterized by powder X-ray diffraction, scanning electron microscopy, and energy dispersive X-ray spectrometer, respectively. The *p-c* isotherms were measured using a homemade fully automatic device. In-situ X-ray diffraction measurements under hydrogen atmosphere were carried out and the results will be discussed. This work has been supported by New Energy and Industrial Technology Development Organization (NEDO) under "Development of fundamental technologies in the safe utilization of hydrogen". [1] N.Terashita, K.Kobayashi, T.Sasai and E.Akiba: J. Alloy Compd. 327 (2001) 275-280.

P-317 **Crystal Structure and Properties of La-Mg-Ni-Co Alloy.** Y. J. Chai,[1] K. Sakaki,[1] H. Hayakawa,[1] E. Akiba,[1] T. Kohno,[2] – [1]National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki, Japan; [2]Corporate Research & Development Center, Toshiba Corporation, Kawasakai, Kanagawa, Japan

New interests are devoted to ABn (n=3.0-4.0) types of La-Mg-Ni-Co system due to the larger discharge capacity (410mAh/g) than AB_5-type alloys (330mAh/g), good cyclic stability and significant rate capability [1-2]. These types of alloys show several kinds of the superlattices consisted of $[LaNi_5]$ layer and $[LaMgNi_4]$ layer along [001] [3-4]. We analyzed the crystal structure of these alloys, $La_{0.67}Mg_{0.33}Ni_{2.5}Co_{0.5}$ (A1), $La_{0.7}Mg_{0.3}Ni_{2.8}Co_{0.5}$ (A2) and $La_{0.75}Mg_{0.25}Ni_{3.0}Co_{0.5}$ (A3) using the Rietveld method. The alloys A1 and A2 were composed of $PuNi_3$-type $La_2Mg(Ni,Co)_9$, Ce_2Ni_7-type $La_3Mg(Ni,Co)_{14}$ and Pr_5Co_9-type $La_4Mg(Ni,Co)_{19}$. The alloy A3 consisted of Ce_2Ni_7-type $La_3Mg(Ni,Co)_{14}$ and Pr_5Co_9-type $La_4Mg(Ni,Co)_{19}$. The lattice parameters of these phases were a=5.055 and c=24.35Å for $PuNi_3$-type $La_2Mg(Ni,Co)_9$, a=5.035 and c=24.18 Å for Ce_2Ni_7-type $La_3Mg(Ni,Co)_{14}$ and a=5.038 and c=32.20 Å for Pr_5Co_9-type $La_4Mg(Ni,Co)_{19}$, respectively. Hydrogen absorbing properties of the alloys such as the *P-C-T* results will also be discussed. [1] T. Kohno, H. Yoshida, F. Kawashima et al., *J. Alloys Compd.* 311 (2000) L5-L7; [2] H. G. Pan, Y. F. Liu, M. X. Gao et al., *J. Alloys Compd.* 351 (2003) 228–234; [3] E. Akiba, H. Hayakawa and T. Kohno, *J. Alloys Compd.*408-412 (2006) 280-283; [4] H. Hayakawa, E. Akiba, M. Gotoh and T. Kohno, *Mater. Trans.* 46(6) (2005)1393-1401.

P-318 **Hydrogen Release of Catalyzed Lithium Aluminum Hydride by Mechanochemical Reaction.** Y. Kojima, Y. Kawai, M. Matsumoto, T. Haga, – Toyota Central R&D Labs., Inc., Nagakute, Aichi, Japan

The effects of various catalysts on the H_2 release characteristics of $LiAlH_4$ were studied. The catalysts studied included $TiCl_3$, $ZrCl_4$, VCl_3, $NiCl_2$, $ZnCl_2$, Ni and nano-Ni. $LiAlH_4$ doped with 5 wt% of $TiCl_3$ desorbed 7.2 wt% of H_2 and transformed into LiH and Al during ball-milling at room temperature; this reaction didn't occur at ambient conditions without prolonged ball-milling for up to 24 h and the catalyst. X-ray diffraction, transmission electron microscopy and energy dispersive X-ray spectroscopy revealed that nano-Al_3Ti particles, which are several 10 nm, were dispersed in the matrix of LiH and Al. It was established that the catalytic activity defined by the H_2 desorption capacity at room temperature decreased in the series $TiCl_3$>$ZrCl_4$>VCl_3>$NiCl_2$>$ZnCl_2$. The high catalytic activity of $TiCl_3$ was attributed to the small percentage d-character and the low electronegativity of Ti. Transition metal trialuminides Al_3X (Ti, Zr, V, Ni) prepared by the mechanochemical reaction of $LiAlH_4$ and the metal chlorides were considered as dehydrogenation catalysts. The ball-milled $LiAlH_4$ doped with nano-Ni desorbed H_2 of 5.0 wt% at room temperature, while that doped with Ni only desorbed H_2 of 0.7 wt% at the temperature. We found that the catalytic activity was also improved with decreasing Ni size.

P-319 **Facilitated Hydrogen Storage over Nano-sized Sodium Alanate on Carbon Nanofibers.** C. P. Baldé, J. H. Bitter, K. P. de Jong, – Faculty of Chemistry, Department of Inorganic Chemistry and Catalysis, Utrecht University, Utrecht, The Netherlands

Sodium alanate ($NaAlH_4$) is a promising H_2-storage material. However due to kinetic barriers, hydrogen desorption rates are slow and reloading of undoped desorbed $NaAlH_4$ is challenging under practical conditions. Ti doping enhances the kinetics to a certain extent [1] but further improvements, which imply new strategies and methods, are needed. A possible strategy is to change the particle size, from which it is known that the physico-chemical properties may change considerably [2,3]. The nanosized $NaAlH_4$ were supported on carbon nanofibers, and the hydrogen desorption, absorption properties were related to the structural properties of the materials. Characterization was performed by X-Ray Diffraction (XRD), Scanning/Transmission Electron Microscopy (SEM/(S)TEM), Temperature Programmed Desorption (TPD) and H_2-absorption measurements. It will be shown that nanosized $NaAlH_4$ shows significant improvement compared to the physical mixture for dehydrogenation of $NaAlH_4$ at low temperatures ($T \leq 160$ °C). Moreover, reloading of a desorbed sodium alanate is facilitated. This is tentatively attributed to the limitation for long-

range phase segregation when nano-sized $NaAlH_4$ is (de)hydrogenated. [1] Bodganovic B., and Schwickardi M., *Journal of Alloys and Compounds* **1997** 253-254, 1-9; [2] C.P. Baldé, B.P.C. Hereijgers, J.H. Bitter, K.P. de Jong, accepted for publication in Angewandte Chemie Int. Ed.; [3] R.W.P. Wagemans, J.H. van Lenthe, P.E. de Jongh, A.J. van Dillen, K.P. de Jong, *J. Am. Chem. Soc.* **2005**, 127(47), 16675-16680.

P-320 **Interaction of Hydrogen with Complex Metallic Alloys: the Mg-Al Case Study.** J. F. Fernández,[1] F. Leardini,[1] J. Bodega,[1] J. M. Joubert,[2] F. Cuevas,[2] M. Baricco,[3] M. Di Chio,[3] H. Figiel,[4] M. Feuerbacher,[5] – [1]Dpto. Física de Materiales, Facultad de Ciencias, Universidad Autónoma de Madrid, Madrid, Spain; [2]Laboratoire de Chimie Métallurgique des Terres Rares, ISCSA, CNRS, Thiais, France; [3]Dipartimento di Chimica IFM and NIS/INSTM, Universití di Torino, Torino, Italy; [4]Faculty of Physics and Applied Computer Science, AGH - University of Science and Technology, Krakow, Poland; [5]Institut für Mikrostrukturforschung, Forschungszentrum, Jülich, Germany

As a part of a European project for the study of Complex Metallic Alloys [1], a number of laboratories around Europe have recently started an integrated research on hydrogen storage on the Mg-Al system. This system shows, at least, five regions of possible interest for hydrogen storage: the Mg(Al) solid solution, the eutectic Mg(Al) - g phase, the g phase ($Mg_{17}Al_{12}$), the l and e phases (around $Mg_{45}Al_{55}$) and the β phase (Al_3Mg_2). Hydrogenation characteristics of some of these phases have already been reported [2-3] but still unknowns remain in relation to their capabilities as hydrogen storage media. Recently, the feasibility of the magnesium alanate prepared by a metathesis reaction for hydrogen storage has also been reported [4]. To start with, the study has been concentrated on the β phase and their two adjacent two-phase fields. Careful characterisation of the starting samples as well as the products of the decomposition and the thermodynamics and kinetics of the H-absorption and desorption process will be presented. [1] Network of excellence of the EU. NMP3-CT-2005-500140; [2] P. Selvam et al. Int. Journal of Hydrogen Energy Vol11,Nº3, 169-192, 1986; [3] S.E. Guthrie et al. SAND97-8220.UC-404; [4] M. Fichtner et al. J. of Alloys and Compounds 356-357(2003)418-422

P-321 **Hydriding Properties of Mechanically Alloyed Magnesium-Salt-Transition Metal Composites.** I. Konstanchuk,[1] E. Ivanov,[2] V. Boldyrev,[1] – [1]Institute of Solid State Chemistry, Siberian Branch of R.A.S., Novosibirsk, Russia; [2]Tosoh SMD, Grove City, OH, USA

Some inorganic salts have been found to promote metal powdering and modify metal particle surfaces being mechanically alloyed with magnesium [1]. This leads to an acceleration of the hydriding and dehydriding reactions of magnesium and to quite high hydrogen capacities. But the kinetics of hydriding and dehydriding processes for magnesium-salt mechanical alloys were still slower than for mechanical alloys of magnesium with metal-catalyst (such as Ni, Fe and so on). The mutual action of salt and metal-catalyst has been investigated in this work. It has been shown that mechanical alloying of magnesium with salt and transition metal additives is able to improve both reaction rate and hydrogen capacity of obtained composites. [1] Ivanov E.Yu., Konstanchuk I.G., Bokhonov B.B., Boldyrev V.V., J. Alloys and Comp. 359 (2003) 320.

P-322 **Investigation on the Hydriding/Dehydriding Properties of Ti-doped Sodium Aluminum Hydride.** L.-X. Chen, X.-Z. Xiao, X.-H. Wang, L. Li, C.-P. Chen, – Department of Materials Science and Engineering, Zhejiang University, Hangzhou, P.R. China

Since Bogdanovic and Schwickardi reported the reversible hydriding-dehydriding behavior of catalyzed $NaAlH_4$ at moderate temperatures, the sodium aluminum hydride with high hydrogen capacity has been attractive for its potential application in the hydrogen storage system for vehicles. However, its achieved reversible hydrogen capacity of only ~4 wt.% is lower than its theoretical capacity of 5.6 wt.%. In this study, we chose Ti as a dopant and prepared the sodium aluminum hydride by hydrogenating the ball-milled composites of (NaH/Al) + *x* mol% Ti (*x*=0, 4, 6, 10) at 100–120 ℃, and their hydriding/dehydriding properties and microstructure were investigated. The result shows that the hydriding/dehydriding properties are affected greatly by the milling parameters, Ti content introduced, hydrogenation/dehydrogenation temperatures and hydrogenation pressure. The composite with *x*=10 ball-milled for 12 h under hydrogen atmosphere can absorb 4.21 wt.% hydrogen at 120 ℃ and 13.5 MPa hydrogenation pressure, and desorb 4.01 wt.% hydrogen at 160 ℃. It is also found that the surface morphology of the composite changes in different stage of hydrogenation-dehydrogenation process. The hydrogen storage properties of system are deteriorated due to the slow reaction dynamics of Na_3AlH_6.

P-323 **Mechanical Alloying of Graphite and Magnesium Powders, and Their Hydrogenation.** A. Takasaki,[1] Y. Furuya,[2] – [1]Shibaura Institute of Technology, Toyosu, Koto-ku, Tokyo, Japan; [2]Nagasaki University, Bunkyo-machi, Nagasaki, Japan

Graphite and magnesium elemental powders whose chemical compositions were $C_{100-x}Mg_x$ ($0 \le x \le 40$) were mechanically alloyed (milled) in an argon gas atmosphere, and these powders were loaded with hydrogen in a high pressure vessel at a room temperature. The initial hydrogen gas pressure for hydrogenation experiment was 4 MPa. The graphite crystal structure easily broke at an early stage of mechanical alloying (MA) for all powders. Although elemental magnesium still remained in $C_{60}Mg_{40}$ powder even after longer MA (80h), but other powders reached to mostly the amorphous state. Hydrogen concentration levels after hydrogenation for C_{100} powder were 0.1 wt.% after MA for 25 h and 0.4 wt.% after MA for 80 h, suggesting that nanostructured graphite uptakes more hydrogen. On the other hand, hydrogen concentration level for $C_{90}Mg_{10}$ powders was less than 0.1 wt.% after MA for 15h, but the concentration level increased to about 1 wt.% after MA for 25 h, indicating that appropriate MA could improve the hydrogenation property. Furthermore hydrogenation occurred smoothly and quickly for $C_{90}Mg_{10}$ powders, although longer induction time was required for C_{100} powders. It is implied that fine magnesium powders were distributed on the graphite powders during MA and would act as catalyst for hydrogenation. Further addition of magnesium to graphite reduced the hydrogen concentration level in the powders.

P-324 **A Comparison of the De-Hydriding Behavior of Lithium Alanate and Sodium Alanate.** P. Ogaro, A. J. Goudy, – Delaware State University, Dover, DE, USA

The de-hydriding behavior of lithium alanate, sodium alanate, and mixtures of these two materials were studied by TGA and PCI analyses. Prior to thermal analysis, samples were ball milled with 4 mole percent titanium (III) chloride catalyst. The results, obtained under an argon atmosphere and in the temperature range up to 200 C, show that the desorption temperature of sodium alanate is higher than that of lithium alanate. This indicates that $NaAlH_4$ is a more stable hydride than $LiAlH_4$. Both materials release approximately 4% of the hydrogen in a moderate temperature interval. Several mixtures of $NaAlH_4$ and $LiAlH_4$ were made by mechanically alloying these two materials. Comparisons were made among the various materials with and without the presence of a catalyst. In all cases, the presence of the catalyst lowered the desorption temperature. Pressure composition isotherms were also determined for $NaAlH_4$ at temperatures up to 200 C. The curves show that, at temperatures below 200 C and at pressures below 50 atmospheres, a phase transition occurs corresponding to the decomposition of Na_3AlH_6. The fact that both desorption and absorption curves can be determined shows that the process is completely reversible.

P-325 **High-pressure Synthesis of Novel Hydride in Mg-Ni-H System.** R. Kataoka, Y. Goto, A. Kamegawa, H. Takamura, M. Okada, – Department of Materials Science, Graduate School of Engineering, Tohoku University, Sendai, Japan

High-pressure synthesis has been used for exploring novel compounds for hydrogen storage. In Mg-Ni-H system, Synthesis of new hydride such as $Mg_2Ni_3H_{3.4}$ and phase transformations of Mg_2NiH_4 under high pressure have been reported. We will report the newly found hydride of $MgNi_2H_2$ synthesized by high pressure. A cubic-anvil-type apparatus, which can yield high pressure of 2 to 5 GPa, was adopted in synthesizing the new compound in Mg-Ni-H system. By using the GPa-order high pressure, samples of MgH_2-x%Ni (x = 50 - 75) have been prepared. The novel hydride with composition of x = 65 - 67 was synthesized at 973 K for 2 h under 2 GPa or higher. This newly synthesized hydride was also synthesized by hydrogenation of C36-type $MgNi_2$ at 973 K for 8 h under 2 GPa or higher. This novel hydride exhibited black color and was stable under air. For the sample of x = 67, the crystal structure was similar to tetragonal $MoSi_2$-type structure (space group *I4/mmm*) and its lattice constant was found to be a = 0.32768 nm and c = 0.8787 nm. In the case of x > 67, the distortion of crystal structure increased with increasing x. From thermogravimetric analysis, the hydrogen content of novel hydride was estimated to be 1.37 mass% for x = 67. Therefore, the chemical formula can be expressed as approximately $MgNi_2H_2$. For the samples of x = 63, 67 and 70, endothermic peaks were observed in DSC curves around 480 K, 460 K and 450 K, respectively.

P-326 **Synthesis and Hydrogenation Property of YMgIn.** H. Nishi,[1] M. Sato,[2] S. Kato,[2] H. Hotta,[3] Y. Matsumura,[2] T. Kuji,[4] H. Uchida,[2] H. H. Uchida,[5] J. P. Maehlen,[6] V. A. Yartys,[6] – [1]Dept. of Applied Science, School of Engineering, Tokai University, Kanagawa, Japan; [2]School of Engineering, Tokai University, Kanagawa, Japan; [3]Graduate School of Engineering, Tokai University, Kanagawa, Japan; [4]School of High-Technology for Human Welfare, Tokai University, Shizuoka, Japan; [5]School of Humanities and Culture, Tokai University, Kanagawa, Japan; [6]Institute for Energy Technology, Kjeller, Norway

RENiIn (RE=La, Ce, Nd) intermetallic compound crystallises with the ZrNiAl-type hexagonal structure, which adopt P -6 2m space group. Two different deutrides, β-$RENiInD_{0.66}$ and γ-$RENiInD_{1.33}$ were structurally characterised by Powder Neutron Diffraction (PND). Crystal structures of the higher deutrides $RENiInD_{1.33}$ pose unusual feature, which do not obey the rule of 2.0 Å empirically known for the metal hydrides. The formation of D…D pair shows the shortest found separation between hydrogen atoms in the rage 1.56-1.64 Å. The decreases in the distance between hydrogen atoms down from 2.0 Å leads to a corresponding rise in the volumetric content of hydrogen in the metal matrices. This work is aimed on studies of the synthesis and hydrogen absorption characteristics in the substituted intermetallic compounds by Y for RE and by Mg for Ni. The present work is the first contribution to this extensive study.

P-327 **Effect of Mixing of $LiAlH_4$ with $NaAlH_4$ on its Hydrogenation Properties.** H. T. Takeshita, Y. Kamada, D. Waki, Y. Inoue, T. Oishi, – Kansai University, Suita, Japan

Complex hydrides with high gravimetric hydrogen storage densities are a promising candidate for hydrogen storage in hydrogen energy systems. But there has been a problem of hydrogenation kinetics which should be solved. The addition of catalysts such as Ti results in a trade-off effect of improvement of the kinetics problems and decrease in hydrogen storage capacity. We propose a new idea of lowering of melting temperature by mixing a target hydride with another hydride. In order to certify our idea, $LiAlH_4$ which exhibits exothermic heat in its decomposition accompanied by hydrogen desorption was chosen due to the ease of the detection of hydrogen desorption and the effect of mixing with $NaAlH_4$ on the hydrogenation properties was examined. Starting materials of $LiAlH_4$ and $NaAlH_4$ were purified in advance and the purification effect was confirmed from the change in color from beige to white. Mixing was performed with a ball mill machine. The thermal properties were examined with a DSC instrument. The endothermic heat corresponding to melting of mixture was detected around 390K, which is 45K lower than the melting point of pure $LiAlH_4$,and it was shown that $LiAlH_4$ in the mixture tended to decompose immediately after melting, as well as pure one. Interestingly, the dehydrogenation temperature was also lowered by 45K by mixing with $NaAlH_4$, implying that decrease in melting temperature can contribute to lowering of dehydrogenation temperature.

P-328 **Hydrogenation Properties of Ca-Pd-Si Based Alloys.** N. Matsumoto,[1] K. Watashi,[1,2] H. T. Takeshita,[1] – [1]Kansai University, Suita, Japan; [2]Ishikawajima-Harima Heavy Industries Co, Tokyo, Japan.

New hydrogen storage alloys with high volumetric and gravimetric hydrogen storage densities are required for the application to hydrogen fuel tank in hydrogen energy system. $CaPdH_{2.4}$[1], $CaPd_3H$[2]and Ca_3Pd_2H[3] were reported as ternary hydrides in Ca-Pd-H system, whereas there is no report for the hydrogenation of other Ca-Pd alloys such as $CaPd_2$. In addition, there are several Ca-Pd-Si alloys of which the hydrogenation properties are not reported yet. The purpose of this study is to clarify the hydrogenation properties of Ca-Pd and Ca-Pd-Si alloys. Raw materials were granular Ca, powder Pd and Si. Samples were alloyed by sintering of the raw materials. The constituent phases of the samples were identified by XRD and with EPMA. The hydrogenation properties of the samples were examined with DSC. All the procedures for sample preparation were conducted in He atmosphere to avoid oxidation of the materials. A new ternary phase was obtained and its structure was identified to be $Ca(Pd, Si)_3$ with a cubic $AuCu_3$ type structure. Hydrogenation of binary $CaPd_2$ alloy at high temperatures resulted in the formation of $CaPd_3H$ by disprotionation reaction. [1] E. Rönnenbro et al., Mater. Res. Bull. *35*(2002), 315-323; [2] A. Palenzona, P. Manfrinetti, J. Less-Common Met. *85*(1982), 307-312; [3] C. Stanitski, J. Tanaka, J. Solid-State Chem. *4*(1972), 331-339.

P-329 **Effect of Mixing of $LiAlH_4$ with MBH_4 (M: Li, Na) on its Hydrogenation Properties.** H. T. Takeshita, Y. Inoue, – Kansai University, Suita, Japan

Complex hydrides with high gravimetric hydrogen storage densities are promising materials for hydrogen storage in hydrogen energy systems. But the hydrogenation kinetics remains as a problem to be drastically improved. The addition of catalysts such as Ti significantly improves the kinetics problems but often leads to decrease in hydrogen storage capacity. We proposed a new idea of lowering of melting temperature by mixing a target hydride with another one, and found that dehydrogenation temperature of $LiAlH_4$ was lowered by about 45K by mixing with $NaAlH_4$, accompanied by the lowering of melting temperature of about 45K. In the present study, we report for the results about mixing of $LiAlH_4$ with MBH_4 (M: Li, Na), in order to clarify in a different system that controlling of melting temperature can contribute to lowering of dehydrogenation temperature. Raw materials of about 95% in purity were supplied to the experiments, except for $LiAlH_4$ purified in advance. Mixing was conducted by ball milling method and by hand using an agate mortar. The melting temperature of the system was lowered to about 400K by mixing of $LiAlH_4$ with $LiBH_4$ or $NaBH_4$, as well as $NaAlH_4$, and the shape of the mixture after the experiment significantly changed, for example, powder to ball, impling the melt has high viscosity. It was found that the hydrogen desorption temperature for $LiAlH_4$ was insignificantly lowered by mixing, different from mixing with $NaAlH_4$, probably due to the high viscosity of melt.

P-330 **Aluminum Trihydride: Thermal Stabilities and *in-situ* Analysis of Dehydriding Process.** T. Kato,[1] Y. Nakamori,[1] S. Orimo,[1] C. Brown,[2] C. M. Jensen,[2] – [1]Institute for Materials Research, Tohoku University, Sendai, Japan; [2]Department of Chemistry, University of Hawaii, Honolulu, HI, USA

Aluminum trihydride (AlH_3, alane) is recently regarded as a candidate for advanced hydrogen storage materials [1], because of its high gravimetric hydrogen density, 10.1 mass%. Among some variations of the crystalline structures of AlH_3, we have reported the intrinsic and mechanically modified thermal stabilities of the α-, β-, and γ-phases [2]. The thermogravimetric profiles of the α- and γ-phases exhibit the dehydriding reactions around 370 – 450 K, and the amounts of hydrogen released are nearly 9 mass%. The profile of the β-phase shows the continuous dehydriding reactions, which differs from the other two phases. In the present study, the dehydriding processes of the α-, β-, γ-phases will be examined by *in-situ* measurements of X-ray diffraction and Raman spectroscopy. This work was financially supported, by the Ministry of Education, Culture, Sports, Science and Technology, "Grant-in-Aid for Encouragement of Young Scientists (B) #17760555", and by the Office of Hydrogen, Fuel Cells, and Infrastructure technologies of the US Department of Energy. [1] G. Sandrock, J. Reilly, J. Graetz, W.-M. Zhou, J. Johnson, J. Wegrzyn, *Appl. Phys. A*, 80 (2005) 687; [2] S. Orimo, Y. Nakamori, T. Kato, C. Brown, C.M. Jensen, *Appl. Phys. A*, 83 (2006) 5.

P-331 **Optimizing the Kinetics of Hydrogenation and Dehydrogenation in $LiH + MgB_2$ / $LiBH_4 + MgH_2$.** T. T. Salguero,[1] J. J. Vajo,[1] J. Graetz,[2] – [1]HRL Laboratories, Malibu, CA, USA; [2]Brookhaven National Laboratory, Upton, NY, USA

The hydrogen storage system that cycles between $LiH + MgB_2$ and $LiBH_4 + MgH_2$ exhibits very good capacity (~10 weight %) and reversibility properties. However, the reaction kinetics of this system are too slow to be practical. For this reason, we have examined the effects of additives on hydrogen exchange. We have found that $TiCl_3$ and other Ti-containing additives improve the kinetics substantially. In the case of $TiCl_3$, XAS studies show the formation of Ti(II) in the form of TiB_2 during cycling. Other transition metal halides, including VCl_3, $CrCl_3$, $NbCl_5$, and $NiCl_2$, also accelerate hydrogen exchange. In contrast, we have found several metal chlorides (e.g., $ScCl_3$, $ZrCl_4$) that completely poison the initial hydrogenation of $LiH + MgB_2$. Additional strategies to accelerate hydrogen exchange involve the use of nanoparticulate additives and creative milling conditions.

P-332 **Virtual High Throughput Screening of Complex Hydrides for Hydrogen Storage.** J. J. Low,[1] J. W. A. Sachtler,[1] G. J. Lewis,[1] D. A. Lesch,[1] C. M. Jensen,[2] – [1]UOP Research Center, Des Plaines, IL, USA; [2]Hawaii Hydrogen Carriers, LLC, Honolulu, HI, USA

High throughput screening can accelerate the rate of discovery of improved materials through a combination of Virtual High Throughput Screening (VHTS) and Combinatorial Synthesis and Screening (CSS). VHTS exploits a molecular mechanics method to screen a thousand phases in a month. The combination of these two techniques can be used scan a wide range of compositions. VHTS has been carried out on mixtures of $NaAlH_4$, $LiAlH_4$ and $Mg(AlH_4)_2$. Molecular Mechanics were used to estimate heats of mixing for VHTS. The parameters for the interatomic potentials used in the molecular mechanics were derived from potentials calculated derived from the electronic structure. These potentials have been validated using them to predict crystal structures and heats of mixing and comparing to experimental results and the predictions of density functional theory. Simulated annealing (SA) was used to estimate the crystal structure of the mixed alanates. It is possible for us use SA to scan a thousand

phases per month. VHTS was demonstrated on mixtures of $NaAlH_4$, $LiAlH_4$ and $Mg(AlH_4)_2$. Only two mixtures of these alanates are predicted to have small negative heats of mixing (<10 kJ/mole). Neither of these phases is predicted to be stable with respect to dehydriding. We have not found any stable mixtures of $NaAlH_4$, $LiAlH_4$ and $Mg(AlH_4)_2$ with either CSS or VHTS. Mixtures of alkali and alkaline earth alanates are not likely to be good candidates for hydrogen storage.

P-333 **Study of Mg_2CoH_5 Prepared by a Combined Milling-Sintering Procedure.** I. González Fernández,[1] G. O. Meyer,[1,2,3] F. C. Gennari,[2,3] – [1]Instituto Balseiro, Universidad Nacional de Cuyo, Bariloche, Argentina; [2]Centro Atómico Bariloche (CNEA), Bariloche, Argentina; [3]Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Bariloche, Argentina

The ternary Mg_2CoH_5 hydride is worth studying because of its high gravimetric (4.4 wt%) and volumetric (about 100 kg H_2. m^{-3}) hydrogen storage capacity, better absorption-desorption kinetics than MgH_2 and low cost. Due to the absence of its parent intermetallic compound (Mg_2Co), the synthesis method is an open issue. The Mg_2CoH_5 hydride was synthesized in a two step procedure: a 2Mg-Co powder mixture was mechanical alloyed under inert atmosphere at room temperature, pressed to form a pellet and heated at 450°C under 5MPa hydrogen pressure for 1 week, following a procedure reported [1]. We observed the hydrogenation of the sample in only 20 hours. This improvement in the hydride formation can be associated with the enlargement of the milling stage. The microstructure and Mg-Co distribution was studied by scanning electron microscopy (SEM) on resin-mounted and polished samples. The formed phases after each step were identified by X-ray diffraction (XRD). The thermal behavior was investigated by differential scanning calorimetry (DSC). From XRD and DSC measurements the transition from tetragonal to cubic structure of Mg_2CoH_5 at 202°C and the decomposition of the hydride starting at 390°C were observed. The hydriding-dehydriding reaction was studied by pressure-composition isotherms and absorption/desorption kinetics up to 400°C in the range of 0 to 5MPa. Two plateaus were identified in the P-x isotherms and associated to the formation of Mg_2CoH_5 and $Mg_6Co_2H_{11}$ hydrides. [1] P. Selvam, K. Yvon, Int. Hydrogen Energy 16 (1991) 615.

P-334 **Sorption Reactions in Reactive Hydride Composites: The Example of $LiH+MgB_2$.** U. Boesenberg,[1] S. Doppiu,[2] A. Borgschulte,[1] G. Barkhordarian,[1] O. Gutfleisch,[2] M. Dornheim,[1] T. Klassen,[3] R. Bormann,[1] – [1]GKSS Research Center, Geesthacht, Germany; [2]IFW Dresden, Dresden, Germany; [3]Helmut Schmidt University, Hamburg, Germany

A new class of promising hydrogen storage materials for mobile applications are Reactive Hydride Composites. These systems show reduced total reaction enthalpies as well as significantly improved rehydrogenation kinetics. The system of $LiBH_4$ and MgH_2 is of special interest due to its high storage capacity of 11.4 wt%. The hydrides are effectively destabilized by forming LiH and MgB_2, since the formation of MgB_2 is exothermic whereas the desorption reactions are endothermic. The reaction principle has been recently proven but the experimental results still show too slow sorption kinetics at enhanced temperatures for application. Thermodynamic and kinetic studies have been performed to follow the reaction. Ball milled $LiBH_4+MgH_2$ is studied using High Pressure Differential Calorimetry combined with thermogravimetric and mass spectrometric measurements, a Sieverts Apparatus and X-ray diffractometry. A two-step desorption reaction with a simultaneous release of hydrogen is observed, ending in the formation of LiH and MgB_2. Hydrogen uptake again takes place in a two-step reaction, regenerating $LiBH_4$ and MgH_2. Cycling improves the sorption reactions significantly. Quantitative evaluation shows reversibility after the first cycle of about 80%. Kinetics of the reactions is investigated in relation to particle size distribution and various additives. The desorption temperatures can be significantly lowered by suitable dopants and appropriate preparation methods.

P-335 **Hydrogenation Properties of Ti-Mn based Alloys for Hybrid Hydrogen Storage Tank.** M. Shibuya, K. Sakaki, E. Akiba, – National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki, Japan

A hybrid hydrogen storage tank has been proposed as one of the realistic solutions for on board hydrogen storage. The alloys suitable for the hybrid hydrogen storage tank are required to show hydrogen equilibrium pressure of a few bars at 243K. Ti-Mn based AB_2-type alloys have been synthesized by arc melting. As the third elements V and Zr were added to Ti-Mn binary alloys. The pct measurements of the products were carried out in the range of 293 to 243K under a maximum hydrogen pressure of 7 MPa. All the alloys synthesized consisted of the C14 Laves phase as a major phase and the BCC phase as a minor phase. The alloys with V and Zr simultaneous addition had a larger hydrogen capacity than TiMn1.5 with a hydrogen absorption amount of 2.0 wt% (H/M=1.03) at 243K, however, the hydrogen equilibrium pressure decreased to lower than 0.1 MPa at the several temperatures. In the case of Ti0.5V0.5Mn, the amounts of hydrogen absorption was 1.84 wt% (H/M=0.89) at 243K, however, the hydrogen desorption pressure was in the range of 0.2 to 0.4 MPa at 243K. The hydrogen capacity of this alloy seemed to increase with hydrogen pressure and the measurements are under way up to a hydrogen pressure of 35 MPa that is the estimated working pressure of the hybrid hydrogen storage tank.

P-336 **Hydrogen Sorption in Metal-Organic Microporous Crystals.** G. Cao,[1] D. Sun,[2] G. Chen,[2] M. Latroche,[3] – [1]Department of Information Science and Engineering, Dalian Institute of Light Industry, Dalian, P. R. China; [2]Department of Materials Science, Fudan University, Shanghai, P. R. China; [3]LCMTR, CNRS, Thiais, France

The development for commercialization of fuel-cell powered vehicles will require new materials that can storage large amounts of hydrogen effectively. Among the various candidate storage materials including metal hydrides, porous carbon, carbon nanotubes, none is capable of meeting the performance targets. A new class of crystalline porous materials commonly referred to as metal-organic frameworks (MOFs) represents a promising new entry to the field of hydrogen storage materials. In the present work, we reported the structure and hydrogen ad/desorption of metal-organic porous crystals $[Zn(im)_2]$ with pore dimensions approximately 10 Å at room-temperature and 77K. Two structures of $[Zn(im)_2]$ were synthesized, i.e. $[Zn_5(im)_{10}\cdot DEF]$ (im = imidazolato = $C_3H_3N_2$, DEF = N, N-dimethylacetamide with zeolite-like topology and $[Zn_2(im)_4\cdot DMF]$ (im = imidazolato = $C_3H_3N_2$, DMF = N, N-

dimethylformamide) with $CaGa_2O_4$ topology. It is found that $[Zn(im)_2]$ uptakes no hydrogen at room temperature, but about 0.9 wt. % at 77 K under 20 bar. A relatively flat isotherm and good structure stability were observed as well. The authors would like to thank Prof. Dong-Yuan Zhao and Dr. Yun-Qi Tian from Department of Chemistry, Fudan University for synthesizing $[Zn(im)_2]$.

P-337 **Modification of Hydrogen Reactivity of Complex Alkali Hydrogen Storage Materials by Carbon Fibers Mixing.** A. Uemura,[1] Y. Nishi,[1] H.-H. Uchida,[2] – [1]Department of Materials Science, Tokai University, Hiratsuka, Kanagawa, Japan; [2]Department of Human Development, Tokai University, Hiratsuka, Kanagawa, Japan

For obtaining hydrogen storage substances with higher hydrogen density, we prepared complex alkali metal hydrides of Na_2LiAlH_6 (expressed 3.0-3.5wt% H) using a simple process of mechanical alloying(MA) of the mixture $2NaH+LiAlH_4$. Because of the intrinsic characteristics of the compound, which decreases the hydrogen absorption rate with increasing amount of hydride phase, we examined a mechanical addition of nano- materials of carbon fibers to the samples during the MA. In the former research[1], drastically modified sorption reactions were reported. The rare-earth oxides possible gave diffusion ways in the hydride phase, which resulted in the increased reaction rates. However, the mass of rare-earth elements was larger than the sample alkaline elements, the contribution of the chemically stable oxide addition to the modification of hydrogen density of Na_2LiAlH_6 as a storage material was rather limited. From this point of view, we examined a carbon fibers mixture to the sample during the MA. Initial reaction rate was improved by the carbon fiber addition, while the absorbed hydrogen amount of the sample with carbon fiber was less than the standard sample. Some alkali carbide was possibly formed during the MA, which resulted in the reduction of hydrogen content of the sample. The mixing condition was the most sensitive factor for modification of the reaction kinetics. [1] N. Okada, R. Genma, Y. Nishi, and H. H.Uchida: J. Mat. Sci., 39, 5503, 2004.

P-338 **Characterisation of Polymers of Intrinsic Microporosity (PIMs) for Hydrogen Storage.** N. B. McKeown,[1] B. Ghanem,[1] K. J. Msayib,[1] P. M. Budd,[2] C. E. Tattershall,[2] K. Mahmood,[2] S. Tan,[2] D. Book,[3] H. W. Langmi,[3] A. Walton,[3] – [1]School of Chemistry, Cardiff University, Cardiff, UK; [2]Organic Materials Innovation Centre, School of Chemistry, University of Manchester, Manchester, UK; [3]Department of Metallurgy and Materials, School of Engineering, University of Birmingham, Birmingham, UK

In most organic polymers, the molecular chains are so flexible that they can form tightly packed structures: this means there are no cavities inside, and thus no appreciable internal surface. However, in the case of polymers constructed from interlinked five- and six-membered rings, at defined points in the molecule, two five-membered rings are connected in such a way as to provide a contorted shape to the stiff macromolecular structures. The contorted molecules cannot pack together efficiently and leave gaps and interstices. These Polymers of Intrinsic Microporosity (PIMs) have large internal surface areas of over 800 m^2/g. In the context of hydrogen adsorption, PIMs may offer an attractive combination of properties including low intrinsic density (they are composed of only light elements, such as C, H, N, and O), chemical homogeneity, thermal and chemical stability, and synthetic reproducibility. We have recently reported [1] how PIM samples (CTC-network-PIM, PIM-1 and HATN-network-PIM) with uniform pore size distributions of 0.6–0.7 nm, can reversible adsorb 1.4–1.7 wt% hydrogen at 77 K and 10 bar. In this work, we report hydrogen sorption measurements (gravimetric and volumetric techniques) made at temperatures between 77 – 298 K and at pressures up to 100 bar. [1] N.B. McKeown, B. Ghanem, K.J. Msayib, P. M. Budd, C.E. Tattershall, K. Mahmood, S. Tan, D. Book, H.W. Langmi, and A.Walton, Angewandte Chemie International Edition, 45, 1804-1807 (2006).

P-339 **Studies on the Structure and Electrochemical Properties of $La_{0.7}Mg_{0.25}M_{0.05}(Ni_{0.85}Co_{0.15})_{3.5}$ (M=Ti, Zr, Mn, V) Hydrogen Storage Electrode Alloys.** H.-L. Chu, F. Xu, Y. Zhang, L.-X. Sun, T. Zhang, – Dalian Insititute of Chemical Physics,Chinese Academy of Sciences, Dalian, China

AB_3-type La–Mg–Ni alloys are promising candidates for the negative electrode materials of Ni/MH batteries in view of their higher electrochemical capacity and low costs. Kohno et al. [1] reported that the discharge capacity of $La_{0.7}Mg_{0.3}Ni_{2.8}Co_{0.5}$ alloy reached 410 mAh/g, with fairly good cycling stability within 30 cycles. Liao B. et al. found that the La_2MgNi_9 alloy with $PuNi_3$ type structure has a large capacity around 400 mAh/g [2]. However, the cycle stability and the overall electrode properties of these alloys hardly meet the need of commercial applications, which need to be further improved. It is well known that element substitution is one of the effective methods for improving the overall properties of the hydrogen storage alloys. In the present work, $La_{0.7}Mg_{0.25}M_{0.05}(Ni_{0.85}Co_{0.15})_{3.5}$ (M = Ti, Zr, Mn, V) alloys samples were prepared. The effects of Mg-site partial substitution by a metallic element in $La_{0.7}Mg_{0.3}(Ni_{0.85}Co_{0.15})_{3.5}$ on the structure and electrochemical properties (discharge capacity, electrochemical kinetic properties and cycling stability) were systematically investigated. The experimental results showed that the substitutions remained the main phase structure of original alloys and resulted in some decrease of the discharge capacity. However it led to an improvement in cycling stability and high rate discharge ability due to the formation of an oxidized but active layer on the powders surface of the alloys. [1] T. Kohno, H. Yoshida, F. Kawashima, T. Inaba, I. Sakai, M.Yamamoto, M. Kanda, J. Alloys Comp. 311 (2000) L5; [2] B. Liao, Y.Q. Lei, G.L. Lu, L.X. Chen, H.G. Pan, Q.D. Wang, J.Alloys Comp. 356/357 (2003) 746.

P-340 **Clustering of H_2 Molecules around Alkaline Earth Metal Ions: a Systematic Density Functional Theory Study.** S. Shi,[1] R. H. Scheicher,[2] R. Pandey,[2] J.-Y. Hwang,[1] – [1]Institute of Materials Processing, Department of Materials Science and Engineering, Michigan Technological University, Houghton, MI, USA; [2]Computational Solid State Theory and Materials Science Group, Department of Physics, Michigan Technological University, Houghton, MI, USA

We have used density functional theory to carry out a systematic study of the bonding geometries of hydrogen molecule clusters around individual alkaline earth metal ions. For Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}, we determined the equilibrium geometry of n H_2 molecules with n taking on values 2, 3, 4, 6, and 8. We were able to observe some clear trends in the clustering of H_2 molecules. The highest binding energy of the system is achieved with a large number of H_2 molecules for heavier alkaline earth ions. The H_2

molecules are found to be trapped fairly close to the smaller alkaline earth ions, while for heavier/larger ions, the H_2 molecules move further away. For smaller ions, H_2 molecules are pushed out when space becomes insufficient in the neighborhood of the given ion. The H–H bond length of H_2 is affected most strongly for lighter ions when few H_2 molecules are present, in other words when the H_2 molecules can be closer to the ion. We have analyzed the charge transfer taking place between the doubly positively charged ion and neutral H_2 molecules. The amount of transferred charge increases with the number of H_2 molecules present, since the ion has more partners to distribute its charge to. However, for lighter ions, we can see a saturation effect setting in, and the amount of charge transferred approaches an asymptotic limit. We will discuss potential consequences of these results for new H-storage materials containing alkaline earth metal ions.

P-341 **Metathesis Reactions for Hydrogen Storage.** T. J. Richardson, X. Chen, – Lawrence Berkeley National Laboratory, Berkeley, CA, USA

Light metal hydrides such as those of magnesium and lithium contain large amounts of hydrogen but are too stable for convenient use as hydrogen storage media. While some progress has been made in reducing their stability [1,2], a more promising approach has been to stabilize the metallic phase through alloy formation with elements such as aluminum [3] or silicon [4] that form less stable hydrides. Other metathesis reactions such as those between hydrogen and nitrides [5] or psuedoreversible reactions with oxides [6] have also been studied. Here we will present the results of investigations of hydrogen storage in Mg alloys containing alternative alloying elements and of metathesis reactions involving oxides and fluorides. [1] G. Liang, J. Huot, S. Boily, A. Van Neste, R. Schulz, Journal of Alloys and Compounds 291 (1999) 295; [2] P.H.L. Notten, M. Ouwerkerk, H. van Hal, D. Beelen, W. Keur, J. Zhou, H. Feil, Journal of Power Sources 129 (2004) 45; [3] M. H. Mintz, Z. Gavra, G. Kimmel, and Z Hadari, Journal of the Less-Common Metals 74 (1980) 263; [4] J. J. Vajo, F. Mertens, C. C. Ahn, R. C. Bowman, and B. Fultz, Journal of Physical Chemistry B 108 (2004) 13977; [5] T. Ichikawa, S. Isobe, N. Hanada, and H. Fujii, Journal of Alloys and Compounds 365 (2004) 271; [6] K. Otsuka, C. Yamada, T. Kaburagi, and S. Takenaka, International Journal of Hydrogen Energy 28 (2003) 335.

P-342 **Destabilisation of $LiAlH_4$: The crystal Structure of Li_3AlN_2 Investigated by *in-situ* Synchrotron X-ray Diffraction.** L. Mosegaard,[1] M. Olesen,[1] S. Kristensen,[1] J.-E. Jørgensen,[1] W. Wen,[2] J. C. Hanson,[2] E. DiMasi,[2] F. Besenbacher,[1] T. R. Jensen,[1] – [1]Interdisciplinary Nanoscience Center (iNANO) and Department of Chemistry, University of Aarhus, Aarhus, Denmark; [2]Department of Chemistry, Brookhaven National Laboratory, Upton, NY, USA

The complex hydride $LiAlH_4$ is of interest as a hydrogen storage material due to its high gravimetric hydrogen content of 10.6 w/w%, but the reversibility has to be improved for practical applications. The $2LiAlH_4/LiNH_2$ mixture was previously investigated by thermogravimetry and indicate a hydrogen release of ca. 8.1 w/w% [1]. In this study lithium aluminium hydride is destabilised by adding different amounts of lithium amide. The complex reaction mechanism for dehydrogenation of the $LiAlH_4$-$LiNH_2$ mixtures has been investigated by in situ synchrotron radiation powder diffraction. The samples were placed in a sapphire tube and heated from R*T* to a maximum of 700°C in an inert atmospher. Several intermediate phases are observed during dehydrogenation, e.g. Li_3AlH_6, Li_2NH and Al. The nitride, Li_3AlN_2, is observed as a product that stabilises the dehydrogenated state and the cubic structure (a = 9.461(3) Å) of this phase was refined from the powder diffraction data. [1] J. Lu, Z. Z. Fang, *J.Phys. Chem. B*, 2005, **109**, 20830.

P-343 **Mechanochemical Synthesis and Characterisation of Multi-component Mg-based Hydrogen Storage Materials.** C. X. Shang, Z. X. Guo, – Department of Materials, Queen Mary, University of London, London, UK

A systematic investigation of the structural stability, evolution and hydrogen-storage properties of Mg-based hydrides was carried out, involving mechanical milling and chemical alloying. The effects of milling on particle size, lattice parameters, microstructure, and phase composition of the powder mixtures were characterised by SEM and X-Ray diffraction. Mechanical milling was shown to be effective in refining particle size, particularly when MgH_2 is involved. The influences of selected chemical elements on hydrogen desorption of various milled mixtures were clearly identified using coupled Thermogravimetry (TG) and Differential Scanning Calorimetry (DSC). The as-received MgH_2 shows an onset desorption temperature of 420°C. Mechanical milling reduces the onset temperature to 330°C. Milling MgH_2 with rare earth metals, Y and Ce, does not seem to influence desorption temperature, but the formation of CeO_2 in the (MgH_2+Ce) mixture provides a beneficial effect on desorption kinetics. A multi-component mixture of (MgH_2+Al+Ni+Y+Ce) exhibits a relatively low desorption temperature of 220°C with relatively high kinetics, which is a significant improvement towards practical targets for on-board applications.

P-344 **Systematic Study for Reaction of Complex Hydrides with NH_3.** T.-H. Izuhara, H. T. Takeshita, – Kansai University, Suita, Japan

It was reported that the dehydrogenation of $LiNH_2$ was composed of two-step reactions accompanied by the formation of NH_3 [1,2]. Imperfect reaction of NH_3 to produce H_2 can cause the degradation of $LiNH_2$ which leads to decrease in hydrogen storage capacity as well as the existence of toxic NH_3 impurity in H_2 gas. To clarify the reason of the imperfect reaction of hydrides with NH_3, we systematically studied the reaction rate of several complex hydrides with NH_3.The reaction rates of hydride samples with NH_3 were determined with a pressure-composition-temperature instrument equipped with mass spectrometer (PCT-MASS). The amount of H_2 and NH_3 were calculated from pressures at room temperature and 77K before and after the reaction. In addition, the generated gas species were identified with the mass spectrometer. It was reported that LiH and NH_3 reacted almost completely [3], whereas the reaction of $LiAlH_4$ with NH_3 was incomplete, independent of the amount of $LiAlH_4$, which means that Al in $LiAlH_4$ disturbs the progress of hydride with NH_3. [1] P. Chen et al., Nature, 420 (2002), 302-304; [2] T. Ichikawa et al, J. Alloys Compd., 365 (2004), 271-276; [3] Y. H. Hu and E. Ruckenstein, J Phys. Chem. A., 107(2003), 9737-9739.

P-345 **Effects of Microwave Irradiation on Metal Hydrides and Complex Hydrides.** Y. Nakamori,[1] T. Tsutaoka,[2] S. Orimo,[1] – [1]Institute for Materials Research, Tohoku University, Sendai, Japan; [2]Graduate School of Education, Hiroshima University, Higashi-hiroshima, Japan

Effects of microwave irradiation on metal hydrides and complex hydrides have been systematically investigated for the first time. For example, TiH_2 is heated to 600 K by microwave irradiation rapidly, at which less than 0.16 mass% of hydrogen is desorbed from surface of the powder. On the other hand, $LiBH_4$ is heated rapidly above 380 K, at which almost all hydrogen, 13 mass%, is desorbed [1]. The rapid heating of TiH_2 is mainly due to conductive loss, while that of $LiBH_4$ is related to a structural transition at approximately 380 K. The energy saving microwave process can be applied to the hydrogen storage system. [1] Y. Nakamori, S. Orimo, T. Tsutaoka, Appl. Phys Lett., in press.

P-346 **Hydrogen Storage of Graphite Carbon/Mg Nanocomposite Prepared by Ball Milling.** H. Imamura,[1] I. Kitazawa,[1] Y. Tanabe, Y. Sakata, – Department of Advanced Materials Science and Engineering, Yamaguchi University, Ube, Japan

Carbon nanocomposites obtained by ball milling of graphite and magnesium with organic additives (benzene or cyclohexane) under different conditions have been studied with the aim of preparing novel hydrogen storage materials [1]. It has been proved by temperature programmed desorption (TPD) and neutron diffraction measurements that the hydrogen taken up by the nanocomposites exists in at least two states; the one is the hydrogen strongly associated with the carbon component and the other the hydride in the magnesium component. The ball milling resulted in the generation of large amounts of dangling carbon bonds in graphite, which acted as active sites to take up the hydrogen. When D_2 gas was brought into contact with such composites, the isotope exchange reaction with the hydrogen in the magnesium hydride occurred at 453 K, and not with the hydrogen associated with the carbon. The properties of such hydrogen taken up were also discussed from the standpoint of isotope effects. [1] H. Imamura, et al., Acta Materialia, 51 (2003) 6407.

P-347 **Microfabricated Pd and Pd-25Ag Alloy Membranes.** Y. Zhang,[1] J. Lu,[1] R. Maeda,[1] C. Nishimura,[2] – [1]National Institute of Advanced Industrial Science and Technology,Tsukuba, Ibaraki, Japan; [2]National Institute of Materials Science, Tsukuba, Ibaraki, Japan

It is necessary to know intrinsic hydrogen permeation behaviors of Pd alloy membranes with thickness of several microns or less, which are widely used for hydrogen separation applications. In this work, dense Pd and Pd-25Ag alloy membranes with the thickness ranged from 1.2 to 2.5 mm were successfully fabricated by micro-system technology. The membranes were supported by a patterned Ni layer so that hydrogen permeation could be performed in a conventional gas permeation apparatus. Hydrogen permeation of the as-prepared membranes was investigated within the temperature range of 473 – 673 K using high purity hydrogen. Hydrogen permeability of the 2.5 mm-thick Pd membrane was 50 ~ 65% of that of Pd membrane with the thickness of about 0.70 mm, while that of the 1.2 mm-thick Pd-25Ag alloy membrane was almost one order lower than that of the 0.51 mm-thick Pd-25Ag alloy membrane. Pressure exponent of hydrogen permeation through the thin Pd membrane decreased from 0.86 to 0.73 when permeation temperature increased from 473 K to 673 K. Grain growth was found in the thin Pd membrane after permeation. There was no visible grain growth in the thin Pd-25Ag alloy membrane. Through comparisons with literature results, it was inferred that the surface status of Ag element had significant effects on hydrogen permeation in thin Pd-25Ag alloy membranes.

P-348 **The Effect of Grain Size and Strain on Hydrogen Storage Content, Hydriding Reaction Enthalpy and Entropy of an AB_5-type Alloy.** C. H. Peng, T. Robert, M. Zhu, – College of Mechanical Engineering, South China University of Technology, Guangzhou, P. R. China

The average grain size and internal strain of an AB_5 type Ml(NiCoMnAl)$_5$ alloy (Ml denotes La- rich mish metal) were manipulated by combining high energy ball milling and annealing. Peak broadening analysis of X-ray diffraction was used to estimate the grain size and internal strain of the prepared sample. According to the pressure composition isothermals measured at different temperature, hydrogen storage content, hydriding reaction enthalpy and entropy with different strain and grain size were determined. It has been found that hydrogen storage content decreases with the increasing of the milling time and the hydrogen storage content of the milled sample nearly recovers the original value of the as cast sample after annealing. It has also been found that hydriding reaction enthalpy and entropy related to the grain size and internal strain. The results present in this work proved that the hydrogen storage content, hydriding reaction enthalpy and entropy would substantially affected by nanometerization of grain size and strain. These phenomena have been discussed in point of non-equilibrium structure on hydriding reaction and influence of grain boundary on hydrogen storage.

P-349 **H-sorption Behaviour of Mechanically Activated Mg-Zn Powders.** S. Deledda,[1] B. C. Hauback,[1] H. Fjellvåg,[2] – [1]Department of Physics, Institute for Energy Technology, Kjeller, Norway; [2]Department of Chemistry, University of Oslo, Oslo, Norway

Ball milling techniques are becoming increasingly important for processing potential hydrogen storage materials. On one hand, this is due to the grain-size reduction process, which occurs during the continuous fracturing and cold welding of the powder particles and which results in an improved H-sorption kinetics [1]. On the other hand, the mixing of elements/compounds at an atomic scale and the extended solid solubility of metals, which has been observed upon ball milling, allows the production of metastable alloys, which might show interesting hydrogen storage properties [2]. This contribution focuses on powder mixtures, with nominal composition Mg_7Zn and Mg_7Zn_3, which were ball milled (i) at room temperature in an inert Ar atmosphere, (ii) at liquid nitrogen temperature (cryomilling), and (iii) at room temperature in a reactive H_2 atmosphere (reactive milling). The structural and

microstructural evolution of the powders was followed by powder diffraction analysis and scanning electron microscopy. Results on the hydrogen sorption behaviour and hydride phase formation upon reactive milling or during conventional hydrogenation in a Sievert-type apparatus, are presented. The effect of different processing conditions, i.e. milling temperature and milling atmosphere, on the hydride phase formation is discussed. [1] A. Zaluska, L. Zaluski, J.O. Ström-Olsen, J. Alloys Comp. 288 (1999) 217; [2] Y. Zhang, Y. Tsushio, H. Enoki, E. Akiba, J. Alloys Comp. 393 (2005) 147.

P-350 **High-pressure Ball Milling Synthesis of Magnesium-based Hydrogen Storage Materials.** J. M. Bellosta von Colbe,[1] H. Fjellvåg,[2] B. C. Hauback,[1] – [1]Physics Department, Institute for Energy Technology, Kjeller, Norway; [2]Department of Chemistry, University of Oslo, Oslo, Norway

Mg-based compounds are among the promising materials for hydrogen storage. Ball-milling is one of the interesting methods for synthesis of new compounds. A milling vial has been designed and constructed for synthesis of materials under a hydrogen pressure of up to 100 bar. The setup has been used to synthesize different materials for hydrogen storage including $MMgH_3$-type materials and Mg-transition metal alloys. Mg-based amides and imides have also been synthesized in this system. The compounds were characterized by X-ray and neutron diffraction, and their absorption/desorption properties were investigated with a Sievert's apparatus. Financial support from the RENERGI programs in the Research Council of Norway is acknowledged

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P-351 **Hydrogen Storage Properties in a Composite of Lithium Hydride and Boron Nitride with Hydrocarbon Radical.** H. Miyaoka,[1] T. Ichikawa,[2] S. Isobe,[2] H. Fujii,[2] – [1]Department of Quantum Matter, ADSM, Hiroshima University, Higashi-Hiroshima, Japan; [2]Materials Science Center, N-BARD, Hiroshima University, Higashi-Hiroshima, Japan

Recently, we reported the hydrogen storage properties of the nano-structural carbon ($C^{nano}H_x$) and LiH composite. The $C^{nano}H_x$ product was synthesized by ball-milling graphite under hydrogen atmosphere. After that, the composite was prepared by ball-milling the mixture of $C^{nano}H_x$ and LiH. Each product needs more than 600 ℃ to completely release the hydrogen. Nevertheless, the composite desorbed hydrogen below 350℃, suggesting that this hydrogen desorption proceeded due to an interaction between the ionic crystal of LiH and the polarized C-H radicals. Since the radicals should be located at the edge of nano-structural graphene sheets in the $C^{nano}H_x$ product, we have paid attention to other layer structure materials. With the same layer structure as graphite, we next focused on the hexagonal boron nitride (hBN), and we tried to synthesize $BN^{nano}CH_x$ by ball-milling hBN under methane atmosphere. Of course, this $BN^{nano}CH_x$ product itself desorbed not only hydrogen but also hydrocarbons in wide temperature range from 300 to 900℃. Moreover, the FT-IR measurement for $BN^{nano}CH_x$ indicated the existence of the C-H bonding in the product. On the analogy of the $C^{nano}H_x$-LiH composite, we prepared the mixture of $BN^{nano}CH_x$ and LiH. This composite successfully desorbed hydrogen around 200℃, in which the emission of the hydrocarbon gases was strongly suppressed due to the interaction as we expected. These results indicated that we succeeded in designing the $BN^{nano}CH_x$ and LiH composite.

P-352 **Microstructure and Properties of MmM_5/Mg Multi-layer Thin Films Prepared by DC Magnetron Sputtering.** L. Z. Ouyang,[1] S. Y. Ye,[1] H. Wang,[1] M. Zhu,[1] J. Zou,[2] C. Y. Chung,[3] – [1]College of Mechanical Engineering, South China University of Technology, Guangzhou, China; [2]Division of Materials and Centre for Microscopy and Microanalysis, The University of Queensland, St. Lucia, Queensland, Australia; [3]Department of Physics and Material Science, City University of Hong Kong, Kowloon, Hong Kong

$MmNi_{3.5}(CoAlMn)_{1.5}$/Mg (abbreviated as MmM_5, here Mm denoted for mischmetal) multi-layer thin films were deposited on (001) Si substrate by direct current (DC) magnetron sputtering with dual-target. Five-layer films were prepared with the starting and finishing layers being the MmM_5. The total film thickness is 2510 nm with the thickness of Mg layer and the MmM_5 layer being 1000 nm and 170 nm respectively. X-ray diffraction (XRD), scanning electron microscopy (SEM) and cross-sectional transmission electron microscopy (XTEM) analysis revealed that the microstructure of MmM_5 layer is amorphous and/or nanocrystalline and that the microstructure of Mg layer is fine grained crystalline with preferential orientation, saying typical columnar crystallite with their [001] and [103] direction nearly parallel to the growth direction. XRD patterns of MmM_5/Mg multi-layer thin film hydrogenated at 392k illuminate that the Mg diffraction peak (103) disappeared, while the (001) peak still existed and MgH_2 peaks appeared, which shows that the Mg layer with (103) orientation absorb hydrogen in the lower temperature than that of the Mg layer with (001) orientation. Phase analysis and pressure-composition-isothermal (PCI) measurement show that MmM_5/Mg multi-layer thin films Mg could absorb hydrogen at 392 K. A maximum hydrogen absorption content of 5.6 mass% is obtained at 573 K. The improvement of the hydrogen storage properties of Mg is attributed to the catalytic roles of the MmM_5 phases.

P-353 **Amorphous and Nanocrystalline Magnesium Alloys and Composites with Improved Hydrogen Storage Properties.** T. Spassov,[1] V. Petkov,[2] N. Drenchev,[1] M. Gateshki,[2] – [1]University of Sofia, Dept. Chemistry, Sofia, Bulgaria; [2]Dept. of Physics, Central Michigan University, Mount Pleasant, MI, USA

Amorphous and nanocrystalline Mg-based hydrogen storage alloys and composites are synthesized by high-energy ball milling and rapid quenching. Controlled annealing of the as-cast and as-milled materials is applied, resulting in desired microstructures. Structural and microstructural characterization of the materials before, during and after hydrogen absorption, including crystallite size, defects and atomic scale structure is carried out. Depending on the preparation conditions the alloys possess nanocrystalline or nano-/amorphous microstructure with different particles and grain size distributions. The hydriding/dehydriding properties of the Mg-based materials are studied from a hydrogen gas phase and electrochemically. Strongly reduced hydriding temperatures due to the fine particle size and nanocrystalline structure are found for some of the compositions. Hydrogen absorption at room temperature is detected for the Mg-AB_5 composites. Relatively high hydrogen storage capacity and fast kinetics of hydriding and dehydriding are detected. The maximum discharge capacity, measured with an electrode prepared from Mg-based alloys is found to be higher than that measured with an electrode prepared from AB_5-type alloys, while the cycle life performance and

charge/discharge kinetics are still unsatisfactory. The influence of the microstructure on the electrochemical properties and on the gas phase hydriding characteristics of the alloys investigated is also discussed.

P-354 **A Comparison of Hydriding Properties of Mg + Mm(NiCoMnAl)$_5$, Mg + TiFe$_{0.95}$Mn$_{0.05}$ and Mg + Mg$_{1.8}$La$_{0.2}$Ni Nano-composites.** H. B. Yang, H. L. Sun, W. Mo, H. C. Zhang, Z. X. Zhou, – Institute of New Energy Material Chemistry, Nankai University, Tianjin 300071, China

Among metal-hydrogen systems, Mg-based alloy is recognized to be a promising one due to its higher storage capacity, lower specific gravity and cost. Its limitation for practical applications, however, lies on slow sorption kinetics and high thermodynamic stability of its hydride [1]. Recent developments indicated that Mg-AB$_5$, Mg-AB and Mg-A$_2$B composites, with nano-structure, could deliver promising performance [2-4]. Although extensive researches have been done to those composites, much confusion still arises up because all the previous work has been done under different conditions. In order to investigate the difference in the hydriding performance of Mg-based composites combined with different alloys, Mg was ball-milled with Mm(NiCoMnAl)$_5$, TiFe$_{0.95}$Mn$_{0.05}$ and Mg$_{1.8}$La$_{0.2}$Ni alloys, which had different hydriding plateau pressures, leading to the formation of three kinds of nano-composites. The results showed that Mg + 10 wt.% Mg$_{1.8}$La$_{0.2}$Ni, Mg + 20wt.% Mm(NiCoMnAl)$_5$ and Mg + 40 wt.% TiFe$_{0.95}$Mn$_{0.05}$ composites had the best hydriding performance in each series and could absorb 4.4 wt.%, 3.7 wt.% and 3.5 wt.% of hydrogen within 50s at 423K, respectively. [1] H. B. Yang, H. T. Yuan et al., J. Alloys Comp., 330-332 (2002) 640; [2] G. Liang, J. Huot et al., J. Alloys Comp., 297 (2000) 261; [3] P. Mandal, O. N. Srivastava, J. Alloys Comp., 205 (1994) 111; [4] A. Zaluska, L. Zaluski, J. O. Ström-Olsen, J. Alloys Comp., 289 (1999) 197.

P-355 **Hydrogenation of Pd-capped Pure Mg Thin Film at Room Temperature.** K. Yoshimura, S. Bao, Y. Yamada, M. Okada, – AIST, Nagoya, Japan

Much attention has been paid to the magnesium-hydrogen system from both fundamental and practical viewpoints. Especially for the purpose of hydrogen storage, magnesium has been extensively studied because magnesium can absorb 7.65 wt% of atomic hydrogen. However, its operation temperature is over 600 K, and it strongly restricts applications of magnesium. Through the study of thin film storage, Yamamoto *et al.* found that Pd/Mg thin films can be hydrogenated and made to be transparent at a temperature of 373 K [1]. We have studied switchable mirror thin films and found that Pd-capped pure Mg film which is prepared by DC magnetron sputtering, can be hydrogenated at room temperature (295K) when the thickness of Mg layer is below 20 nm. Our sample which consists of 4 nm Pd layer and 20 nm Mg layer on the glass substrate shows drastic optical change from the metallic state to the transparent state after exposure to 4% hydrogen in Ar at 295K. The hydrogenation of Mg layer is completed within a few seconds. This change is too fast than we expected from the hydrogen diffusion constant in Mg. We investigated the structure of Pd-capped pure Mg film by TEM observation and found that this film has very special interface structure and that may be the reason of such a fast hydrogenation at room temperature. [1] K. Yamamoto, K. Higuchi, H. Kajioka, H. Sumida, S. Orimo, H. Fujii, J. Alloys and Compounds,330-332 (2002) 352

P-356 **Titanium Nitride Coating to Inner Walls of Narrow Tubes for Prevention of Hydrogen Permeation.** H. Hyakawa,[1] M. Takeuchi, Y. Matsumura, H. Uchida, M. Yamawaki, – Tokai University, Hiratuka, Japan

Titanium nitride shows considerable hydrogen impermeability and is expected as a prevention coating of hydrogen gas for a cladding tube of metal hydride fission fuel. Inner coatings of narrow tube have been studied in Al_2O_3, TiN, TiC and their composite films, which are formed by using plasma processes. However, the coating processes are very complicated because the cladding tube is not wide enough to create stable plasma. In this study, TiN coating to inner walls of narrow tubes was formed by a simple evaporation method. Ti and Ti-N thin film was prepared by a vacuum evaporation. The deposition chamber was evacuated down to 6.0×10^{-4} Pa, the films were thermally deposited on stainless steel sheets coiled around inner walls of glass tubes. A Ti wire twisted with a W filament was used for the evaporant. In case of Ti-N deposition, N_2 gas was induced into the chamber and the pressure was kept at 1.0×10^{-1} Pa during the deposition. As a result, thin films with dark gold color were obtained. From XRD result, distinct diffraction patterns of TiN phase were observed. The film structure of TiN was found dense enough by SEM observations.

P-357 **Hydrogen and Methane in MOF – Isotherms, Heat of Absorptions and INS Data.** W. Zhou,[1,2] T. Yildirim,[2] – [1]Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA, USA; [2]NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD, USA

Metal-organic framework (MOF) compounds are a relatively new class of nano-porous material that show promise for methane storage. Here we present a detailed study of hydrogen and methane adsorption in MOF5 using elastic and inelastic neutron scattering (INS) along with first-principles calculations. We developed a fully computer-controlled Sieverts apparatus to measure the adsorption capacity and the heat of adsorption over a large temperature and pressure range. The adsorption sites were directly determined from the difference-Fourier analysis of neutron powder diffraction data. Initial adsorption occurs at the MOF5 cup site for both H_2 and CH_4. Using INS, we studied the hydrogen and methane dynamics. The experimental data including absorption site positions, phonon-libron energies and the rotational tunnel-spectrum is then used to test widely used phenomenological force fields and potentials obtained from first-principles. All these results hold the key to tuning MOF structures further for better hydrogen and methane storage applications.

P-358 **Comparison of Hydrogen Uptake in Various Stoichiometries of Ball Milled TiMgNi.** D. A. Sheppard,[1] C. E. Buckley,[1] Z. T. Jiang,[2] A. Mawson,[1] – [1]Department of Applied Physics, Curtin University of Technology, Perth, Australia; [2]Department of Applied Chemistry, Curtin University of Technology, Perth, Australia

The study of the interaction of hydrogen with various metal and metal alloys has a long history. Recently Lomness et al. [1] investigated hydrogen absorption in a mechanically alloyed mixture of $Ti_{53}Mg_{47}Ni_{20}$ based on promising hydrogen absorption results published for the Ti-Zr-Ni system [2]. Though their results could not be confirmed in our laboratory we found that the hydrogen uptake characteristics of a $Ti_{53}Mg_{47}Ni_{20}$ mechanically ball-milled for 36 hrs rapidly absorbed 2.5 wt% of hydrogen at room temperature (296K) [3]. X-ray diffraction shows that our ball-milled sample comprises low crystallinity elemental Ti, Mg and Ni which converts to more crystalline Ti_2Ni, Ti and Mg during temperature cycling. Examination of the hydrided sample shows the presence of Ti_2NiH_x ($x > 0.5$), TiH_y ($0.7 < y < 2$) and MgH_2. Here we examine the effect of altering the molar ratio of the constituent elements and ball-milling time on the hydrogen adsorption characteristics of Ti-Mg-Ni. Initial results for $Ti_{62}Mg_{117}Ni_{20}$ show an extremely rapid hydrogen absorption of 3.8 wt% at room temperature. [1] J. K. Lomness, M. D. Hampton, L. A. Giannuzzi. Int. J. Hydrogen Energy 27 (2002) 915; [2] K. F. Kelton, P. C. Gibbons. MRS Bull 22 (1997) 69; [3] D. A. Sheppard, Z. –T. Jiang, C. E. Buckley, Submitted to Int. J. Hydrogen Energy (2006).

P-360 **Hydrogen Absorption and Desorption Properties of Mg-20wt%$Ti_{28}Cr_{50}V_{22}$ Composite Prepared by Ball Milling.** X. P. Liu, Z. N. Li, L. J. Jiang, S. M. Wang, – General Research Institute for Nonferrous Metal, Beijing, China

The Mg-20wt% $Ti_{28}Cr_{50}V_{22}$ hydrogen storage composite was successfully prepared by high power mechanical milling of a mixture of magnesium powder and $Ti_{28}Cr_{50}V_{22}$ body center cubic solid solution alloy powder. The hydrogen absorption and desorption kinetic under different temperature were investigated. The experimental results showed that the milled Mg-20wt% $Ti_{28}Cr_{50}V_{22}$ composite did not need to activate on the first hydrogen absorption process. The composite exhibits a high hydrogen storage capacity and good hydriding and dehydriding kinetic properties. All hydrogen absorption process of milled composite can be finished in 4 mins, and its hydrogen absorption capacity can reach to 3wt% and 5.3wt% under 3MPa hydrogen pressure at 298K and 573K, respectively. The DSC experimental on the heating process for the hydriding Mg-20wt% $Ti_{28}Cr_{50}V_{22}$ composite results showed that the hydrogen desorption temperature of the mechanical milled composite decreases nearly about 100°C in contrast to that of the milled pure MgH_2. It is indicated that the both the catalyst effect of $Ti_{28}Cr_{50}V_{22}$ hydrogen storage alloy distributed in Mg substrate and the many crystal defects formed by the mechanical milling process are the main reason for improving hydrogen absorption and desorption kinetic of Mg-20wt%$Ti_{0.28}Cr_{0.50}V_{0.22}$ hydrogen storage composite.

P-361 **Structural and Optical Properties of Hydrogenenated Zr Thin Film.** I. P. Jain, R. K. Jain, C. Lal, A. Jain, – Centre for Non-Conventional Energy Resources, University of Rajasthan, Jaipur, India

Recently lot of research interest has been generated in scientific world with the discovery of hydrogenated switchable mirrors showing dramatic changes in the optical properties of the thin film metal hydride. Structural and optical properties of hydrogenated Zr thin films with different coatings have been presented. Thin films of Zr with 200nm thickness were deposited onto glass substrate by electron beam evaporation technique at 10^{-8} Torr Vacuum. 30 nm thick films of Ni, Cu and Co have also been deposited on Zr films. Crystal structure was investigated by GIXRD of thin film samples before and after hydrogenation and annealing as well. The surface modifications of the films due to hydrogenation have been viewed by optical microscope. Optical transmission changes in the UV-VIS range of metal hydride films have been presented.

P-362 **Operation of a PEM Fuel Cell with $LaNi_{4.8}Sn_{0.2}$ Hydride Beds.** P. R. Wilson,[1] R. C. Bowman, Jr.,[1] J. L. Mora,[1] J. W. Reiter,[2] – [1]Jet Propulsion Laboratory, Califorina Institute of Technology, Pasadena, CA, USA; [2]Swales Aerospace, Pasadena, CA, USA

A series of measurements were performed using metal hydride sorbent beds to operate a 1.0 kW capacity PEM fuel cell hybrid power system. Two sorbent beds were filled with $LaNi_{4.78}Sn_{0.22}$ alloy and each unit had a maximum storage capacity of ~280 sL hydrogen. A single sorbent bed was able to supply hydrogen gas for ~20-25 minutes operation at 30 amps net current and ~900 W output power. These hydride beds were also capable of supplying sufficient hydrogen flows and pressures to produce up to ~1.1 kW output power from the fuel cell for shorter durations. Good correlations for hydrogen consumption rates and power outputs were obtained and boundaries parameters for continual operation were identified. Various input and output parameters were recorded and analyzed to relate hydride bed, fuel cell, and battery behavior and assess their dynamic interactions. The equilibrium absorption and desorption pressures for the $LaNi_{4.78}Sn_{0.22}H_x$ used in these sorbent bed have been measured from 273 K to 473 K. In order for the desorption pressures across the plateau region of x~0.5 to x~ 5.0 to exceed the minimum fuel cell input pressure of 1.7 bar, the $LaNi_{4.78}Sn_{0.22}H_x$ was heated above ~333 K to operate the fuel cell.

P-363 **Hydrogen Desorbing Properties of Nanocrystalline Mg-Based Alloys Studied by PCT and TDS Measurements.** K. Tanaka, – Toyota Physical & Chemical Research Institute, Nagakute, Aichi, Japan

Hydrogen desorbing properties of Mg-rich Mg-Ni and Mg-Ni-La alloys have been studied by measuring pressure-composition isotherms (PCT) and thermal desorption spectra (TDS). Nanocrystalline samples have been prepared by rapid quenching from the melts to form amorphous alloys and then by crystallizing at elevated temperatures. The nanocrystalline Mg-Ni-La alloy, composed of Mg(α), Mg_2Ni(γ) and LaH_2 phases (3-30nm in size) after initial activation treatment, provides with a large H-capacity of ~4.6wt% and fast absorbing and desorbing rates compared with the nanocrystalline Mg-Ni alloy containing Mg amd Mg_2Ni phases. The PCT curve of this ternary alloy exhibits flat two-stage plateaus, corresponding to the formation of MgH_2(β) and Mg_2NiH_4(τ) hydrides, with very small hysteresis at temperatures between 240 and 330□. TDS spectra of this alloy measured between RT and 400□ at a heating rate of 2□/min exhibit four characteristic desorption peaks. Peaks *a* (~190□) and *b* (~220□), which always appear in parallel, correspond to the decomposition of τ and β hydrides, respectively. Peak *c* (~270□), which is rather unstable to thermal

cycling, is attributed to release of hydrogen from nanograin boundaries of the α phase. Peak *d* (~360□) is due to decomposition of LaH_2. The segregation and rapid transport of hydrogen along the nanograin boundaries increase the reaction rates between hydrogen and the metallic phases, and give rise to excellent hydrogen storage properties of this nanostructured alloy.

P-364 **Studies on Hydrogen Loaded Fe/V Multilayers.** R. Gemma, P. Kesten, T. Al-Kassab, R. Kirchheim, A. Pundt, – Institut für Materialphysik, Universität Göttingen, Göttingen, Germany

In this study, we have prepared 1nm ~ 10nm Fe/V multilayer packages to study their layer structure and H/D distribution. They were deposited at room temperature by ion sputtering on W tip for 3d-tomographic atom probe (TAP) analyses. As well, polycrystalline Fe/V/Fe sandwich packages with each layer thickness of 40nm and 10nm on Al_2O_3(11-20) substrate were also prepared for electromotorical force (EMF) measurement. The TAP results showed that layers near the center pole were grown epitaxially in <110> direction in relation to the (110) plane of W tip. However, the Fe concentration in V layer was found to be relatively high, ranging 8 ~ 15% depending on the double layer thickness; the thinner the thickness is, the higher the Fe concentration is. It has already been reported that even several % of Fe in V can increase the dissociation pressure of V-H ($\alpha+\beta_1$) by a factor of 10 ~ 100 [1]. In accordance with this observation, our samples exhibited clear dependence of Fe content on EMF curves. But in each sample, the increase in the plateau pressure of VH was slightly higher than expected from Fe concentration obtained by TAP analysis. This deviation will be discussed by taking the result of the stress measurement with inductive strain gauge into account. Also, the surface segregation behavior of H atoms observed at SIMS depth profile measurement carried out at room temperature will be presented.
[1] H. Yukawa *et al.*, *J. Alloys. Comp.*, 356-357 (2003) 45-49.

P-365 **Hydrogen Storage Mg_2Ni Alloy Produced by Induction Field Activated Combustion Synthesis.** Y. Kodera,[1] T. Yamamoto,[1] T. Kawasaki,[1] M. Ohyanagi,[1] Z. A. Munir,[2] – [1]Ryukoku University, Ohtsu, Shiga, Japan; [2]University of California, Davis, CA, USA

We tried to synthesize pure Mg_2Ni from elemental Mg and Ni by induction field activated combustion synthesis in spite of large difference in vapor pressure and melting point between Mg and Ni. The formation energy of Mg_2Ni is ΔH= -40kJ/mol and is generally not enough to self-sustain the combustion reaction without any external heat support. Reactions which are weakly exothermic can not be initiated or sustained. We, herein, applied the field-activated process that arising from the use of induction for the external heat support. The reactants sample coated by MgO is covered with a conductive carbon foil and is placed inside an induction coil. The induction current is generated in the foil and in the sample. Since the induction current is localized in a surface layer of the foil and the sample, ignition takes place in this region and is expected to propagate in an inward radial direction. The effect of mechanical milling on hydroden storage behavior in the Mg_2Ni is also described..

P-366 **AFM and Resistivity Studies on Metal Nanowires and their Hydrogen Sorption.** S. Schmidt, A. Pundt, – Institut für Materialphysik, Universität Göttingen, Göttingen, Germany

Nanowire arrays of different metals (Pd, Fe, Nb, V) were produced by small angle sputtering on facetted sapphire, using the self shadowing effect of the facets [1]. Minimum wires widths of about 20 nm were achieved, with a wire height of 15 nm and a length in the cm range. The wire length is given by the length of the facet, i.g the length of the sample. Surprisingly, in the case of Pd, Nb and Fe, island growth was also found on the facets back side. This could be attributed to surface diffusion. The behaviour of wires during the exposure to hydrogen was investigated with AFM, using Contact mode, Lateral Force Microsopy (LFM) and Force Spectroscopy (FS). Massive tip-induced surface changes were observed in long-time mesaurements. Therefore, short-time measurements were performed by instantanously changing the hydrogen gas pressure above the solubility limit. By this, hydrogen formation could be monitored. Resistivity measurements on Palladium wires arrays during hydrogen loading show a reduced pressure-dependence compared to bulk. The influence of hydride formation on the resistivity of wires will be discussed. Hysteresis effects were found even for 2 nm thin wires. [1] Huth et al., Highly Ordered Fe and Nb Stripe Arrays on Facetted α-Al2O3 (10-10), Adv. Funct. Mater., 2002,12, No.5 (pp. 333-338).

P-367 **Hydrogenation Characteristics of Laminated Magnesium-Nickel Alloys.** H. Miyamura,[1] R. Mori,[1] S. Kikuchi,[1] K. Tanaka,[2] H. Tanaka,[2] N. Takeichi,[2] N. Kuriyama,[2] T. T. Ueda,[3] M. Tsukahara,[3] – [1]Univ. Shiga Prefecture, Hikone, Japan; [2]AIST, Ikeda, Japan; [3]IMRA Material R&D Co. Ltd., Kariya, Japan

Microstructures and hydrogenation properties of Mg-Ni laminate composites were investigated. Laminated Mg-Ni alloy films with various Mg:Ni ratios were prepared by cold rolling of alternatedly-stacked Mg and Ni foils. The stacked foils were subjected to repetition of rolling down and the thickness of each layer was reduced less than 1 micrometer. Some of the laminate composites were subjected to heat-treatments at various temperatures between 473K and 673K, and then their microstructures were observed by scanning electron microscopy and X-ray diffractometory. The hydroegnation behaviors were investigated by use of a Sieverts type apparatus. The laminate composites were activated in the first hydrogenation and turned into a mixture of magnesium hydride and magnesium-nickel hydride. The P-C isotherms had slightly higher dissociation pressures and smaller histerisis gaps than those for the alloys prepared by conventional casting. The hydrogen storage capacity (H/M) of a laminate composite with the ratio Mg:Ni=3:1 amounted upto 4.3 mass% at 573K. Hydrogen absorption rates were also evaluated by measuring the pressure change as a function of time. As-rolled laminates quickly absorbed hydrogen when they were exposed to hydrogen, but heat-treated laminates showed slower absorption rates. This study was adminisrated through the New Energy and Industrial Technology Development Organization(NEDO), Japan.

P-368 **Hydrogen Storage Property of MgH_2 Single-Crystal Nano-Fiber.** I. Saita, H. Hayashi, T. Toshima, S. Tanda, T. Akiyama, – Hokkaido University, Sapporo, Hokkaido, Japan

Nano-fibers of MgH_2 was synthesized by *hydriding chemical vapor deposition (HCVD)*, which used high pressure hydrogen [1]. The MgH_2 fiber was made of single crystalline with the **diameter less than 500 nm and the length larger than 100 mm**. In this study, we examined the hydrogen storage property of the HCVDed MgH_2. As the results of Pressure-Composirion-Isotherm (PCT) measurement, the HCVDed MgH_2 reversibly absorbed and desorbed hydrogen as much as 7.6 mass% without any activation treatment, keeping the fiber shape. The decomposition pressure of the HCVDed MgH_2 was slightly lower, 0.07 MPa at 560 K, than the reported value, 0.1 MPa at 563 K. Each hydrogenation/dehydrogenation operation in the PCT measurement took about 2 hours. That is, the hydrogenation/dehydrogenation rate of the HCVDed MgH_2 was relatively large while it is difficult to obtain high purity MgH_2 by current solid-gas reaction between magnesium and hydrogen even under the conditions of repeting hydrogenation/dehydrogenation, adding second element as a catalyst, or pulverizing into micro- or nano-orders. The results appealed a revolutionary productive route for metal hydride, which offers many benefits for simplifying the productive procedure, minimizing processing time, saving energy, and upgrading the product. [1] I. Saita et al., Mater. Trans., in press for 47 (2006).

P-369 **Hydrogen Purification Membrane Stability: Interdiffusion of Thin and Bulk Palladium-Stainless Steel Couples.** S. Fletcher, D. Prosperi, R. Barlow, A. Walton, J. D. Speight, I. R. Harris, D. Book, – Department of Metallurgy & Materials, School of Engineering, University of Birmingham, Birmingham, UK

Polymer Electrode Membrane (PEM) fuel cells are very sensitive to impurities (such as CO, H_2S, etc) and therefore require a very pure hydrogen feed. Palladium alloy films supported by stainless steel (SS) substrates are the favoured method to achieve a ppm-pure hydrogen supply. We have investigated bulk (25µm) and thin film (<2.5µm) Pd – SS (SS-430-S15) couples and found widely differing behaviour. Bulk couples demonstrate grain boundary / defect enhanced diffusion of Fe and Cr into the Pd film at 600℃ with rapid bulk interdiffusion beginning at around 900℃. Thin film Pd deposited on SS annealed at 500℃ demonstrates a relaxing of the high as-deposited Pd film stresses. A strong [111] texture develops before the onset of rapid film-substrate interdiffusion. Further kinetic and crystallographic results, together with the effects of interdiffusion on the hydrogen permeance of the membrane will be presented.

P-370 **Hydrogen in Si Clathrates.** C. L. Condron, D. Neiner, S. M. Kauzlarich, – University of California Davis, Davis, CA, USA

Solid State clathrate phases provide an exciting area of research. These phases show rich crystal chemistry and display a wide variety of physical properties. Solid state clathrate phases are typically studied for superconductivity and thermoelectricity, and hydrogen storage applications have typically been focused on their hydrate counter phases. However, due to the stability of the clathrate framework, it is possible to encapsulate hydrogen in the framework cages of the type I clathrate phase $H_xNa_{8-x}Si_{46}$. Since the type I framework structure of solid state type I clathrate phases is stable even under extreme conditions, this may result in a new and renewable means of hydrogen storage. Synthesis, structural characterization (NMR, IR, powder x-ray diffraction), and thermal stability will be presented.

P-371 **Nanocrystalline Mg-based Alloys for Hydrogen Storage.** A. Palacios-Lazcano, J. Luna-Sánchez, L. Dámaso-Custodio, J. G. Cabañas-Moreno, – Instituto Politécnico Nacional, ESFM, México, D. F., México

Magnesium hydride is particularly interesting for mobile applications of hydrogen because of its low density and high storage capacity. Despite numerous studies, Mg alloys still draw considerable research efforts. Probably the most important problem related to hydrogen storage in Mg resides in the sluggish kinetics of dehydriding at moderate temperatures, so that operation temperatures above 350 °C are usually required. A number of alloying elements, additives and processing treatments (e.g., ball milling) have been shown to improve kinetics and lower both hydriding and dehydriding reaction temperatures. However, many questions remain regarding what exactly is the role of the alloying elements and additives in previous studies. In the present work, we report the preparation by mechanical alloying of binary Mg alloys containing 5 and 10 wt. % of the elements M = Zn, Ag, Al, and Y. These alloying additions were chosen on the basis of the extent of solid solubilities and on the results of geometry optimization calculations to determine the enthalpy of formation of $(Mg,M)H_2$. Milling parameters have been adjusted so that nanocrystalline Mg-M alloys could be produced. Special attention has been given to the determination of the actual state of the alloying additions (dissolved or dispersed in the matrix). Qualitative phase analysis is performed by XRD and TEM; while powder morphology and average chemical composition of the mechanically alloyed powders is determined by SEM-EDS. The hydriding behavior of the Mg-M powder alloys is being characterized at the present time and these results will be correlated with the structural and chemical characterization of the mechanically alloyed materials. Work supported by CONACYT and IPN in Mexico and the AIEJ program in Japan. We thank Profs. M. Morinaga and H. Yukawa)Nagoya University, Japan) for supplying the results of molecular simulations.

P-372 **Hydrogen Permeation and Diffusion of Ni-Nb-Ta Amorphous Alloy Membrane.** D.-Y. Lee,[1] K.-D. Kim,[1] S.-W. Kang,[1] K.-B. Kim,[1] Y.-S. Song,[2] – [1]Korea Institute of Science and Technology, Cheongryang, Korea; [2]Amosense Co. Ltd, Gimpo city, Gyunggi-Do, South Korea

The pressure and temperature dependence of hydrogen permeability in Ni-Nb-Ta ternary amorphous alloys will be described. The ribbon of Ni-Nb-Ta ternary amorphous alloys was produced on a single roller and thin film of Pd was coated on it by a sputtering method. The hydrogen permeation of Pd-coated Ni-Nb-Ta ternary amorphous alloy membrane was investigated within a temperature range of 573-723K under a pressure range of 0.3-0.5MPa, using a gas permeation technique. The amorphous and surface property of the amorphous alloy was examined in SEM, AES, AFM, DSC, and XRD analysis. From the XRD and SEM

analysis, it was clarified that the ribbon of Ni-Nb-Ta ternary alloy had amorphous character and no defects on its surface. Hydrogen permeability was increased with increasing the operating temperature and a difference of hydrogen pressure between input and output hydrogen pressure. Also during the permeation of hydrogen gas the surface characteristics of the amorphous membrane were not changed and there were no indications of interdiffusion of the metallic atoms in the membrane. The relationship between the diffusion and the hydrogen permeation of the Ni-Nb-Ta ternary amorphous alloy membrane will be discussed.

P-373 **Phase Evolution of Li_2ND LiD and $LiND_2$ in Hydriding/Dehydriding of Li_3N.** W. M. Chien,[1] D. Chandra,[1] A. Huq,[2] J. Richardson, Jr,[2] E. Maxey,[2] M. Kunz,[3] S. Fakra,[3] – [1]University of Nevada, Reno, NV, USA; [2]Argonne National Laboratories, IPNS, Argonne, IL, USA; [3]Lawrence Berkeley National Laboratories, Berkeley, CA, USA

Several studies have been performed on Li_3N and it hydrides after the pioneering work of, by Chen et al. [1]. For example, research by Ichikawa et al. [2], Meisner et al. [3], and Orimo et al. [4], Neutron and synchrotron studies have been performed on in-situ hydriding of Li_3N. Commercial Li_3N is composed of α phase (~70 wt.%) and β phase (~30 wt.%). In this study, we have performed thermal expansion studies between 10 to 300K of the α and β (both hexagonal phases). In this temperature range, the α phase has shown 0.56% and the β phase 1.1%. Further, we performed experiments to convert β→α, and then performed in-situ deuteration during neutron diffraction experiments. In this we found concurrent phase evolution of Li_2ND, LiD, and $LiND_2$. Mass percents of the phase evolved as a function of time and temperature have been quantified using GSAS refinement of the neutron diffraction data. The problem of formation of the stable LiD is discussed in light of decreasing of the amount of LiD phase when the temperature is increased from 200 to 320°C during dehydriding, and in addition the concentration of Li_2ND phase increased at this temperature. Lattice parameters, volume changes, phase evolutions in wt.% as a function of temperature and time will be presented. [1] P. Chen et al., *Nature* 420 (Nov. 2002) 302; [2] Ichikawa et al., *J. Alloys Compds.* 404-406 (2005) 435 and 439; [3] Meisner et al., *J. Alloys Compds.* 404-406 (2005) 24; [4] Nakamori and Orimo, *Materials Sci. and Engineering* B108, (2004), 48, and *J. Alloys Compds.* 370 (2004) 271. *This research Program support by US DOE, neutron experiments were performed at IPNS, Argonne.*

P-374 **Correlation Between Defects and Stress Level in MgD_2 Thin Films Studied by Positron Annihilation Spectroscopy and Thermal Desorption Analysis.** R. S. Brusa, R. Checchetto, N. Bazzanella, A. Miotello, – Dipartimento di Fisica dell'Università di Trento, Povo, Italy

Measurement on the D_2 desorption kinetics of nanocrystalline MgD_2 thin films have shown deuterium desorption peaks at temperatures lower than 390 K [1]. This temperature is lower than the temperature pertinent to bulk MgH_2 and to the mechanically milled nanocrystalline material. The low desorption temperature was explained by the presence of fast diffusion channels for D atoms in the nanostructured film and by lattice stresses due to the clamping effect of the Pd capping layer producing open volume defects, as evidenced by Positron Annihilation spectroscopy (PAS) [1]. In this paper we experimentally analyse the role of interface stresses due to the substrate on the deuterium desorption kinetics of Pd capped MgD_2 thin film. Mg films were grown by e-gun deposition on different substrate material (Si and g-C wafers, microscope glass) and than submitted to thermal treatment in D_2 atmosphere to promote the MgD_2 phase formation. The influence of the different substrates on the D_2 release was analysed by Thermal Desorption Analysis while the presence of different level of open volume defects and stresses was studied by PAS [2]. [1] R. Checchetto, N. Bazzanella, A. Miotello, R. S. Brusa, A. Zecca, P. Mengucci, J. Appl. Phys. 95, 1989 (2004); [2] R. S. Brusa, C. Macchi, S. Mariazzi, G. P. Karwasz, N. Laidani, R. Bartali, M. Anderle, Appl. Phys. Lett. 86, 221906 (2005).

P-375 **Hydrogen Trapping at Defects in Thin Nb Films Studied by Positron Annihilation.** J. Cizek,[1] I. Prochazka,[1] S. Danis,[1] O. Melikhova,[1] N. Zaludova,[1] M. Vlach,[1] G. Brauer,[2] W. Anwand,[2] A. Mücklich,[2] E. Nikitin,[3] R. Gemma,[3] R. Kirchheim,[3] A. Pundt,[3] C. Bähtz,[4] M. Knapp,[4] – [1]Faculty of Mathematics and Physics, Charles University, Prague, Czech Republic; [2]Institut für Ionenstrahlphysik und Materialforschung, Forschungszentrum Rossendorf, Germany; [3]Institut fur Materialphysik, Universität Göttingen, Germany; [4]Institut of Materials Science, Darmstadt University of Technology, Germany

Hydrogen trapping at defects in Nb films were investigated in this work. Thin Nb films were prepared by cold cathode sputtering at various temperatures. The films were covered by a thin Pd cap in order to prevent oxidation and to facilitate hydrogen absorption into the Nb layer. Microstructure of the as deposited films were characterized. The films sputtered at room temperature exhibit nanocrystalline grains. On the other hand, high temperature sputtering (T = 850°C) lead to formation of epitaxial films. Subsequently, the films were step-by-step electrochemically charged with hydrogen. Development of microstructure and evolution of defects with increasing hydrogen concentration were investigated by variable energy positron annihilation spectroscopy combined with X-ray diffraction. We have found that hydrogen in nanocrystalline films is trapped at open volume defects at grain boundaries. Formation of the β-phase (NbH) at higher hydrogen concentrations leads to introduction of new defects most probably dislocation loops emitted by the growing β-phase particles.

P-376 **Solubility and Diffusivity of Hydrogen in TiC.** T. Nozaki, H. Homma, Y. Hatano, – Hydrogen Isotope Research Center, University of Toyama, Toyama, Japan

Carbides of group 4 metals have unique physical and chemical properties such as extreme hardness and good resistance against chemical corrosion. Hence, systematic and quantitative survey of the interactions between these carbides and hydrogen may lead to the development of new functional materials. From this viewpoint, hydrogen absorption, desorption and diffusion in TiC was examined in the present study. Powder of TiC (99% in purity) supplied by Kojundo Chemical Lab. Co. was first analyzed by means of X-ray diffraction (XRD), and then hydrogen absorption was examined at 873 K and H_2 pressure from 1 Pa to 45 kPa. Diffusion coefficeint of hydrogen was evaluated from the absorption curves obtained in the high pressure region. Desprotion of hydrogen was also examined by heating hydrogen-charged specimen from room temperature to 973 K in a closed volume. XRD analysis showed

that the specimen had NaCl-type strucutre with lattice constant of 0.424 nm. No impurity phase was detected. Reversible hydrogen absorption and desorption were obeserved in the whole range of hydrogen pressure examined. The hydrogen content was 0.01 mol% at 1 Pa and 1 mol % at 45 kPa. Namely, the pressure dependence of hydrogen content was much weaker than that expected from Sieverts' law. No significant change was observed in the crystal structure and lattice constant after hydrogen absorption. The diffusion coefficent of hydrogen at 873 K was evaluated to be 10^{-16} m^2s^{-1}.

P-377 **First-Principles Study on Light-Element Materials for Hydrogen Storage.** T. Tsumuraya, T. Shishidou, T. Oguchi, – ADSM, Hiroshima University, Higashihiroshima, Japan

Light-element materials such as lithium amide $LiNH_2$, magnesium amide $Mg(NH_2)_2$ and lithium imide Li_2NH have been noticed as one of the most promising candidates for hydrogen storage due to their high gravimetric densities of hydrogen.The hydrogenating and dehydrogenating reaction mechanism and fundamental properties of these hydrides still remain as a matter to be investigated. In particular, the crystal structure of Li_2NH is not fully determined yet. Recently, various transition-metal compounds have been examined with ball-milling technique for exploring catalysis to promote reaction processes, and it is found that some of the Ti compounds show good performance for the lithium hydride system. Measurements of x-ray absorption spectroscopy (XAS) at Ti K-edge are currently under way to have a clue for understanding the catalysis mechanism. To address these issues and to get fundamental insights from microscopic point of view, we perform first-principles electronic structure calculations for light-element hydrides as well as catalytic materials by using all-electron full-potential linear augmented plane wave method. We also discuss structural stability and the heats of formation in reaction processes.

P-378 **Ammonia Borane (NH_3BH_3): Hydrogen Storage and Generation Catalyzed with Porous Hollow $Ni_{100-x}Pt_x$ (x=3, 6, 9, 12) Spheres.** H. Ma,[1] F. Cheng,[1] J. Chen,[1] Q. Xu,[2] – [1]Institute of New Energy Material Chemistry, Nankai University, Tianjin, P. R. China; [2]National Institute of Advanced Industrial Science and Technology, Ikeda, Osaka, Japan

The hydrolysis of ammonia borane (NH_3BH_3) associated with porous hollow metal/alloy catalysts at room temperature is a promising route for hydrogen generation. Submicrometer $Ni_{100-x}Pt_x$ (x=3, 6, 9, 12) hollow spheres, which were synthesized though the assistance of soft polymer spheres, are successfully employed as catalysts in the hydrolysis of NH_3BH_3. The as-synthesized $Ni_{88}Pt_{12}$ hollow spheres exhibit the highest catalytic activity, with which the reaction is completed in about 30 min with H_2 to NH_3BH_3 atomic ratio up to 3, corresponding to 8.9 wt% of the starting materials NH_3BH_3 and H_2O. It is also found that the high activity of $Ni_{88}Pt_{12}$ hollow spheres can be kept by increasing concentrations of the NH_3BH_3 solution. In addition, the probability of the products BO_2^- and NH_4^+ to NH_3BH_3 is also investigated primarily to realize the reversibility of the reaction. On the other hand, the as-synthesized $Ni_{88}Pt_{12}$ hollow spheres also demonstrated the catalysis of NH_3BH_3 thermolysis. The novel alloy hollow spheres are intriguing catalysts to meet the demand for on-board hydrogen storage/generation with ammonia borane.

P-379 **Does the Type/Origin of Carbon Nanotube Affect its Electrochemical Capacity for Hydrogen Storage?** X Qin, – Department of Chemistry, TianJin University, TianJin, P. R. China

In a comparative study of the electrochemical hydrogen storage capacity of various types of CNTs, three different kinds were synthesized and examined. The CNTs that were produced were: i) Aligned multi-walled carbon nanotubes (40 nm) prepared by the decomposition of C_2H_4 in the AAO templates, ii) normal multi-walled carbon nanotubes catalytically prepared by the decomposition of CH_4 on a surface of Ni-Mo/Mg_2O, and iii) Single-walled carbon nanotubes produced by catalytic arc-discharge using the $LaNi_5$ hydrogen storage alloy as a catalyst. Electrodes of each of these CNTs were prepared by pressing together a 1:10 mass ratio of CNTs to nickel powder in order to measure their electrochemical hydrogen storage capacity. Electrochemical measurements of CNTs were performed using a sintered nickel electrode as the counter electrode and an Hg/HgO electrode as the reference electrode in a 6 mol/l KOH electrolyte at room temperature under normal atmosphere. Results showed that electrodes produced from aligned CNTs showed the highest electrochemical discharging capacities i.e. up to 205 mAh/g (corresponding to a hydrogen storage capacity of 0.77 wt%). This was followed by single-walled CNTs (160mAh/g) and finally by catalytically prepared multi-walled CNTs (60 mAh/g). These results suggest that aligned CNTs produced by the AAO template method, could be promising materials for electrochemical hydrogen storage in the future. 1] Iijima S. Nature 1991, 354:56–8;] Thess, A; Roland, L; Pavel, N, et al., Science 1996, 273:483–7; [3] Geng, J.F.; Singh, C; Shephard, D.S., *et al.* Chem Commun. 2002, 2666-7; [4] Nutzenadel, C.; Zuttel, A.; Chartouni, D.; Schlapbach, L. Electrochem. Solid-State Lett. 1999, 2(1):30–2; [5] Dai, G.P.; Liu, C.; Liu, M., *et al.* Nano letters 2002, 2(5): 503-6; [6] Qin, X.; Gao, X.P.; Liu, H., *et al.* Electrochem. Solid-State Lett. 2000, 3 (12):532–5; [7] Gao, H.; Wu, X.B.; Li, J.T., *et al.* Appl.Phys.Lett. 2003, 83(16),3389-91.

P-380 **Magnetic Carbon Hydride.** V. A. Somenkov,[1] S. A. Lushnikov,[2] – [1]Russian Research Center "Kurchatov Institute", Moscow, Russia; [2]Moscow State University, Moscow, Russia

Have been revealed a formation of the graphitelike crystal phase through interaction of amorphous ballmilling fullerenes with hydrogen at pressure exceeding 100 atm and temperature more 400^0C with $c \approx c_{gr}$, $a \approx 2a_{gr}$ and composition close to CH_x with $x \approx 0.5$. This phase has clearly expressed ferromagnetic properties, which have been stable during nine month. The structure of this compound has been studied by X-ray and neutron diffraction and properties have been investigated with magnetic methods. The work has been supported by RFBR under the grants 06-02-17062, 06-02-17515.

P-381 **Hydrogen-Initiated Synthesis of Indium Antimonide in the Presence of Aluminum Hydride.** I. Sh. Normatov, N. Shermatov, – Institute of Chemistry, Academy of Sciences Republic of Tajikistan, Dushanbe, Tajikistan

Fine-particle indium antimonide was prepared by continuously bombarding Sb_2S_3, + In and Sb_2O_3 + $InCl_3$ mixtures with hydrogen atoms in the presence of aluminum hydride. The reaction intermediates were identified by x-ray diffraction. Atomic hydrogen was generated in an rf plasma reactor by passing hydrogen gas through the discharge produced between two electrodes, one connected to the feeder of an rf generator and the other grounded. The starting chemicals used were extra pure-grade Sb_2S_3, reagent-grade $InCl_3$, reagent-grade Sb_2O_3, and Extra-grade In.Sb_2S_3 and In (1 : 1) were mixed under a flowing inert gas. The mixture (5 g) was placed on a quartz substrate, which was then introduced into the reactor. After pumping to 0.13 Pa and purging with hydrogen, the hydrogen pressure in the reactor was set at -70 Pa. The chemical transformations induced in the reaction system by hydrogen bombardment were followed by x-ray diffraction (XRD). X-ray patterns were taken on a DRON-1.5 powder diffractometer (CuK_α radiation) at -30 min intervals.Since aluminum hydride was shown earlier to appreciably accelerate some chemical reactions, we examined the processes in mixtures of Sb_2S_3 and In with aluminum hydride additions. In that case, notable changes in the XRD pattern were detected after just 40 min of bombardment. With increasing bombardment duration, the reflections from InSb became progressively stronger. After 240 min of hydrogen bombardment, the XRD pattern showed a set of reflections due to InSb and Al metal. InSb was found to have a cubic structure with a lattice parameter a = 6.475 ± 0.005 Å. The heterogeneous reaction in a mixture of Sb_2O_3 and $InCl_3$ with aluminum hydride additions under hydrogen bombardment was studied with the aim of assessing the nature of the reaction intermediates and their role in the formation of fine-particle InSb (in the Sb_2S_3-In system, we failed to detect reaction intermediates). The effect of bombardment duration on the phase composition of the reaction products in this system is illustrated that hydrogen bombardment for 80 min led to the formation of antimony oxychloride. After bombardment for 200 min, the peaks from SbOCl were missing, and the XRD pattern showed peaks from $SbCl_3$, $Al(OH)_3$, and In. After 300 min, we observed sharp reflections from InSb and Al_2O_3. Hydrogen atoms bombarding the mixture recombine on its surface to release an energy of 434 kJ/mol, which causes local heating and gradual decomposition of aluminum hydride. The hydrogen atoms resulting from this process are involved in exchange reactions. In the case of the Sb_2S_3 + In mixture, they react with In to form the volatile compound InH, which then adsorbs on the surface of Sb_2S_3. The subsequent exchange reaction yields InSb. This process is favored by the generation of anion vacancies in Sb_2S_3, under hydrogen bombardment. InSb may also be formed by mechanism — through adsorption of the volatile compound SbS on the In surface. This mechanism is, however, unlikely, because the affinity of In for S is much higher than that of Sb for In, and the interracial reaction of SbS with In would, most likely, yield InS, which was not detected in our studies. The formation of InSb from mixtures of Sb_20_3 and $InCl_3$ under hydrogen bombardment may follow the next mechanisms: The hydrogen atoms resulting from the decomposition of aluminum hydride reduce $InCl_3$ to metallic In. The forming hydrogen chloride adsorbs on the Sb_2S_3 surface. Subsequent exchange reactions yield antimony oxy-chlorides and, finally, $SbCl_3$. Atomic hydrogen reacts with indium metal to form InH, which then adsorbs on the surface of $SbCl_3$ and reacts with it to form InSb. Concurrently, aluminum hydride hydrolyzes to $Al(OH)_3$, which then decomposes.Our XRD studies showed that powder InSb can be prepared by continuously bombarding Sb_2S_3+ In and Sb_2O_3 + $InCl_3$ mixtures with hydrogen atoms. In this process, gaseous reaction intermediates and aluminum hydride play a key role.

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