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Diffraction Studies of the Thermal Properties of Nanocrystalline Pd and Cr*

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Abstract

Quantitative X-ray and neutron diffraction measurements were made on nanocrystalline and coarse-grained samples of Pd and Cr. For both materials, Debye-Waller parameter comparisons over a temperature range of approximately 20-300 K indicate that the nanocrystalline materials have increased static displacements of atoms from their equilibrium sites compared to coarse-grained material. No grain-size-correlated differences in thermal vibrational amplitude, lattice parameter, or thermal expansion coefficients were observed in either material. In contrast to earlier results on nanocrystalline Pd, significantly more non-peak intensity is observed from a nanocrystalline Cr sample than from a coarse-grained Cr sample. Impurities may account for the increased background intensity from nanocrystalline Cr. These results indicate that there is no significant grain boundary excess volume in nanocrystalline Pd, and therefore the reduced density typically observed in nanocrystalline Pd samples must be due to porosity.

Introduction

Characterizing the microstructures of nanocrystalline materials is necessary to understand and control any altered properties in nanocrystalline materials compared to conventional coarse-grained materials. Studies of temperature dependent properties can provide important information related to the detailed structures of nanocrystalline materials. This paper summarizes recent thermal property measurements of nanocrystalline Pd [1] and Cr [2] by X-ray and neutron diffraction. Along with other pertinent conclusions, the results can be interpreted to provide information on the grain boundary excess volume in nanocrystalline Pd.

Results

X-ray diffraction θ-2θ scans from coarse-grained and 8 nm grain-sized nanocrystalline Pd samples were acquired over the temperature range 16-300 K using beamline X7A at the National Synchrotron Light Source, Brookhaven National Laboratory. Experimental details are described elsewhere [1]. A comparison of the diffraction data from the two samples at 300 K is shown in Fig. 1(a), where the abscissa is the magnitude of the scattering vector τ, where $\tau = 4\pi \sin\theta/\lambda$. As expected, the intensity peaks are considerably broader for the nanocrystalline sample due to the much smaller grain size, and due to the presence of
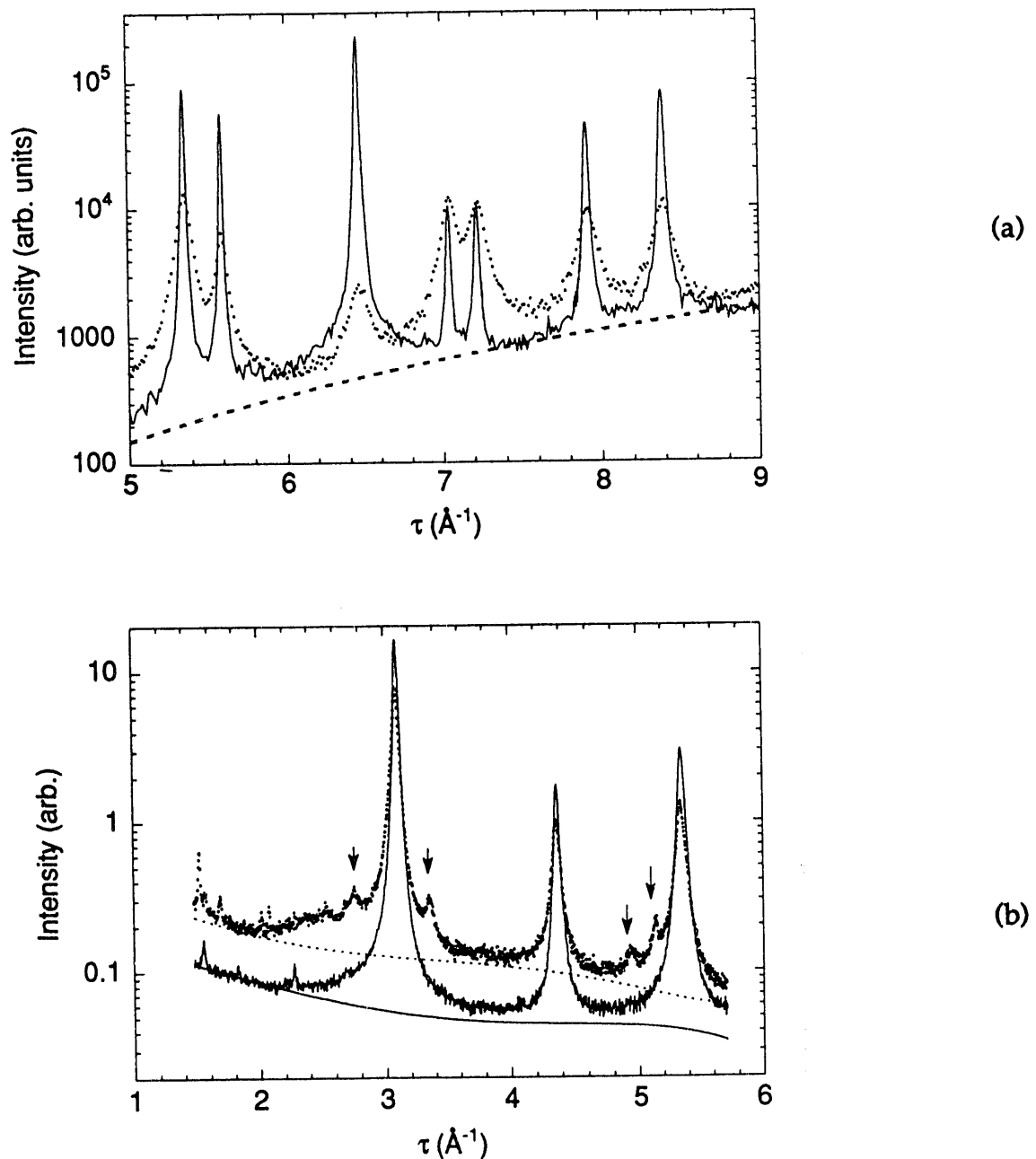
Figure 1. (a) Corrected X-ray data from nanocrystalline (points) and coarse-grained (solid line) Pd samples. The non-peak portions of the intensities from both samples overlap and are shown as dashed lines. The intensities are plotted on a logarithmic scale versus scattering vector magnitude, $\tau = 4\pi \sin\theta/\lambda$. (b) Raw X-ray data from nanocrystalline (points) and coarse-grained (solid line) Cr samples. The non-peak portions of the intensities are shown as a dashed line for nanocrystalline Cr, and as a solid line for coarse-grained Cr. Arrows indicate weak intensity peaks from a non-bcc Cr phase [5]. Additional weak peaks due to CrO_2 and CrO phases are seen for both samples. From [4].
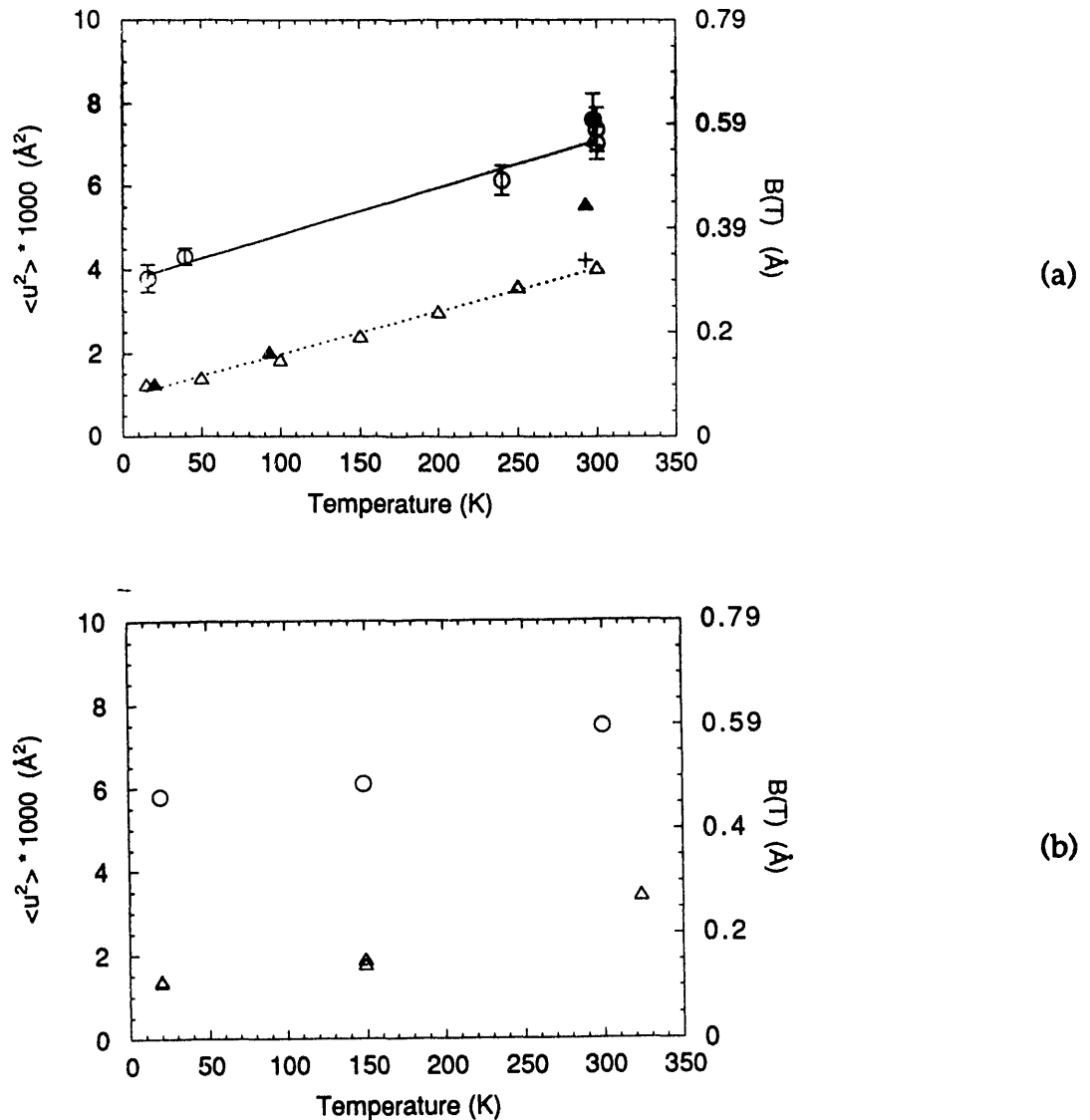
Figure 2. (a) Mean-squared atomic displacements versus temperature for nanocrystalline Pd (o -- [1], ● -- [3]), and coarse-grained Pd literature values (Δ, ▲, and +). Linear fits are provided as a guide to the eye. From [1]. (b) Mean-squared atomic displacements versus temperature for nanocrystalline (o) and coarse-grained (Δ) Cr.

increased strain broadening in the nanocrystalline material. The intensity data were analyzed and separated into peak and non-peak components. The dashed lines in Fig. 1(a) represent the non-peak intensities deduced from this analysis. The lack of any significant differences in these non-peak intensity components from nanocrystalline and coarse-grained Pd samples over the measured τ range is evidence that the atomic relaxations in nanocrystalline Pd must be small in magnitude and/or extremely localized [3]. Differences were observed in the total integrated intensities from the two samples due to increased peak intensities from the coarse-grained sample. This difference is believed to arise from possible

increased small angle scattering from the nanocrystalline sample and texture in the coarse-grained sample [1].

Coarse-grained and 11 nm grain-sized nanocrystalline Cr samples were examined by both X-ray (rotating anode source) and neutron diffraction. The neutron diffraction data were acquired at the Los Alamos Neutron Scattering Center using the High Intensity Powder Diffractometer. A room temperature X-ray diffraction comparison of nanocrystalline and coarse-grained Cr is shown in Fig. 1(b). In contrast to the results for Pd, the nanocrystalline Cr sample exhibits significantly more non-peak scattering (dashed line) than does coarse-grained Cr (solid line). However, this difference in intensity is believed to be due primarily to substantial impurities in the Cr nanocrystalline sample [4]. Weak peaks of intensity indicated with arrows in the nanocrystalline Cr scan are believed to be due to the presence of a small amount of a second cubic Cr phase that is known to occur when Cr is evaporated in an inert-gas environment [5]. Additional weak peaks have been identified with the presence of mixtures of CrO_2 and CrO phases.

The Debye Waller parameters and corresponding atomic mean squared displacements for nanocrystalline and coarse-gained Pd and Cr samples were deduced from an analysis of the peak integrated intensities. The results shown in Fig. 2 demonstrate that the atomic thermal vibrational amplitudes do not differ in either case between nanocrystalline and coarse-grained material, but that both Pd and Cr nanocrystalline samples exhibit increased static (temperature independent) displacements compared to their coarse-grained counterparts. Strong similarities with previous results for a variety of nanocrystalline powders indicate that the origins of these increased displacements are most likely due to the powder production process, rather than arising from possible grain boundary relaxations [1].

Lattice parameter data seen in Fig. 3 demonstrate that there are no differences in lattice parameters or thermal expansion behavior of nanocrystalline and coarse-grained samples in the cases of either Pd or Cr. This is in contradiction to earlier reports of factor 2-3 increases in the thermal expansion coefficient of nanocrystalline materials [6]. In the case of Pd, the lack of any significant differences in the non-peak intensity components (Fig. 1(a)) indicates that the grain boundary regions in nanocrystalline Pd must be scattering into the observed intensity peaks. In this case lattice parameter comparisons can be used to estimate the grain boundary excess volume, ΔV, which is defined as
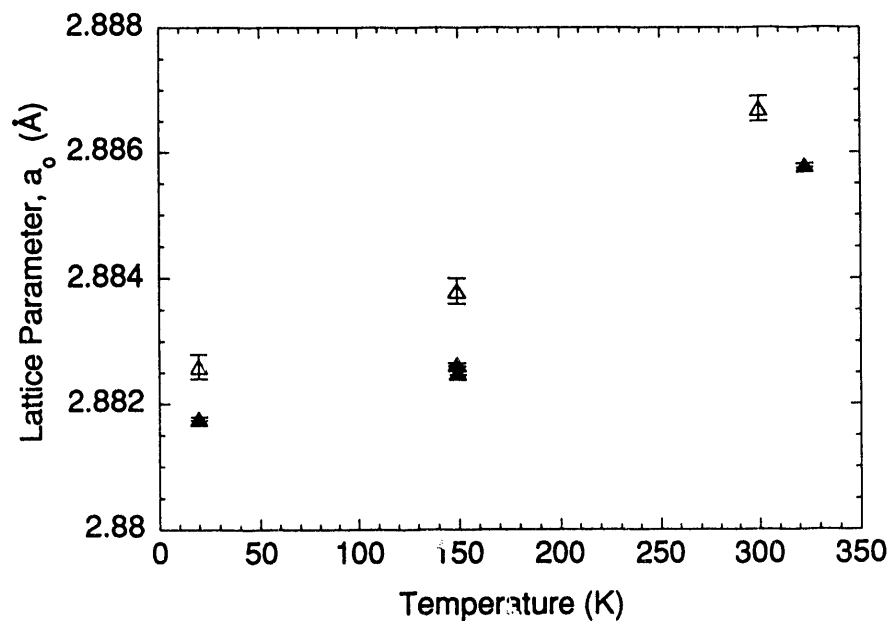
$$\Delta V = (V_{gb}/V_{bulk}) - 1 \qquad (1)$$

where V_{gb} and V_{bulk} are the grain boundary and bulk volumes, respectively for equal masses of material. Defining $V = a_0{}^3$, where a_0 is the lattice parameter, it follows that

$$a_0(gb)^3 = (\Delta V + 1) * a_0(bulk)^3 \qquad (2)$$
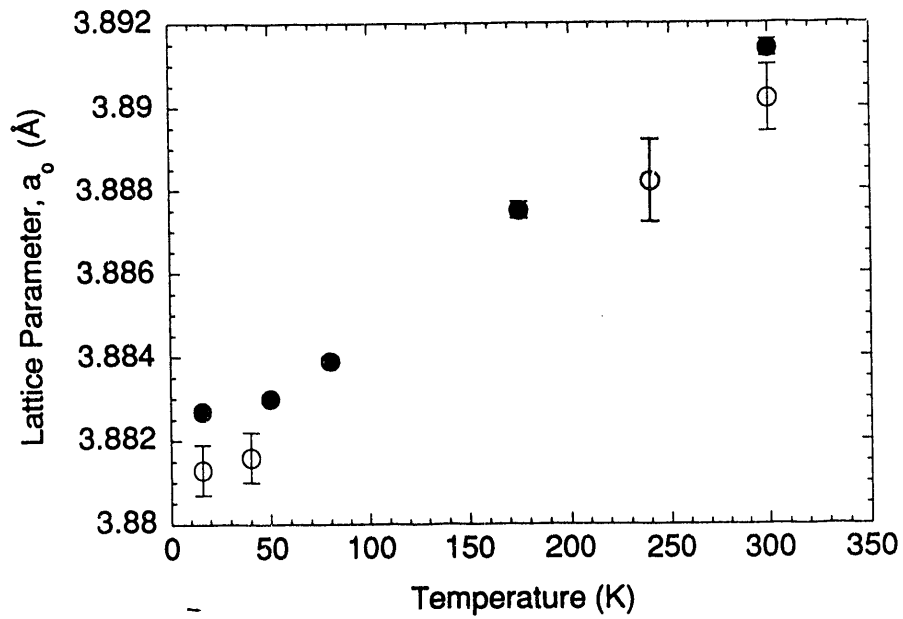
Figure 3. (a) Lattice parameter as a function of temperature for nanocrystalline (o), and coarse-grained (●) Pd. From [4]. (b) Lattice parameter as a function of temperature for nanocrystalline (Δ), and coarse-grained (▲) Cr.

If the measured lattice parameter of a nanocrystalline material, a_o(nanocrystalline), is defined as the weighted average of grain boundary and bulk components,

$$a_o(\text{nanocrystalline}) = GBF * a_o(gb) + (1 - GBF) * a_o(\text{bulk}) \qquad (3)$$

where GBF is the grain boundary volume fraction in the material, the following relationship between grain boundary excess volume and observed lattice parameters for coarse-grained (bulk) and nanocrystalline materials as a function of grain boundary volume fraction is obtained

$$a_0(\text{nanocrystalline})/a_0(\text{bulk}) = (\text{GBF}) * (\Delta V + 1)^{1/3} + (1 - \text{GBF}) \qquad (4)$$

Recently it has been suggested that observations of reduced density imply that the grain boundaries in nanocrystalline Pd exhibit a large excess volume of ~30% [7]. An 8 nm grain size and 1 nm boundary width would correspond to a 33% grain boundary volume fraction in the absence of porosity in the material. From Eq. 4, it can be seen that this would result in approximately a 3% increase in lattice parameter in nanocrystalline Pd compared to coarse-grained Pd. The actual lattice parameters for nanocrystalline Pd with an average grain size of ~8 nm and coarse-grained Pd differ by less than 0.04% at both 16 and 300K (and the lattice parameter of nanocrystalline Pd is lower than that of coarse-grained Pd). Even if porosity reduces the grain boundary volume fraction to 10% in the nanocrystalline Pd sample, the volume difference between the bulk and grain boundary regions derived from Eq. 4 would be only approximately 0.1% for the observed lattice parameters. From this analysis it is clear that grain boundary regions in nanocrystalline Pd do not exhibit a large excess volume, and therefore the reduced density typically observed in nanocrystalline Pd is due to porosity. Further experiments with clean samples are required before it can be determined whether this is also true for Cr. These experiments are planned in the near future.

Acknowledgments

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