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ON THE HARDENING AND SOFTENING OF NANOCRYSTALLINE MATERIALS*

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DISCLAIMER

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Abstract- *Nanocrystalline Pd and Cu samples have been thermally treated to determine whether the relationship between hardness and grain size depends upon the method used to vary the grain sizes. Previous reports indicate that hardening with decreasing grain size resulted from data obtained using individual samples, while softening with decreasing grain size resulted from data from a given sample that had been thermally treated. Hardening and softening regimes were evident for the nanocrystalline Cu, and the hardness improvements over the original as-consolidated state were maintained throughout the thermal treatments. This review examines our hardness results for Cu and Pd and those for other nanocrystalline materials.*

INTRODUCTION:

In studies of the mechanical behavior of nanocrystalline metals and alloys, conflicting results have been obtained for the dependence of hardness on grain size. For example, Jang and Koch [1], Nieman,Weertman and Siegel [2], Ganapathi, Aindow, Fraser and Rigney [3], Hughes, Smith, Pande, Johnson and Armstrong [5], and Koch and Cho [13] found an increase in hardness with decrease in grain size. The conventional relationship for this behavior in coarser grained materials is described by the Hall-Petch equation [6]:

$$H_V = H_O + kd^{-1/2}$$

where H_V is the hardness, H_O and k are constants, and d is the average grain size. According to these investigators, the increase in hardness with decreasing grain size is observed down to the finest grained material examined, although its variation with grain size may be less than in the case of conventional grain size material.

In apparent contrast with this behavior, Lu, Wei and Wang [7], Christman and Jain [8], Chokshi, Rosen, Karch and Gleiter [9], Chang, Hofler, Altstetter and Averback [10], and Kim and Okazaki [12] reported that decreasing the grain size produces softening in their nanocrystalline materials. Softening with decreasing grain size has been attributed to the increasing contribution of diffusional accommodation to deformation processes at the finest grain sizes [9].

Whether a nanocrystalline sample hardens or softens with decreasing grain size does not appear to correlate with the synthesis method. Table I represents a synopsis of the current literature for nanocrystalline materials; it lists the grain sizes or ranges examined, the method of synthesis, the material studied, how the grain size was increased, and the resultant hardening or softening. The subset of these results, plotted in Fig. 1, appear to indicate that increased hardening with decreasing grain size is observed generally when hardness is measured on a series of as-prepared samples labeled as "various samples" (e.g., Refs. 1-5,11). Softening has been often found for cases in which hardness measurements are carried out on a single sample that is successively heated to produce ever-increasing grain sizes, labeled as an "annealed sample" (e.g., Refs. 7-10,12,13); the results for these samples are plotted in Fig. 2. Hardness changes from nanocrystalline sample to sample were negligible in the investigations of Pd [2] and Ni-P [12], and the hardness data for Cu in [4] were limited. The hardening of intermetallics can be complicated by the development of different phases (e.g., Refs. 12,13).

The objective of the present review is to compare our previously reported hardness measurements on Cu and Pd [17] with other published results of hardness measurements of nanocrystalline materials.

EXPERIMENTAL DETAILS:

In the previously reported study, two samples each of nanocrystalline Cu and Pd (n-Cu and n-Pd) were prepared by inert gas condensation and consolidation [2]. The grain sizes were determined from X-ray line broadening measurements using the Warren-Averbach analysis method and the Scherrer formula [14]. Vickers microhardness was measured with a load of 100 g applied for 20 s at room temperature, and the mean of 10 measurements is reported. Density measurements of the Pd samples were performed by the Archimedes technique. Residual strain was calculated from Warren-Averbach analyses of (111) & (222) X-ray peaks. The annealing of individual samples was done at 0.315 T_m (423 K for Cu and 569 K for Pd) in an Ar atmosphere.

DISCUSSION:

As-consolidated Pd and Cu samples hardened during the initial stages of thermal treatment. The n-Pd samples hardened by 7-11% during the first 60-90 minutes of annealing [17]. The n-Cu samples hardened by 4-5% during the first 20-30 minutes of annealing. Further annealing of both the Pd and Cu resulted in softening as shown by the slope reversal in Figs. 3 and 4. In Fig. 3, the hardness data from a representative Cu sample are shown along with the data from the as-consolidated samples of Nieman [2]; the grain sizes are determined by the Warren-Averbach method. The Cu hardness values exceed those of the as-consolidated samples throughout the thermal treatments, indicating that the hardness improvement is maintained. Fig. 4 presents the data from our Cu sample along with the data of Chokshi et al. [9], and these grain sizes are determined by the Scherrer formula.

The reason for hardening with exposure to elevated temperature is unclear. The residual strain measurements after each thermal treatment showed negligible change for the n-Pd and a reduction by a factor of 3 for n-Cu samples [17]. Density measurements for the n-Pd showed little change and were hindered by the small sample size.

CONCLUSIONS:

Individual nanocrystalline Cu and Pd samples have hardened and then softened when thermally treated to increase their grain size. Hardening could be caused by densification or changes in internal strains, although measurements of these quantities were inconclusive. Hardness improvements could be attributed to interparticle bond growth and neck development as seen in powder metals [15] and proposed for nanophase ceramics [16]. Studies by Valiev [18] of submicron grain size alloys produced by severe plastic deformation indicate that a rearrangement of the grain boundary structure concurrent with heating may be responsible for strengthening the material. Softening follows the trend observed in earlier work on sets of as-prepared samples and appears to result from the increased ease in forming and moving dislocations as the grains grow larger. Hardening or softening of nanocrystalline metals can depend upon the method used to vary the grain size. Annealing a sample to produce grain growth can result in hardness values greater than those of as-prepared samples with similar grain sizes and this improvement can be maintained throughout the thermal treatment.

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TABLE I: Hardness Studies of Nanocrystalline Materials

d (nm)	Method of Synthesis	Mat'l	Hardness vs. $d^{-1/2}$ data from	Effect with decreasing d	[Ref.]
6-60	Mechanical Attrition	Fe	Various Samples	Hardening	[1]
8-16	Inert Gas Condensation	Cu	Various Samples	Hardening	[2]
7-13	Inert Gas Condensation	Pd	Various Samples	Negligible	[2]
50 & 70	Wear Debris	Cu	Various Samples	Hardening	[3]
25 & 35	Inert Gas Condensation	Cu	Various Samples	N.A.	[4]
50 & 70	Wear Debris	Cu	Various Samples	N.A.	[4]
12-12,500	Electrodeposition	Ni	Various Samples	Hardening	[5]
4 -8	Electrodeposition	Ni-P	Various Samples	Negligible	[11]
9-120	Crystallization of Amorphous Alloy	Ni-P	Annealed Sample	Softening	[7]
10 & 20	Mechanical Alloying	TiAlNb	Annealed Sample	Softening	[8]
8-16	Inert Gas Condensation	Cu	Annealed Sample	Softening	[9]
7-13	Inert Gas Condensation	Pd	Annealed Sample	Softening	[9]
10-21	Sputtering	TiAl	Annealed Sample	Softening	[10]
42-61	Mechanical Alloying	$NbAl_3$	Annealed Sample	Softening	[12]
6-100	Mechanical Alloying	Nb_3Sn	Annealed Sample	Hardening	[13]

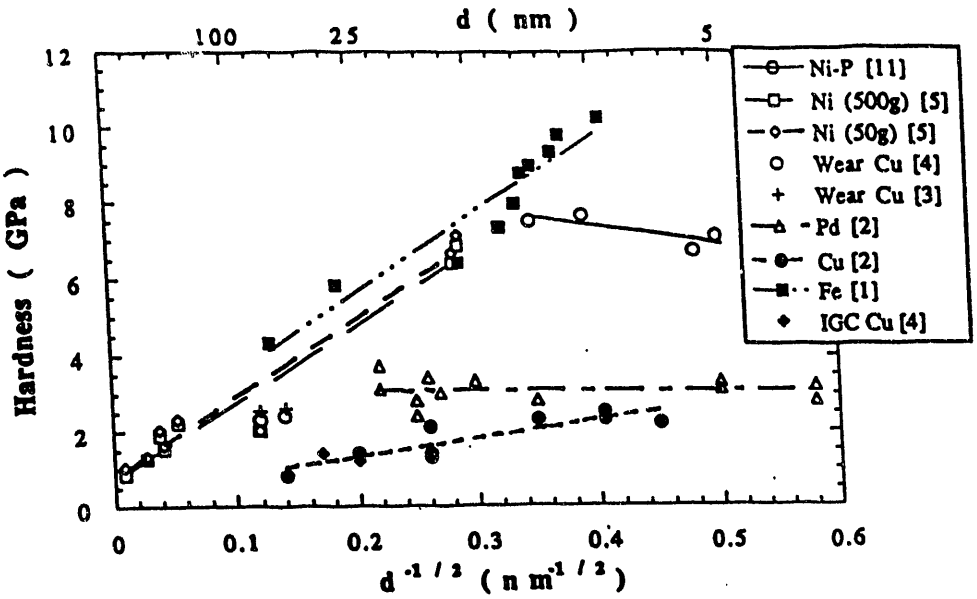

Figure 1: Hardness vs. $d^{-1/2}$.
The grain size was varied by using different samples.

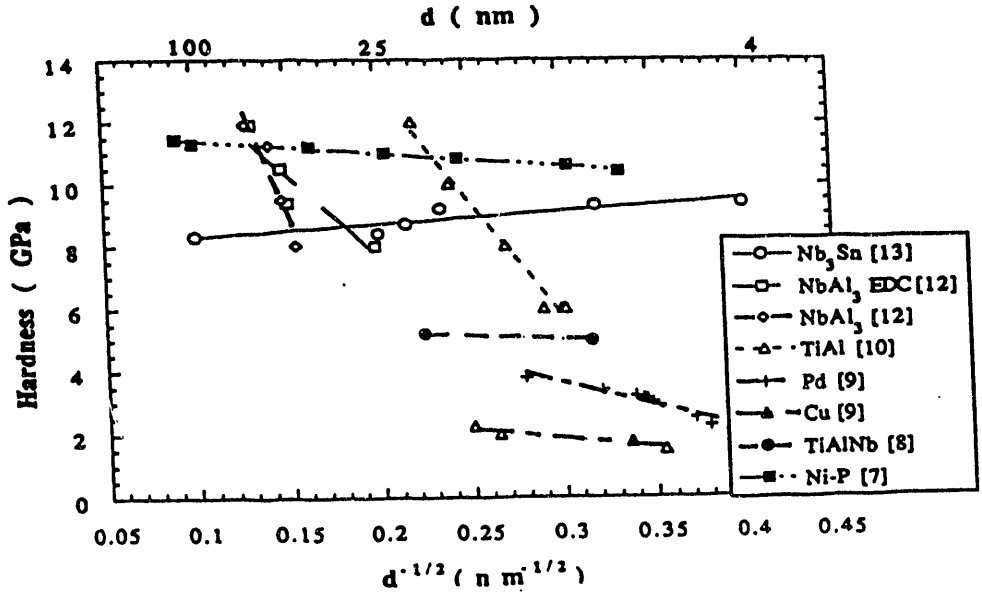

Figure 2: Hardness vs. $d^{-1/2}$.
The grain size was varied by annealing.

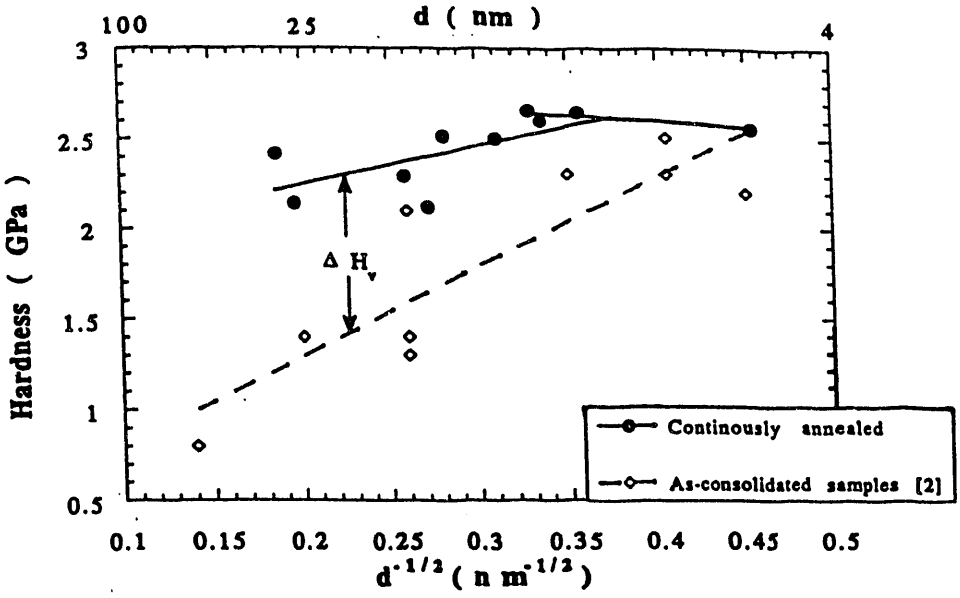

Figure 3: Vickers Microhardness vs. $d^{-1/2}$ for Cu. The grain sizes were determined by the Warren-Averbach method.

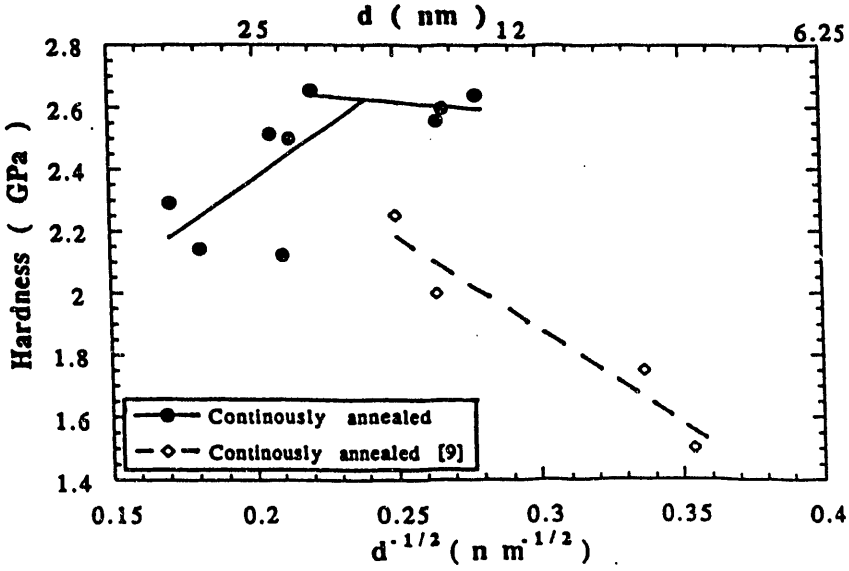

Figure 4: Vickers Microhardness vs. $d^{-1/2}$ for Cu.
The grain sizes were determined by the Scherrer method.

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