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Residual Stress, Strain, and Faults in Nanocrystalline Palladium and Copper*

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Abstract

Nanocrystalline Pd and Cu, prepared by inert gas condensation and warm compaction, were studied using x-ray diffraction techniques. A sample of Cu with sub-micrometer grain size produced by severe plastic deformation was also examined. The Warren-Averbach technique was used to separate the line broadening due to grain size, root-mean-squared strain, and faults. Peak shifts and asymmetry were used to determine the long range surface stresses, stacking fault probability, and twin probability. The Young's modulus of a Pd sample was determined by an ultrasonic technique, and compared with the coarse-grained, fully-dense value.

Introduction

The ultimate goal of this investigation is the determination of the intrinsic mechanical behavior of nanocrystalline (n-) Pd and Cu. Toward this end, it is important to understand the structure of these materials. For this reason, grain size, residual stress, stacking faults, and twins are significant structural features to understand so that their impact on mechanical properties may be evaluated. Twins and root-mean-squared (rms) strains are commonly observed in fine-grained materials, but their variation as a function of grain size and preparation conditions is not fully understood. In addition, it is important to compare materials made by different processes, because techniques and methods of structural determination may vary between laboratories. In this study, the structure of Cu with sub-micrometer grain size, denoted as ultrafine-grained (UFG-), was compared to that of n-Cu.

Experimental Procedure

The n-Pd and n-Cu samples were prepared by inert gas condensation (IGC) and warm compaction at Argonne National Laboratory [1]. High (metallic) purity Pd wire (99.997%) and Cu shot (99.999%) were evaporated from alumina lined boats into an atmosphere of 650 Pa of ultrahigh-purity He (99.9999%). The resulting powder, after being warmed following collection on a liquid nitrogen cooled surface, was compacted with 1.4 GPa of pressure for 10 min at temperatures ranging from 100 to 300°C. Typical samples were 9 mm in diameter and 0.1 to 0.5 mm thick. The UFG-Cu sample was prepared by severe plastic deformation by torsion under high pressure at room temperature to a true logarithmic strain $\varepsilon \approx 7$ [2]. (In the following graphs of Cu, this sample is denoted as #8 or the sample with the largest grain size.) Density measurements were made on each sample using Archimedes principle, with particular care used to insure minimal thermal effects in the liquid measurement. X-ray diffraction (discussed below) was used to determine the grain size, rms strain ($\langle\varepsilon^2\rangle^{1/2}$), stacking fault probability (α), twin probability (β), and residual surface stress. The residual stress was remeasured after the samples were polished to 0.05 μm surface finish. A measurement of the Young's modulus by an ultrasonic technique was used to estimate the error resulting from assuming the coarse-grained,

fully-dense values of the elastic constants. The transmission electron microscopy (TEM) was performed on a Hitachi H-700 microscope operating at 200 kV.

For the Warren-Averbach (W-A) analysis [3] in n-Pd and n-Cu, the 111, 200, 311, 222, and 400 x-ray peaks were scanned over a range of ± 5 times the full-width-half-maximum (fwhm). A pseudo-Voight or Lorentzian function was fit to the data only to remove the background and deconvolute overlapped tails. The data were then corrected for functions which vary with two-theta, including the Lorentz-polarization factor, the variation of the structure factor, the Debye-Waller factor, and the dispersion-corrected scattering factor. The range of the data was selected to correspond to a 1 nm interval in real space, and then the Fourier transform was numerically integrated. The instrumental function was deconvoluted using the Stokes correction [4] with a standard sample made from annealed, compacted filings of high purity Pd or Cu. The data were then normalized using the method of Rothman and Cohen [5], and only a cosine expansion was used to separate the broadening due to size and strain. Two orders of a reflection (e.g., 111-222) were used to separate size and strain, while two different sets of peaks (e.g., 111-222 and 200-400) were used to separate the grain size broadening from that due to intrinsic stacking faults and twins (deformation and growth faults, respectively, in Warren's terminology). Independent confirmation of these results was obtained by determining α using peak shifts between a standard and the sample [3], and β using the difference between the peak maximum and the centroid [6].

Residual surface stress measurements were made with Cr Kα radiation on n-Pd samples using the 311 peak ($2\theta \approx 155°$), where the 1/e penetration depth is 0.3 μm. All 5 samples received identical processing treatments, including a 200°C compaction. The samples ranged between 0.15 and 0.48 mm thick, and all were ≥ 94% dense. The biaxial residual stress was determined using the $\sin^2\psi$ technique [7], where scans were performed for 6 different values of $\sin^2\psi$. After background subtraction and correcting for all the angular corrections listed above, plus the absorption factor (which varies with ψ), the top ≈15% of the peak was fit with a parabola [7]. For biaxial stress, a plot of $\sin^2\psi$ vs d is linear with a slope proportional to the residual surface stress, where the Young's modulus and Poisson's ratio used in the calculation were an average of the single crystal elastic constants [9]. As a test of the method's accuracy, the annealed Pd standard used in the W-A analysis was tested, and the residual stress was found to be -3.8 ± 0.1 MPa, or practically zero compared with all the other measurements, which were usually about an order of magnitude higher.

All x-ray data uncertainties in this paper are standard deviations propagated from counting statistics using standard methods (e.g., Beers [9]); other sources of error have not been quantified. Propagation of errors through the W-A analysis follows the treatment of Wilson [10] and Schlosberg and Cohen [11].

Results

Warren-Averbach

Grain size data from the W-A analysis of n-Pd and n-Cu are shown in Fig. 1. The first feature noticed is the measurable difference between the 111-222 W-A value, which is typically reported, and the grain size after removal of the stacking fault and twin contributions (W-A (no α & β)). The TEM grain size was found to be in the same range as the x-ray data, but more work is necessary to get quantitative data. The x-ray grain size of the UFG-Cu was found to be 52.8 ± 0.5 nm, which is smaller than the ≈ 170 nm size observed in TEM [2]. However, this

difference may be due to the high dislocation density (ρ). Using a relation from Mikkola and Cohen [12], where ρ can be calculated from the 111-222 and 200-400 W-A sizes and rms strains, ρ was found to be 6-12 × 10^{14} m^{-2}, which agrees well with the TEM value of 5-10 × 10^{14} m^{-2} [2]. Also plotted in Fig. 1 is the grain size calculated from the Scherrer formula, where an attempt has been made to remove the instrumental function by subtracting the square of the standard's full-width-half-maximum (fwhm) from that of the nanocrystal. Without going into too much depth, it must be noted that the Scherrer method assumes the only source of broadening is the small size of the crystallites. In addition, the Scherrer method volume averages, while the W-A method area averages grain size.

The grain size and faulting probabilities (only the sum 1.5α+β can be obtained from W-A) were separated using the 111-222 and 200-400 W-A sizes. In n-Pd and n-Cu, α is practically zero, considering the standard deviation of the measurement (Fig. 2). This is not surprising because stacking faults are typically remnants of plastic deformation and dislocation motion in face-centered cubic crystals, and little of this has occurred in these nanocrystalline samples. However, α was about an order of magnitude higher (0.002 with a small uncertainty compared to about 0.0002 for the n-Cu) in the UFG-Cu, which makes sense considering it was made by severe plastic deformation. Since α is small, values of β should agree with those of (1.5α + β) from W-A. As seen in Fig. 2, the agreement is excellent. Both the magnitude of β and the trend of decreasing β with increasing grain size are similar in n-Cu and n-Pd, even though the twin energy is higher in Pd. Large numbers of twins in n-Cu made by IGC have been observed with high resolution electron microscopy (HREM) [13].

TEM studies have shown that twins are very common in small clusters [e.g., 14], perhaps due to growth faults and/or to reduce surface energy. In accordance with these observations, it was postulated that the twins form during cluster condensation, and not during compaction. To test this hypothesis, loose powder and a compacted sample from a Pd evaporation were x-rayed and their respective β's calculated. The β's for both the powder and the compacted sample were in the same range considering experimental error (which was larger for the powder sample), so it can be concluded that most of the twins are present in the original powder.

The rms strain was measured for the 111-222 and 200-400 peaks at a coherence length of 5 nm. As shown in Fig. 3, the 200-400 strain is always higher than the 111-222 strain for a given sample. It was noticed that the strains also seemed to decrease with increasing grain size in n-Pd and n-Cu. This trend is weaker in n-Cu, due in part to the poor counting statistics. The n-Pd powder and a consolidated sample from the same evaporation analyzed by the W-A method showed nearly identical rms strains, which implies that the high strains are inherent in the free clusters. The rms strain in UFG-Cu is slightly higher than that predicted by the rms strain curve for the IGC samples. The local strain near the grain boundaries in this severely deformed material may be even higher, but the large fraction of grain interior that is less strained would cause the average rms strain to be closer to that for n-Cu. Other measurements of the rms strain in UFG-Cu have given values in exactly the same range [2].

Residual Stress

All measurements made, without exception, showed negative biaxial strain, which implies that the surface layer is under compression. The $\sin^2\psi$ vs d plots were linear, signaling that the stress state can be accurately described as biaxial. After polishing off 0.02 to 0.04 mm of the surface, the biaxial stress increased by a statistically significant margin about half the time. Before polishing, the surface stresses ranged between -20 and -40 MPa, while after polishing the

stresses were -40 to -105 MPa. No strong correlations were observed between the residual stress and density, thickness, or amount of material removed during polishing. One sample was accidentally broken after testing in the unpolished state. While not showing the general trend of increasing residual stress with polishing, the measured stress in this broken sample did not decrease either, meaning that the stress state is not completely dependent on having a fully formed disc.

As mentioned previously, the Young's modulus and Poisson's ratio used to calculate the residual stress were the coarse-grained, fully-dense values. Many investigators have seen changes in the elastic properties of nanocrystalline metals (e.g., [15]). Ultrasonic techniques provide one method of measuring the Young's modulus. Using the density and the longitudinal wave speed (and assuming Poisson's ratio is 0.33), the Young's modulus for a 97.17 ± 0.05% dense n-Pd sample (d = 12.2 ± 0.5 nm) was found to be 82 ± 4 % of the standard's modulus [16]. The lower modulus may result from the 3% density decrement and/or the slight increase in the overall atomic spacing in these grain-boundary dense materials. In any case, the residual stresses calculated from the handbook value of the elastic modulus may be high by ≈ 18%.

Conclusions

The W-A grain size corrected for the effect of $(1.5\alpha + \beta)$ agrees with the TEM grain size, at least in the small grain size regime. In n-Pd and n-Cu, the stacking fault probability (α) is virtually 0, while the twin probability (β) is significant. Both β and the rms strains decrease with increasing grain size. Similar trends for β were seen in the UFG-Cu, although the rms strain and α seemed to be slightly higher. Uncompacted n-Pd powder showed similar values of β and rms strain to those in n-metals, signalling that these structural features may result from the fine particle size, and not compaction. The residual surface stresses in n-Pd are compressive and relatively low in magnitude. The Young's modulus of n-Pd was found to be smaller than the coarse-grained, fully-dense value by a significant amount.

Acknowledgements

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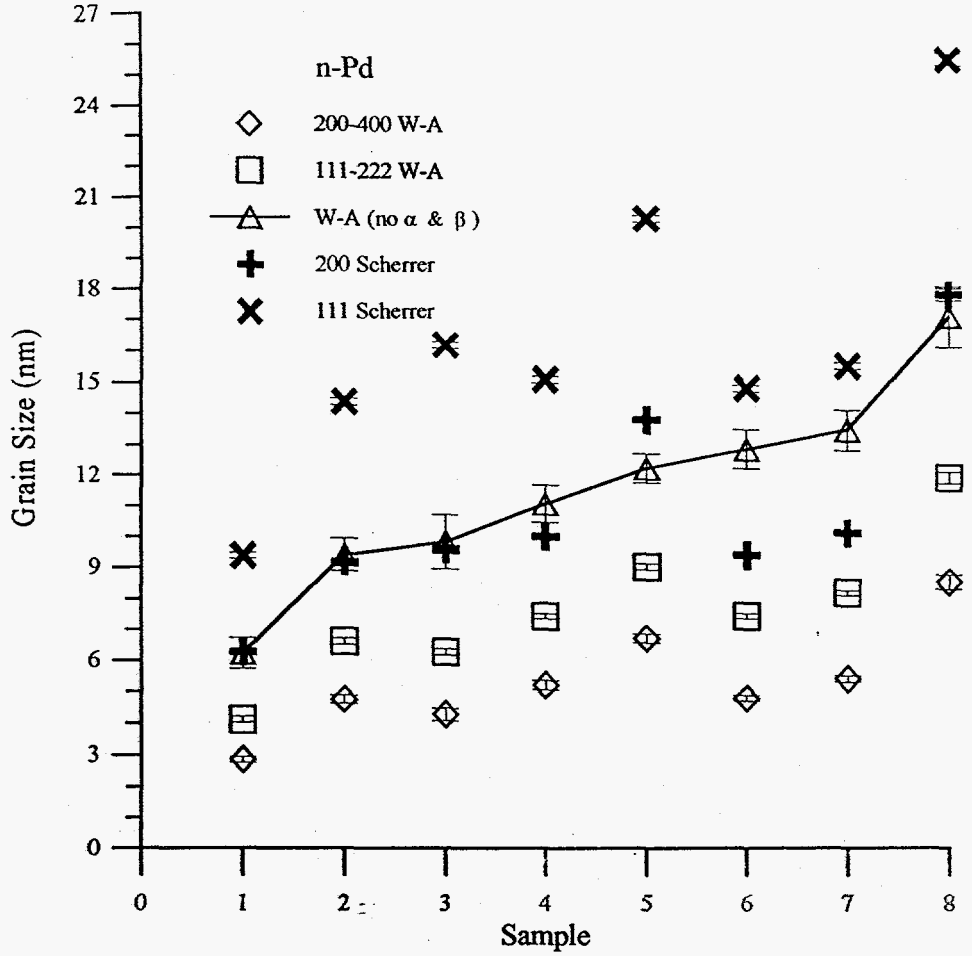
Fig. 1. Comparison of grain sizes determined from x-ray analysis of line broadening for n-Pd (a) and n-Cu (b). Sample #8 in (b) is UFG-Cu.

Fig. 2. Stacking fault (α) and twin (β) probability as a function of grain size for n-Pd (a) and n-Cu (b). Also note the agreement for the two methods used to determine α and β. The sample with the largest grain size in (b) is UFG-Cu.

Fig. 3. Root-mean-squared (rms) strain as a function of grain size for n-Pd (a) and n-Cu (b). The sample with the largest grain size in (b) is UFG-Cu.


n-Pd
200-400 W-A
111-222 W-A
W-A (no α & β)
200 Scherrer
111 Scherrer
Grain Size (nm)
Sample
0
3
6
9
12
15
18
21
24
27
0
1
2
3
4
5
6
7
8

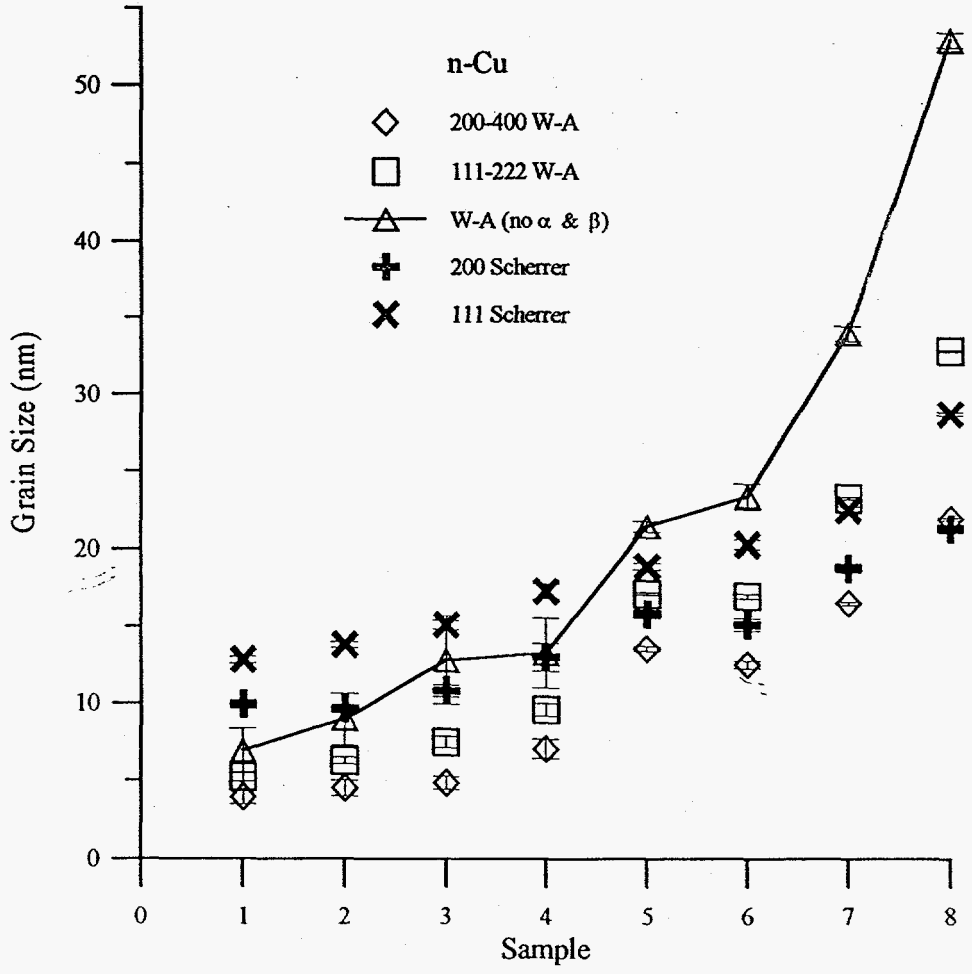
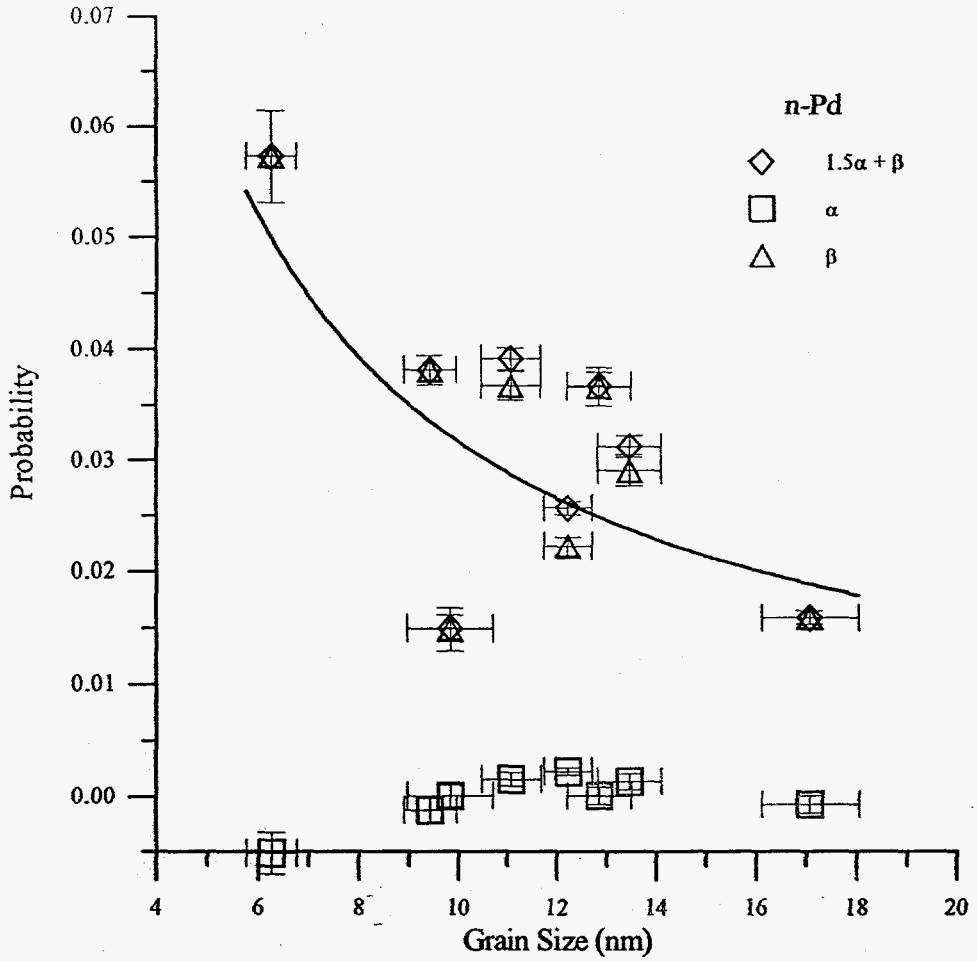

n-Cu
200-400 W-A
111-222 W-A
W-A (no α & β)
200 Scherrer
111 Scherrer
Grain Size (nm)
Sample
0
10
20
30
40
50
0
1
2
3
4
5
6
7
8

Fig 1 a, b


n-Pd
1.5α + β
α
β
Probability
Grain Size (nm)
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
4
6
8
10
12
14
16
18
20

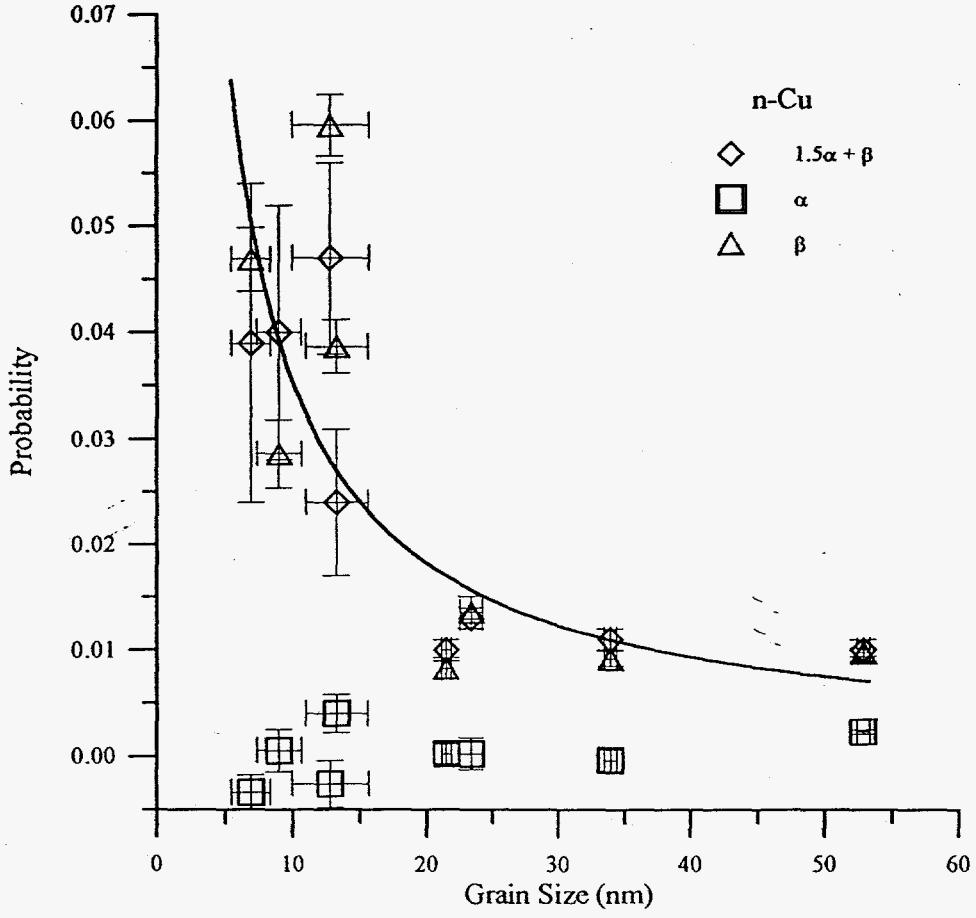
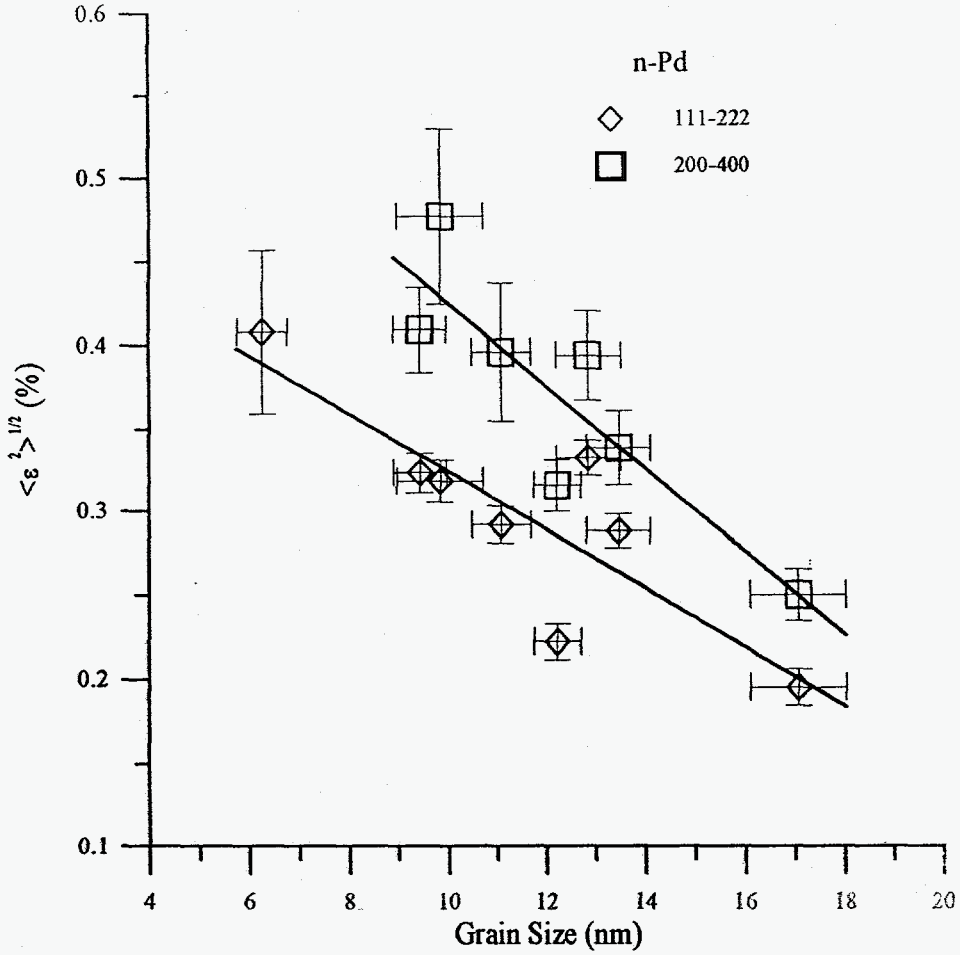

n-Cu
1.5α + β
α
β
Probability
Grain Size (nm)
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
0
10
20
30
40
50
60

Fig 2a,b


n-Pd
111-222
200-400
0.6
0.5
0.4
0.3
0.2
0.1
$\langle \varepsilon^2 \rangle^{1/2}$ (%)
4
6
8
10
12
14
16
18
20
Grain Size (nm)

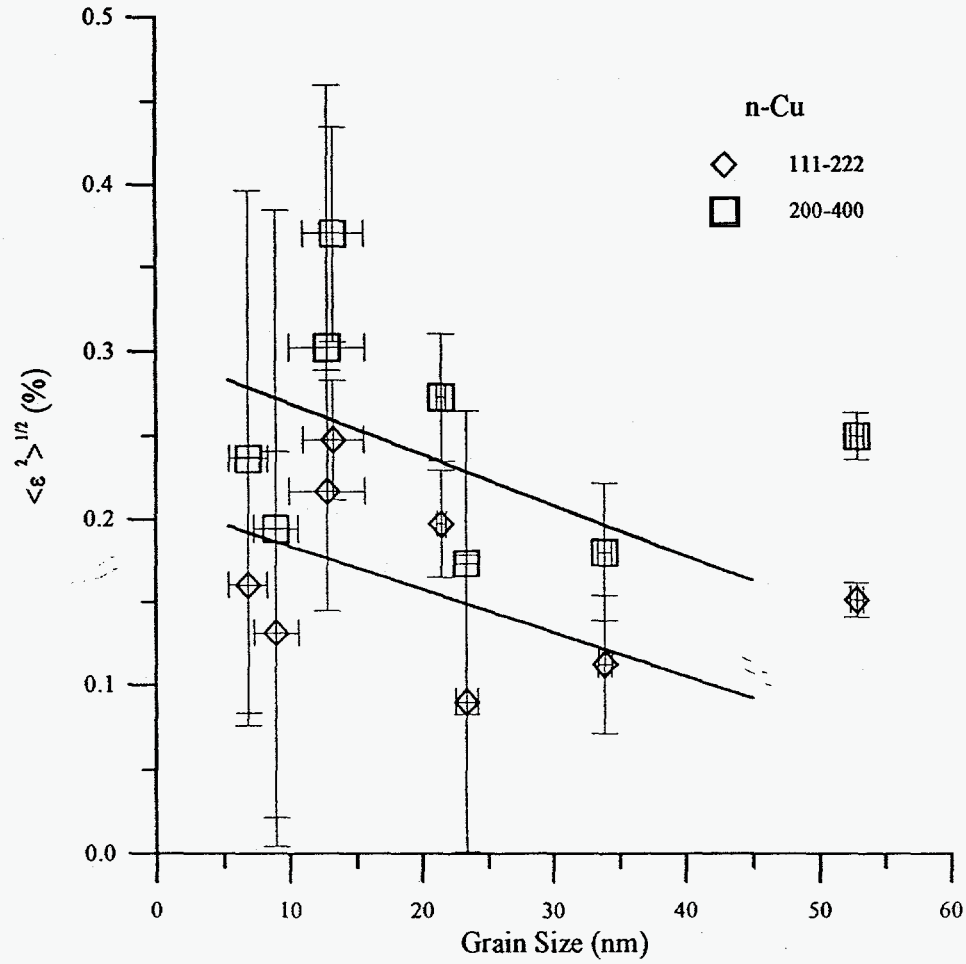

n-Cu
111-222
200-400
0.5
0.4
0.3
0.2
0.1
0.0
$\langle \varepsilon^2 \rangle^{1/2}$ (%)
0
10
20
30
40
50
60
Grain Size (nm)

Fig 3a,b