Pressure-Composition Isotherms for Nanocrystalline Palladium Hydride

Ralph J. Wolf and Myung W. Lee
Savannah River Technology Center, Westinghouse Savannah River Company, Aiken, South Carolina 29808

John R. Ray
Department of Physics and Astronomy, Clemson University, Clemson, South Carolina 29634-1911

(Received 23 February 1994)

We present results from Monte Carlo simulations of the pressure-composition isotherms of nanometer-size palladium clusters under hydrogen loading. In contrast to simulations of bulk samples, the clusters do not show a phase transformation upon hydriding. A study of the hydrogen loading of the clusters shows that they load the surface first and then the interior, with no evidence of a phase transformation. We relate this behavior of our models to the observed narrowing of the plateau (miscibility gap) in the phase boundary of the pressure-composition phase diagram of nanocrystalline palladium.

PACS numbers: 61.46.+w, 05.20.Gg, 64.10.+h, 64.75.+g

Nanocrystalline materials have attracted much attention due to their altered physical properties, which include, among others, increased microhardness and yield stress as well as increased hydrogen solubility [1]. Recently we have presented Monte Carlo simulations in which we successfully modeled the phase transformation from the low composition α palladium hydride (Pd-H) phase on the high composition β Pd-H phase [2]. In the previous study [2] we employed embedded atom method potentials that we developed for the Pd-H system. We employed these same potentials, which we refer to as PDW3, in the present study; further details of our potential may be found in Wolf *et al.* [3]. For a general discussion of embedded atom method we refer to papers by Daw and Baskes [4]. Our earlier [2] Monte Carlo simulations were performed in the $(TP\mu_H N_{Pd})$ ensemble [5], in which the temperature T, the pressure P, the hydrogen chemical potential μ_H, and the number of palladium atoms N_{Pd} are held constant. The simulated transformation is very sharp in the hydrogen pressure or chemical potential variable, with a change in the chemical potential from -2.477 to -2.476 eV resulting in the system transforming from the α phase to the β phase. Since we used three-dimensional periodic boundary conditions in these simulations, our results correspond to bulk samples.

Mütschele and Kirchheim [6,7] and Eastman, Thompson, and Kestel [8] have shown that the width of the plateau (miscibility gap) for the Pd-H phase boundary shows significant narrowing, in the composition variable [H/Pd], for nanocrystalline samples as compared to conventional polycrystalline samples. For example, in a nanocrystalline sample with average grain diameter 8–12 nm Mütschele and Kirchheim [7] reported the maximum α phase composition (α_{max}) is increased from 0.015 to 0.03 while the minimum β phase composition (β_{min}) is decreased from 0.58 to 0.44 as compared to a polycrystalline sample with an average grain diameter of 20 μm; comparable results were reported by Eastman; Thompson, and Kestel [8].

Mütschele and Kirchheim [7] concluded that the increase in α_{max} for nanocrystalline palladium hydride (n-PdH) was due to an increase in H solubility at the grain boundaries. The decrease in β_{min} was attributed to the fact that the grain boundary regions, which were estimated to occupy 27% of the sample volume, do not transform to the β phase. However, it was shown by Eastman, Thompson, and Kestel [8] by carrying out very detailed *in situ* x-ray diffraction studies that the narrowing of the plateau in the n-PdH phase diagram is not related to the inability to form the hydride phase in the grain boundary regions; the entire sample is converted to the β phase upon hydriding. Eastman, Thompson, and Kestel did not give any new microstructural explanation of the narrowing but argued that such behavior was thermodynamically possible and consistent with the observed results.

More recently Sanders and Weertman [9] have shown using small angle neutron scattering (SANS) that the grain boundary regions in n-Pd are associated with voids ranging in size from 1 nm to 0.1 μm. No evidence for any structure in the grain boundary regions except voids was necessary to explain the SANS over 8 orders of magnitude.

The above experimental results suggest that the narrowing of the plateau in the n-PdH phase diagram is associated with loading of hydrogen onto the surface of the voids in the nanocrystalline samples; this means that the narrowing of the plateau is a surface effect associated with the much larger surface area of the grains contacting the voids in n-PdH. In order to test this hypothesis we constructed Pd clusters of 500 Pd atoms and studied the hydrogen loading of these clusters. These clusters are not a detailed model of n-Pd, but they should show the effect of surface area on the hydriding of Pd in a case of extreme surface area. In our clusters approximately 88% of the Pd atoms are within 0.5 nm of the surface, while in a nanocrystalline sample with 5 nm grain size, approximately 50% of the atoms are within 0.5 nm of one or more grain boundaries [8]. As we shall discuss, the

0031-9007/94/73(4)/557(4)$06.00

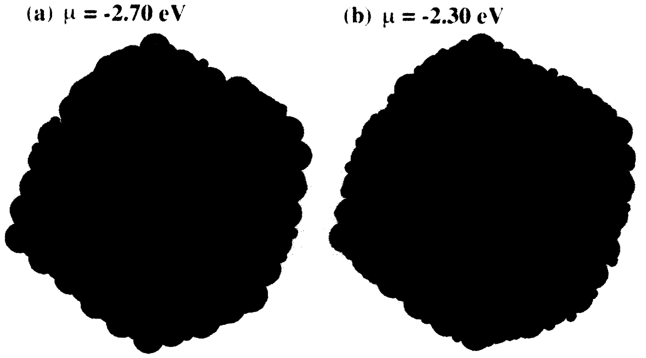

FIG. 1. (a) A view of the Pd-H cluster at a chemical potential of −2.70 eV. The average number of hydrogen atoms adsorbed on the cluster at this chemical potential is 64. The palladium atoms are shown as blue spheres while the hydrogen atoms are shown as red spheres. (b) A view of the Pd-H cluster at a chemical potential of −2.30 eV. The orientation of the cluster is the same as in (a). The average number of H atoms adsorbed onto and absorbed into the cluster is 635.

pressure-composition relation we determine for the clusters does not show a hydride phase transformation.

In order to form the cluster we removed the three-dimensional periodic boundary conditions from a 500 particle fcc crystal and equilibrated the cluster at a temperature of 300 K for several hundred thousand Monte Carlo moves. At this temperature the cluster ends up with multiple facets. We formed two clusters which have different facet structure but had very similar pressure-composition isotherms; we shall present results for the first cluster. By studying the density of the cluster as measured from the center of mass of the cluster, we determined the radius of the cluster to be approximately 1.3 nm.

Next we employed grand canonical Monte Carlo simulations to study the hydrogen loading of the cluster at 300 K. The procedure used is described in some detail in Ref. [2] and in Ray and Wolf [10] and we shall, therefore, not repeat all the details. We used a grid of 1000 ghost hydrogen atoms spread randomly over the cluster and attempted 10 creation and 10 destruction trials for each spatial Monte Carlo move of all the particles. When a real particle was deleted (turned into a ghost) it was not allowed to be created for 10 Monte Carlo moves, where a Monte Carlo move means an attempt to move all the real particles and 10 creation attempts and 10 destruction attempts. At selected times during the simulation the ghosts were randomized over the volume of the system. These are the same strategies that we employed in Refs. [2] and [10]. All of the simulations reported in this paper were performed at a temperature of 300 K.

In Fig. 1 we show pictures of the Pd cluster loaded with hydrogen at chemical potentials of −2.70 and −2.30 eV with equilibrium numbers of 64 and 635 H, respectively. Palladium atoms are represented by blue spheres and hydrogen by red spheres. Both (111) and (100) facets appear on the surface as well as various defects. The hydrogen loads mainly into the bridge and hollow sites on the facets. In order to further illustrate that H load first on the surface of the cluster we determined the density of H atoms as measured from the center of mass of the Pd cluster. In Fig. 2 we show the average hydrogen number density determined from the center of mass of the palladium cluster for four chemical potentials: −2.70, −2.65, −2.50, and −2.40 eV, which correspond to increasing hydrogen pressure; the [H/Pd] compositions at these chemical potentials are 0.131, 0.276, 0.529, and 0.886, respectively. It is clear from Fig. 2 that the hydrogen first loads on the surface of the cluster and then loads in the interior. We can also verify the

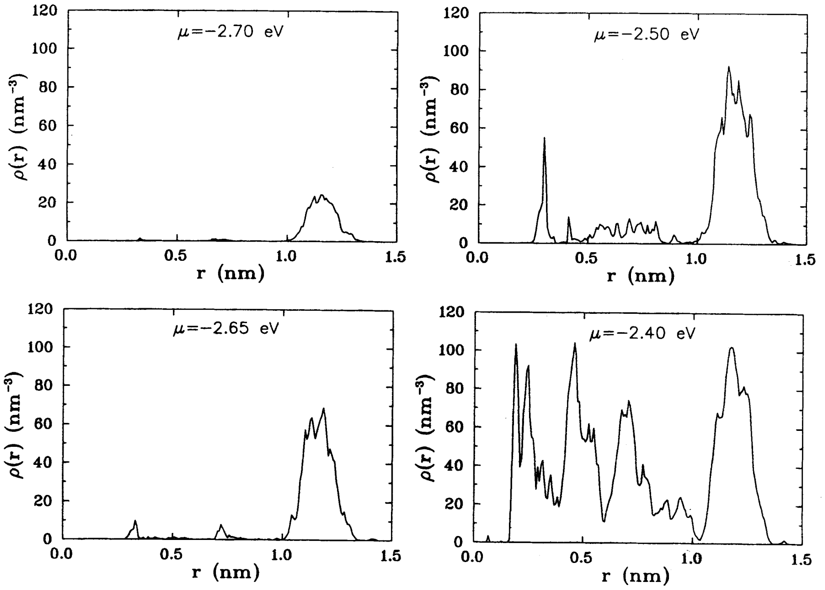

FIG. 2. The density of the hydrogen as seen from the center of mass of the Pd cluster for four different chemical potentials: −2.70, −2.65, −2.50, and −2.40 eV; the compositions of H can be found from Table I. This shows that H loads on the surface of the cluster and then into the interior.

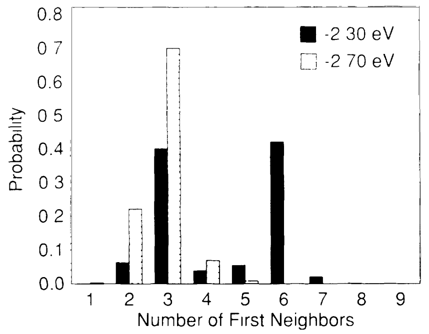

FIG. 3. The probability of H atoms having first nearest-neighbor Pd atoms in the two clusters shown in Fig. 1. The cross-hatched values are for Fig. 1(a) while the nonhatched values are for Fig. 1(b).

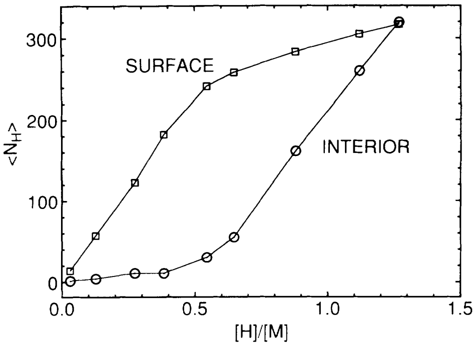

FIG. 4. Average number of surface and interior hydrogen atoms versus [H/Pd]. A hydrogen atom is identified as occupying a surface site (squares) if it has fewer than 5 nearest-neighbor palladium atoms or an interior site (circles) if it has 5 or more nearest-neighbor palladium atoms. The lines through the data are just a guide.

surface loading by calculating the number of Pd atoms that are first nearest neighbors of H atoms. For an H atom on the surface this number is 2 at a bridge site, 3 at a threefold hollow site, and 4 at a fourfold hollow site, whereas in the interior the H atoms load into octahedral sites [2] where the number of Pd neighbors is 6. In Fig. 3 we show the probability distribution for Pd neighbors of H atoms for the two clusters shown in Fig. 1. The neighbors are determined by averaging over the number of neighbors up to the first minimum (0.265 nm) of the pair distribution function for each H atom. Figure 3 shows that there are no atoms with 6 Pd neighbors for the cluster in Fig. 1(a); that is, the H atoms are on the surface of the cluster. For the cluster in Fig. 1(b) there are H atoms with 6 Pd neighbors which shows that atoms are also loaded into the interior of the cluster in this case. In order to further quantify the changeover from mainly surface loading to mainly interior loading of the clusters, we determined the number of surface and interior hydrogen atoms as a function of [H/Pd]. For this purpose a hydrogen atom is defined as occupying a surface site if it has fewer than 5 first nearest-neighbor palladium neighbors and an interior site if it has 5 or more first nearest-neighbor palladium neighbors. No significant change occurs if we use 6 neighbors instead of 5 in these definitions since there are few atoms with 5 neighbors. In Fig. 4 we show the average number of surface and interior hydrogen atoms loaded on and in the cluster as a function of composition. Notice the sharp increase in the slope of the number of interior versus the sharp decrease in the slope of the number of surface hydrogen atoms around the composition of [H/Pd] =0.65. Figure 4 clearly shows the changeover from mainly surface to mainly interior loading of hydrogen at around [H/Pd] =0.65. The fact that both the surface and interior numbers are approximately equal at the last point in Fig. 4 is a reflection of the size of the cluster and has no other significance.

In Fig. 5 we show the pressure-composition isotherm at 300 K for the cluster along with the bulk experimental desorption data of Frieske and Wicke [11] and the bulk simulation data from Ref. [2]. Hydrogen loading of the cluster starts at a very low pressure; for example, [H/Pd] =0.0322 at $P=1.33\times10^{-12}$ atm, corresponding to a chemical potential of -2.75 eV, and $\log_{10}P$(atm) increases with composition up to the highest pressure studied. The slope of $\log_{10}P$(atm) decreases near the composition 0.65 which is the changeover from mainly surface loading to mainly interior loading of the cluster. It is interesting that the cluster can be loaded to compositions larger than 1.0; this is due to the large number of H

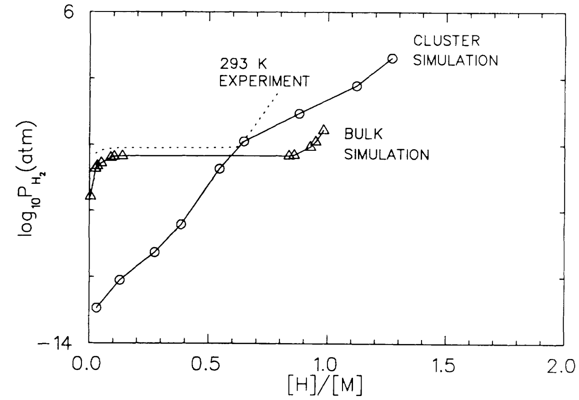

FIG. 5. Pressure-composition isotherms at 300 K for palladium hydride. The experimental values are from Ref. [11] and are shown by the dashed line with no symbols with the temperature label 293 K Experiment. The bulk simulation data at 300 K from Ref. [2] are shown by the solid line with triangles. The cluster simulation data at 300 K are shown by the solid line with circles; the pressures are calculated from the chemical potentials in Table I by using Eqs. (5) and (6) of Ref. [2]. The lines through the data are just a guide.

TABLE I. Chemical potential, hydrogen compositions, and pressure for hydrogen loading of a 500 atom palladium cluster at 300 K. The pressure is calculated using Eqs. (5) and (6) from Ref. [2].

μ (eV)	[H]/[Pd]	P (atm)
−2.75	0.0322	1.33×10^{-12}
−2.70	0.129	6.38×10^{-11}
−2.65	0.275	3.05×10^{-9}
−2.60	0.384	1.46×10^{-7}
−2.50	0.545	3.47×10^{-4}
−2.45	0.648	1.60×10^{-2}
−2.40	0.879	0.766
−2.35	1.12	36.7
−2.30	1.27	1755.0

atoms that are adsorbed on the surface. In Table I we give the data used to construct Fig. 5. The value of the pressure is obtained from the chemical potential by equating the chemical potential of H in the cluster to the chemical potential of an ideal gas of H_2 molecules using Eqs. (5) and (6) given in Ref. [2]. Our simulations are carried out at zero pressure since the pressure of the H_2 gas outside the cluster is too small to have an appreciable effect on the cluster volume. The maximum pressure is 1755 atm whereas the bulk modulus of palladium is around 2×10^6 atm.

From Fig. 5 we see that there is no hydride phase transformation for the Pd cluster; although there is a slope change there is no plateau region. The slope change near [H/Pd] =0.65 is associated with the changeover from mainly surface loading to mainly interior loading. In actual nanocrystalline palladium samples the surface area associated with the voids is much larger than in coarse grain samples but less than in our clusters. There would be a shrinkage of the plateau region in the phase diagram with decreasing grain size. Our cluster corresponds to a grain size of approximately 2.6 nm.

The details of the boundary region in actual nanocrystalline samples are, of course, more involved than simple voids. In simulations we are currently performing [12] on bulk systems with large scale defects such as grain boundaries and dislocations, we also see a modification of the pressure-composition phase diagram for palladium hydride. Moody and Foiles [13] have studied the change in the grain boundaries regions of models of nickel when hydrogen is present.

We have determined the pressure-composition isotherms for palladium clusters undergoing hydrogen loading. There is no phase transformation for the clusters due to the ease of hydrogen adsorption which starts at very low hydrogen pressures; there is a slope change in the pressure-composition relation which occurs as the loading changes from mainly surface loading to mainly interior loading. Our results suggest that the narrowing of the plateau in nanocrystalline palladium hydride is associated with the loading of hydrogen onto the surface of voids. The narrowing should be correlated with the grain size of the sample, narrowing further as the grain size decreases.

We acknowledge support from the U.S. Department of Energy under Contract No. DE-AC09-88SR18035 and through SCUREF. We thank Dr. Khalid Mansour, Dr. Elliot Clark, Dr. Jeff Eastman, and Professor Dick Manson for helpful discussions.

[1] R. W. Siegel, Phys. Today, **46**, No. 10, 64 (1993).
[2] R. J. Wolf, M. W. Lee, R. C. Davis, P. J. Fay, and J. R. Ray, Phys. Rev. B **48**, 12415 (1993).
[3] R. J. Wolf, K. A. Mansour, M. W. Lee, and J. R. Ray, Phys. Rev. B **46**, 8027 (1992).
[4] M. S. Daw and M. I. Baskes, Phys. Rev. Lett. **50**, 1285 (1983); Phys. Rev. B **29**, 6443 (1984).
[5] Since Ref. [2] was published we have learned from Dr. Khalid Mansour that the $(TP\mu_H N_{Pd})$ ensemble has been mentioned in T. L. Hill, *An Introduction to Statistical Mechanics* (Addison-Wesley, Reading, MA, 1960), p. 363. Hill credits Stockmayer with first introducing this ensemble in W. H. Stockmayer, J. Chem. Phys. **18**, 58 (1950).
[6] T. Mütschele and R. Kirchheim, Scr. Metall. **21**, 135 (1987).
[7] T. Mütschele and R. Kirchheim, Scr. Metall. **21**, 1101 (1987).
[8] J. A. Eastman, L. J. Thompson, and B. J. Kestel, Phys. Rev. B **48**, 84 (1993).
[9] P. G. Sanders, J. R. Weertman, J. G. Barker, and R. W. Siegel, Scr. Metall. **29**, 91 (1993).
[10] J. R. Ray and R. J. Wolf, J. Chem. Phys. **98**, 2263 (1993).
[11] H. Frieske and E. Wicke, Ber. Bunsen-Ges. Phys. Chem. **77**, 48 (1973).
[12] R. J. Wolf, M. W. Lee, and J. R. Ray (to be published).
[13] N. R. Moody and S. M. Foiles, Mater. Res. Soc. Symp. Proc. **229**, 1 (1991).

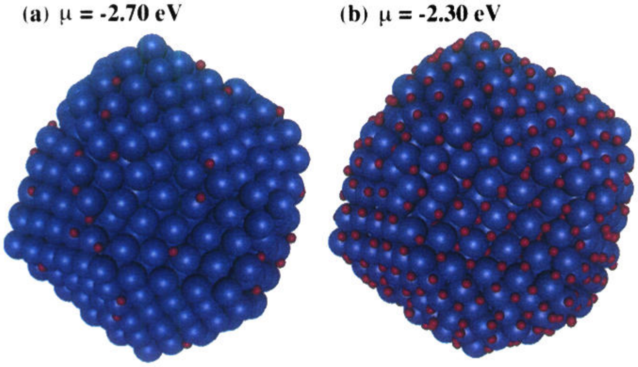

FIG. 1. (a) A view of the Pd-H cluster at a chemical potential of -2.70 eV. The average number of hydrogen atoms adsorbed on the cluster at this chemical potential is 64. The palladium atoms are shown as blue spheres while the hydrogen atoms are shown as red spheres. (b) A view of the Pd-H cluster at a chemical potential of -2.30 eV. The orientation of the cluster is the same as in (a). The average number of H atoms adsorbed onto and absorbed into the cluster is 635.

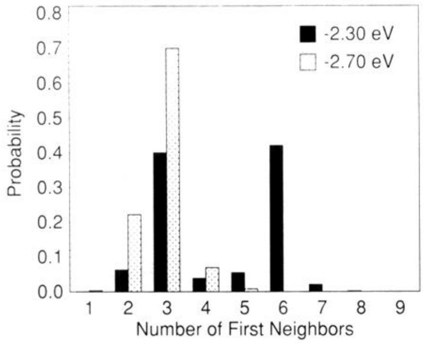

FIG. 3. The probability of H atoms having first nearest-neighbor Pd atoms in the two clusters shown in Fig. 1. The cross-hatched values are for Fig. 1(a) while the nonhatched values are for Fig. 1(b).