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Journal of Alloys and Compounds 404–406 (2005) 523–528

Journal of ALLOYS AND COMPOUNDS

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Hydrogen absorption behaviour in nanometer sized palladium samples stabilised in soft and hard matrix

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Received 7 September 2004; received in revised form 28 December 2004; accepted 5 January 2005

Available online 15 July 2005

Abstract

The reduction in the length scale of materials to the nanometer range brings about fundamental changes that lead to novel and unusual phenomena, very different from their coarse-grained counterparts. These differences are not only due to the different physical properties of the small-size system but it is also affected by the type of the stabiliser used on these materials.

In situ X-ray diffraction (XRD) investigations of the hydrogen absorption behaviour in different nanometer sized palladium samples were performed during loading and unloading. Pressure-lattice parameter isotherms were constructed for three different samples: surfactant stabilised clusters, and two types of polymer stabilised samples (clusters and closed clusters layers sample). The pressure-lattice parameter isotherms for the samples show a narrowed *lattice parameter miscibility gap*. The closed clusters layers sample shows the smallest lattice parameter expansion values. The effect of the samples morphology on the lattice expansion will be discussed. It will be shown that not only the sample sizes affect the expansion but also the cluster surrounding plays an important rule.

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Keywords: Synchrotron radiation; Hydrogen; Clusters; Polymers; Surfactants

1. Introduction

Nanometer sized metal clusters have been extensively studied because of the intense scientific interest in exploring the properties of small metal particles, and because of the anticipation in new technological applications [1]. They can be used as quantum dots for understanding the quantum size effects and for designing new optical and electronic materials [2]. The transition metal nanometer sized clusters also serve as a bridge between homogeneous and heterogeneous catalysis and provide new opportunities for catalysis [3].

Clusters in free form, non-stabilised, can be prepared and studied only in vacuum. Clusters tend to agglomerate because of the large cohesion energy of the metals. In this case the cluster size is not stable and structural investigations such as XRD and high resolution electron microscopy (HREM) can not be accomplished under these conditions. To prevent undesired agglomeration clusters have to be stabilised. A large variety of stabilisers can be used such as ligands [4], surfactants [5], polymers [6] and solid matrix [7].

The effect of the stabiliser on the properties of the cluster is a fundamental question. However, detailed reports on the effect of the stabiliser on the cluster are very limited [8]. The stabiliser can influence the physical properties of the cluster because the cluster adapts the stabiliser or it can not change its volume in a way a free cluster would. In a recent study on the binding energy of different stabilisers with the cluster surface, Fu et al. [8] found that the binding between the stabiliser and the cluster surface is larger in case of polymer stabilised clusters than the surfactants (amine) stabilised cluster.

Additionally, the number of anchoring points between the polymers and the clusters is different for polymers and surfactants. Tannenbaum et al. found more anchoring points in the case of polymer stabilisation [9]. Therefore, stabilisers can be classified with regard to the bonding strength to the clusters. This bonding strength contains both the number of anchoring

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doi:10.1016/j.jallcom.2005.01.118

points and the binding energy. Both contributions are larger in the case of polymers. Therefore, we assume polymers to be strong stabilisers compared to the soft surfactant or ligand stabilisers.

In this work tetraoctylammonium bromide (TOAB) and polymethylmethacrylate (PMMA) are used as stabilisers. Studies on films deposited on polycarbonate and PMMA show that stress up to −2 GPa can appear when the substrate is thick [10]. This stress is lower for thinner substrates. Interfacial stress between the stabiliser and the adhered cluster can occur, especially during hydrogen uptake. Measurements on thin films deposited in Si and Al_2O_3 show that the interfacial stress reaches several GPa and influences the thermodynamic properties of the samples [11].

To analyse the stabiliser effect on the cluster isotherm the Pd–H system was chosen. The bulk Pd–H system is one of the most well studied metal–hydrogen systems because of the noble character of the Pd metal and the good hydrogen solubility. These advantages also help studying the small-size system. Furthermore, sample preparation and surface-oxide reduction can be done [12].

In this work the hydrogen solubility of nanometer sized Pd samples will be studied. In situ XRD investigation of the hydrogen absorption behaviour of the different Pd samples will be discussed. The effect of the stabiliser type and hence the morphology of the sample on the hydrogen uptake will be studied. Using the in situ XRD measurements the pressure-lattice parameter relation, which we will call from now on *pressure-lattice parameter isotherm*, will be constructed. Usually, the pressure-lattice parameter isotherms are similar to the pressure concentration isotherms [13] and therefore can be used to identify the behaviour of hydrogen in the samples [14].

2. Experimental

2.1. Cluster preparation

2.1.1. Surfactant stabilised clusters

The surfactant-stabilised (S-clusters) clusters were stabilised in TOAB. The Pd clusters were prepared by using an electrochemical technique described by Reetz et al. [5]. The clusters syntheses were preformed in a two-Pd-electrodes containing cell using a constant current density, where TOAB was used as electrolyte and stabiliser. Applying constant current to the electrodes causes dissolution of the Pd anode with the formation of Pd(II)-cations which are reduced at the cathode forming the so-called "adatoms". The adatoms aggregate into surfactant stabilised clusters. The electrolysis was preformed at room temperature and stopped after a charge of 720 C is passed. Elemental analysis show that an amount of 75% of palladium is within the cluster stabiliser mixture. A schematic picture of the surfactant stabilised cluster is shown in Fig. 1(a).

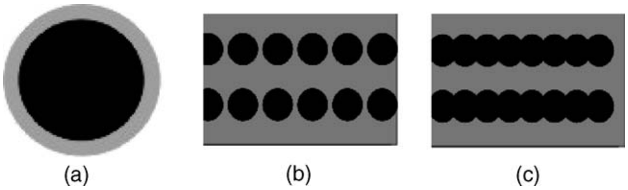

Fig. 1. Schematic illustration of the morphology of the three samples; S-cluster is quasi-free with surfactant stabilisation shell (grey colour) (a). P-clusters having multi-layers stacking form (b) and closed cluster multi-layers (c).

2.1.2. Polymer stabilised clusters

The polymer stabilised clusters (P-clusters) were stabilised in PMMA. The Pd-clusters in PMMA were prepared using pulsed-laser-deposition (PLD). A KrF excimer laser (pulse length 30 ns) at a repetition rate between 5 and 10 Hz and energy density of 2–6 J/cm^2 was applied. As targes a high purity metal foil (99.99+%) and PMMA foil was used. Both, polymers and metals were prepared under ultrahigh vacuum conditions, with a base pressure of less than 10^{-8} mbar. Metal clusters are formed by strong island growth of Pd on the polymer surface. The complete PLD-setup has been described in detail earlier [15]. Samples of 10×10 mm^2 size are prepared on a polymer (PMMA) foil of 50 μm thickness. By using different numbers of laser-pulses the size of the Pd-clusters can be controlled, ranging from nm-sized clusters at 500 pulses to closed layers at 2000 pulses, see Fig. 1(b) and (c). To increase the total mass of the clusters a "multilayer" stack of alternating polymer and cluster layers were prepared. Up to 400 double layers were prepared using PMMA as ground and cap layer.

2.2. In situ X-ray measurements

In situ XRD measurements were performed in a special high vacuum gas loading cell which allows stepwise and controlled hydrogen loading and unloading between 10^2 and 10^5 Pa. All the measurements were conducted at beam line B2 at the Hamburg synchrotron laboratory (HASYLAB) at DESY. The wavelength was selected by a Ge(1 1 1) double-crystal monochromator. All samples were pre-treated with hydrogen to remove any oxide layer. Each loading cycle starts at a base pressure of 10^{-3} Pa, the hydrogen pressure was increased stepwise to 10^5 Pa. The pressure was monitored by using MKS pressure gauges with 0.01% precision. The purity of the hydrogen gas was 99.9999%, all the measurements were performed at room temperature. The measurements are restricted with the time it takes to reach equilibrium pressure and the time needed to take one diffractogram at a selected 2θ range (24–70 °C) with reasonable statistics. The high intensity synchrotron source makes it possible to perform such measurements and reduce enormously the time needed for such experiments.

3. Results and discussion

3.1. Samples characterisation

The cluster size and size distribution was determined by transmission electron microscopy (TEM) and HREM. The S-clusters have medium size of 4.8 nm (see Fig. 2). All sizes were determined from electron microscopy images by measuring more than 150 clusters spread over amorphous carbon sample holders. The full width at half the maximum is about 0.8 nm, and thus, quite narrow. The S-clusters are stabilised by the adsorption of TOAB at their surface, thus providing a protective layer or a *stabilisation shell*. HREM images demonstrate that the distance between individual clusters is about 2 nm, as can be seen in Fig. 3. This indicates that the thickness of the *stabilisation shell* is 1 nm, which means that the Pd cluster is stabilised by one monomolecular layer of TOAB (chain length is about 1.1 nm), which is in accordance with the finding of Reetz and co-workers [16]. The size and the size distribution of the P-stabilised samples were determined from TEM and XRD. Fig. 2(b) shows the TEM picture of a sample prepared at 500 laser-pulses. The sample consists of clusters that are slightly coalesced. The size obtained from counting more than 100 single clusters show that they have a lateral size of 4.8 nm with relatively narrow size distribution of 1.8 nm. Up to now, it was not possible to avoid this slight coalescence in the 4.8 nm sample prepared by using the PLD technique. However, the majority of clusters have free sides.

Fig. 2(c) shows the TEM pictures of the sample, prepared at 2000 laser-pulses. It is a closed clusters layer; no free cluster sides can be detected. The lateral grain size of the closed clusters layer sample was estimated from a transmission XRD experiment and was found to be equal to 9.3 nm. 3.2 hydrogenation measurements in situ XRD measurements for three Pd samples with different morphologies (4.8 nm S-cluster, 4.8 nm P-cluster and 9.3 nm closed cluster layers sample) were performed during hydrogen loading and unloading at different hydrogen pressures. A typical experiment consists of one loading and one unloading cycle. During loading up to 16 pressure steps were taken. Fig. 4a and b, shows diffraction pattern of (a) the 4.8 nm S-clusters and (b) the 4.8 nm P-clusters at four different equilibrium hydrogen pressures, monitoring the lattice expansion by a shift of the peak positions. During hydrogen loading, a shift to smaller 2θ values is observed in the diffraction patterns, indicating a lattice expansion. The shift in the peaks positions increases with increasing the hydrogen pressure. During unloading the peaks positions shift to higher 2θ values indicating a shrinking of the lattice. After unloading the diffraction patterns of the samples are at the exact starting position (Fig. 4a and b). Thus, hydrogen can absorb and desorb reversibly in these samples. The results verify the fast kinetics of the hydrogen sorption and desorption process.

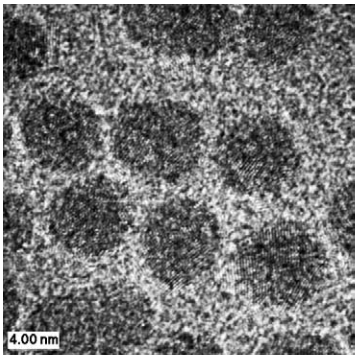

Fig. 3. HREM micro graph of S-clusters showing a distance of about 2 nm between each individual cluster.

Using the X-ray diffractograms obtained from the XRD measurements at different equilibrium hydrogen pressures the pressure-lattice parameter isotherms for the three samples were constructed (Fig. 5). The lattice parameter of each Pd sample, at a given pressure, was calculated from the position of the lower angle peak (near bulk fcc (1 1 1) reflection). The pressure-lattice parameter isotherms show three distinguished regions (I, II and III in Fig. 5). These parts are comparable to the parts found in the pressure–concentration isotherms. Region I is the solid solution. Region II represents the two-phase region (miscibility gap); results supporting this interpretation will be given in the coming discussion. In this current work it's called the *lattice parameter miscibility gap*,

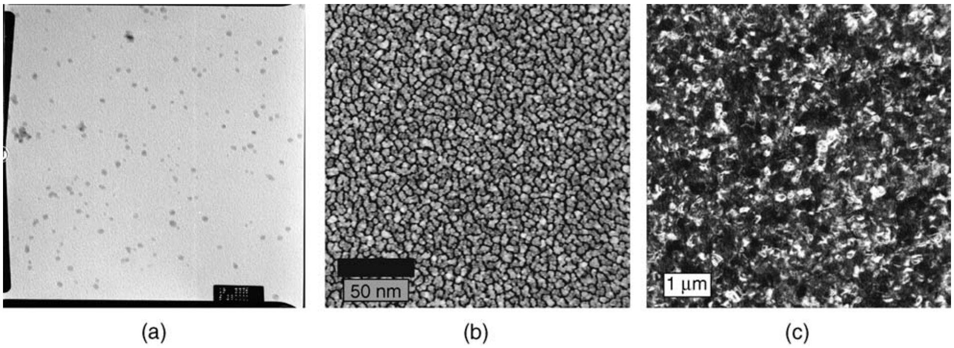

Fig. 2. TEM micro graphs of (a) surfactant stabilised clusters (S-clusters), (b) polymer stabilised clusters (P-clusters) and (c) TEM micro graph of the closed cluster layers sample.

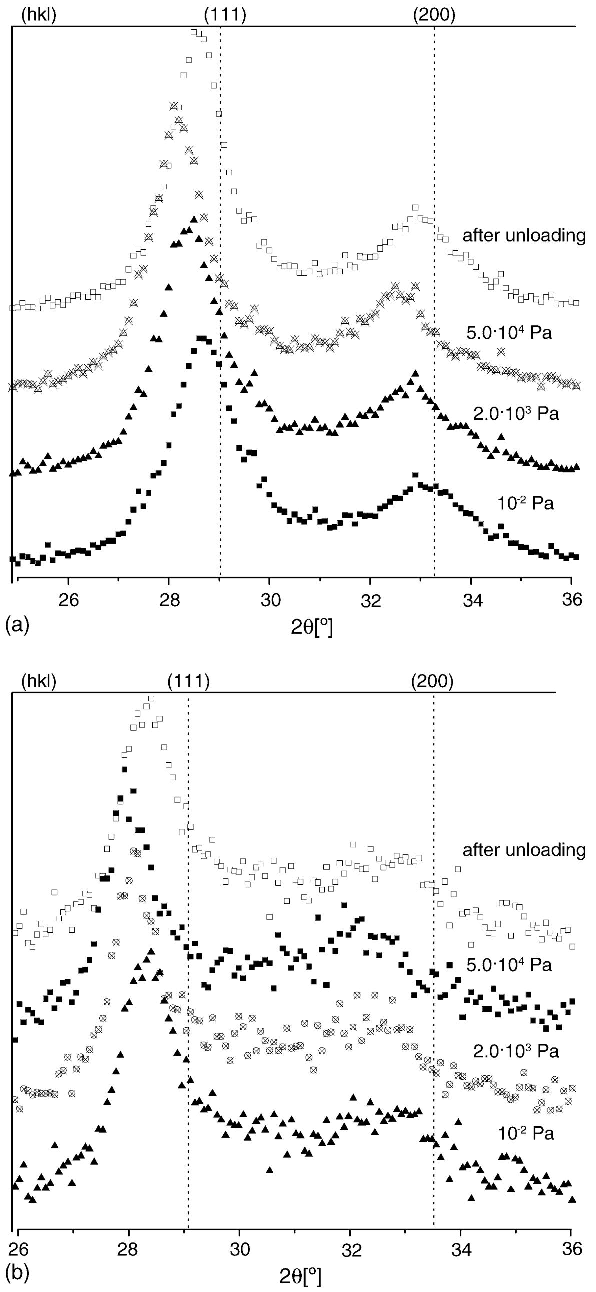

Fig. 4. Diffraction patterns of the 4.8 nm S-clusters (a) and the 4.8 nm P-clusters (b). During hydrogen loading, a shift to smaller 2θ values is observed in the diffraction patterns. During unloading the peaks positions shift to higher 2θ values indicating a shrinking of the lattice. After unloading the diffraction patterns of the samples are at the exact position of the unloaded one (10^{-2} Pa). ($\lambda = 1.2438$ Å).

since pressure-lattice parameter isotherms are presented. In contrast to bulk Pd, where ideally no pressure dependency exists, this region has, for clusters, a pressure dependency and is occurring over a pressure range. This behaviour was also found in pressure–concentration isotherm measurements [17–19]. Region III, is comparable to the metal hydride where the lattice parameter rises steeply with increasing pressure.

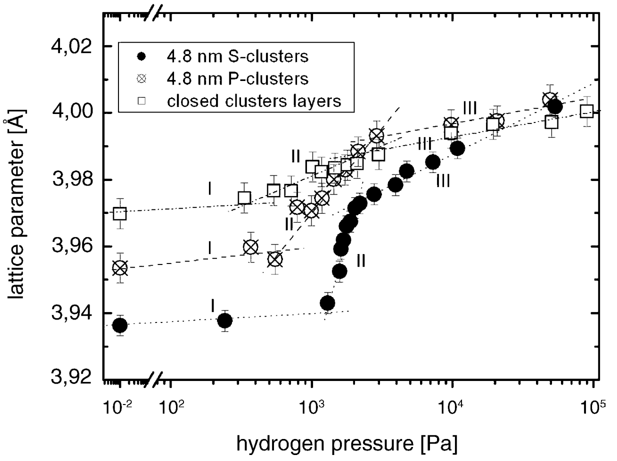

Fig. 5. The pressure-lattice parameter isotherms of the 4.8 nm S-cluster (circles), the 4.8 P-cluster (crossed-squares) and the closed film sample (squares). The isotherms show three distinguished regions.

By examining Fig. 5 the following features can be seen; First, the lattice parameters of the pure Pd-cluster samples are larger than that for bulk Pd ($a_0 = 3.890$ Å): Secondly, region II (the *lattice parameter miscibility gap*) for the polymer stabilised samples is occurring in a wider pressure range than that for the surfactant stabilised clusters. Lastly, the total lattice expansion for the polymer stabilised samples is smaller than that for the surfactant stabilised samples. These findings will be discussed in the following.

The lattice parameter values of the pure Pd samples (at 10^{-2} Pa) were not only found to be larger than that for bulk Pd but also different from each other; the lattice parameter of the closed cluster layers ($a_0 = 3.9701$ Å) is larger than that of the P-cluster ($a_0 = 3.9534$ Å) and the S-cluster ($a_0 = 3.9369$ Å). Especially the last two cluster types that have a comparable size of 4.8 nm but a different stabiliser strongly differ in their low-concentration lattice parameter. The results show that the mean Pd–Pd interatomic distance expands with changing the stabiliser from soft to strong. Furthermore, the lattice dilation does not have the expected size dependency.

In a previous work we have found that the lattice parameter of pure Pd clusters increases with decreasing the clusters size. Other reports also show this dilation of the lattice constant with decreasing clusters size [6,20,21]. This was attributed to an incorporation of gases at the sample surface sites [22], subsequent lattice stretching [23] and, furthermore, a different structure especially for small size samples [14]. In this work such an explanation can not explain our results since the largest Pd-clusters sample has the largest lattice parameter. There has to be another reason for the present finding.

The closed cluster layer sample and P-cluster sample are stabilised in PMMA (strong matrix) [9] whereas the S-cluster sample is stabilised in TOAB (soft matrix) [8]: the samples have different morphologies and different surface surrounding. We attribute the dilation of the lattice parameter to mechanical stress between the sample surface and the stabiliser.

The mechanical stress seems to be larger in the case of the polymer stabilised samples. Therefore they have larger lattice parameter values than the surfactant stabilised cluster. This can be interpreted by a mechanically harder matrix in the case of the polymer compared to the mechanically softer surfactant.

The larger lattice parameter value for the closed clusters layers in comparison to the cluster sample (P-clusters) can be explained by the coalescence effect during cluster film growth. As soon as the clusters coalesce surface tension will be reduced and the in-plane lattice parameter will be stretched.

Secondly, the different pressure ranges in which region II (the "*lattice parameter miscibility gap*") is occurring, Fig. 5. The pressure range is different even for the clusters with the same size. For the 4.8 nm S-clusters sample it appears in the pressure range of 1.0×10^3–2.0×10^3 Pa (during H-loading) which is smaller than that for the polymer stabilised samples. Our results on clusters with different sizes show that this region (the "*lattice parameter miscibility gap*") is similar to the pressure change in the miscibility gap found in apparent pressure–concentration isotherms [12,19]. The *lattice parameter miscibility gap* of the 4.8 nm P-cluster sample appears in a wide pressure range of 6.0×10^2–2.7×10^3 Pa. The closed clusters layers sample shows a lattice parameter miscibility gap almost in the same pressure range 6.0×10^2–2.8×10^3 Pa.

Now the questions are arising: if this region really is marking the miscibility gap (*lattice parameter miscibility gap*) and why it occurs in a wider pressure range for the polymer stabilised samples.

Region I and III seem to mark different phases which can be also different from the well-known bulk phases [14]. In situ XRD measurements performed during stepwise hydrogen unloading of the S-clusters and P-clusters samples show the existence of a hysteresis in region II. If such a hysteresis can be taken as a finger print of a phase transition even for the small-size system, as done in an earlier work [19], this indicates that a transition is occurring in this pressure range (region II in Fig. 5), although the apparent reflections can not be separated. Thus region II is marking the miscibility gap between two phases and in our case it is the *lattice parameter miscibility gap*.

The wide pressure range is most probably due to lateral stress which grows up during hydrogen loading [24]. It is assumed that a larger mechanical stress change results in a larger width of the pressure change in the miscibility gap of the small size system.

According to our results on the lattice parameter shift of the unloaded samples, the mechanical stress is smaller in S-clusters sample, the matrix is mechanically softer. Fig. 5 shows that the *lattice parameter miscibility gap* occurs in a narrower pressure range. Exactly this is expected for the softer matrix and, therefore, supports the above given interpretation. This interpretation can also be applied for understanding literature results. Salomons et al. [7], for example, measured isotherms of 17 nm and 7.3 nm Pd–H clusters stabilised in SiO_2 and Al_2O_3. They attributed the wide pressure range of the miscibility gap, visible as slope in the plateau region, to a size dependent shift of the chemical potential whose origin should have been the size dependent surface tension. Sachs et al. [8] and Pundt' [25] both showed that this contribution can not explain the order of magnitude of their experimental data obtained from surfactant stabilised (soft matrix) Pd clusters. However, mechanical stress between the cluster particles and the stabiliser might explain the steep slope, for the mechanically very hard SiO_2 and Al_2O_3 substrates these contributions are expected to be huge.

To summarise, the wider pressure range of the polymer-stabilised clusters compared to the surfactant-stabilised clusters can be understood by the larger mechanical stress in case of the polymer matrix. The width of the *lattice parameter miscibility gap* is strongly affected by mechanical stress between the cluster and the matrix.

Lastly, the total lattice expansion of the polymer stabilised samples is smaller than the surfactant stabilised sample. Using the data in Fig. 5, S-clusters show a total lattice expansion value ($\Delta a = 0.065$ Å) which is larger than that for P-clusters ($\Delta a = 0.051$ Å). The closed-clusters layers sample shows the smallest lattice expansion value ($\Delta a = 0.029$ Å). This result is also not expected. In a previous study performed on S-clusters (in the size range between 3.0 and 6.0 nm), we have found that the lattice expansion is strongly size dependent [14]. The lattice expansion values for larger clusters are larger than those for smaller ones, but still smaller than those for bulk Pd. For example, after loading cycle, $\Delta a = 0.123$ Å for the 6.0 nm cluster but $\Delta a = 0.036$ Å for the smallest cluster (3.0 nm) [12,14]. The narrowing in the miscibility gap on going from the large-size system to the small-size system was reported by many workers [19,26,27]. This behaviour is mostly related [7,8,26] to the large surface-to-volume atom ratio which leads to an increased α-solubility and a decreased α'-solubility.

In this work the *lattice parameter miscibility gap* for the cluster samples was found to be larger than that for the closed cluster layers sample. This behaviour is surprising, since one would expect a narrowing in the miscibility gap on going from large-size system to small-size system. The arguments based on the increased α-solubility and the decreased α'-solubility discussed above is not enough to explain this observation. The three Pd samples have different morphologies and matrices and this has to be taken into account. We attribute this difference in the behaviour of the clusters samples to the difference in type of the stabiliser and different morphology of the samples.

S-clusters are stabilised with one mono-molecular layer of TOAB and since the modulus of elasticity of the surfactant is an order of magnitude lower than that of the clusters [5], the S- Pd cluster is soft stabilised and the cluster can expand well. In earlier works, we even regarded these clusters as expanding quasi-free [8]. The narrowing in the miscibility gap observed in these cluster samples [7,8] was explained in terms of a two-site model, whereby hydrogen atoms can only occupy subsurface or bulk-sites. According to these calculations two sub-surface sites do not contribute to the phase transition. The question if such a simple treatment is allowed when stress contributions take part is an open question. However our results suggest that this simple treatment can not be used in the case of large stress contribution.

The P-cluster is stabilised in PMMA, so one would expect that the mechanically hard stabilizer, also having a stronger bonding and more anchoring points [9] will prevent the cluster from changing its volume quasi-freely. In this case the cluster expansion will be hindered by arising compressive stress, and it will have smaller Δa values in comparison to the S-cluster. This was exactly found in our measurements.

The effect of the stabiliser is more pronounced in the closed clusters layers sample ($\Delta a = 0.029\,\text{Å}$). Due to the morphology of this sample, no free cluster sides, the lateral expansion is expected to be even more difficult than in the case of the P-clusters. Expansion of clusters is hindered by adjacent clusters, since the cluster layers are closed (see Fig. 2c).

All the results presented in this paper confirm the important impact of mechanical stress on isotherm measurements of clusters. Mechanical stress changes low-concentration lattice parameter values, increases the width of the pressure range in which the *lattice parameter miscibility gap* is occurring and, furthermore, changes the lattice parameter values of the high-concentration phase.

4. Conclusions

In situ XRD measurements on Pd nanometer samples, (surfactant-stabilised cluster, polymer-stabilised cluster and cluster-layer sample) show that the lattice dilation during hydrogen loading and unloading strongly depends on the sample morphology and the type of the stabiliser. Low-concentration lattice parameters, lattice parameter expansion, phase transition as well as the high-concentration lattice parameter values are affected by these contributions. Polymer (PMMA) stabilised cluster (4.8 nm P-cluster) show larger low-concentration lattice constants and smaller lattice expansions than their surfactant (TOAB) stabilised counterparts (4.8 nm S-cluster). This can be attributed to the different hardness of the stabilisers and the mechanical stress arising between the cluster and its stabiliser during hydrogen uptake. Our results suggest that the PMMA stabiliser is mechanically harder than the TOAB stabiliser. All experimental results can be interpreted by taking the mechanical hardness of the stabiliser into account. The closed cluster layers sample shows the smallest lattice parameter expansion. This behaviour is attributed to the hard polymer stabiliser and the fact that side expansion is hindered by neighbouring clusters.

Acknowledgements

Financial support by the DAAD and SFB602 (A9) is greatly acknowledged. Beam time provided by HASYLAB, Hamburg, Germany is highly appreciated.

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