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MECHANICAL BEHAVIOR OF NANOCRYSTALLINE METALS*

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MECHANICAL BEHAVIOR OF NANOCRYSTALLINE METALS

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Introduction

The influence of grain size or cell size on the mechanical behavior of metals is well known, although debate continues about details of defect control mechanisms. In the past, difficulty in producing bulk samples with grain sizes smaller than about 1 μm limited mechanical behavior studies in finer-grained materials. Expressions relating strength to grain size, determined from studies of coarse-grained materials, suggest that reducing grain size into the sub-micrometer range results in increased mechanical strength at low homologous temperatures. At high temperatures, diffusional creep effects may lead to increased ductility. This paper reports the major results to date of an ongoing study of the mechanical behavior of nanocrystalline metals produced by the inert-gas condensation method; some results have been reported elsewhere (1-3). Studies of the tensile strength, low-temperature creep and Vickers microhardness of Cu, Pd and Ag reported here are complemented in this broader study by processing studies, x-ray grain-size and strain analyses, and high resolution microscopy studies of nanostructure and microstructure. The work provides a basis for predicting low-temperature mechanical behavior of ultrafine-grained metals, subject to some significant constraints imposed by the processing conditions.

The inert-gas condensation process is capable of producing small crystallites with a narrow size distribution. Mean crystallite size is controlled by the evaporation temperature and the inert-gas pressure (4,5). In the present experiments, the powder produced is consolidated under vacuum using a uniaxial pressure of 1.4 GPa. The samples produced are ≤ 9 mm in diameter and 0.2-1.0 mm thick, and are amenable to mechanical properties testing. We used 0.7 kPa of He gas in the evaporation chamber and performed evaporations ranging from <1 to >3 hours duration, while maintaining temperature near the melting temperature (T_m) of the pure metal source material.

Surface roughness and cracks, spherical and string-like surface features, and micrometer-size pores are visible in as-consolidated pellets by optical microscopy. Smaller

pores and cracks, still vastly larger than the grain size, are visible by SEM. Polishing reduces the size and abundance of surface flaws, but does not remove all flaws that are larger than the nanometer grain size. Precision density measurements were made on 16 nanocrystalline Cu, Pd, and Ag samples, using the Archimedes method in ethyl phthalate (3). These results, which represent lower-bound values for the density of as-consolidated samples, range from 82% to 99% of that of coarse-grained standards. The measured density for a given sample is reproducible to within $\approx 2\%$. The lowest densities occur in samples having significant low-compacted rims. Ag samples tend to have the smoothest as-consolidated surfaces and the highest densities of the materials studied.

A total of 24 as-consolidated and annealed samples of Cu, Pd and Ag have been studied by x-ray diffraction methods (6) to estimate grain sizes and mean lattice strains. The grain sizes were determined by the area-averaging Warren-Averbach (WA) double peak method, after removing instrumental broadening, and by area- and volume-averaging single peak methods. Grain size estimates (WA method) for all the as-consolidated samples measured range from 3-21 nm for the Pd samples, from 5-60 nm for Cu samples, and from 51-74 nm for Ag samples (Table 1). Errors in the grain size estimates are greater for larger grain-size samples than for the smaller grain-size samples. For samples with grain sizes smaller than about 25 nm, the error is probably on the order of 10-25%, while it is as large as 100% for samples with grain sizes larger than about 50 nm. Mean strains range from 0.0 to 34×10^{-3} for as-consolidated samples, with most strains below 4×10^{-3} . This range of strains indicates that strains in cold-consolidated nanocrystalline samples are of the same magnitude as those found in ceramics and cold-worked metals with similar grain sizes (6). The variation in estimated grain size obtained from different diffraction lines or from using different methods of analysis points to the difficulty in knowing precisely the effective grain size of nanocrystalline materials.

Table I. Comparison of the ranges in mean grain size estimates (in nm) obtained by several methods, and the range in mean long range strains ($\langle \epsilon_{10^2} \rangle^{1/2}$) calculated at $10 \text{ \AA}$ scattering length from double peak XRD data.

Sample	Scherrer	Single-peak		Double-peak	$\langle \epsilon_{10^2} \rangle^{1/2}$ ($\times 10^{-3}$)
		111 peak	200 peak		
Pd	7-54	3-17	6-15	3-21	0.7-34
Cu	15-112	5-59	4-28	5-59	0.0-12
Ag		46-59	33-38	51-74	0.6-1

Microhardness Tests

Vickers microhardness measurements have been made on as-consolidated and polished specimens of nanocrystalline Cu, Pd and Ag using a 100 g load applied for 20 seconds. The results of these tests are summarized in Fig. 1, showing mean Vickers microhardness (H_V) as a function of $1/\sqrt{d}$ (d = grain size) and composition. The error bars for the grain size are taken to be 25%, a typical value. The error bars for H_V are the standard deviations for the measurements on each specimen. As a group, the Pd samples are the finest-grained and show the greatest hardness, ranging from 2.4 to 3.7 GPa compared to the hardness of a coarse-grained Pd sample of 0.8 GPa. Microhardness for the Cu samples ranges from 0.9 to 2.3 GPa compared to 0.5 for a coarse-grained sample. The two Ag samples, both comparatively large-grained, have a hardness of 0.5 GPa, compared to 0.4 GPa for a coarse-grained sample. Hardness varies greatly for a given Pd specimen. This has been interpreted in conjunction with density measurements as indicating the presence of a distribution of flaws that are much larger than the grain size

(3): The Cu and Ag samples have much more uniform hardness from point to point on the sample surface.

As shown in Fig. 1, hardness appears to increase with a decrease in grain size. However, the dependence of hardness on grain size in the nanocrystalline range is apparently much less than at conventional grain sizes (3). A low rate of strengthening in nanocrystalline Fe produced by ball-milling has also been observed (7) recently. Previously, the yield stress in pure Ni with $\leq 1 \mu\text{m}$ grain size was found to show a small rate of increase as a function of $1/\sqrt{d}$ (8). Armstrong (9) has suggested this result is due to the influence of small inclusions. Mathematical models based on dislocation pile-ups or stress/strain concentrations at grain boundaries have been developed to explain the small slopes at sub-micrometer grain sizes (10-12).

Fig. 1 Vickers microhardness of 23 samples of nanocrystalline Cu (12 samples), Pd (9 samples), and Ag (2 samples) as a function of (grain size) $^{-1/2}$.

Tensile Tests

Tensile tests have been performed on 5 nanocrystalline Pd samples and on 6 nanocrystalline Cu samples. Dogbone-shaped test specimens were machined from the as-consolidated samples by electric discharge machining. After polishing, the samples were tested using a miniaturized servo-electric test apparatus built to test the small specimens (3). Strain was monitored by an LVDT attached to the ends of the machine grips rather than to the gage section of the sample.

Results of the tensile tests completed to date are shown in Table 2. The Pd samples were found to have yield stresses ranging from ≈ 140 MPa to > 330 MPa with no clear trend towards increased strength as a function of decreasing grain size between 5 and 15 nm. The maximum strain reached in any of the Pd samples is 1.75%, but a typical value is $\approx 0.5\%$. The yield stress of the Cu samples range from ≈ 125 MPa to 225 MPa, with a clear indication of increased strength with decreasing grain size. Fig. 2 is a plot of the Cu yield stress data as a function of $1/\sqrt{d}(\text{nm})$. The slope of the line, equal to k in the empirical Hall-Petch equation, $\sigma_y = \sigma_{y0} + k/\sqrt{d}$

(9,13,14), is $\approx 470 \text{ MPa}\sqrt{\text{nm}}$, with an intercept, σ_{y0} of 82 MPa. This value of k is about an order of magnitude smaller than the corresponding constant for the flow stress in conventional Cu cited by Hansen and Ralph (15). True strains of as much as 6% were reached in the nanocrystalline Cu, although a more typical value is 1.5-2%. The effective Young's modulus for both the Cu and Pd samples ranges from 21 to 66 GPa with a typical value for both materials of about 47 GPa. In contrast, Young's modulus for conventional Pd is ≈ 120 , and for Cu is ≈ 130 GPa.

Table 2. Tabulation of data from tensile tests on nanocrystalline Pd and Cu: E = Young's modulus, σ_y = yield stress, True ϵ = % true strain at failure, $\dot{\epsilon}$ = strain rate; (d) = displacement control, (l) = load control.

Sample	Grain Size (nm)	E (GPa)	σ_y (MPa)	True ϵ (%)	$\dot{\epsilon}$ (mm/mm·sec)
Pd1205(l)	5	43	192	0.59	1E-5
Pd1203(l)	8	47	>200	>0.26	1E-5
Pd7061(d)	11	46	140	0.56	7E-5
Pd8031(l)	14 ^a	21	249	1.75	2E-5
Pd1202(l)	15 ^b	66	>330	>0.52	2E-5
Cu3012(l)	15	47	225	1.52	6E-4
Cu3081(l)	20	47	175	0.79	3E-4
Cu1104(l)	25	45	185	>6.3	1E-5
Cu1103(l)	50	36	162	>2.2	1E-5
Cu3061(l)	61	53	140	2.2	5E-4

^a Reported as 7 nm grain size in Ref. 2

^b Reported as 10 nm grain size in Ref. 2

Fig. 2 Yield Stress of 5 samples of nanocrystalline Cu as a function of (grain size) $^{-1/2}$.

All of the Pd samples, and 3 of the Cu samples, failed in a brittle manner along a fracture path with traces oriented normal to the tensile axis. As shown in a previous report (2), the tensile behavior of the Pd samples is correlated to the quality of the surface polishing to reduce the size of flaws. This is not surprising in view of the density and microhardness data cited above. As with the microhardness data, the Cu tensile test data suggest less of a flaw sensitivity.

Creep Tests

Room temperature creep tests have been performed on several nanocrystalline Cu and Pd samples in order to determine whether the ultrafine grain size and possibly enhanced diffusivity (16) result in creep at abnormally low temperatures (2,3). The results of several tests are shown in Table 3. The creep rates observed are all near the resolution limit of the test apparatus. The nanocrystalline samples appear to show strong creep resistance at room temperature, and creep curves have been found to be well described by logarithmic creep expressions typical of conventional grain size materials.

Table 3. *Tabulation of room temperature creep test data on nanocrystalline Pd and Cu: ϵ = true strain (%), $\dot{\epsilon}$ = average strain rate.*

Sample	Grain Size (nm)	Time (minutes)	Constant Stress (MPa)	$\dot{\epsilon}$ (mm/mm·sec) ($\times 10^{-8}$)	Apparent Total ϵ (%)
Pd1203	8	1091	150	0.5	0.343
Pd1203	8	1071	130	1	0.409
Cu3012	15	1160	47	2	0.363
Cu1104	25	45	145	7	1.203
Cu1104	25	850	150	14	1.161
Cu1103	50	1070	100	4	0.545
Cu3061	61	1035	51	0.7	0.219

Conclusions

The mechanical behavior of nanocrystalline Pd, Cu and Ag samples with well-characterized mean grain sizes have been evaluated by Vickers microhardness measurements, uniaxial tensile tests, and creep measurements. The strength of the materials appears to increase with decreasing grain size, similar to conventional grain-size materials. There is a large increase in yield strength and microhardness as grain size drops from the micrometer to the nanometer scale, but the slope of H_v and σ_y vs $1/\sqrt{d}$ is much lower in the nanometer range than is seen at ordinary grain sizes. No evidence of diffusional creep at room temperatures could be found. All mechanical measurements were handicapped by the small amounts of material available for study, but this serves to point out the importance of developing improved processing methods.

Mechanical properties of the samples described here appear to be influenced by processing-induced features that are not yet well characterized, including grain size distributions; "nanoscale" porosity, cracks, and impurity concentrations; and delamination microcracks and consolidation process-related texture. The strengthening as a function of grain size observed in the present results must be interpreted cautiously, since knowledge of

the relative importance of these processing effects is presently lacking. Yet the tensile yield and compressive microhardness tests give consistent strength vs grain size results. At room temperature, the strength of a nanocrystalline metal is increased significantly over that of a coarse-grained material, while the rate of increase of strengthening with decreasing grain size is significantly reduced. Detailed knowledge of the mechanisms that result in the increased strength of nanocrystalline metals are lacking, but restrictions on dislocation activity (both generation and mobility) imposed by small grain size are likely to be the dominant factor in raising strength.

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