

MM 20: Topical session (Symposium MM): Hydrogen in Materials

Hydrogen absorption in nano-materials

Time: Tuesday 10:15–13:00

Location: H 0107

Topical Talk MM 20.1 Tue 10:15 H 0107**Sensing Hydrogen with (Single) Nanoparticles** — ●CHRISTOPH LANGHAMMER — Chalmers University of Technology, Göteborg, Sweden

Using particles as signal transducers in a hydrogen sensor offers the ultimate miniaturization limit of the single nanoparticle. At the same time, metallic nanoparticles exhibit localized surface plasmon resonance, which provides unique opportunities for optical sensing. In this talk, I will discuss the concept of (single nanoparticle) nanoplasmonic hydrogen sensing on two examples:

A plastic-plasmonic optical hydrogen sensor platform using PdAu alloy nanoparticles embedded in a polymer matrix acting as molecular sieve, which enables deactivation-resistant hysteresis-free hydrogen detection with unprecedented sub-second response time at room temperature, and with sub-5 ppm detection limit.

Single nanoparticle plasmonic hydrogen sensing as a tool to unravel size- and shape effects in the thermodynamics and hysteresis of metal-hydrogen interactions in individual Pd nanocrystals with different size and shape, as well as to understand the role of grain boundaries in the hydrogenation process of individual polycrystalline Pd nanoparticles.

MM 20.2 Tue 10:45 H 0107

Thermodynamic and elastic properties of palladium-hydrides from first principles — ●BEATRIX ELSNER, GREGOR FELDBAUER, and STEFAN MÜLLER — Hamburg University of Technology, Institute of Advanced Ceramics, Denickestr. 15, D-21073 HH

Palladium and Pd-based alloys exhibit a huge potential for widespread applications ranging from hydrogen storage to catalytic processes. Because of its ability to reversibly embed a significant amount of hydrogen into interstitial sites, palladium is often characterized as a "hydrogen sponge". With increasing amount of absorbed hydrogen, the mechanical properties of palladium-hydride (PdH_x) are affected, e.g. it becomes more susceptible to brittle fracture. In order to understand such phenomena in more detail, the thermodynamic stability and elastic properties of PdH_x are here investigated via ab initio methods. Dispersion-corrected density functional theory (DFT) calculations are performed to obtain the energetics as well as the elastic properties of PdH_x for hydrogen concentrations up to 100%. The significant effect of phonon contributions is considered within the harmonic approximation. Using the DFT results as input data, cluster-expansion Hamiltonians for the phase formation energy as well as for the elastic properties are constructed to scan exhaustively the entire configuration space of PdH_x . This approach allows us to identify the most favorable configurations (ground states) as well as to identify trends for the elastic properties, such as a decrease of the shear constant c_{44} with increasing hydrogen concentration.

MM 20.3 Tue 11:00 H 0107

Tunable elasticity of nanoporous palladium by hydrogen insertion — ●SHAN SHI^{1,2}, JÜRGEN MARKMANN^{1,2}, and JÖRG WEISSMÜLLER^{1,2} — ¹Institut für Werkstofforschung, Werkstoffmechanik, Helmholtz-Zentrum Geesthacht, Geesthacht — ²Institut für Werkstoffphysik und -technologie, Technische Universität Hamburg-Harburg, Hamburg

Nanoporous metals with large specific surface area fabricated by dealloying are well-defined model systems for studying the mechanical behavior of nanostructured metals via conventional mechanical testing approaches. It has been demonstrated that mechanical properties such as macroscopic strain and stiffness of nanoporous gold could be tuned via changing the surface state. Most recently, a synthesis protocol for uniform and strong bulk samples of nanoporous Pd has been established. The material is readily equilibrated with H at controlled chemical potential. We have demonstrated that hydrogen electroabsorption could result in more than 3% reversible strain variation with np Pd. Here, we explore the elasticity change of np Pd during hydrogen absorption/desorption. It concluded that hydrogen induced over 30% compliance change with np-Pd. Furthermore, the relationship between experimentally measured elastic coefficient and hydrogen content agrees quantitatively with the theory of open system elasticity by Larché and Cahn.

30 min. break

MM 20.4 Tue 11:45 H 0107

Strain Response of Nanoporous Palladium upon Hydrogenation: Contributions of Hydride Phases, Stresses and Strain Rate — ●MARKUS GÖSSLER, EVA-MARIA STEYSKAL, and ROLAND WÜRSCHUM — Inst. of Mater. Phys., TU Graz, Austria

Nanoporous (np) palladium is an interesting candidate to study hydrogen and hydride phases in nanoporous systems [1]. The high surface stresses in nanoscaled structures can affect hydrogen interactions substantially, including the formation of metal hydrides. A novel method to achieve particularly fine porosities is electrochemical dealloying, a selective dissolution process from an alloy. In this work the strain response of dealloyed np Pd samples upon electrochemical hydrogenation was studied, using an in-situ dilatometric technique [2]. Unexpected yielding of np Pd during hydrogen desorption could be associated with an enhancement of plasticity, based on the activation of an additional pathway for plastic deformation. There are indications that hydrogen solutes interact with dislocations upon hydrogen desorption at high strain rates which are discussed by analogy with the well-known mechanism of dynamic strain aging. The impact of the np-structure related surface stress on the behaviour of the strain curve will be elucidated. Acknowledgement: This work is financially supported by the Austrian Science Fund (FWF): P30070-N36.

[1] M. Hakamada et al., J.Phys.Chem.C **114** (2010) 868. [2] E.-M. Steyskal et al., Beilstein J. Nanotech. **7** (2016) 1197.

MM 20.5 Tue 12:00 H 0107

Mechanical stress upon hydrogen absorption in Nb-Fe Films — ●PHILIPP KLOSE, MAGNUS HAMM, VLADIMIR RODDATIS, and ASTRID PUNDT — Institut für Materialphysik, Friedrich-Hund-Platz 1, 37077 Göttingen, Deutschland

Hydrogen absorption in thin films adhered to rigid substrates results in compressive mechanical in-plane stresses.[1,2,3] These stresses can lead to changes in the material's properties. While the in-plane film stress increases linearly on the hydrogen content for low hydrogen concentrations, deviations from the linearity appear at the yield stress [3,4]. The yield stress inversely depends on the film thickness.[5] For hydrogen loaded Niobium films, linearity is maintained to 1 H/Nb, for films below 6 nm and mechanical stress of up to -10 GPa is achieved.[5]

The yield stress can also be affected by alloying.[6] In this presentation we study the stress-development upon hydrogen loading in niobium-iron films of differing compositions. Films of different thickness were prepared by argon-cathode beam sputtering. Electrochemical hydrogen loading was performed during in-plane stress and in-situ XRD-measurements. By alloying the yield stress is shifted to much higher values. This will be discussed with respect to the Hall-Petch relation and the lattice coherency.

This work is financially supported by the DFG via project PU131/12-1. [1] J. Weissmüller et al., Phil. Mag. Lett. **80** (2000), [2] S. Wagner et al., Appl. Phys. Lett. **92** (2008), [3] U. Laudahn et al., JALCOM (1999), [4] A. PunDT et al., Phys. Rev. B **61.15** (2000), [5] Hamm, M., et al. APL **106** (2015), [6] P. Klose et al. IJHE (2017).

MM 20.6 Tue 12:15 H 0107

Depth-resolved hydrogen content measurement using Laser-induced Ablation-Quadrupole Mass Spectrometry (LIA-QMS) — ●JANNIS OELMANN, SEBASTIJAN BREZINSEK, CONG LI, and CHRISTIAN LINSMEIER — Institut für Energie und Klimaforschung - Plasmaphysik, Forschungszentrum Jülich GmbH, 52425 Jülich, Deutschland

Monitoring the quantitative sample's material composition is important for both- industrial process control as well as for post mortem analysis in research and industrial development. Still there is a lack of diagnostics, providing depth resolved information without using standard samples, although those cannot be used in several cases. We present a new method for measuring volatile sample species, using residual gas analysis with quadrupole mass spectrometry after picosecond laser-induced ablation.

A layer-wise sample analysis in the order of $\mathcal{O}(100 \text{ nm})$ is achieved

by using the third harmonic ($\lambda = 355$ nm) of a Nd:YVO₄ laser with a pulse duration of $\tau = 35$ ps and pulse energies up to $E = 50$ mJ for material ablation. To show the capability of the method, results for well characterized multilayer thin film solar cells (μ c-Si:H and a-Si:D on ZnO:Al) are shown and compared to standard techniques like Thermal Desorption Spectroscopy (TDS). Additionally, hydrogen content measurements of graphite samples from the fusion test reactor Wendelstein 7-X (W7-X) are shown to study the impact of heat flux on the graphite limiter tiles on hydrogen retention, which is essential for an in-depth understanding of the plasma wall interaction processes.

MM 20.7 Tue 12:30 H 0107

Sensitive 3D Microscopy of H and D in Metals using MeV Protons. — ●PATRICK REICHART and GÜNTHER DOLLINGER — LRT2, Universität der Bundeswehr München, Neubiberg, Germany

At the Munich microprobe SNAKE (Superconduction Nanoscope für Applied nuclear (Kern-) physics Experiments) a coincidence detection system has been installed to analyze proton-proton scattering events with up to 25 MeV incident protons. This allows to quantitatively analyze atomic H distributions in three dimensions with micrometer resolution. Due to transmission geometry the sample or foil thickness is limited to maximum $50\ \mu\text{m}$ e.g. for W or $150\ \mu\text{m}$ for Si.

The technique is the only nuclear microscopy method with low enough irradiation damage, i.e. not altering the H distribution before sufficient signal is detected. Sub-ppm sensitivity has been achieved for light materials like diamond, worse sensitivity of few ppm is demonstrated in heavy metals like Fe or W. We present a selection of previous studies of H in materials e.g. H in nominally anhydrous minerals of the

earth mantle, H adsorption in thin metal films, H retention in irradiated tungsten that is of large interest for potential diverter material in future fusion reactors.

We also demonstrate that sensitive D detection is possible by using a deuteron beam and detect deuteron-deuteron coincidences. This gives the possibility to study adsorption, retention as well as diffusion processes of H in materials by isotope marking.

MM 20.8 Tue 12:45 H 0107

Hydrogen influence on diffusion in nickel from first-principles calculations — ●DÔME TANGUY¹, YU WANG^{1,2}, and DAMIEN CONNÉTABLE² — ¹University Lyon 1, Villeurbanne, France — ²ENSIACET, Toulouse, France

The diffusion coefficient of vacancy-hydrogen clusters (VH_n), at equilibrium, in Ni is evaluated. The key is a good separation of timescales between H diffusion and the metal-vacancy exchange so that cluster diffusion can be treated as an uncorrelated random walk and that H is always in equilibrium before the vacancy-metal exchange. Then, the diffusion coefficient is a sum over jump paths of the equilibrium probability of being in a specific VH_n configuration times the corresponding activation terms. The influence of H on the energy barriers for the metal-vacancy exchange are calculated ab initio. It is shown that vacancies are drastically slowed down by H. Nevertheless, at equilibrium, VH_n clusters always induce a speed up of metal diffusion, because of the overall enrichment in vacancies. The implications concerning H induced damage, in particular in regards to Ni-Cr oxidation and GB embrittlement, are discussed. Details in Phys. Rev. B 91 094106.