

MM 22: Hydrogen in Metals

Time: Tuesday 10:15–11:30

Location: H5

MM 22.1 Tue 10:15 H5

First-principles and thermodynamic description of hydrogen interaction with vacancies in fcc iron — ●ROMAN NAZAROV, TILMANN HICKEL, and JOERG NEUGEBAUER — Max-Planck-Institut für Eisenforschung GmbH, Duesseldorf, Germany

Several mechanisms of hydrogen embrittlement are associated with a significant increase of the vacancy concentration in a H-rich atmosphere. These superabundant vacancies can form vacancies clusters or even microvoids in regions of high stress (for example crack tips), facilitate the formation of brittle phases and reduce elastic properties of crystalline structure.

In order to reveal the physics of this phenomenon we have employed density-functional theory (DFT) together with thermodynamic concepts. Our systematic comparison of isolated and hydrogen loaded vacancies in fcc iron with various magnetic configurations reveals that hydrogen reduces the formation energy of a vacancy. This decrease can be significant, as up to 6 hydrogen atoms can be incorporated into a vacancy.

Based on our ab-initio results we developed a thermodynamic model which determines the concentrations of vacancies, of hydrogen in different interstitial positions and of vacancy-hydrogen complexes as a function of pressure, temperature and external hydrogen chemical potential. Applying this model we find dramatically increased vacancy concentrations and total hydrogen concentration in fcc iron if the material is exposed to a H-rich atmosphere.

MM 22.2 Tue 10:30 H5

First-principles studies of the La-H system — GUNTHER SCHÖLLHAMMER¹, PETER HERZIG¹, WALTER WOLF², ●TOBIAS KERSCHER³, and STEFAN MÜLLER³ — ¹Institut für Physikalische Chemie, Universität Wien, 1090 Wien, Austria — ²Materials Design s.a.r.l., 72000 Le Mans, France — ³Universität Erlangen-Nürnberg, Lehrstuhl für Theoretische Physik 2, Staudtstr. 7, 91058 Erlangen, Germany

The LaH system is the epitome of an interesting candidate for theoretical investigations: Its structural details are still not well understood, and – at $\text{LaH}_{\approx 2.8}$ – a concentration-dependent metal-insulator transition (“switchable mirror”) is observed. At low H concentrations our first-principles study found a preference of the H atoms for the occupation of the octahedral interstitial sites instead of the expected tetrahedral sites. Close to LaH_3 a stabilization of the structure either by an orthorhombic distortion or by the presence of (pairs of) H vacancies was observed. This coincides with opening up a band gap predicted via density functional theory [1]. Recently we have applied the cluster-expansion approach (see e.g. [2]) in the framework of the UNCLE code [3] in order to study configurational diversity. The objective is the calculation of a phase diagram from first-principles.

[1] G. Schöllhammer, W. Wolf, P. Herzig, K. Yvon, P. Vajda, *J. Alloys Comp.* **480**, 111–113 (2009)

[2] S. Müller, W. Wolf, R. Podloucky, *Ab-initio Methods and Applications*, in *Alloy Physics*, ed. W. Pfeiler, Wiley 2007

[3] D. Lerch *et al*, *Modelling Simul. Mater. Sci. Eng.* **17**, 055003 (2009)

MM 22.3 Tue 10:45 H5

Strain-induced metal-hydrogen interactions across the first transition series: An ab initio study of hydrogen embrittlement — ●JOHANN VON PEZOLD, LIVERIOS LYMPERAKIS, and JÖRG NEUGEBAUER — Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf, Deutschland

The attractive interaction between hydrogen and distorted regions of the host matrix underlies all the currently discussed mechanisms of

hydrogen-induced embrittlement of metals, such as hydrogen enhanced local plasticity (HELP), hydrogen enhanced decohesion (HEDE) and stress-induced hydride formation. In this study we investigate these interactions systematically by determining heat of solutions, H-H binding energies within the metal matrix, as well as phase diagrams as a function of the lattice strain and the H chemical potential across the first transition series (3d elements) using density functional theory (DFT) calculations. It will be shown that these provide a very direct insight and allow an identification of the likely embrittlement mechanisms within these metals.

MM 22.4 Tue 11:00 H5

Li-Al-borohydride as a potential candidate for on-board hydrogen storage — ●INGE LINDEMANN¹, ROGER DOMÈNECH FERRER¹, LOTHAR DUNSCH¹, YAROSLAV FILINCHUK², HANS HAGEMANN³, RADOVAN ČERNÝ³, LUDWIG SCHULTZ¹, and OLIVER GUTFLEISCH¹ — ¹IFW Dresden, PO Box 270016, D-01171 Dresden, Germany — ²Swiss-Norwegian Beam Lines at ESRF, BP-220, 38043 Grenoble, France — ³University of Geneva, Crystallography and Physical Chemistry Department, 1211 Geneva, Switzerland

Recently, double-cation borohydride systems have attracted great interest. It was found that the desorption temperature of the borohydrides decreases with increasing electronegativity of the cation. Consequently, it is possible to tailor a feasible on-board hydrogen storage material by combination of appropriate cations. Li-Al-borohydride shows a desorption temperature suitable for applications ($\approx 70^\circ\text{C}$) combined with an high hydrogen density (17.2 wt.%). It was synthesised via high energy ball milling of AlCl_3 and LiBH_4 . The structure of the compound was obtained from high-resolution synchrotron powder diffraction and shows a unique complex structure within the borohydrides. The material was characterized by means of in-situ-Raman, DSC, TG and thermal desorption measurements to study its decomposition pathway. The desorption at $\approx 70^\circ\text{C}$ results in the formation of LiBH_4 while the high mass loss of about 20% points to the release of not only hydrogen but also diborane. This is right now the main drawback for applications because it hinders reversibility.

MM 22.5 Tue 11:15 H5

Effects of recrystallization on the deuterium retention in tungsten — ●ARMIN MANHARD and KLAUS SCHMID — Max-Planck-Institut für Plasmaphysik, EURATOM Assoziation, Boltzmannstr. 2, 85748 Garching

Tungsten is a promising material for plasma-facing surfaces in nuclear fusion devices such as ITER. In these machines the surface material is exposed to large fluxes and fluences of hydrogen isotope ions and energetic neutrals. The retention of hydrogen isotopes in tungsten is generally considered small. The underlying mechanisms are yet only poorly understood despite continued research efforts. Especially the microstructure of the material can have a large influence on the hydrogen inventory.

To investigate this, the microstructure of tungsten samples from the same base material is systematically modified by recrystallization. After a thorough characterization by electron microscopy, strongly deformed samples and samples recrystallized by different degrees are loaded with deuterium in a low-temperature plasma device. The ion energy is adjusted by sample biasing. The deuterium inventory is then measured by nuclear reaction analysis and thermal effusion spectroscopy. The surface morphology is investigated by optical and atomic force microscopy. Microscopic markers applied to the sample surface allow to observe the identical surface region after each treatment step. The results are presented and compared for the different microstructures.