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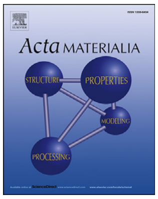

Full length article

Dislocation/hydrogen interaction mechanisms in hydrided nanocrystalline palladium films

Behnam Amin-Ahmadi [a], Damien Connétable [b], Marc Fivel [c], Döme Tanguy [d], Renaud Delmelle [e], Stuart Turner [a], Loic Malet [f], Stephane Godet [f], Thomas Pardoen [e], Joris Proost [e], Dominique Schryvers [a], Hosni Idrissi [a, e, *]

[a] Electron Microscopy for Materials Science (EMAT), Department of Physics, University of Antwerp, Groenenborgerlaan 171, B-2020 Antwerp, Belgium
[b] CIRIMAT, CNRS-INP-UPS UMR 5085, Ecole Nationale d'Ingénieurs en Arts Chimiques et Technologiques (ENSIACET) 4, allée Emile Monso, BP 44362, F-31030 Toulouse Cedex 4, France
[c] SIMaP-GPM2, Université Grenoble Alpes-CNRS, F-38000 Grenoble, France
[d] Institut Lumière Matière, UMR5306 Université Lyon 1-CNRS, Université de Lyon 69622 Villeurbanne Cedex, France
[e] Institute of Mechanics, Materials and Civil Engineering, Université catholique de Louvain, Place Sainte Barbe 2, B-1348 Louvain-la-Neuve, Belgium
[f] Université Libre de Bruxelles, Matters and Materials Department, 50 Av. FD Roosevelt CP194/03, 1050 Brussels, Belgium

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ABSTRACT

The nanoscale plasticity mechanisms activated during hydriding cycles in sputtered nanocrystalline Pd films have been investigated *ex-situ* using advanced transmission electron microscopy techniques. The internal stress developing within the films during hydriding has been monitored *in-situ*. Results showed that in Pd films hydrided to β-phase, local plasticity was mainly controlled by dislocation activity in spite of the small grain size. Changes of the grain size distribution and the crystallographic texture have not been observed. In contrast, significant microstructural changes were not observed in Pd films hydrided to α-phase. Moreover, the effect of hydrogen loading on the nature and density of dislocations has been investigated using aberration-corrected TEM. Surprisingly, a high density of shear type stacking faults has been observed after dehydriding, indicating a significant effect of hydrogen on the nucleation energy barriers of Shockley partial dislocations. Ab-initio calculations of the effect of hydrogen on the intrinsic stable and unstable stacking fault energies of palladium confirm the experimental observations.

1. Introduction

Owing to its fast and reversible hydriding kinetics, palladium (Pd) is an ideal model system to study hydrogen purification and sensing applications. This is essential for hydrogen energy technology, one of the cleanest alternative to fossil fuels [1,2]. Pd has a high sensitivity and selectivity with respect to hydrogen and can release hydrogen at room temperature [2].

Recently, nanocrystalline (nc) Pd thin films have been widely used in hydrogen applications because of large surface and sub-surface site densities and of the presence of a high fraction of grain boundaries (GBs) which can facilitate the hydriding process [2,3]. These layers must be thin enough to ensure high hydrogen permeability while remaining mechanically stable [4]. The crystalline structure of Pd is a face centered cubic (fcc) lattice, also referred to as the α-phase, in which interstitial hydrogen atoms occupy part of the octahedral sites. During hydriding, as long as the H/Pd ratio stays below $\alpha_{SSmax} \approx 0.02$ (atomic ratio) at room temperature, the fcc α-Pd lattice parameter can expand from 3.889 Å to 3.895 Å. When H/Pd ratio reaches 0.02 a so-called β-phase appears with a lattice constant near 4.025 Å, and again an fcc structure. The two phases coexist up to a ratio H/Pd $\beta_{SSmin} \approx 0.58$ at which the α-phase entirely disappears. The initial volume of the Pd structure expands by about 10% when the H/Pd ratio reaches about 0.5. This dilatation can generate extremely large overall compressive stresses if the deformation is impeded by a mechanical constraint imposed to the material, such as in the case of a film lying on a thick substrate. If the material is unconstrained, it can still undergo large local stress variation if the transformation does not take place homogenously. The large local or overall stress can induce severe local or global plastic deformation, respectively [2–8]. It was first

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* Corresponding author Electron Microscopy for Materials Science (EMAT), Department of Physics, University of Antwerp, Groenenborgerlaan 171, B-2020 Antwerp, Belgium; Institute of Mechanics, Materials and Civil Engineering, Université catholique de Louvain, Place Sainte Barbe 2, B-1348 Louvain-la-Neuve, Belgium.

E-mail address: hosni.idrissi@uantwerpen.be (H. Idrissi).

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shown by Wise et al. [9] that coarse-grained Pd after being subjected to a hydriding/dehydriding cycle contains a large dislocation density which is comparable with the dislocation density of a heavy cold-worked Pd [9,10]. Flanagan et al. [11] also reported that plastic deformation occurs both during hydriding and dehydriding in Pd which leads to an increase of the dislocation density. It has also been shown by transmission electron microscopy (TEM) results that after cold-working Pd, dislocations are arranged in cell walls with only a few dislocations within the cells, but when dislocations are created by a hydriding/dehydriding cycle, they are distributed more uniformly and it is difficult to discern a cell structure [9,12].

Robertson et al. also intensively investigated the mechanisms of hydrogen-dislocation interactions using environmental TEM for stainless steel [13], Ti [14,15] and pure Al [16]. They reported that hydrogen decreases the stacking fault energy in 310s stainless steel (SFE) and enhances the dislocation mobility (the movement of dislocations occurred at a lower applied stress). They interpreted these results by a shielding of the elastic interactions between defects (dislocation–dislocation and dislocation-pinning points). They have also investigated the separation distance between dislocations in a pileup during H absorption/desorption in pure Al. The results showed the reversible movement of dislocations in a pileup after an absorption/desorption cycle, coherent with elastic shielding in the absence of solute pinning effects in high purity Al. Several other experimental studies have been dedicated to the study of the effect of hydrogen on the microstructure and mechanical properties of bulk coarse-grained Pd such as the evolution of dislocation density and hardness after hydriding [17–21]. The nanoindentation experiments on coarse-grained Pd showed that local hardness is increased by 50% after hydriding the Pd to β-phase [19]. However, in depth experimental investigations on the elementary plasticity mechanisms activated in nc Pd films under hydrogen loading are still missing in the literature. Because of the complexity of the microstructure of nc metals, the microstructural changes associated to the effect of hydrogen loading may strongly differ from coarse-grained metals. Indeed, in nc metals, depending on the grain size and the local stress, the nucleation of leading partial dislocations from GBs and twinning can be favored over the formation of full lattice dislocations even in high SFE metals [22]. Furthermore, GB processes such as grain growth and grain rotation can be activated due to the increase of the local or overall stress during hydriding [23]. Another unexplored aspect concerns the experimental investigation of the nanoscale mechanisms controlling the dislocation/hydrogen interactions in Pd. Only a few investigations based on numerical simulations have recently tackled these questions but on other metallic materials such as nickel (Ni), aluminum (Al) and α-iron (Fe) [24–26]. Lu et al. [27] performed *ab-initio* calculations and found that both unstable and stable SFE in Al decrease by 50% when hydrogen atoms occupy the octahedral sites of fcc Al. Similarly, Taketomi et al. [28] showed through molecular statics simulations that the stable SFE decreases with increasing hydrogen concentration in α-Fe. Wen et al. [29] also investigated the effect of hydrogen on the dissociation of screw dislocations in Ni using the embedded-atom method, and showed that the stacking fault width of screw dislocations increases with increasing hydrogen concentration. Tang et al. [25] reported that the increase of the hydrogen concentration in Ni decreases the stable SFE due to the resulting negative binding energy of hydrogen to the SF, while the unstable SFE increases with increasing hydrogen concentration.

However, direct experimental evidences on the effect of hydrogen on the nucleation energy barriers of partial dislocations in fcc metals are still absent in the literature.

Finally, there is no doubt that the accumulation of irreversible microstructural changes during hydriding cycles on nc Pd films can alter the mechanical properties of these films (i.e., ductility, hardening, creep, etc). Defects generated in hydrided nc Pd used in sensing applications can also have other effects such as shortening of a sensing cell's lifetime, interruption of the electrical circuitry and lowering of the device's sensing sensitivity and proficiency [30]. Therefore, it is of primary importance to uncover the elementary plasticity mechanisms activated during hydriding of nc Pd thin films.

In the present study, we have performed detailed TEM characterizations on nc Pd thin films prepared using sputter deposition and hydrided at low and high pressures for α-phase and β-phase transformation, respectively. The internal stress developing within the films during hydriding has been monitored in-situ using an original experimental setup based on the measurement of the curvature of the Pd films during hydriding [2,31]. Statistical analyses of the grain size/morphology as well as the crystallographic texture have been performed using automated crystal orientation mapping in TEM (ACOM-TEM) while aberration corrected high resolution TEM (HRTEM) has been used to unravel the nature and the near-core properties of the defects generated during hydriding. The results revealed strong interaction of hydrogen with extended defects as well as a clear effect of hydrogen on the nucleation energy barriers of Shockley partial dislocations of Pd which was confirmed using *ab-initio* calculations. The results also provide insightful information for the validation of atomistic simulations on the interaction of hydrogen with extended defects and for better understanding of the effect of hydriding on the macroscopic mechanical properties of nc metallic thin films.

2. Materials and methods

In the present study, 150 nm thick Pd films were sputter-deposited at room temperature with a deposition rate of 0.3 nm s^{-1} under an argon (Ar) plasma pressure of 1.07 Pa. Hydriding cycles were performed after pumping down a vacuum chamber to base pressures better than 10^{-6} mbar, followed by the introduction of ultra-pure Ar/H_2 gas mixtures to instantaneously impose a desired partial pressure. The hydriding cycles were performed at partial pressure of $p_{H_2} = 2.26$ mbar for α-phase and 97.5 mbar for β-phase formation. The gas mixture was then pumped out of the chamber, resulting in a gradual decrease of the internal stress within the films due to reversible dehydriding at room temperature. A high-resolution curvature measurement setup is mounted onto the hydriding chamber and continuously detects the positions of multiple laser beams reflecting off a cantilevered sample, hence monitoring the sample curvature in real time [31]. The change in internal stress in the Pd layer, which is the result of the restricted in-plane expansion during Pd–H interaction in the film-on-substrate geometry, can be derived from the measured changes in curvature [2,32]. After dehydriding, the system returns to ambient conditions, i.e. room temperature and atmospheric pressure. The hydrogen is released from the film and cross-sectional and plan-view TEM thin foils were prepared using Focused Ion Beam (FIB) thinning with the "lift-out" procedure. Conventional and HRTEM characterizations of the Pd films before and after hydriding were carried out using a FEI Tecnai G2 (FEG, 200 kV). A FEI Titan 80–300 ″cubed″ microscope with aberration correctors for imaging and probe was used to reveal the near-core properties of defects induced by the hydriding. Spatially resolved electron energy loss spectroscopy (EELS) technique was also used to detect the residual hydrogen on the core of dislocations after hydriding.

The dislocation density was measured by counting extra half planes in HRTEM images. For better visualization of the extra half planes, a mask was applied on each **g**-vector and the corresponding Inverse Fast Fourier Transform (IFFT) was generated showing one family of planes. This procedure was used for all main spots present in the FFT pattern. Thus, the dislocation density was calculated