TENSILE STRENGTH AND CREEP RESISTANCE IN NANOCRYSTALLINE Cu, Pd AND Ag

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ABSTRACT

Measurements of tensile strength and creep resistance have been made on bulk samples of nanocrystalline Cu, Pd and Ag consolidated from powders by cold compaction. Samples of Cu-Cu_2O have also been tested. Yield strength for samples with mean grain sizes of 5-80 nm and bulk densities on the order of 95% of theoretical density are increased 2-5 times over that measured in pure, annealed samples of the same composition with micrometer grain sizes. Ductility in the nanocrystalline Cu has exceeded 6% true strain, however, nanocrystalline Pd samples were much less ductile. Constant load creep tests performed at room temperature at stresses of >100 MPa indicate logarithmic creep. The mechanical properties results are interpreted to be due to grain size-related strengthening and processing flaw-related weakening.

INTRODUCTION

Two well-established relations developed from studies of coarse-grained materials are generally used to predict mechanical behavior as a function of grain size. At low homologous temperatures ($T \leq 0.3T_m$) the yield or flow strength (σ_y) has been related to grain size (d) through the empirical Hall-Petch expression (1-3): $\sigma_y = \sigma_o + kd^{-1/2}$, where σ_o and k are constants. At temperatures in the range $0.3T_m \leq T \leq 0.5T_m$, diffusional creep is predicted to be dominated by grain boundary processes, leading to a creep rate proportional to $\sigma\delta D_b/d^3$ (δ = grain boundary thickness; D_b = grain boundary diffusivity; [ref. 4]). These relationships predict material strength will increase as grain size decreases as long as grain boundary diffusivity is very slow. Reports of exceptionally high diffusivity in nanocrystalline Cu (5,6) suggested that diffusional creep would be significant even at room temperature in ultrafine grain samples. Nanocrystalline materials might therefore be expected to soften with decrease in grain size.

This paper reports on tensile strength, low-temperature creep and Vickers microhardness studies of several samples of nanocrystalline Cu, Pd and Ag produced by the inert-gas condensation method. Grain-size and long range strain have been measured by x-ray diffraction (XRD) analyses, and high resolution microscopy (HREM) studies are in progress to identify elements of nanostructure that may influence mechanical properties (7-12).

The inert-gas condensation process was used to produce powders with ultrafine grain sizes. Mean crystallite size is controlled by the evaporation temperature and the inert-gas pressure (13-15). 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. The powder produced was consolidated under

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vacuum ($\geq 10^{-5}$ Pa) using a uniaxial pressure of 1.4 GPa. Grain size estimates for 24 as-consolidated samples measured range from 3-21 nm for nine Pd samples, from 5-60 nm for 13 Cu samples, and from 51-74 nm for two Ag samples (12). The samples produced were ≤9 mm in diameter and 0.2-1.0 mm thick, and were amenable to mechanical properties testing using conventional Vickers microhardness equipment and a custom tensile testing apparatus (9).

Precision density measurements were made on 16 nanocrystalline Cu, Pd, and Ag samples, using the Archimedes method in ethyl phthalate (9). Densities range from 82% to 99% of that of coarse-grained standards. The measured density for a given sample is reproducible to within ≈ 2%. The lowest densities occur in samples having significant low-compacted rims. The presence of these rims determines that all density measurements represent lower limits of the density of the well-consolidated central parts of the specimens used in the mechanical properties tests. For Cu and Pd samples, the lowest densities were observed in the finest-grained specimens. Density measurements were repeated on several samples after annealing for 1 h at 200 °C or after hot-recompacting at 100 °C. The changes in density that resulted were insignificant with respect to the range of the measurement errors for the method.

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. While polishing reduced the size and abundance of surface flaws, it could not remove all flaws that are larger than the nanometer grain size. The mechanical properties test results therefore reflect net material strength, i.e., the strength provided by grain size constraints and the weakness due to trapped porosity and other processing flaws.

MECHANICAL PROPERTIES TESTS

Tensile tests have been performed on 6 nanocrystalline Cu samples, 5 nanocrystalline Pd samples, and on 2 Ag samples. Dogbone-shaped test specimens were cut from the as-consolidated samples by electric discharge machining, then polished carefully. Tests were run on a miniaturized servo-electric test apparatus built to test the small samples (9). 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 1. The yield stress of the nanocrystalline Cu samples ranges from ≈ 125 MPa to 225 MPa, with a clear indication of increased strength with decreasing grain size. A coarse-grain Cu sample gave a yield stress on the order of 85 MPa. Fig. 1 is a plot of the Cu yield stress data as a function of $1/\sqrt{d(nm)}$. The error bars for the grain size are taken to be ±25%, a value typical for samples with mean grain sizes greater than about 15 nm (10,12). The slope of the line, equal to k in the Hall-Petch equation, is ≈ 470 MPa$\sqrt{nm}$, with an intercept, σ_0 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 (16). True strains of as much as 6% were reached in the nanocrystalline Cu. More typically, strains reached only 1.5-2% before brittle failure occurred.

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

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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 ≈ 0.5%. Coarse grain samples tested gave yield stresses on the order of 55 MPa and large strains.

The two Ag samples gave similar yield stress values (54 & 48 MPa) despite the fact that their mean grain sizes are apparently different by a factor of two. One sample failed by cracking after about 1.6 % strain, while the second sample was tested repeatedly to a cumulative strain of > 6% without failing. This second sample showed strain hardening during repeated tests (Fig. 2), as would be expected in coarse-grained samples from dislocation interactions.

Vickers microhardness measurements were also made on as-consolidated and polished specimens of nanocrystalline Cu, Pd and Ag using a 100 g load applied for 20 seconds (9,11). 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. Two Ag samples tested, including one of the samples tested in tension, are comparatively large-grained and show little increase in hardness over a coarse-grained sample. The hardness of the nanocrystalline Ag samples is about 0.5 GPa, compared to 0.4 GPa for a coarse-grained sample. Spatial variability in hardness for a given Pd specimen 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 (7,9). The Cu and Ag samples have much more uniform hardness from point to point on the sample surface.

Table 1. *Tabulation of data from tensile tests on nanocrystalline Pd, Cu and Ag: σ_y = yield stress, True ε = % true strain at failure, $\dot{\varepsilon}$ = strain rate; (d) = displacement control, (l) = load control. After ref. (9).*

Sample	Grain Size (nm)	σ_y (MPa)	True ε (%)	$\dot{\varepsilon}$ (mm/mm·sec)
Pd1205(l)	5	192	0.59	1E-5
Pd1203(l)	8	>200	>0.26	1E-5
Pd7061(d)	11	140	0.56	7E-5
Pd8031(l)	14[a]	249	1.75	2E-5
Pd1202(l)	15[b]	>330	>0.52	2E-5
Cu3012(l)	15	225	1.52	6E-4
Cu3081(l)	20	175	0.79	3E-4
Cu1104(l)	25	185	>6.3	1E-5
Cu1103(l)	50	162	>2.2	1E-5
Cu3061(l)	61	140	2.2	5E-4
Cu3051(l)	60	125	1.3	3E-4
Ag2081(l)	51	54	>2.5	3E-4
Ag2091(l)	21	48	1.6	8E-4

[a] Reported as 7 nm grain size in Ref. 7

[b] Reported as 10 nm grain size in Ref. 7

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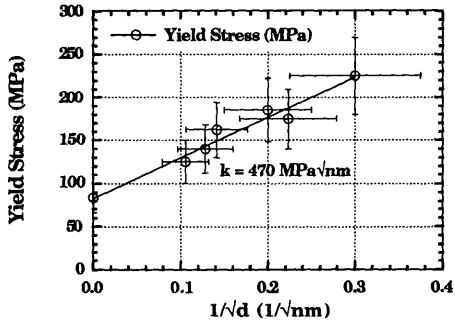

Fig. 1 Yield Stress of 6 samples of nanocrystalline Cu as a function of (grain size)$^{-1/2}$. (After ref. 11)

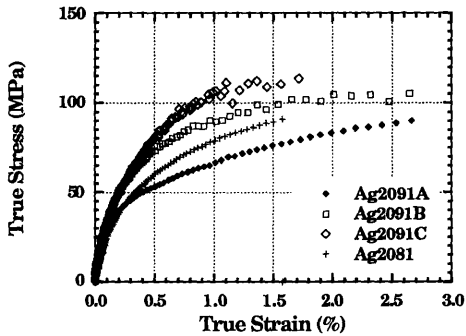

Fig. 2 Comparison of stress -strain curves for 2 samples of nanocrystalline Ag, showing strain-hardening in Sample Ag2091. A = first tensile test, followed by B, then C.

All of the Pd samples, 3 of the Cu samples, and one of the Ag samples failed in a brittle manner after ≤ 3% strain, generally along a fracture path with traces oriented at ≈ 90° to the tensile axis. This is not surprising in view of the density and microhardness data cited above. It was shown previously (8) that tensile behavior of nanocrystalline Pd is correlated to the quality of the surface polishing to reduce the size of processing flaws. As with the microhardness data, the Cu tensile test data suggest less of a flaw sensitivity. Two samples that were annealed at 200 °C for 1 h and two samples that were hot compacted in air at 100 °C also failed in a brittle manner. These two samples had been consolidated in air and showed significant Cu_2O peaks in XRD profiles. They failed at loads so low that large flaws must have been present.

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Room temperature creep tests were performed on several nanocrystalline Cu and Pd samples to determine whether the ultrafine grain size and possibly enhanced diffusivity result in creep at abnormally low temperatures (9). The nanocrystalline samples show strong creep resistance at room temperature, giving creep rates near the resolution limit of the test apparatus even at constant loads of twice the yield stress of coarse grain materials. The creep curves have been found to be well described by logarithmic creep expressions typical of conventional grain size materials at room temperature.

CONCLUSIONS

The mechanical behavior of nanocrystalline Pd, Cu and Ag samples with well-characterized mean grain sizes have been evaluated by uniaxial tensile tests, Vickers microhardness measurements, and room temperature creep measurements. The results of tensile, creep, and compressive microhardness tests are consistent at room temperature. The strength of a nanocrystalline metal is increased significantly over that of the coarse-grained material. However, the slope of microhardness and yield strength vs $1/\sqrt{d}$ is much lower in the nanometer range than at ordinary grain sizes. No evidence of diffusional creep at room temperature could be found in nanocrystalline Cu or Pd.

These significant increases in strength were observed despite the fact that processing flaws much larger than the nanocrystalline grain size are present in our small samples. Processing-induced features are not yet well characterized, but include nano- and micrometer-scale porosity and cracks, impurity concentrations, and delamination microcracks. The degree of strengthening as a function of grain size observed in the present experiments must be interpreted cautiously, due to incomplete knowledge of the relative importance of these effects, but represent at least a lower limit to that possible in nanocrystalline metals.

By analogy with coarse grain materials, restrictions on dislocation activity (both generation and mobility) imposed by small grain size are considered to be the dominant factor in raising strength. Geometrical constraints, proposed by Ashby (17) and developed into a Hall-Petch equation form by Thompson et al. (18), may play an important role in controlling deformation. As shown in Fig. 1, yield strength appears to increase with a decrease in grain size. However, the dependence of yield strength on grain size in the nanocrystalline range is apparently much less than at conventional grain sizes, in agreement with other microhardness (19) and tensile test (20) results in metals with grain sizes ≤ 1 μm. Armstrong (3) suggested that small slopes at sub-micrometer grain sizes result from 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 (21-25). In our nanocrystalline samples, processing induced flaws probably develop through Griffith crack behavior (e.g., 26) to account for the strain and fracture observed. Evidence from HREM studies (12) suggests that twinning is influential in plastic behavior in the finest grain samples. Samples that show significant plastic strains may do so as a result of plastic deformation of larger grains in samples with broader grain size distributions.

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