CHARACTERIZATION OF NANOCRYSTALLINE Pd BY X-RAY DIFFRACTION AND EXAFS*

J. A. Eastman¹, M. R. Fitzsimmons^{2**}, M. Müller-Stach², G. Wallner² and W. T. Elam³

¹Materials Science Division, Argonne National Laboratory, Argonne, IL 60439

²Ludwig Maximilians-Universität, München, Germany

³Naval Research Laboratory, Washington, DC 20375

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¹Argonne National Laboratory, Argonne, IL 60439

²Ludwig-Maximilians-Universität, München, Germany

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Introduction

Since the fraction of atoms located within a few atomic distances of one or more internal interfaces increases rapidly with decreasing grain size in the nanometer regime, it is expected that the structure of grain boundaries plays an important role in determining and controlling the properties of nanocrystalline materials. Studies characterizing the nature of the structure of grain boundaries in nanocrystalline materials have been controversial. Zhu, et al. [1] studied nanocrystalline Fe by x-ray diffraction and concluded, based on a comparison of observed and calculated diffuse background intensities, that grain boundary regions in nanocrystalline materials lack both short- and long-range order. Haubold, et al. [2] concluded from an EXAFS investigation of nanocrystalline Cu and Pd that the boundary component of nanocrystalline materials represents a new solid-state structure with random atomic arrangement. In contrast to these conclusions, however, a high resolution electron microscopy study of nanocrystalline Pd found no evidence for extended, disordered boundary regions that would differ from boundaries in coarse-grained materials [3]. Recent results from x-ray diffraction [4], EXAFS [5] and hydriding studies [6] have yielded clear evidence that the boundaries in nanocrystalline Pd are ordered and/or extremely localized in nature. The present paper will summarize and discuss the principal results of these latter three studies.

X-Ray Diffraction Studies at Ambient Temperature

Nanocrystalline Pd was produced by the gas-condensation method [7] using the process first suggested by Gleiter [8]. In the present study 99.997% purity Pd wire was evaporated from a ceramic crucible in 500 Pa of 99.9999% He gas. The resulting ultrafine powder was collected and consolidated at ambient temperature using a pressure of ~1.4 GPa. Except during the evaporation of the Pd, the entire process took place under vacuum conditions (~10⁻⁵ Pa) in order to ensure minimum sample contamination. The sample was disk-shaped with a diameter of 9 mm, a thickness of 0.18 mm and a density estimated at 80±10% of the literature value (12.02 g/cm³ [9]). A coarse-grained reference foil cut to the same dimensions as the nanocrystalline sample was examined in order to obtain a direct comparison of the effect of grain size on diffracted intensity. The grain size of the nanocrystalline sample was estimated as 9 to 16 nm, based on an analysis of x-ray Bragg peak broadening, while the coarse-grained sample had a grain size of several microns.

* Current Address: Los Alamos National Laboratory, Los Alamos, NM 87545

Powder x-ray diffraction measurements were taken at the medium resolution two-axis spectrometer, G3 HASYLAB, Germany, in reflection mode at ambient temperature. X-rays of wavelength 0.92 Å were selected from the synchrotron ring. Scattered intensity was collected using a Ge energy dispersive counter with an energy window of ~300 eV width centered about the fundamental radiation of 13.48 keV. Intensity was recorded as a function of scattering angle 2θ , and was normalized to the incident beam intensity. The position of the sample remained fixed during the experiment, and only the detector was scanned. Intensity measurements were corrected for absorption, Lorentz, polarization and atomic form factors. Corrected intensity data is shown in Figs. 1(a) and 1(b) for coarse-grained and nanocrystalline Pd, respectively, as a function of scattering vector magnitude, $\tau = 4\pi \sin\theta / \lambda$. Experimental intensity profiles were fit by a combination of a quadratic polynomial plus a Lorentzian function for each of the 16 observed Bragg peaks. Optimized parameters for the integrated intensity, the full-width at half-maximum intensity and the peak centroid position were obtained for each peak.

A quadratic was found to adequately represent the intensity not accounted for by the Lorentzian peaks and a direct comparison of optimized quadratics for both samples is shown in Fig. 1(c). If atomic relaxations in grain boundary regions are large enough to produce significant amounts of broadly distributed diffuse scattering, then the intensity of the quadratic for the nanocrystalline sample should be significantly greater than that of the coarse-grained sample, since the coarse-grained sample contains a negligible total grain boundary volume. An increase of only $8 \pm 8\%$ is observed in the region where $\tau > 4 \text{ Å}^{-1}$, however. Larger differences are seen below this angle, but these differences are believed due to low intensity in this region and to artifacts of the fitting procedure. Zhu et al. [1] compared measured and computed interference functions for Fe and found that their model required large-magnitude random displacements of up to 50% of a nearest-neighbor distance in a four plane grain boundary region (~50% of the total sample volume) in order produce enough background intensity to satisfactorily match that observed. The intensity between Bragg peaks was ~50% too low if smaller, but still significant, random displacements of up to 15% of a nearest-neighbor distance in the grain boundary region were used in their model (see Fig. 4 of [1]). An important limitation of the Zhu et al. study was that no direct experimental comparison was made of diffuse background intensities for nanocrystalline and coarse-grained samples. While it is possible that grain boundary structures in nanocrystalline Pd and Fe differ dramatically due to differences in crystal structure (fcc versus bcc) or due to the greater affinity of Fe for boundary contaminants such as oxygen (the presence of which would produce diffuse intensity), our results demonstrate convincingly that random grain boundary relaxations lacking short-range order that would produce large broadly distributed diffuse background intensity do not occur in nanocrystalline Pd.

A significant difference between nanocrystalline and coarse-grained Pd was observed when comparisons were made of the two materials' Debye-Waller factors. The nanocrystalline Pd sample was found to have a significantly larger Debye-Waller factor than the literature value for Pd ($0.56 \pm 0.04 \text{ Å}^2$ versus $0.44 \pm 0.03 \text{ Å}^2$, respectively). This implies that the mean-squared displacements of atoms in the nanocrystalline Pd sample are ~27% larger than in coarse-grained Pd at room temperature. Since the scattered intensity observed is averaged over the entire sample it is impossible to unambiguously determine the origin of these increased displacements. This behavior could result from differences in structure between grain boundaries and grain interiors (such as enhanced atom vibrations in the grain boundaries or ordered atomic relaxations in the boundaries that give rise to scattered intensity in the tails of the Lorentzian Bragg peaks) or from uniform displacements throughout the sample. The displacements may be of thermal and/or static origin and temperature measurements to discern between these two possibilities are currently in progress.

The Hydriding Behavior of Nanocrystalline Pd

In situ x-ray diffraction studies of the hydriding behavior of nanocrystalline Pd were carried out at Argonne National Laboratory. A previous study by T. Mütschele and R. Kirchheim [10] found, based on the results of electrochemical hydrogen charging experiments, that the hydrogen solubility of nanocrystalline Pd differs from that of conventional, coarse-grained material. In particular they observed a narrowing of the miscibility gap in nanocrystalline Pd such that the maximum hydrogen solubility in the α -Pd phase (α -max) approximately doubled while the minimum solubility in the β -PdH_x phase (β -min) decreased by ~25% at 333K. They attributed the increase in α -max to a larger solubility in the grain boundaries, while the decrease in β -min was proposed to be due to the presence of a disordered boundary region of thickness 0.7 to 1.1 nm that resisted transformation to the β -phase. Samples were produced for our study by the technique described above. Two nanocrystalline samples and one coarse-grained reference foil were examined. The two nanocrystalline samples had mean grain sizes of approximately 10 and 50 nm, respectively. X-ray θ -2 θ scans were obtained using Cu K α radiation ($\lambda=0.1542$ nm) while exposing the samples to controlled gaseous hydrogen pressures of 0 to 100 kPa at ambient temperature. The smaller-grained nanocrystalline sample was cycled repeatedly through the α -Pd $\leftrightarrow$ β -PdH_x transformation, while the reference foil and larger-grained nanocrystalline samples were observed at several pressures, but were only subjected to one transformation cycle.

Lattice parameter changes as a function of hydrogen pressure were determined for all three samples and results for the α -phase regime are shown in Fig. 2. The data clearly show that the change in lattice parameter at a given pressure depends on grain size, with the largest change occurring for the smallest-grained sample. Changes in lattice parameter can be directly related to changes in hydrogen concentration [11]. From lattice parameter measurements in the mixed-phase regime it was determined that the α -max concentration of the coarse-grained reference sample agrees well with the literature value at room temperature (H/Pd ~0.01 [12]), while the α -max concentration of the smallest-grained nanocrystalline sample is approximately twice that, in agreement with the observations of Mütschele and Kirchheim [10]. Likewise, lattice parameter measurements of the β -phase in the mixed-phase regime showed that the β -min concentration decreased with decreasing grain size, indicating a narrowing of the miscibility gap as seen previously. A hydrogen pressure of ~3 kPa was required to cause the nanocrystalline samples to begin transforming to the β -phase, while a lower pressure of ~2 kPa caused the coarse-grained sample to begin transforming, indicating a change in the plateau pressure.

If the observed decrease in average β -min concentration is due to a significant fraction of the sample resisting transformation to the β -phase, this would be directly observable by x-ray diffraction. Since it is known from the background intensity comparisons described in the previous section that little additional broadly distributed diffuse scattering is produced in nanocrystalline Pd, one would expect to see a portion of the Pd Bragg peaks remaining even after prolonged hydrogen exposure above the plateau pressure. We found clear evidence that this is not the case for nanocrystalline Pd. Intensity data is shown in Fig. 3 for the smaller-grained nanocrystalline sample prior to hydrogen exposure (Fig.3(a)), in the mixed-phase regime (Fig.3(b)) and following complete transformation to the hydride phase (Fig.3(c)). This means again that there is no evidence for the presence of extended, disordered grain boundary regions in nanocrystalline Pd, and that the observed narrowing of the miscibility gap must occur for another reason. An alternative explanation that we propose is that nanocrystalline Pd behaves as if it has a higher effective temperature than its coarse-grained counterpart. This is consistent with the observed increase in the Debye-Waller factor for nanocrystalline Pd, which corresponds to a decrease in Debye temperature of ~60K. A change in effective temperature of this magnitude

would be consistent with the observed change in solubility since α -max for coarse-grained Pd is known to approximately double when the temperature is increased from 25 to 90 °C [12].

EXAFS Studies

Haubold and co-workers [2] observed reductions in EXAFS amplitudes in nanocrystalline Pd and Cu compared to coarse-grained material. In order to verify and extend these results, we made EXAFS measurements on nanocrystalline Pd samples in both powdered and compacted forms, as well as on a Pd coarse-grained reference foil. Samples were produced in the manner described above. Measurements were made at Beamline X23A2 of the National Synchrotron Light Source, Brookhaven National Laboratory. Foil and powder spectra were collected in transmission mode, while the spectra from compacted samples were acquired using electron detection in a He gas detector. Reductions in amplitude similar to those seen previously were observed for the compacted nanocrystalline samples, but, surprisingly, an even larger amplitude reduction was seen in uncompact powder. A comparison of the data for the three types of samples is seen in Fig. 4. The fact that larger reductions in amplitude are seen for nanocrystalline powder, in which the grain boundary volume is negligible, suggests that large-magnitude, disordered boundary relaxations are not responsible for the observed behavior, in contrast to the conclusion of [2]. A detailed analysis of the data aimed at understanding the role of several effects such as surface oxidation, particle size, vacancies and pores on EXAFS amplitudes is in progress. Comparisons of possible structures derived by molecular dynamics calculations as well as from simple models are being made. Methods have also been developed to extract grain radii from EXAFS amplitudes of different atomic shells. These techniques are expected to prove useful in making connections between diffraction and EXAFS results.

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Fig. 1 Corrected intensity data from (a) coarse-grained and (b) nanocrystalline Pd plotted on a logarithmic scale versus scattering vector magnitude, $\tau = 4\pi \sin\theta / \lambda$. Dashed lines indicate the intensity not accounted for by the Lorentzian-shaped Bragg reflections. (c) Quadratic polynomial representation of the background intensity from coarse-grained (dashed line) and nanocrystalline Pd (solid line).

Fig. 2 Change in Pd lattice parameter versus hydrogen pressure for 10 nm (open circles), 50 nm (stars) and coarse-grained Pd (closed circles).

Fig. 3 Intensity data for 10 nm grain-sized Pd prior to H₂ exposure (a), in the mixed-phase (Pd + PdH_x) regime (b) and following complete transformation to the hydride phase. The hydrogen pressure was 5.5 kPa.

Fig. 4 Fourier transform of the k^2 weighted EXAFS above the Pd edge for a coarse-grained Pd foil sample, for a compacted nanocrystalline sample and for nanocrystalline powder. The radial coordinate is not corrected for atomic phase shifts (about 0.4 Å).

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