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Phase transition and lattice expansion during hydrogen loading of nanometer sized palladium clusters

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Abstract

In situ X-ray diffraction (XRD) measurements for Pd-clusters (3.8 and 6.0 nm) are performed during hydrogen loading and unloading. The lattice parameter increases as a function of the hydrogen partial pressure. The expansion is smaller than that of bulk palladium and is shown to be cluster-size dependent. An (α–α') phase transition was observed for the large clusters but small clusters do not show this transition. XRD analysis of the as-prepared clusters show that the 3.8-nm sized clusters predominantly have an icosahedral structure, while the 6.0-nm sized clusters have a cubic structure. The effect of size and structure of the cluster on the lattice expansion and on the phase transition will be discussed.

Keywords: Clusters; Metals; Hydrogen storage materials; Crystal structure and symmetry; Synchrotron radiation

1. Introduction

Hydrogen is absorbed by many metals and occupies interstitial sites in the host lattice. In most known metal–hydrogen alloys, the dissolved hydrogen expands the crystal lattice of the host metal, thus displacing the metal atoms from their regular sites [1]. The distortion of the crystal lattice gives rise to a series of physical property changes. The hydride of bulk palladium has been intensively investigated [2] because of the relatively high hydrogen concentration for an elemental metal and the noble character of palladium.

The physical and chemical properties of nanometer sized materials, such as nanocrystalline materials and clusters, are of particular interest because they are often size dependent and are different from bulk properties [18,19]. For nanometer-sized materials, the Pd–H system can be regarded as a model system. A nanocrystalline material was used to investigate the hydrogen palladium interaction in small grains [3,16]. Mütschele and Kirchheim [3] found that, in a nanocrystalline Pd-sample (grain diameter of 8–12 nm), there is an increase in the maximum α-phase concentration from 0.015 H/Pd to 0.03 H/Pd, while the α'-phase concentration decreases from 0.58 H/Pd to 0.44 H/Pd as compared to a polycrystalline sample with an average grain diameter of 20 μm. Similar results were obtained by other workers such as Natter et al. [4] and Stuhr et al. [5], in conformity with Mütschele and Kirchheim's interpretation, explaining the results in terms of the influence of grain boundaries which undergo no phase transition. Using neutron energy loss scattering, Stuhr et al. [5] found that two types of hydrogen sites exist at low hydrogen concentrations: interstitial sites in the lattice and in the grain boundaries. The latter are occupied at a lower chemical potential and could therefore increase the α-phase solubility.

Structural information was given by Eastman et al. [6] who performed in situ XRD gas-phase hydrogenation studies of nanocrystalline palladium produced by gas condensation. They proved that the hydrogenated nanocrystalline samples transform into the α'-phase.

An increased solubility of hydrogen in the α-phase and a

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narrowing of the miscibility gap in clusters were also observed [7–9], in good accordance with results on nanocrystalline materials. This behaviour was attributed to interface-lattice sites that differ from bulk sites [3–5]. It was found that the width of the plateau decreases with the decreasing cluster size. In thermodynamical studies on the clusters [7–9] no information about the lattice structure was given. It is known that small clusters possess structures different from that of the bulk metal, such as the icosahedral structure. Thus, it is of importance to know the cluster's lattice structure, especially in the range of the two-phase field where the isotherms show an (α–α')-like phase transition. Firstly, because the mean pressure is similar to that of the bulk phase transition and secondly, the cluster behaviour can be described by simply splitting the cluster into a surface part, that undergoes no phase transition, and a bulk-like inner part, as known from nanocrystalline metals. Recently, Pundt et al. [10] found evidence for a structural transition in small palladium clusters from cubic into icosahedral structure during hydrogen loading.

In this work we employ in situ XRD measurements which give structural information and enable us to monitor the sample lattice structure directly during hydrogen loading. The aims of this work are to: (1) determine the lattice parameter of the cluster as a function of the partial hydrogen pressure and (2) identify the effect of the cluster size and structure on the lattice expansion and phase transition during hydrogen absorption.

2. Experimental

2.1. Cluster preparation

The Pd-clusters were stabilised by tetraalkylammonium salts and were synthesised by an electrochemical method [11,12] in which a simple electrolysis cell consisting of two electrodes (a Pd anode and cathode) is used. Applying constant current to the electrodes, causes dissolution of the Pd anode with formation of Pd(II)-cations which are reduced at the cathode forming the so-called 'adatoms'. The tetraalkylammonium salt serves as the electrolyte and as the stabiliser (surfactant). In the current work, we used tetraoctylammonium bromide. The adatoms aggregate into surfactant stabilised clusters. This method has many advantages over other methods including a very narrow size distribution and the quasi-free nature of the stabilised clusters, because the modulus of elasticity of the surfactant is orders of magnitude lower than that of the clusters [11]. For details about the preparation technique see Refs. [12,13].

2.2. Hydrogenation measurements

In situ X-ray diffraction measurements were performed on the beam line B2 at the Hamburg synchrotron laboratory HASYLAB at DESY. The wavelength was selected by a Ge(111) double-crystal monochromator, the 3.8-nm cluster sample was measured at $\lambda=1.12617$ Å and the 6-nm cluster sample at $\lambda=1.24438$ Å. A special high vacuum gas loading cell was used that allows stepwise and controlled hydrogen loading as well as unloading between 10^2 and 10^5 Pa. Each loading cycle starts at a base pressure of about 10^{-3} Pa, the hydrogen pressure was increased stepwise to 10^5 Pa. All samples were pretreated with hydrogen to remove the oxide layer. The hydrogen pressure was measured using MKS pressure gauges with 0.01% precision. The purity of hydrogen gas was 99.9999%, all measurements were performed at room temperature.

3. Results and discussion

3.1. Determination of the size and structure of the as-prepared clusters

The cluster size of the investigated samples was determined by transmission electron microscopy (TEM). TEM analysis shows that clusters of one sample have a diameter of 3.8±0.4 nm and those of the other sample have a diameter of 6.0±1.3 nm.

The lattice structure of the clusters was obtained by using X-ray analysis. The X-ray patterns of each sample were obtained at about 10^{-3} Pa. Fig. 1 shows the diffractograms of (a) the 6.0-nm and (b) the 3.8-nm cluster samples. The two diffraction patterns have different characteristic features. In Fig. 1a, all the diffraction patterns have peak intensities similar to that of bulk Pd. In Fig. 1b, there is a considerable intensity decrease of the high angle diffraction peaks (near bulk (200) and (222)) in comparison with that of the bulk (111) diffraction pattern. In addition, there is an intensity increase between 50 and 53° in the diffractogram of the 3.8-nm clusters which was not found for the 6.0-nm clusters (marked with an arrow). Furthermore, the reflection close to the bulk (200) position is slightly shifted towards the reflection near the bulk (111) peak position. Comparing the experimental XRD patterns with those obtained from MD-simulated clusters [14] shows that the 3.8-nm clusters have predominantly icosahedral lattice structure, while the 6.0-nm clusters have a cubic lattice structure.

In the 3.8-nm clusters, all the diffraction peaks are shifted to lower 2θ values. This can be attributed to incorporation of hydrogen in Pd-surface sites [15] and subsequent lattice stretching. Weissmüller et al. [16] reported a similar phenomenon in nanocrystalline Pd–H. This shift was less in the 6.0-nm cluster, which we attribute to the decreased surface-to-volume fraction.

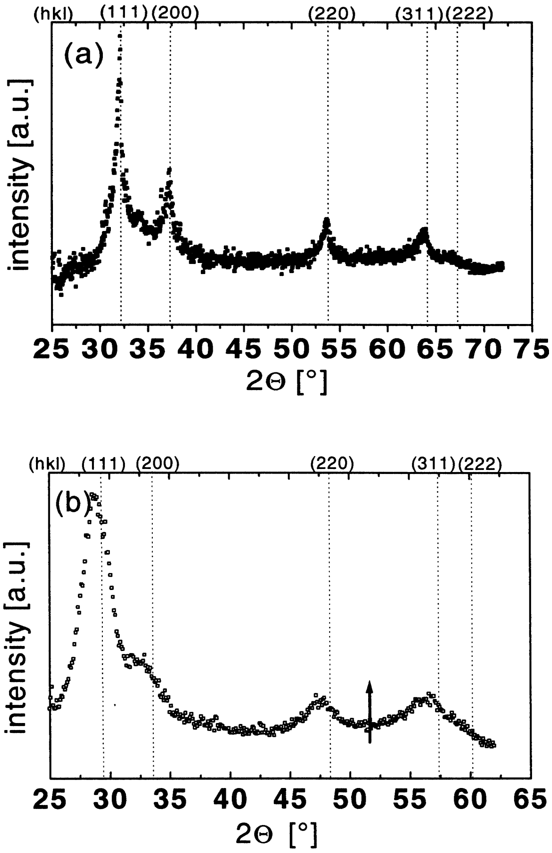

Fig. 1. Diffraction patterns of the as-prepared sample: 6.0-nm cluster (a) and 3.8-nm cluster (b). The vertical dotted lines are position of peaks for bulk Pd: (a) at λ=1.24438 Å, (b) at λ=1.12617 Å.

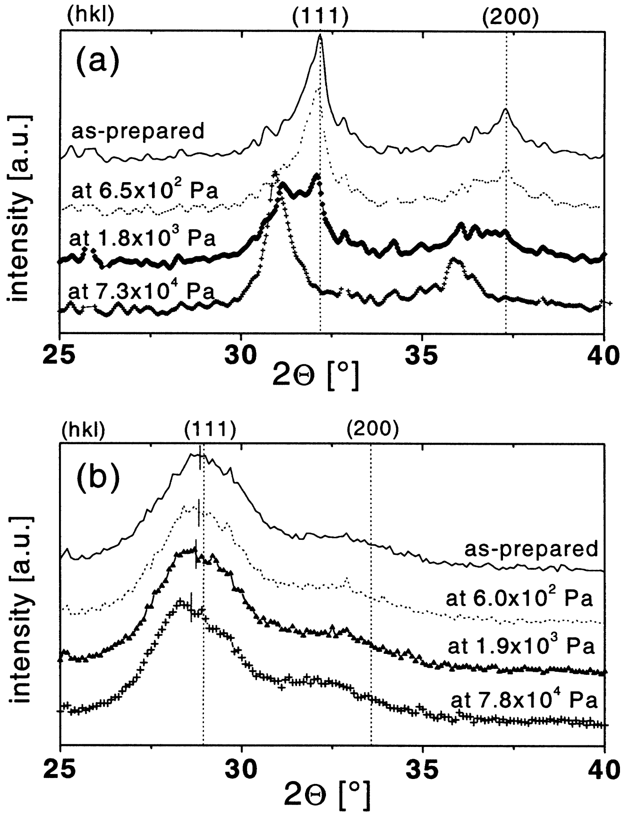

Fig. 2. Diffraction patterns of the 6.0-nm (a) and 3.8-nm (b) cluster samples at four different hydrogen pressures monitoring the lattice expansion. (a) Diffraction pattern of the as-prepared 6.0-nm clusters (solid line), at 6.5×10^2 Pa (dotted line), at 1.8×10^3 Pa (diamond) and at 7.3×10^4 Pa (cross line). The α′-Pd–H phase is visible at 1.8×10^3 Pa. At the largest pressure the whole sample is in the α′-Pd–H phase. (b) Diffraction pattern of the as-prepared 3.8-nm cluster (solid line); at 6.0×10^2 Pa (dotted line), at 1.9×10^3 Pa (up-triangle) and at 7.8×10^4 Pa (cross line). Only a small peak shift is visible. The (111) peak positions have been marked with vertical bars.

3.2. Lattice expansion and phase transition

A typical experiment consists of one loading and one unloading cycle (in about 30 pressure steps). During hydrogen loading, a shift to smaller 2θ values is observed in the diffraction patterns, indicating a lattice expansion. Fig. 2 shows diffraction patterns of the (a) 6.0-nm and (b) 3.8-nm cluster samples at four different pressure steps, monitoring the lattice expansion by a shift of the peak positions. It is clearly seen that the lattice expansion of the 6.0-nm cluster is larger than that of the 3.8-nm cluster. In the 6.0-nm cluster (Fig. 2a) a transition is observed. Since these clusters have a cubic lattice structure and, since, the observed transition occurs at a pressure typical for bulk palladium, this transition is interpreted as a (α–α′) phase transition. That indicates that such a transition is possible in the 6.0-nm clusters. Fig. 2a shows diffraction patterns at four different hydrogen pressure stages monitoring the (α–α′) phase transition. At 1.8×10^3 Pa another set of Bragg reflections start to appear indicating the formation of the (α′-Pd–H) phase. At higher pressure, the whole 6.0-nm cluster sample transfers into the (α′-Pd–H) phase and the (α-Pd–H) phase peaks completely vanish. No such (α–α′) phase transition was found in the 3.8-nm cluster sample, as shown in Fig. 2b. Increasing the hydrogen pressure leads to a very small dilation of the lattice, shifting the Bragg reflection to smaller 2θ values. Moreover, there is no change in the peak intensity which excludes a possible structural change [10].

Mütschele and Kirchheim [3] and Eastman et al. [6] have shown that the width of the plateau (miscibility gap) for the Pd–H phase boundary exhibits significant narrowing, for nanocrystalline samples as compared to that of the conventional polycrystalline samples. Similar results were observed for nanometer sized clusters [7–9]. Plotting the lattice parameter as a function of the hydrogen partial pressure (Fig. 3) shows some interesting features. There is slight narrowing of the plateau region (miscibility gap) in the 6.0-nm cluster sample, whereas there is no plateau region at all in the 3.8-nm cluster sample. Comparing the lattice parameters of the clusters with those of the bulk

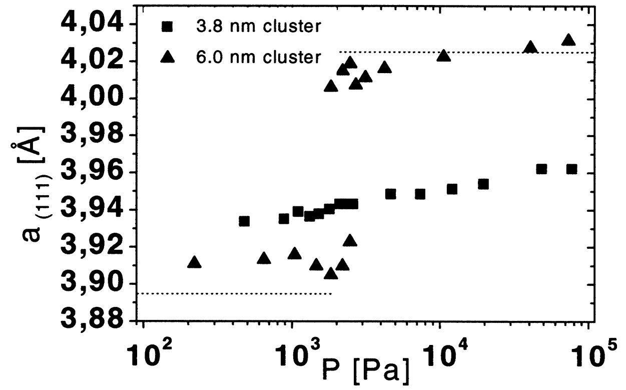

Fig. 3. The lattice parameter at different hydrogen partial pressures of 6.0-nm clusters (up-triangle) and 3.8-nm clusters (shaded squares). The (dotted line) represents the Pd bulk values. The lattice parameter of the large clusters strongly increases at 2×10^3 Pa, whereas the lattice parameter of the small clusters shows a continuous increase.

palladium as a function of the hydrogen pressure (Fig. 3) shows that the lattice expansion is strongly size dependent. The 6.0-nm cluster has lattice expansion values larger than those for the 3.8-nm cluster, but still smaller than those for bulk palladium. Again, that indicates a narrowing of the lattice parameter miscibility gap on going from bulk to nanometer sized material and is in accordance with the narrowing of the miscibility gap found in nanometer sized materials observed by other groups [3,6–9]. In an electrochemical hydrogen loading study of small Pd clusters (about 1.2-nm diameter), Nützenadel et al. [9] found that it was not clear if the 1.2-nm cluster exhibited a phase transition. Nützenadel et al. explained this by a lowering of the critical temperature (T_c) of the α–α'-miscibility gap below room temperature, resulting in no phase transition for this cluster size. In addition, calculations by Wolf et al. [17] showed that, for small Pd clusters (500 Pd atoms with about 2.6-nm diameter), no phase transition is expected. These calculations were based on a cubic lattice structure.

We found that the 3.8-nm clusters have an icosahedral structure which should be taken into account when discussing an (α–α') phase transition in clusters. It is known that, for bulk Pd, both the α-Pd–H phase and α'-Pd–H phase have a face-centred-cubic (fcc) structure with hydrogen occupying the octahedral sites in the palladium lattice, which cannot be the case in our 3.8-nm icosahedral cluster sample. We relate the absence of the phase transition to the icosahedral structure of the small Pd–H clusters. Recently, it was shown by Pundt et al. [10] upon performing in situ X-ray diffraction studies that small clusters (cubic structure) can undergo a new phase transformation (α-ico phase transformation) occurring in the same pressure range or chemical potential as for the (α–α') phase transformation in bulk Pd. This is not the case for our 3.8-nm cluster samples, since the α-phase is a characteristic feature of a cubic lattice structure. Additionally, an explanation based on the lowering in the T_c below room temperature, which could be possible for cubic clusters [9], is not acceptable in the case of icosahedral clusters. We attribute the absence of the phase transition in the case of the 3.8-nm clusters to their size and structure. This could lead to a new way of understanding Pd–H-cluster systems, especially for small clusters which prefer to have an icosahedral lattice structure [13,14].

4. Conclusions

In situ XRD measurements performed during hydrogen loading–unloading of Pd clusters show that the lattice dilation strongly depends on the hydrogen partial pressure and the cluster size. Larger clusters (6.0 nm) show much higher lattice expansion values in comparison to those of the small clusters (3.8 nm) at the same hydrogen partial pressure. The 6.0-nm clusters undergo an (α–α') phase transition in the same pressure range of bulk Pd, while the 3.8-nm clusters do not show an obvious phase transition. We attribute this difference in behaviour to the different structure of the investigated clusters. The small Pd–H clusters have an icosahedral structure, whereas the larger ones are cubic.

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