

A remarkably clear experiment has been designed in order to investigate the influence of stress on reactive diffusion in spherical symmetry. Thin film Al/Cu/Al and Cu/Al/Cu triple layers with approximately 10 nm single layer thickness are deposited on curved substrates of 25 nm radius and investigated by atom probe tomography. The experiments demonstrate that the reaction rate depends significantly on the deposition sequence of the metals. The thickness of the product formed at the interfaces at which Cu is deposited on top of Al is approximately 1.5 to 2 times thicker than that of the opposite stacking sequence. This observation may be explained naturally by Laplace tension of the curved interfaces. By quantitative analysis, the level of induced stress can be determined from the modified growth rates.

MM 38.5 Thu 12:45 H 0111

Twinning during low-temperature deformation of nanocrystalline pulsed-electrodeposited nickel — ●KLEMENS REUTHER, LUTZ HOLLANG, and WERNER SKROTZKI — Institut für Struktur-

physik, Technische Universität Dresden, 01062 Dresden

Pure 'nanocrystalline' nickel was produced by pulsed electro-deposition without additives for grain refinement. The average grain size of the material is $d_{EBSD} = 150$ nm and $d_{XRD} = 30$ nm if determined by electron backscatter diffraction (EBSD) and by X-ray diffraction (XRD), respectively. Tensile tests between 4 K and 320 K reveal that the material is ductile in the whole temperature range. Generally, the stress-strain curves are parabolic and the stress reaches its maximum after about two percent plastic strain, with the ultimate stress strongly increasing with decreasing temperature. However, there exists a critical temperature $T_T = 9$ K below which the deformation mode suddenly changes towards twinning if the stress level reaches 2400 MPa. The twinning events are characterized by substantial stress drops accompanied by loud acoustic emissions. The microstructural changes connected with twinning will be discussed on the basis of results obtained by scanning and transmission electron microscopy.

MM 39: SYM Hydrogen in Materials: New Developments III

Time: Thursday 14:00–16:00

Location: H 1058

Invited Talk

MM 39.1 Thu 14:00 H 1058

Hydrogen Chemisorption to Clusters — ●GERD GANTEFOER — Department of Physics, University of Konstanz, Germany

The properties of nanoclusters consisting of up to 100 atoms are different from the ones of the corresponding bulk materials. Their geometric and electronic structures change with each additional atom. As a consequence chemical properties also vary dramatically with size. The interaction of such nanoparticles with hydrogen exhibits a broad variety of new and unexpected effects. E.g., single hydrogen atoms behave like gold atoms if attached to a small Au cluster. The interaction of small Al clusters with atomic hydrogen results in the formation of a new, previously unknown family of Aluminum hydrides. These examples demonstrate, that chemistry of nanoclusters is different and provides a new approach to the problem of hydrogen storage.

Invited Talk

MM 39.2 Thu 14:30 H 1058

Hydrogen Storage in Light Weight Metal Hydrides: Mg-based Reactive Hydride Composites — ●M. DORNHEIM, U. BÖSENBERG, C. PISTIDDA, G. BARKHORDARIAN, J. BELLOSTA V. COLBE, and R. BORMANN — GKSS-Research Centre Geesthacht, Institute of Materials Research, Max-Planck-Str. 1, 21502 Geesthacht, Germany

Compared to conventional room temperature hydrides light weight metal hydrides have much higher gravimetric hydrogen storage densities. However, kinetic and/or thermodynamic restrictions limit the potential use of such high capacity hydrides. There is still a large number of hydrides with high storage capacities which have to be considered as irreversible or at least require high pressures and/or very high temperatures for reversible hydrogenation / dehydrogenation as well as very long absorption and desorption times. Prominent examples are borohydrides like LiBH_4 . Another crucial parameter is the reaction enthalpy. Most of the past attempts to alter and tailor the hydrogen reaction enthalpy of light weight metal hydrides like Mg either failed or led to dramatically reduced gravimetric hydrogen storage capacities. An exciting and promising novel approach is the concept of the Reactive Hydride Composites (RHC). RHC consisting of MgH_2 and borohydrides show significantly reduced total reaction enthalpies as well as improved ab- and desorption kinetics compared to the pure borohydrides while a high hydrogen storage capacity is maintained [1]. In this talk, an overview on the sorption behaviour of the doped nanocrystalline RHCs $2\text{LiBH}_4 + \text{MgH}_2$, $2\text{NaBH}_4 + \text{MgH}_2$ and $\text{Ca}(\text{BH}_4)_2 + \text{MgH}_2$ will be given.

[1] Scripta Materialia 56 (2007) 841-846.

MM 39.3 Thu 15:00 H 1058

Direct synthesis of LiBH_4 monitored by in-situ neutron diffraction — ●ARNDT REMHOF¹, OLIVER FRIEDRICHS¹, FLORIAN BUCHTER¹, ANDREAS ZÜTTEL¹, and DIRK WALLACHER² — ¹EMPA, Swiss Federal Laboratories for Materials Research, Dübendorf, Switzerland — ²Hahn Meitner Institut, Berlin Neutron Scattering Facility, Berlin, Germany

Due to its large hydrogen content, LiBH_4 is a promising candidate for

a hydrogen storage material. Recently, we discovered a way to synthesize LiBH_4 directly from the respective elements, by exposing Li and B to hydrogen gas at high temperatures 700°C and at high pressures (150 bar) [1]. The synthesis can be facilitated by using intermetallic Li-B compounds as starting material. We have shown by in-situ neutron powder diffraction that starting from an intermetallic Li-B compound LiBD_4 can be synthesized at 180bar at a temperature of 350°C, which is about 350°C lower than the temperature required for the direct synthesis [1,2]. The experiment was carried out at the powder diffraction instrument E6 of the Hahn Meitner Institut. Support by A. Hoser and N. Stüsser is gratefully acknowledged. Financial support from the 6th Framework Program of the European Commission (NESSHY Contract No.: 518271) and the Swiss Federal Office of Energy is acknowledged.

[1] O. Friedrichs et al., Acta Materialia, in press

[2] D. Goerrig, Deutsches Patent; Auslegungsschrift (1960)

MM 39.4 Thu 15:20 H 1058

Refinement of the phonon analysis in the complex hydride systems LiBH_4 and LiBD_4 — ●ANA MARIA RACU¹, JOACHIM SCHOENES¹, ZBIGNIEW LODZIANA², ANDREAS BORGSCULTE², and ANDREAS ZÜTTEL² — ¹Institut für Physik der Kondensierten Materie, Technische Universität Braunschweig, Germany — ²EMPA Materials Sciences and Technology, Div. Hydrogen and Energy, Dübendorf, Switzerland

In the present study we have performed low temperature micro Raman measurements on small LiBH_4 and LiBD_4 crystals. At the lowest temperature, the spectra compare very well with the calculated phonons for the orthorhombic structure. The spectra are dominated by three separated bands: the external modes, the internal bending and the internal stretching vibrations. Internal refers to vibrations within the BH_4^- tetrahedra while external modes imply motions of Li^+ and BH_4^- . The temperature dependence of the observed phonons corroborates the strong anharmonicity of the system. Due to the anharmonicity, Fermi resonances occur between the first order stretching modes and the second order bending modes of LiBH_4 . Moreover, the linewidths have an Arrhenius-like component, with an activation energy of 40 meV. This value corresponds to the energy of the librational mode determined by inelastic neutron scattering [1] and is strongly related to the reorientation motions of the BH_4^- tetrahedra.

[1] J. Tomkinson, T. C. Waddington, J. Chem. Soc. Faraday Trans 2 72, 528 (1976).

MM 39.5 Thu 15:40 H 1058

Hydrogen release of $\text{Mg}(\text{BH}_4)_2$ under helium and hydrogen backpressure — ●WIEBKE LOHSTROH, NOBUKO HANADA, CHRISTOPH FROMMEN, and MAXIMILIAN FICHTNER — Institut für Nanotechnologie, Forschungszentrum Karlsruhe GmbH, Postfach 3640, 76021 Karlsruhe

$\text{Mg}(\text{BH}_4)_2$ is one of the potential materials to be used in solid state hydrogen storage systems due to its high capacity of 14.9 wt% H_2 and a favourable reaction enthalpy. However, experimentally, hydrogen is only released at temperatures above 300 °C. Depending on the surrounding gas atmosphere (helium or hydrogen) and the applied backpressure several decomposition steps are observed. We will present

thermal analysis and structural investigations at various stages of the

decomposition and the hydrogen release mechanism will be discussed.

MM 40: SYM Hydrogen in Materials: New Developments IV

Time: Thursday 16:30–18:00

Location: H 1058

Invited Talk MM 40.1 Thu 16:30 H 1058
Complex Metal Hydrides — ●MICHAEL FELDERHOFF — Max-Planck-Institut für Kohlenforschung, Kaiser Wilhelm Platz 1, 45470 Mülheim / Ruhr

One important feature for a commercial success of PEM fuel cell for mobile applications is the improvement of the hydrogen storage system. Since the physical storage methods are limited, solid state hydrogen storage are in the focus of research activities. The classical metal hydrides have storage capacities not higher than 2 wt.%. Compared to these materials the storage capacities of the complex metal hydrides are much higher. Sodium aluminium hydride (NaAlH₄) is one of the most interesting material, because it is fully reversible, the thermodynamic properties and the storage capacities are close to the technical requirements for on-board hydrogen storage. The recent work for optimization of the complex metal hydrides and to understand the molecular processes during the de- and rehydrogenation reactions will be summarized.

MM 40.2 Thu 17:00 H 1058

XRD, XPS and Raman analysis of metal and complex hydrides — ●ISABEL LLAMAS JANSÁ¹, CARINE RONGEAT¹, STEFFEN OSWALD², ANGELIKA TERESIAK², MARTIN KALBÁČ³, and OLIVER GUTFLEISCH¹ — ¹IFW Dresden, Institute for Metallic Materials, P.O. Box 270016, D-01171 Dresden, Germany — ²IFW Dresden, Institute for Complex Materials, P.O. Box 270016, D-01171 Dresden, Germany — ³IFW Dresden, Institute for Solid State Research, P.O. Box 270016, D-01171 Dresden, Germany

X-ray diffraction (XRD), photoelectron spectroscopy (XPS), and Raman spectroscopy, preferentially as in-situ techniques, are valuable tools for the characterisation of the chemical state and structure of doped metal- and complex-hydrides and their intermediate products upon absorption and desorption. Examples for ex- and in-situ characterisation of the evolution with temperature and pressure of doped-NaAlH₄ [1] and reactive hydride composites [2] (e.g. LiBH₄ + MgCl₂) are discussed. XPS surface analyses indicated the complete decomposition of the catalyst in the case of TiCl₃ doped NaAlH₄ samples, whereas samples doped with ScCl₃ and CeCl₃ still showed traces of the chloride phases. Raman results demonstrated the formation of the Mg(BH₄)₂ phase after high-pressure ball milling (HP-BM) of a LiBH₄ + MgCl₂ mixture for 12 h. Finally, in-situ XRD was used to monitor the transition from tetrahydride (NaAlH₄) into the hexahydride (Na₃AlH₆) phase during desorption of sodium alanate.

[1] C. Rongeat, I. Llamas-Jansa, and O. Gutfleisch, in preparation

(2007)

[2] U. Boesenberg et al., Acta Materialia 55, 3951 (2007)

MM 40.3 Thu 17:20 H 1058

Seeing Hydrogen — ●ANDREAS BORGSCHULTE — EMPA Materials Science and Technology, Hydrogen & Energy, Überlandstrasse 129, CH-8600 Switzerland

The fact that hydrogen absorption in metals leads to large optical changes is the basis of a new combinatorial method called hydrogenography. We show that hydrogenography provides a high-throughput method to measure quantitatively the key thermodynamic properties (equilibrium properties like heat of absorption and kinetics) of hydride formation. The optical setup involves a good accessibility of the sample, which enables us the measurement of the impact of electric fields on the hydrogen absorption process. We demonstrate that an electric current and the thereby induced heat and electromigration of H⁻ ions can start and control the absorption of hydrogen in Mg thin films. We describe how the optical technique on thin films can be transferred to measure hydrogen dynamics in bulk materials by means of Raman spectroscopy.

MM 40.4 Thu 17:40 H 1058

Opto-mechanical high-throughput characterization of composition spread thin films for the development of new hydrogen storage materials — ●ALFRED LUDWIG^{1,2}, JIALIN CAO², ALAN SAVAN², MICHAEL EHMANN², and HANS-WERNER BECKER³ — ¹Institut für Werkstoffe, Ruhr-Universität Bochum — ²Combinatorial Materials Science, caesar, Bonn — ³Institut für Physik mit Ionenstrahlen, DTL Labor, Ruhr-Universität Bochum

An opto-mechanical high-throughput characterization method was used for the investigation of hydrogen storage materials within the system Mg-B-Ti-Pd. The materials were deposited by magnetron sputtering in form of thin film composition spreads on micromachined Si cantilever arrays. The thin films were characterized by EDX and XRD prior and after hydrogen loading. In a special pressure vessel, the mechanical stress-changes of the coated cantilevers as a function of hydrogen pressure (0.1 to 5.1 MPa) and temperature (20 to 450°C) was measured in parallel using the optical technique. These stress-changes are related to the hydrogen uptake/release of the different materials. The most promising thin films which showed hydrogen storage were further analyzed by RBS and NRA. The latter was used to determine the hydrogen content of the thin films and its depth distribution.

MM 41: Poster SYM Hydrogen in Materials: New Developments

Time: Thursday 18:00–20:00

Location: Poster B

MM 41.1 Thu 18:00 Poster B

Beyond the featureless particle approximation: An extension of quantum-liquid density-functional theory to account for rotational effects. — ●SERGEI YURCHENKO¹, SERGUEI PATCHKOVSKI², THOMAS HEINE¹, and GOTTHARD SEIFERT¹ — ¹Institut für Physikalische Chemie und Elektrochemie, TU Dresden, D-01069 Dresden, Germany — ²Stacie Institute for Molecular Sciences, NRC Canada, 100 Sussex Drive, Ottawa, Ontario, K1A 0R6 Canada

In a different contribution we present QLDFT (Quantum Liquid Density Functional Theory), a Kohn-Sham based extension to DFT for liquids, to describe the adsorption properties of molecules in host structures under consideration of quantum effects. In QLDFT the individual molecules are treated as featureless particles, and rotational contributions to the free energy are neglected. However in the vicinity of strong charges the featureless particle approximation breaks down and rotational contributions become important even at ambient conditions.

We present an extension of QLDFT to account for rotational effects. Then, we apply this new method to examine the effect of electric field-

induced interactions on hydrogen adsorption. These interactions initiated by the atomic charges are stronger than dispersive interactions and can facilitate the H₂/host binding, which can potentially lead to the increase of the hydrogen adsorption. We present results of simulations of the hydrogen adsorption for a number of model and real structures. We analyze the rotational and spatial probability distributions of the adsorbed hydrogen both with slow and fast varying atomic charge fluctuations.

MM 41.2 Thu 18:00 Poster B

Hydrogen Adsorption in Metal-Organic Frameworks — ●IRENA SENKOVSKA and STEFAN KASKEL — Department of Inorganic Chemistry, Technical University Dresden, Germany

Metal-Organic Frameworks (MOFs) have recently received considerable attention because of their high specific micropore volume and the ability to store gas molecules exceeding the storage capacity of traditional adsorbents. A variety of differences in the MOFs structures makes it difficult to analyze the influence of different factors on