

MM 49: Hydrogen in Metals

Time: Friday 10:15–11:45

Location: IFW D

MM 49.1 Fri 10:15 IFW D

Universal trends for the solubility of hydrogen in non-magnetic 3d transition metals derived from first principles — ●UGUR AYDIN, LARS ISMER, TILMANN HICKEL, and JÖRG NEUGEBAUER — Max-Planck Institut für Eisenforschung

Hydrogen is an omnipresent element in many materials which may cause materials failure (e.g. hydrogen embrittlement) or maybe used for hydrogen storage. Therefore a detailed understanding/prediction of H solubility (energetics) and kinetics in metals is crucial. In order to identify chemical trends for the solubility and mobility of hydrogen in metals we have performed an extensive ab initio study. Since the number of valence electrons was supposed to have a decisive influence on the quantity, the complete set of all 3d transition metals has been studied under comparable conditions (pure elements, no magnetism, identical fcc lattice structure). With respect to the site preference of the hydrogen atom in these metals, we have identified two different classes, with either the octahedral or the tetrahedral interstitial site being preferred. The corresponding H solution enthalpies, calculated for different lattice constants of the host metal, revealed a remarkable universal trend for all elements. The universal curve has a minimum formation energy (i.e. maximum hydrogen solubility) at a critical fcc lattice constant of ≈ 4.6 Å. Analyzing the data we find that the shape of the curve is a consequence of a volume dependent contribution and the specific electronic configuration of the host material. Based on these results we discuss strategies to identify systems with a optimum H solubility.

MM 49.2 Fri 10:30 IFW D

Hydrogenation Behaviour of Titanium Thin Films — ●ERVIN TAL-GUTELMACHER, RYOTA GEMMA, ASTRID PUNDT, and REINER KIRCHHEIM — Institute for Materials Physics, University of Goettingen, Friedrich-Hund-Platz 1, 37077 Goettingen

Titanium films of different thicknesses were prepared on sapphire substrates in an UHV chamber, by means of ion beam sputter deposition under Ar-atmosphere at the pressure of $1,5 \cdot 10^{-4}$ mbar. For electrochemical hydrogen loading, the films were covered by a 30 nm thick layer of Pd in order to prevent oxidation and facilitate hydrogen absorption. In-situ stress measurements were conducted during step-by-step electrochemical hydrogen charging of the films. XRD measurements using a Phillips X-Pert diffractometer with a Co-K α radiation were performed before and after hydrogenation in order to investigate the effect of hydrogen loading on the microstructure. The phase boundaries, as well as the stress and strain development during hydrogen absorption, depend strongly on the crystallographic growth orientation of the films. The main characteristics of absorption behaviour of hydrogen, as well as the thermodynamics and phase boundaries of titanium-hydrogen thin films are discussed in detail with specific emphasis on the comparison to titanium-hydrogen bulk system. Shifted grain boundaries and narrowed two-phase field appear in Ti-H film system, which are mainly attributed to the microstructural contribution, as well as to the large stresses in the GPa-range that built up between the films and their substrate.

MM 49.3 Fri 10:45 IFW D

Quantitative determination of the hydrogen in zirconium with high spatial resolution by means of neutron radiography — ●MIRCO GROSSE — Forschungszentrum Karlsruhe, Germany

Due to the high total neutron cross section of hydrogen, neutron radiography is a powerful tool for quantitative hydrogen determination in a lot of materials with a spatial resolution up to 0.030 mm.

As example, studies of the hydrogen uptake during steam oxidation of zirconium based alloys applied as nuclear fuel cladding materials are given.

Correlation parameters between the total neutron cross section of the sample and its hydrogen content were determined. At H/Zr atomic ratios lower than 1.0, linear correlations between the hydrogen content and total cross section exist. The total cross section of Zr is lower and the effect of the hydrogen is higher in radiography measurements with a cold neutron spectrum than with a thermal spectrum.

After an initial phase a dynamical equilibrium is established between the hydrogen released into the gas phase and absorbed into the remaining metal. Due to the parabolic oxidation kinetics the hydrogen

concentration decreases by the power of $-1/4$ with time.

The method provides also the possibility of in-situ measurements. Examples for the hydrogen uptake during isothermal steam oxidation will be given.

MM 49.4 Fri 11:00 IFW D

A multiscale study of hydrogen embrittlement in metals: The hydrogen enhanced local plasticity (HELP) mechanism — ●JOHANN VON PEZOLD and JÖRG NEUGEBAUER — Max Planck Institut für Eisenforschung GmbH, Düsseldorf, Germany

The embrittlement of metals by H is a long-standing problem, whose underlying mechanisms are still largely unclear. In this study we consider the atomistic basis of the HELP mechanism, which asserts that H mobilises dislocations by shielding elastic dislocation-dislocation and dislocation-solute interactions.

Using a combination of density-functional theory calculations, semiempirical EAM potentials and an effective lattice gas Hamiltonian we determine the effect of H on the stress field around edge dislocations in fcc metals. The density of the H distribution around the dislocation core is determined by the H-H interaction: weak H-H interactions give rise to a dilute H distribution, while attractive H-H interactions entail a dense H distribution. The stress field around the dislocation in the presence of a dilute and a dense H distribution is used to critically discuss the H-induced shielding effect postulated by the HELP mechanism.

MM 49.5 Fri 11:15 IFW D

Atom probe tomography analyses of deuterium distribution in Fe/V multi-layered films — ●RYOTA GEMMA, TALAAT AL-KASSAB, REINER KIRCHHEIM, and ASTRID PUNDT — Institut fuer Materialphysik, Friedrich-Hund-Platz 1, D-37077, Goettingen, Germany

Recently, the interaction of hydrogen with metallic multi-layered thin films remains as a hot topic. A detailed knowledge on such chemically modulated systems is required if they are desired for application in hydrogen energy system as storage media. In this study, the deuterium (D) concentration profile of Fe/V multi-layer was investigated by atom probe tomography (APT) between 60 and 20 K. It is firstly shown that a deuterium-loaded sample can easily react with oxygen at Pd capping layer on Fe/V and therefore, it is required to avoid any oxygen exposure after D₂ loading before APT analysis. The analysis temperature also has an impact on the D concentration profile. The results taken at 60 K show clear traces of surface segregation of D atoms diffusing towards the analysis surface. The observed diffusion profile of D regarding analysis time allows us to estimate an apparent diffusion coefficient. The calculated diffusion coefficient at 60 K is in the order of 10^{-17} cm²/s which deviates about 6 orders of magnitude from a value extrapolated from high temperatures. Below 30 K, the D concentration profile shows no segregation anymore and a homogeneous distribution with $c_D = 0.05(2)$ D/Me, which is in good accordance with that measured in corresponding pressure-composition isotherm of H-Fe/V system.

MM 49.6 Fri 11:30 IFW D

Study of complex hydrides prepared by mechano-chemical synthesis — ●CARINE RONGEAT, CHRISTIAN GEIPEL, and OLIVER GUTFLEISCH — IFW Dresden, Institute for Metallic Materials, P.O. Box 270116, D-01171 Dresden, Germany

Ball milling has been widely used for the synthesis of metal hydrides, e.g. MgH₂, with high sorption performances. However, metal hydrides cannot address the requirements imposed for solid state hydrogen storage in mobile application. A new class of hydrides, the complex hydrides are attracting much interest due to their high capacity and predicted moderate temperature of operation. High-pressure reactive milling with in-situ monitoring the pressure and temperature was applied to the synthesis of NaAlH₄ doped with different additives. Useful information on the kinetic properties of the compound could be derived from this system already during synthesis. The same system was applied for the synthesis of Ca(BH₄)₂ but different results were obtained due to the higher stability of the boride compounds used. Finally, another route for the synthesis of complex hydride is to performed the metathesis reaction during milling, e.g. the synthesis of Mg(BH₄)₂ can be obtained (with LiCl) by the reaction between LiBH₄

and MgCl₂. All the compounds synthesized by mechano-chemical synthesis are analyzed by means of advanced structural characterization

techniques (Raman spectroscopy, XPS, in-situ XRD). Their hydrogen sorption properties were also studied by various methods (DSC, TGA).