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TENSILE BEHAVIOR OF NANOCRYSTALLINE COPPER

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Abstract

High density nanocrystalline copper produced by inert gas condensation was tested in tension. Displacements were measured using foil strain gauges, which greatly improved the accuracy of the strain data. The Young's modulus of nanocrystalline copper was found to be consistent with that of coarse-grained copper. Total elongations of ≈ 1% were observed in samples with grain sizes less than 50 nm, while a sample with a grain size of 110 nm exhibited more than 10% elongation, perhaps signifying a change to a dislocation-based deformation mechanism in the larger-grained material. In addition, tensile tests were performed as a function of strain rate, with a possible trend of decreased strength and increased elongation as the strain rate was decreased.

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Introduction

Nanocrystalline materials are those with grain or crystallites sizes in the nanometer regime (1). Since the early days of nanocystalline research, the strengths of nanocrystalline metals have been believed to be extremely high, due to grain size strengthening as exemplified by the Hall-Petch relation. Indeed, early indentation measurements showed that these metals had hardnesses which were 2 to 4 times that of their annealed coarse-grained counterparts (2).

A relatively small amount of research has been done measuring the bulk mechanical properties of pure nanocrystalline metals, perhaps due to the difficulty in producing samples large enough to make mechanical test specimens. By specifying pure nanocrystalline metals, the discussion is mainly limited to materials synthesized by inert gas condensation, although other methods are possible. Among the first tensile tests performed on pure nanocrystalline metals were those done by Nieman et al. (3). They reported yield stresses for nanocrystalline Pd that were 5 times higher than annealed coarse-grained Pd, and total elongations of 1 to 2%.

Later work by Nieman et al. (4) reported the tensile properties of nanocrystalline Cu (Table I). The yield stress was only about 2 times that of annealed coarse-grained copper, but the elongation was found to be greater than 2 to 7%. The Young's modulus from the stress-strain curve was also reported, and it appeared to be less than half of the coarse-grained value (Table I).

Tensile tests by Günther et al. (5) were performed on nanocrystalline Cu, which was 92% dense with an oxygen impurity level of 1.3 at%. They found the yield stress for copper with a 30 nm grain size to be about 5 times higher than annealed coarse-grained Cu (Table I). In addition, they found that a short, low temperature anneal (which didn't increase the grain size) increased the ductility from about 2 to 7%, while it decreased the yield stress from 370 to 300 MPa.

Table I. Previous Tensile Test Results for Pure Copper

grain size	treatment	E (GPa)	σ_y(MPa)	σ_{uts}(MPa)	elong. (%)	ref.
25 nm	none	45	185	> 260	> 2	(4)
50 nm	none	36	162	> 190	> 7	(4)
30 nm	none		370		≈ 2	(5)
30 nm	150°C, 30 min		300		≈ 7	(5)
20 μm	annealed	110	70	220	60	(6)

">": the test was stopped because the load or displacement range was exceeded

The goal of the current work was to determine the intrinsic mechanical behavior of nanocrystalline metals. Extrinsic effects, such as porosity and gaseous impurities, have been found to have a significant impact on the mechanical behavior of nanocrystalline materials, including those made by inert gas condensation (7). Improvements to the synthesis and compaction chambers at Argonne National Laboratory (8) have led to reductions in both the porosity and gaseous impurity levels in the resultant nanocrystalline metals (7), which should facilitate the measurement of the intrinsic mechanical behavior in these materials.

Experimental Procedures

The nanocrystalline Cu was made by inert gas condensation and compaction (1) at Argonne National Laboratory (8). After evacuation of the synthesis chamber to ≈ 5×10^{-8} Torr, it was filled with 5 Torr of 99.9999% purity He, which was continuously pumped to change the atmosphere every 10 min. High purity (99.999%) Cu was then evaporated at ≈ 1110°C from alumina-lined Mo boats for 3 hr. The resultant powder was collected on a liquid nitrogen-cooled cold finger, and was continuously removed during the evaporation by stainless steel scrapers. After completion of the powder synthesis, the system was once again evacuated, and the powder transferred in vacuum to the attached compaction chamber. The powder was placed in a die, and compacted for 10 min at 150°C under 1.4 GPa of pressure. The resultant disks were 9 mm in diameter, and 0.4 to 0.7 mm thick.

Density measurements were made using Archimedes' principle (9), with a precision of ≈ 0.1%. The grain size was determined by x-ray line broadening of the 111 and 222 peaks, using the Warren-Averbach technique (10), where the uncertainty due to counting statistics was less than 0.5 nm for grain sizes smaller than 50 nm. The oxygen and metallic impurity content were inferred from other nanocrystalline samples produced under similar synthesis conditions. The oxygen concentration was found to be less than 0.5 at% (the detectability limit) by neutron activation (11). The largest metallic impurity identified was 0.07 at% Mo (from the boat).

Tensile specimens were electro-discharge machined from the disks. The gauge length was 3mm, the gauge width was 2 mm, and the radius between the gauge length and the grip ends was 1 mm. The faces of the specimen were vibratory polished to a mirror finish using 0.05 μm alumina, while the edges were polished using a dremel tool and a slurry of 5 μm alumina. Strain gauges with a 0.79 mm grid length and 1.27 mm grid width were glued to the center of the gauge section with a cyanoacrylate adhesive. Tensile tests were conducted on an MTS servo-electric machine in stroke control. The samples were held using custom made, clamp-type tool steel grips. An elaborate procedure utilizing an alignment fixture was developed to ensure the specimen was clamped properly in the grips, and to minimize bending during loading.

Results and Discussion

The tensile test results for nanocrystalline copper are shown in Table II. The nanocrystalline samples had grain sizes ranging from 26 to 110 nm, and densities between 98.4 and 99.4%. A cold-rolled copper sample with a grain size of 20 μm tested in the same geometry is shown for comparison. The 0.2% offset yield stress is denoted by σ_y.

Table II. Tensile Test Results for Pure Copper

grain size	density (%)	thickness (mm)	E (GPa)	σ_y(MPa)	σ_{uts}(MPa)	elong. (%)
26 nm	99.0	0.69	108	365	425	0.7
34 nm[1]	98.4	0.42	107		290	0.3
49 nm	99.1	0.45	104	345	460	1.2
110 nm[2]	99.4	0.41	93	300	415	> 10
20 μm[3]	100.0	0.40	103	263	292	15

[1] the sample broke before the yield stress could be determined

[2] the test was stopped because the displacement range was exceeded

[3] cold-rolled, coarse-grained

Young's Modulus

The Young's modulus was determined from the initial slope of the stress-strain plot (from 20 to 80 MPa), as shown in Fig. 1. The elastic modulus for coarse-grained copper was found to be 103 GPa, while the modulus for the 3 nanocrystalline samples measured was 108, 107, and 104 GPa (Table II). Considering the possible errors in the measurement, these values were judged to be essentially the same as the coarse-grained value. This means that high-density nanocrystalline copper has virtually the same elastic modulus as fully-dense coarse-grained copper. Of course, some reduction in the modulus could be expected if the material was not fully dense (6), but this was not apparent due to the normal uncertainty in modulus results from tensile tests.

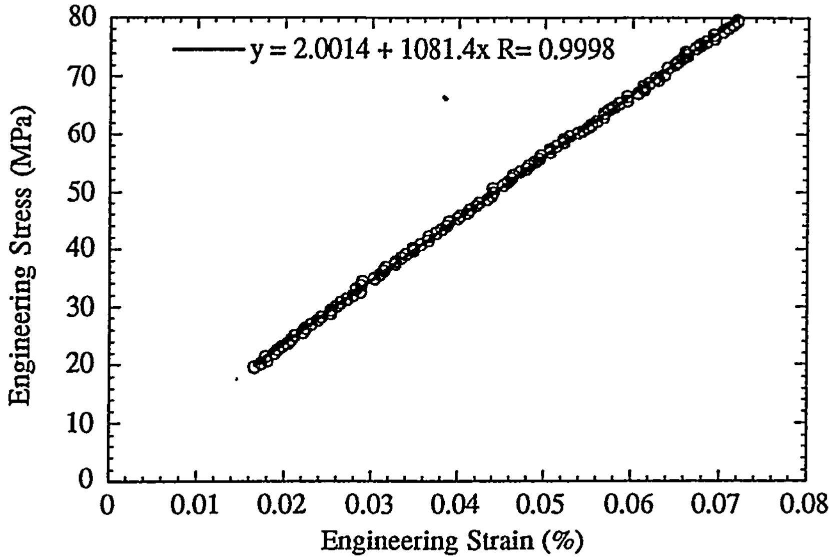

Figure 1. Stress-strain plot used for Young's modulus determination of nanocrystalline copper (26 nm grain size).

The extremely low Young's modulus results reported by Nieman et al. were mainly the result of calculating the strain from the change in displacement across the grips (4). Two effects which must be considered are the machine compliance and the effective gauge length. The correction for machine compliance assumes that there is a linear relation between load and the machine elongation during the tensile test (12). The effective gauge length is the sum of the actual gauge length (3 mm) and the contribution from the flared region between the gauge length and the grip ends (≈ 1.5 mm), since both parts of the specimen stretch during a tensile test. The impact of strain measurement on the stress-strain plot is shown graphically in Fig. 2. The curve labeled grip displacement shows the strain if the gauge length is assumed to be 3 mm, and the machine compliance is neglected. In this case, the modulus appears to be 36 GPa, and the elongation is 3.3%. If corrections are made for the machine compliance and effective gauge length, the modulus is now right at 105 GPa, but the elongation is still 1.8%. The strain gauge also gives the correct modulus, but the elongation is only 0.8%. Perhaps the difference in elongation between the strain gauge and corrected displacement measurements is due to nonlinear machine compliance effects, such as rotation of the grip clamps as the load is applied.

Another explanation for the low Young's modulus found by Nieman et al. (4) could be a lower sample density. Although numbers were not available for the nanocrystalline samples listed in Table I, typical densities for Nieman's nanocrystalline Cu averaged 91% (4). A number of the-

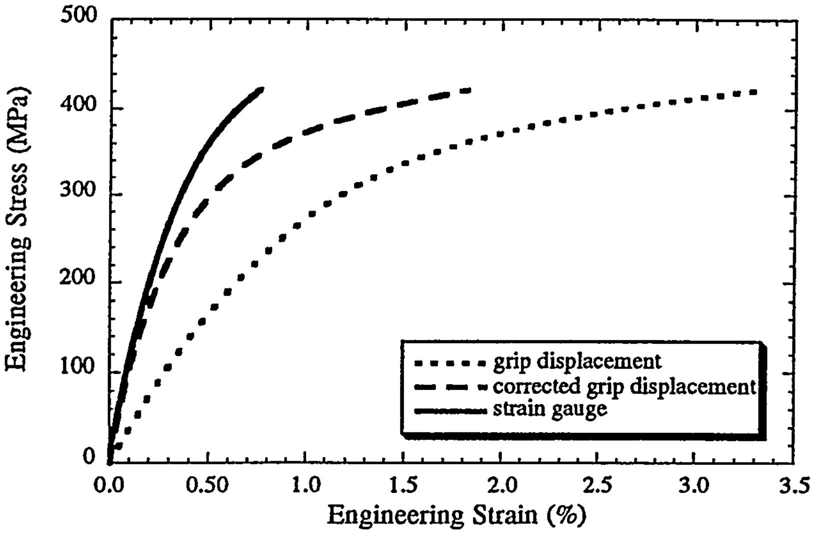

Figure 2. Comparison of small specimen stress-strain curves for different strain measurement techniques (26 nm grain size).

ories have been formed to explain the low modulus in terms of pores and/or cracks (e.g. 13), but the major reason for the decreased Young's modulus was the indirect strain measurement.

Strength and Elongation

Stress-strain plots are shown in Fig. 3 for three nanocrystalline samples and a cold-rolled Cu sample with a 20 μm grain size, all tested with strain gauges. The strain gauges should give accurate strain measurements up to 2 to 4% strain, and seem to perform reliably in the range tested. The most significant result in Fig. 3 is the difference in behavior between the samples with grain sizes below 100 nm, as compared to those with larger grain sizes.

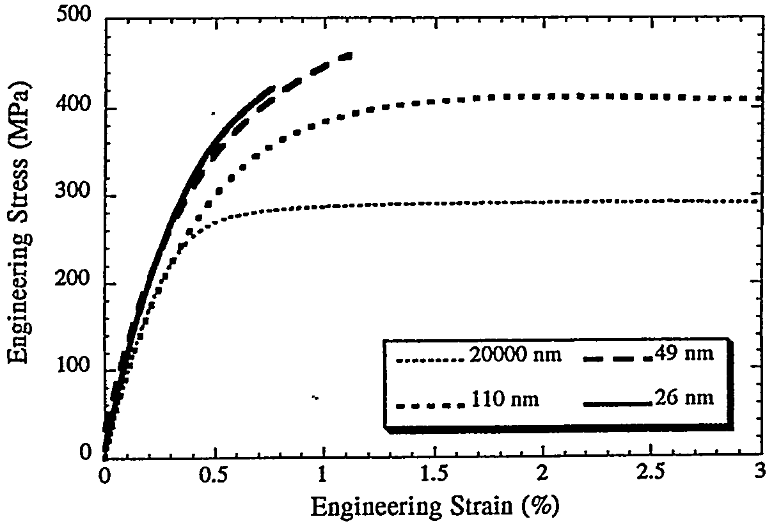

Figure 3. Stress-strain plots for nanocrystalline and cold-rolled coarse-grained Cu.

The 20 μm sample has strengths and elongations similar to those for cold-worked Cu (6), while the 110 nm sample had properties comparable to those observed in R. Z. Valiev's ultra finegrained Cu made by equal channel angular pressing (14). However, at grain sizes below 100 nm, considerably higher strengths, as well as lower elongations were observed (Table II). For the smaller grain sizes, the failure seemed to be flaw dominated, with little deformation and a fracture surface perpendicular to the stress axis. The dislocation-based deformation mechanisms which are likely to be active above 100 nm may not operate at smaller grain sizes. If this is the case, the presence of small processing flaws could lead to brittle failure, especially in the absence of crack tip blunting. Since the theoretical strength of Cu is only about 60 times the ultimate stress observed in nanocrystalline Cu (12), a small elliptical pore or crack could easily lead to a stress concentration higher than the material strength. Pores on the order of the grain size are still observed in high-density nanocrystalline metals produced by inert gas condensation (7), and it is likely that at least one processing flaw of the critical dimensions is present in each sample.

As shown in Table II, the yield strength of copper with a grain size of 26 nm was 365 MPa, which is consistent with that found by Günther et al. (Table I). However, this yield strength was about double that measured by Nieman et al. (Table I). This lower strength observed by Nieman may have resulted from the lower density of his samples, as discussed in the previous section. In addition, the reduced strength may also be explained by the presence of a few large grains in the material. Nieman used different boats in the synthesis of his nanocrystalline powder, and it was more difficult for him to get a uniform evaporation rate from these sources (15). Both the presence of a few large grains, as well as the indirect method of measuring the strain, may have contributed to the considerably higher elongations reported by Nieman et al. for nanocrystalline Cu.

The impact of strain rate on the deformation behavior was investigated by testing several samples with similar densities and grain sizes. The results are shown in Fig. 4, where all the strains were measured by grip displacement, with corrections made for effective gauge length and linear machine compliance. As the strain rate was decreased, a general trend of decreased strength and increased elongation was observed. However, a second sample tested at a strain rate of 10^{-5} /s showed behavior like that of the samples tested at faster strain rates, even though it failed prematurely. Slower strain rates may allow for greater time dependent deformation, but due to sample-to-sample variability, a definite conclusion cannot be drawn.

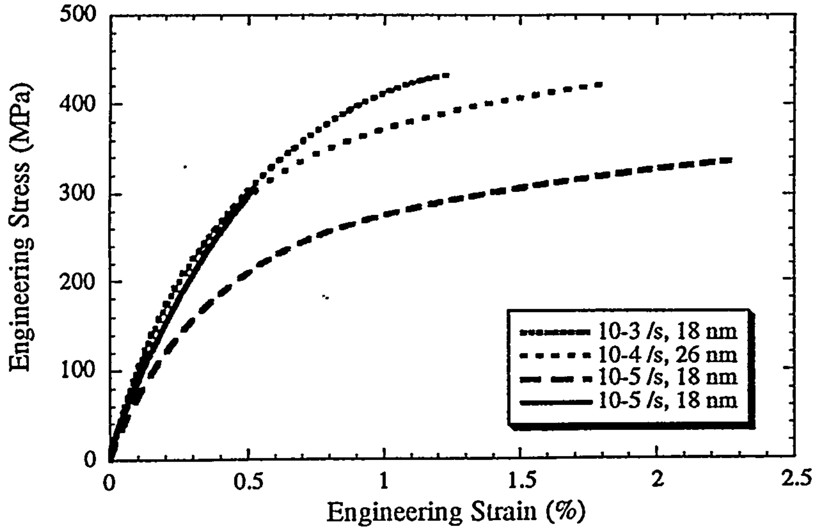

Figure 4. Effect of strain rate on the tensile behavior of nanocrystalline Cu (corrected indirect strain measurement).

Conclusions

Tensile tests were performed on high-density nanocrystalline Cu produced by inert gas condensation and compaction. The Young's modulus was found to be consistent with that of fully-dense coarse-grained Cu. Copper with grain sizes below 50 nm had extremely high strength and low ductility, while Cu with a grain size of 110 nm had an elongation in the range of coarse-grained Cu. The dislocation-based deformation mechanisms operating at grain sizes greater than 100 nm may not be active at smaller grain sizes. In addition, tensile tests as a function of strain rate were performed, with a possible trend of decreased strength and increased elongation as the strain rate was reduced.

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