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Multi-Scale Analysis of Hydrogen-Induced Buckling in Pd Films

J Cizek[a,*], I. Prochazka[a], M. Vlach[a], N. Zaludova[a], P. Dobron[a], F. Chmelik[a], G. Brauer[b], W. Anwand[b], A. Mücklich[b], E. Nikitin[c], R. Gemma[c], A. Pundt[c], R. Kirchheim[c]

[a]*Faculty of Mathematics and Physics, Charles University in Prague,Prague 8 CZ 18000, Czech Republic*
[b]*Institut für Ionenstrahlphysik und Materialforschung, Forschungszentrum Dresden-Rossendorf, Dresden D-01314, Germany*
[c]*Institut für Materialphysik, Universtät Göttingen, D-37073 Göttingen, Germany*

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Abstract

Hydrogen loading causes a significant volume expansion, which is isotropic in free-standing bulk materials. Contrary to bulk samples, thin films are clamped to an elastically stiff substrate, which prevents in-plane expansion. Hence, volume expansion of a thin film is strongly anisotropic because it expands only in the out-of-plane direction. High internal stresses introduced during hydrogen loading may lead to a situation when detachment of film from the substrate is energetically favorable. In the present work, we studied hydrogen-induced buckling of thin Pd films using a multi-scale approach. Defects in buckled films were characterized on the atomic level by positron annihilation spectroscopy combined with microstructure studies by transmission electron microscopy. Meso-scale measurements were performed by acoustics emission. Observations at the macroscopic level were performed by optical microscopy. It was found that buckling of thin films occurs at hydrogen concentrations $x_H > 0.1$. Defect studies of buckled Pd films revealed a significant increase of dislocation density in agreement with acoustic emission studies which demonstrated a correlated movement of dislocations with a well-defined threshold coinciding with the onset of buckling.

Keywords: hydrogen, thin films, dislocations, positron annihilation, acoustic emission

1. Introduction

Hydrogen usually occupies interstitial sites in a host lattice and causes a significant volume expansion, which is isotropic in free-standing bulk samples. However, thin films are clamped at elastically stiff substrates, which hinder the in-plane expansion, while the out-of-plane expansion becomes larger than in bulk samples. As a consequence, high compressive in-plane stresses up to several GPa are introduced into thin films by hydrogen loading[1]. These stresses grow with increasing hydrogen content, and when they exceed a certain critical level, local or global detachment of the film from its substrate occurs. Hydrogen-induced buckling may cause adhesion failure of thin

* Corresponding author. Tel.: +420-221-912-788; fax: +420-221-912-567.
E-mail address: jakub.cizek@mff.cuni.cz

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film systems, but it can also be used to measure the adhesion energy between a film and its substrate[2]. Although formation of buckles was observed on the macroscopic scale in a number of works[2-4], there is still a lack of knowledge about microstructure changes during this process. In the present work hydrogen-induced buckling in thin Pd film was investigated using a multi-scale approach. Defects created during buckling were characterized at the atomic level by slow positron implantation spectroscopy (SPIS). This technique uses moderated slow positrons with tunable energy as probes in the specimen. Momentum of annihilating positron-electron pair is measured through Doppler shift in energy of annihilation photons, which causes broadening of annihilation photopeak in the gamma ray energy spectrum. Open volume defects (e.g. vacancies, dislocations etc.) represent potential wells (trapping sites) for positrons. Because of positron trapping SPIS is highly sensitive to open-volume defects present in the studied material. A detailed description of SPIS can be found e.g. in excellent review by Schultz and Lynn[5]. Microstructure of buckled films was studied by transmission electron microscopy (TEM). These studies were accompanied by meso-scale measurements by acoustics emission (AE) and macroscopic observations performed by optical microscopy (OM).

2. Experimental

Thin Pd films with a thickness of 1080 nm as determined by TEM, were prepared in a UHV chamber (10^{-10} mbar) using cathode beam sputtering at room temperature on optically polished $(11\bar{2}0)$ sapphire substrates. The samples were then step-by-step loaded with hydrogen by electrochemical charging[6] in a galvanic cell filled with a 1M KOH electrolyte. The hydrogen concentration in the sample was calculated from Faraday's Law and is expressed as the atomic ratio H/Pd throughout this paper.

SPIS studies were performed on a magnetically guided positron beam "SPONSOR"[7] with positron energy adjustable from 0.03 to 36 keV. Doppler broadening of the annihilation line was evaluated using the line shape S parameter defined as ratio of suitably selected central area of the annihilation peak (centered at 511 keV) to the net peak area[5]. Usually the central region is selected so that S parameter value is close to 0.5. In the present work the energy interval was (510.54, 511.46) keV. This choice leads to the value $S_0 = 0.4968(7)$ for a well annealed reference Pd sample at positron energy E = 36 keV. All S parameters in this work are normalized to the S_0 value. Narrowing of the annihilation peak (i.e. smaller Doppler shift) leads to higher S parameter. Localization of positron in an open-volume defect leads to a reduction of its overlap with high momentum core electrons. As a consequence, annihilation peak becomes narrower and S parameter increases. Thus, S parameter is a measure of density of open volume defects in the specimen.

The AE studies were performed in-situ during the hydrogen loading a computer-controlled DAKEL-XEDO-3 AE system. Threshold voltage for the AE count was 480 mV (full scale was ± 2.4 V). A piezoelectric sensor MST8S (a frequency band from 100 to 600 kHz) was attached to the back side on the substrate of the loaded film, while the front side with the Pd film was immersed in the electrolyte. The TEM studies were performed with a Philips CM300SuperTWIN microscope operating at 300 kV. Thin foils for cross sectional TEM were produced by conventional preparation using a Gatan precision ion polishing system. A metallographic microscope Arsenal AM-2T was used for the OM observations of the films.

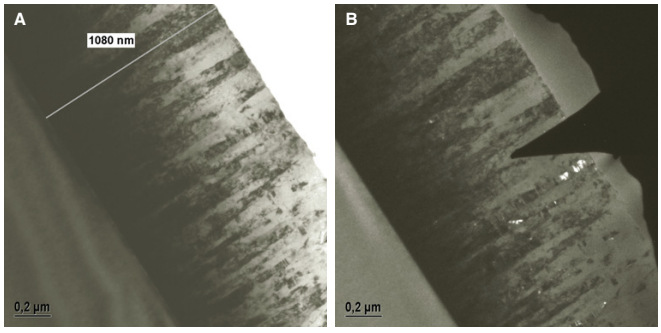

Fig. 1. TEM image of virgin Pd film (A) bright field; (B) dark field.

3. Results and Discussion

Microstructure of virgin Pd film is shown in Fig. 1. TEM revealed the presence of nanocrystalline "column-like" elongated grains with a lateral width around 50 nm.

OM images of hydrogen loaded Pd film are shown in Fig. 2. The film surface appears smooth at hydrogen concentrations $x_H < 0.10$, see Fig. 2A. At higher hydrogen concentrations buckling of the film occurs. Straight buckles are formed in early stages of buckling ($x_H < 0.15$), see Fig. 2B. Such straight buckle can, however, releases the in-plane stresses only in one in-plane direction[2]. Hence, a straight buckle is forced to expand also in the perpendicular direction and buckles become curved at higher hydrogen concentrations ($x_H > 0.15$), see Fig. 2C. Finally, at $x_H > 0.20$ a lot of buckles of undulated shape can be observed in the film, see Fig. 2D.

Dependence of the S parameter on the positron energy E for the virgin film is plotted in Fig. 3A. The S(E) curve for a reference well-annealed bulk Pd sample is plotted in Fig. 3A as well. Low energy positrons annihilate almost exclusively at the surface. With increasing energy positrons penetrate deeper into the sample and the fraction of positrons diffusing back to the surface decreases. This is reflected by shape of the S(E) curve which converges to a bulk value S_0 corresponding to a situation when virtually all positrons annihilate inside the bulk Pd sample. All S parameters in this work are normalized to the S_0 value measured on the bulk Pd sample. Fitting of S(E) curves was performed by numerical solution of positron diffusion-annihilation equation[8] using the code VEPFIT[9]. From fitting of the S(E) curve of reference Pd sample we obtained positron diffusion length of (151 ± 4) nm. This value is comparable to positron diffusion lengths measured in defect-free metals[5] and can be considered as the mean diffusion length of free positrons in a perfect Pd crystal. One can see in Figs. 3A, B that Pd film exhibits significantly higher S parameter and also shorter positron diffusion length than the reference bulk Pd specimen. Thus, in virgin Pd film some positrons are trapped at defects. This occurs due to nanocrystalline grain size, which leads to a significant volume fraction of grain boundaries containing open-volume defects. A significant fraction of thermalized positrons diffuse to grain boundaries and are trapped at open volume defects there.

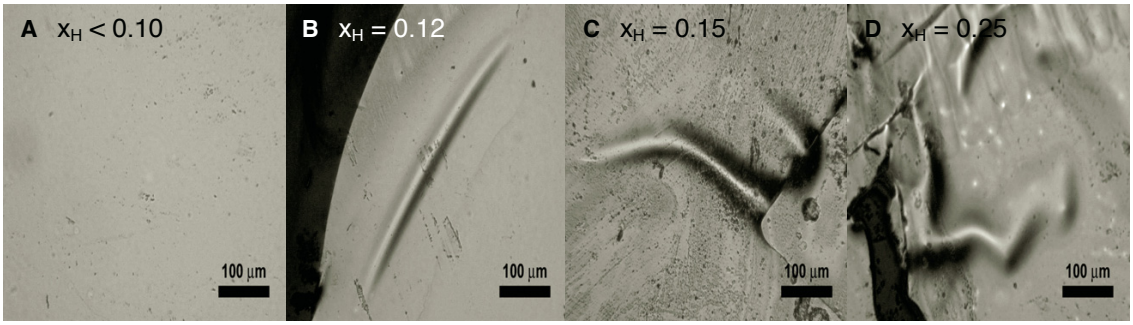

Fig. 2. OM images of Pd film loaded up to various hydrogen concentrations x_H (A) $x_H < 0.10$, (B) $x_H = 0.12$, (C) $x_H < 0.15$, (D) $x_H = 0.25$.

Selected S(E) curves for the hydrogen loaded films are shown in Fig. 3A, while Fig. 3B shows the S parameter values S_{Pd} and the positron diffusion lengths $L_{+,Pd}$ for Pd layer obtained from fitting of the S(E) curves. The open volume defects at grain boundaries do trap not only positrons, but also hydrogen atoms. At low concentrations ($x_H < 0.01$), hydrogen fills the open volume defects at grain boundaries. This is reflected by a decrease of S_{Pd} caused by a reduced localization of the positron wave function due to the repulsive interaction of positron with a hydrogen atom attached to a defect. At higher hydrogen content, all available deep traps are filled and S_{Pd} becomes constant. A dramatic increase of S_{Pd}, accompanied by a drop of $L_{+,Pd}$, can be seen at $x_H \geq 0.10$. The occurrence of first buckles in the film was observed by OM at this concentration. At higher concentrations the number of buckles increases. Thus, the increase in S_{Pd} is due to positron trapping at defects, probably dislocations, introduced into the film by buckling. Note that non-equilibrium vacancies are unstable in Pd at room temperature and cannot, therefore, explain the observed increase of S parameter as SPIS signal from buckled film remains unchanged at least for months.

The cumulative AE counts are plotted in Fig. 4A as a function of hydrogen concentration. Obviously, the number of AE counts begins to increase drastically at $x_H > 0.1$, where the buckling process starts. Taking into account the

experimental results, i.e. (i) a lot of AE signals produced during buckling, and (ii) a clear evidence from SPIS that new defects were formed in the buckled film, the most probable microstructure process operating during buckling is a collective movement of dislocations created in the film during buckling. A time chart of detected AE counts and time dependence of the applied current during the step-by-step hydrogen charging are shown in Fig. 4B. The time interval shown in the figure corresponds to the hydrogen concentration range well, where buckling occurs. One can see that the AE bursts occur during the loading current pulse, i.e. during hydrogen insertion into the film. When the loading current is switched off, i.e. the film is not loaded anymore by hydrogen, the AE counts also disappear. This correlation testifies that dislocations are created in the film during buckling.

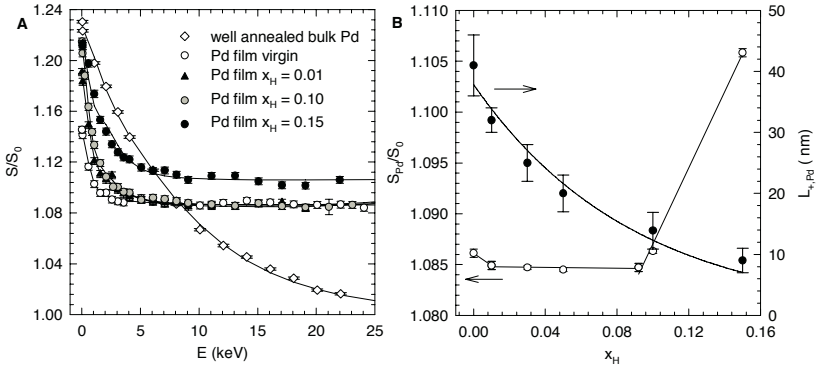

Fig. 3. (A) Selected S(E) curves for the virgin film and the film loaded to various hydrogen concentrations x_H. The solid lines show fits by VEPFIT. The S(E) curve for well annealed bulk Pd reference specimen is plotted in the figure as well by open diamonds, (B) The S parameter S_{Pb} and the positron diffusion length $L_{+,Pd}$ for the Pd layer obtained from fits of the S(E) curves as a function of hydrogen concentration.

Surface effects play an important role in thin films because of the high surface to volume ratio (1000:1 mm^{-1} in the case of Pd film studied in this work). Although buckling increases surface area, it is energetically favorable due to the release of hydrogen-induced in-plane stresses. Buckling is energetically favorable if the released strain energy is higher than the energy of adhesion (i.e. the difference between the surface energies of adjacent materials and the interfacial energy). Note that hydrogen-induced buckling was observed even in films with thickness around 100 nm, which exhibit an order of magnitude higher surface to volume ratio[2].

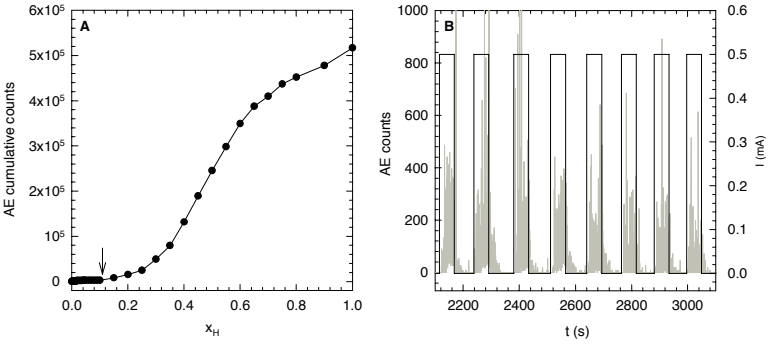

Fig. 4. (A) Dependence of the cumulative AE counts on hydrogen concentration. (B) Time chart showing simultaneously the detected AE counts and the loading current pulses during the step-by-step hydrogen charging in the concentration range $x_H > 0.1$, where buckling takes place.

4. Conclusions

Multi-scale investigations of hydrogen loaded nanocrystalline 1080 nm thick Pd film were performed in the present work. It was found that hydrogen is trapped at vacancy-like open volume defects at grain boundaries.

Buckling of the film occurs at $x_H \geq 0.1$. Experimental results obtained by AE and SPIS indicate that dislocations are generated during the process of buckling.

Acknowledgement

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