Journal of Alloys and Compounds 293–295 (1999) 480–483

Hydrogen sorption in elastically soft stabilized Pd-clusters

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Abstract

Thermodynamic properties of the Pd–H system are studied on 3.1- and 3.6-nm clusters by performing gasvolumetric measurements. To avoid interfacial stress that occurs between an adhering particle and the substrate, the clusters are embedded in an elastic soft polymer matrix and in a surfactant shell, respectively. A largely enhanced H-solubility was found in the α-phase region. Additionally the solubility limit of the α-phase is shifted to a higher H-concentration whereas the minimum α′-phase solubility is lowered compared to that of bulk Pd. This can be attributed to an occupation of subsurface sites. Sorption–desorption isotherms show the existence of a small hysteresis. This hysteresis can not be related to the formation of misfit dislocations because of the small cluster size, but can be explained with regard to the thermodynamics of an open two-phase system with coherent interfaces.

Keywords: Cluster; Palladium; Hydrogen loading

1. Introduction

Nano-structured materials have been attracting increasing interest for basic research and for applications in recent years. This is due to the discovery of new size-related physical properties and their application such as in catalysis [1]. One type of the new catalytic materials is extremely small metal nano-clusters [1,2].

As soon as these nano-clusters come into contact with each other, they agglomerate to lower their surface energy. To maintain the original size of the nano-clusters, they have to be stabilized. Stabilization is often performed by adhesion to a substrate or in a crystalline matrix [3]. Between the adhering particle and the elastically hard substrate interfacial stress occurs. Measurements on thin Nb films deposited on Si and Al_2O_3 [4] show that during hydrogen absorption these interfacial stresses reach several GPa and influence the thermodynamic properties of the samples. Recently, polymers were proposed as elastically soft stabilizers for catalytically active metal nano-clusters [5,6]. Surfactants have been used by a variety of authors to stabilize small clusters [1,7]. Recently, Reetz et al. described an electrochemical method to produce small clusters in a simple manner [8].

Nano-clusters of Pd or Ni appear in the cuboctahedral shape of the fcc lattice with low index surface planes [2]. Studies on hydrogen sorbing thin film surfaces have shown that different surface phases occur [9,10]. A phase with a hydrogen coverage of 1 H/Pd-atom is stable on the Pd (110) surface at approximately room temperature [9].

At appropriate hydrogen pressures an absorption of hydrogen on internal cluster sites takes place [11]. Additional, so-called subsurface sites [12] are occupied in the vicinity of the in Pd film surface. The H-occupation of subsurface sites is energetically favored compared to the occupation of bulk sites.

In clusters the existence of highly coordinated positions such as corners or edges between the low indexed planes leads to additional hydrogen uptake. In extremely small clusters of less than 1 nm, hydrogen to cluster atom ratios of 8 were found [13]. Thus surface and subsurface sites increase the hydrogen solubility of clusters compared to that of bulk material.

Wolf et al. [14] performed Monte Carlo simulations on hydrogen loaded Pd clusters of 500 atoms using embedded atom (EAM) potentials. In contrast to bulk simulations [15] they found a largely enhanced H solubility and no distinct two phase field with constant pressure. Calculating the density of hydrogen as a function of the chemical potential Lee et al. determined a slope change of the pressure-composition isotherm which occurs as soon as the loading changes from mainly surface loading to mainly interior loading [16].

Pressure-composition isotherm measurements by

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0925-8388/99/$ – see front matter
PII: S0925-8388(99)00469-7

Salomons et al. [17] on 17-nm and 7.3-nm Pd-clusters adhered to porous SiO_2 and Al_2O_3, respectively, show deviations from the bulk isotherms. In their model these deviations were attributed to a size-dependent contribution to the chemical potential due to surface tension. Contributions due to interfacial stresses were not taken into account. Consequently, Salomon's model can only be verified by studying soft embedded clusters.

In this paper we present hydrogen loading studies on soft stabilized Pd-clusters with a narrow size distributions. Therefore effects attributed to interfacial stresses and a broad cluster size distribution should not influence our experimental results.

2. Experimental details

Pd nano-clusters in poly (amide imide) matrix were synthesized by using the method of Fritsch et al. [5]. Details concerning this preparation method are given in Ref. [6]. The analyzed polymer sample is a foil with 18.9-cm^2 area and 50-μm thickness containing 15 wt% Pd. Transmission electron microscopy (TEM) study shows a bimodal cluster size distribution. Approximating the cluster projections in the micrographs with circles of diameters *d*, the evaluation of more than 200 clusters in TEM micrographs gives a size distribution that is shown in Fig. 1a. A large amount of $d = 3.6$ nm clusters and a negligible amount of $d = (8–12)$ nm agglomerates is found. The large clusters do not contribute to the gasvolumetric experimental results because of their low number density.

Pd-clusters stabilized in a surfactant shell of $(C_4H_9)_4NBr$ were prepared using the technique proposed by Reetz et al. [8,18]. The analyzed powder sample contains $1.73\cdot10^{-3}$ mol Pd. The size distribution of these clusters is very narrow, as shown in Fig. 1b. The mean cluster diameter is (3.13±0.42) nm. HREM lattice imaging on several clusters gave no hints on grain boundaries inside these clusters [19].

The isotherms were determined by performing gasvolumetric measurements at constant temperature of (37±0.5)°C. The measurements were taken using high purity H_2 gas (99.9996%) at constant pressures between 10^5 and 10 Pa inside a high vacuum chamber with a background pressure of 10^{-1} Pa. Precision pressure gauges from MKS with pressure ranges between $2\cdot10^{-2}-2\cdot10^{2}$ Pa, $1-10^4$ Pa and 10^1–10^5 Pa were used. The sensitivity is within 0.01% of the maximum value. Absorption of other components within the vacuum chamber can be neglected. This was verified by performing comparability measurements without samples.

To reduce the oxide surface layer the samples were twice loaded at 10^5 Pa hydrogen gas pressure for approximately 20 h with subsequent evacuation for 20 h.

The surfactant shell as well as the polymer matrix solve hydrogen in a negligible amount and so do not influence the equilibrium results of the gasvolumetric measurements [5,6]. This was checked in the case of the polymer by measuring the pressure drop of the pure polymer.

3. Results

Experimental gasvolumetric adsorption isotherms of the surfactant stabilized Pd clusters (shaded circles) and the polymer stabilized clusters (shaded squares) are represented in Fig. 2 in logarithmic scale. In clusters (all shaded symbols) the hydrogen solubility at low concentrations is found to be largely enhanced compared to bulk Pd (unshaded squares). It is increased by a factor of about ten.

The isotherm obtained for the polymer stabilized clusters reaches up to pressures of 10^2 Pa. That is due to the hydrogen permeability of the polymer that controls the kinetic of absorption. Assuming an equilibrium pressure of 10^2 Pa, equilibrium is reached after a time exceeding 90 h. Thus measurements above 10^2 Pa were not performed. The

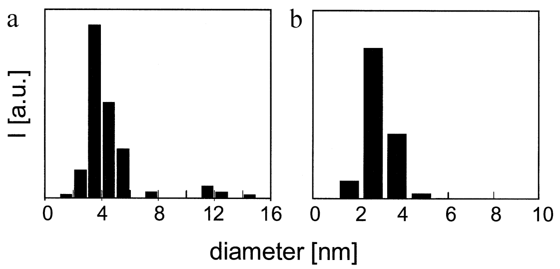

Fig. 1. (a) Bimodal cluster size distribution of Pd-clusters in poly (amide imide) matrix. A large amount of 3.6 nm small clusters and a negligible amount of 8–12 nm large clusters can be seen. (b) Cluster size distribution of Pd-clusters stabilized in a surfactant shell of $(C_4H_9)_4NBr$. A mean diameters of 2.8 nm and a very narrow size distribution can be seen.

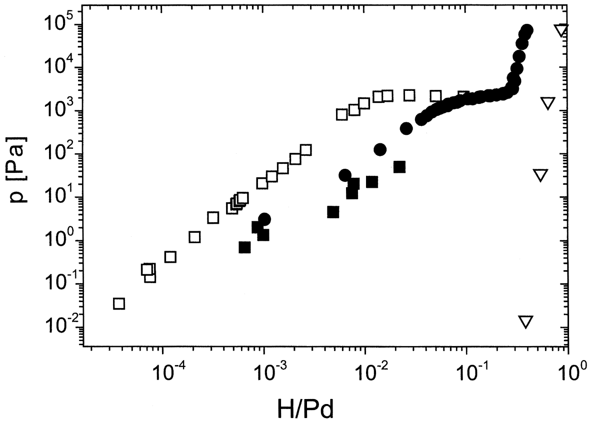

Fig. 2. Pressure–concentration absorption isotherms of Pd-clusters stabilized with surfactants (shaded circles) and in a polymer matrix (shaded squares) obtained at 37°C. For comparison, results for bulk Pd are represented by the unshaded squares. The clusters show a largely enhanced hydrogen solubility compared to that of bulk Pd. The unshaded triangles represent data for a 500 atom cluster calculated by Lee et al.

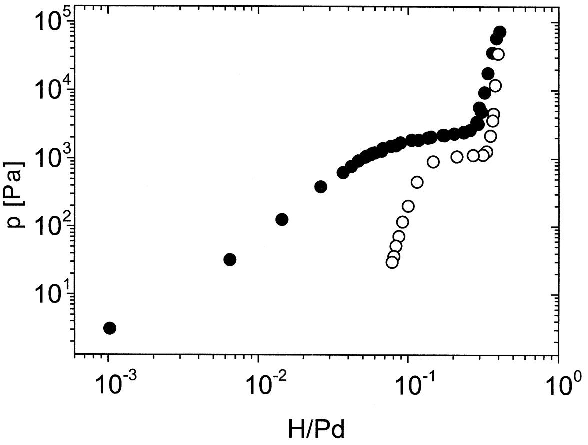

Fig. 3. Pressure–concentration absorption (shaded circles) and desorption (unshaded circles) isotherms of surfactant stabilized 3.1 nm Pd-clusters obtained at 37°C. The existence of a hysteresis is clearly visible. The isotherm branches in the 'plateau' concentration range are not constant in pressure.

kinetic behavior of H-absorption in polymer stabilized clusters will be published elsewhere [19].

For the surfactant stabilized clusters a narrowed two-phase field is detectable indicated by a change in the slope of the chemical potential, respectively the logarithmic gas pressure. The proof for the existence of this two-phase field is given in Fig. 3 where ad- and desorption isotherms of surfactant stabilized clusters are plotted in shaded circles and unshaded circles, respectively. A small hysteresis can be seen.

During desorption the error in the concentration determination successively cumulates. Thus the obtained concentrations are shifted to higher values and after a full cycle the concentrations of ad- and desorption deviate. Nevertheless the pressures at which a plateau appears are determined correctly. Similarly the existence of a slope in the plateau pressure is certain but its absolute inclination cannot be correctly determined.

4. Solubility increase and narrowing of the miscibility gap

The solubility increase compared to that of bulk Pd can be attributed to the additional sorption in surface and subsurface sites. The simulations of Lee et al. [16] on clusters that contain 500 atoms, are plotted in Fig. 2 in unshaded triangles and also show an increase in the solubility. This solubility increase is much larger than that obtained in our experiments. This difference can not be attributed solely to the smaller cluster size (500 atoms ≅ 2.3 nm, by using the lattice constant of bulk Pd). It can be explained by taking into account the fact that at 37°C a monolayer of adsorbed hydrogen is stable on the Pd surfaces [9]. Due to the reduction treatment of the clusters in H_2 the sites on the surface are filled and remain filled during the absorption and desorption runs. Thus the loading only takes place at subsurface and internal sites and the experimental obtained concentrations correspond to this fraction of all sites.

Besides these difficulties in comparing our results with the simulations of Wolf et al. there remains the question whether the chosen potentials describe the system accurately enough, because the same potentials applied to bulk Pd yield a concentration of 1 H/Pd for the α'-phase in contradiction to the experimental value of 0.6 H/Pd [15].

The miscibility gap that occurs during hydrogen loading of 3.1-nm Pd clusters is narrowed compared to bulk material. An α-phase solubility limit $c_l = 0.06$ H/Pd and a minimum solubility $c_r = 0.28$ H/Pd of the hydride phase is obtained from Fig. 3, compared to $c_l = 0.015$ H/Pd and $c_r = 0.58$ H/Pd for polycrystalline Pd determined at 20°C [20].

Similar results were obtained for nano-crystalline Pd (nano) by Mütschele and Kirchheim [20,21]. They have explained the increase in the solubility limit c_l in terms of an increased solubility of hydrogen in grain boundaries. The decreased minimum hydride phase composition c_r was attributed to the assumption that there is no phase transformation in grain boundary regions. The authors give a relation to determine the volume fraction f_t of lattice sites that do not participate in hydride formation

$$f_t = \frac{n_t}{n_{\mathrm{Pd}}} = 1 - \frac{c_r^{\mathrm{nano}} - c_l^{\mathrm{nano}}}{c_r^{\mathrm{poly}} - c_l^{\mathrm{poly}}} \qquad (1)$$

by comparing miscibility limits of poly- and nano-crystalline material. n_t is the number of lattice sites that do not participate in hydride formation. This model can be transferred to clusters by assuming that surface-near sites do not participate in phase transition. Substituting the limits c_r^{nano} and c_l^{nano} in Eq. (1) with c_r and c_l measured on 3.1-nm clusters results in a fraction $f_t = 0.61$. By assuming that the total number of H-sites equals the total number of Pd-atoms this can only be explained if two outer shells of the cluster (3.1 nm ≅ 7 shells, each shell contains $n_i = (10i^2 + 2)$ atoms) are not transforming, $f_t = (n_7 + n_6)/n = 0.60$.

5. Hysteresis

Ad- and desorption measurements of Pd-clusters show the existence of a hysteresis, plotted in Fig. 3. In bulk metal the hysteresis is explained in terms of the generation of misfit dislocations [22,23]. TEM studies carried out in our group have not yet given evidence for the existence of dislocations inside the 3.1-nm clusters. Furthermore, the formation of an incoherent boundary between the matrix and the hydride precipitate is energetically not favored in small clusters. Brook's criterion [24] gives the critical size d_{crit} of a coherent misfitting precipitate, $d_{\mathrm{crit}} = b/g$, where

b is the Burgers vector and g is the misfit between the involved phases. In bulk Pd a coherent hydride precipitate is expected up to a size of about 4 nm. The size of the investigated clusters is smaller than this value. Thus we conclude that the formation of misfit dislocations does not take place and that the explanation for hysteresis in bulk material is not valid in small clusters.

Based on the theory of Cahn and Larche [25], Schwarz and Khachaturyan [26] showed that a thermodynamic treatment of an open two-phase system (like the hydrogen–metal system) with coherent interfaces, already leads to the existence of a hysteresis. The quantitative treatment given in Ref. [26] is in good agreement with the obtained experimental results of this study. The authors give an expression for the relation between adsorption p_{ad} and desorption p_{de} equilibrium plateau pressures

$$\ln \frac{p_{\mathrm{ad}}}{p_{\mathrm{de}}} = \frac{4\Omega G_{\mathrm{s}} \dfrac{1+\mu}{1-\mu} \epsilon_0^2 (c_{\mathrm{r}} - c_{\mathrm{l}})}{kT} \tag{2}$$

where $\Omega = 2.607$ Å^3 is the volume of hydrogen in Pd [27], $G_{\mathrm{s}} = 47.7$ GPa is the shear modulus [28], $\mu = 0.385$ is Poisson's ratio [28], $\epsilon_0 = \mathrm{d}a/a\ \mathrm{d}c = 0.063$ is the lattice expansion [27], k is Boltzmann's constant and T is the temperature. For bulk Pd ($c_{\mathrm{l}} = 0.008$, $c_{\mathrm{r}} = 0.607$ [11]) a pressure ratio $p_{\mathrm{ad}}/p_{\mathrm{de}} = 1.86$ is obtained. Taking the mean equilibrium pressures obtained from Fig. 3 of $p_{\mathrm{ad}} = 2000$ Pa and $p_{\mathrm{de}} = 1100$ Pa gives $p_{\mathrm{ad}}/p_{\mathrm{de}} = 1.8$. Thus we conclude that the hysteresis found in small clusters during hydrogen loading can be explained in terms of the coherent phase transformation of an open system.

Lee et al. [14,16] concluded according to their simulations that phase separation does not occur in small clusters. This disagrees with our experimental results for the 3.1-nm clusters that clearly show a two phase region, as shown in Fig. 3.

The slope of the 'plateau' pressure that can be seen in Figs. 2 and 3 is still unexplained. Contrary to the measurements of Salomons et al. [17] the slope cannot be explained by a broad cluster size distribution. With regard to Fig. 1a and b the narrow size distribution of the investigated clusters can be verified. Hence additional factors influence the 'plateau' slope. We propose that the chemical potential of the H on subsurface sites is influenced by the phase transformation occurring on internal sites. This effect might explain the slope change found in the EAM simulations of Lee et al. as soon as interior sites are filled. Further results concerning this will be given in [19].

6. Summary

Gasvolumetric measurements on H- loaded 3.1- and 3.6-nm Pd clusters show that the H-solubility is ten fold increased in the α-phase range. At higher concentrations the clusters undergo a phase separation into an α- and α′-phase. The miscibility gap is narrower than in bulk Pd. The solubility limit is shifted to a higher H-concentration whereas the minimum α'-phase solubility is lowered. Since surface sites are occupied with hydrogen during all sorption measurements at 37°C, the effects are attributed to an occupation of two shells of subsurface sites.

At higher H gas pressures a hysteresis occurs that can be explained in terms of the thermodynamics of an open two-phase system. The measured plateau pressure ratios are in good accordance with the predictions of the thermodynamic treatment.

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