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Abstract

Bulk samples of Cu with grain sizes in the range of 5-61 nm were produced from high purity Cu by inert gas condensation (IGC) in vacuum ($\approx 10^{-5}$ Pa), and samples of Cu-Cu_2O with grain sizes of 5-7 nm were produced by IGC followed by consolidation in air. Samples produced by IGC from a Cu-7 at. % Si alloy and consolidated in vacuum have grain sizes of 8-20 nm and small to negligible Si contents. Densities of all samples range from 82-99% of standard density. Mechanical properties measurements on nanocrystalline Cu and Pd samples show that strength is increased over that of conventional material, with a slight $1/\sqrt{d}$ dependence. Two nanocrystalline Ag samples (21,51 nm) show apparent work hardening. Constant load creep tests performed at room temperature on nanocrystalline Cu and Pd indicate logarithmic creep typical of coarse-grained samples. High resolution electron microscopy shows nanostructural features, including multiple twinning, that may influence strain behavior.

Introduction

Methods of strengthening used in conventional grain size materials include grain size refinement, precipitation hardening and oxide dispersion strengthening. Strengthening in these types of materials results from restrictions on dislocation generation and motion as dislocations interact with grain boundaries, precipitates, or dispersed oxides. We have used the inert gas condensation (IGC) process (1-3) to produce nanometer grain size materials for mechanical properties tests in order to investigate the effects of ultrafine grain size on mechanical behavior. A detailed report of this processing method has recently appeared elsewhere (4). We have attempted to prepare alloy and composite samples with precipitates and oxide dispersoids of nanometer size in addition to pure metals. Studies of the tensile strength, low-temperature creep and Vickers microhardness of Cu, Pd and Ag (3, 5-7) have been augmented by x-ray grain-size and lattice strain analyses (9,10), and by high resolution microscopy (10) studies of nanostructure and microstructure.

Processing and Physical Properties

Nanocrystalline powders of pure Cu, Pd and Ag were produced by IGC starting with high-purity precursor metals. The powders were consolidated in situ under vacuum ($\geq 10^{-5}$ Pa) using a uniaxial pressure of 1.4 GPa. Two samples of Cu-Cu_2O were produced by consolidating the samples of pure Cu powder after exposure to air. A Cu-7 at. % Si alloy precursor was evaporated in an effort to produce samples of a Cu-Si alloy. The consolidated samples were disk-shaped, $\leq$ 9 mm diameter and 0.2-1.0 mm thick. The grain sizes of consolidated samples were determined by x-ray diffraction (XRD) line broadening methods (9,10). Grain size estimates for 25 as-consolidated samples measured range from 3-21 nm for nine Pd samples, 5-61 nm for 13 Cu samples, and 21-74 nm for three Ag samples. Samples produced from the Cu-7 at. % Si alloy were found to have negligible Si contents, with estimated mean grain sizes of 8-20 nm. The Cu-Cu_2O samples, consolidated in air, showed strong 111 and 200 Cu_2O XRD peaks, with no evidence of CuO peaks in the data. The mean grain sizes of the two Cu-Cu_2O samples were 5 and 7 nm.

Precision density measurements were made on 16 as-consolidated nanocrystalline Cu, Pd, and Ag samples, using the Archimedes method in ethyl phthalate (3). Densities ranged from 82% to 99% of that of coarse-grained standards. The measured density for a given sample is reproducible to within $\approx$ 2%. The consolidation process left rims of poorly consolidated material in some cases and this material was not removed prior to the density tests. Therefore all density measurements represent lower limits of the density of the well-consolidated central parts of the specimens used in the mechanical properties tests. The Cu-Cu_2O and the Cu alloy nanocrystalline samples were compared to a pure Cu standard rather than a fully dense standard of the composition of the nanocrystalline sample. This will have reduced the relative density of these nanocrystalline samples slightly.

gave yield stress values similar to one another (Fig. 3) despite the fact that their mean grain sizes are apparently a factor of two different (21,51 nm). 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 tests subsequent to the first one (Fig. 3), as would be expected in coarse-grained samples due to 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 (4,5). 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 and 1.3 GPa for a cold-worked coarse-grain sample. These microhardness results are shown in Fig. 4, plotted as a function of (grain size)$^{-1/2}$. The slope of the best-fit line for all of the data shown is 4.6 GPa$\sqrt{nm}$, about ten times larger than the value of the Hall-Petch coefficient k for the nanocrystalline Cu tensile test data, but still slightly smaller than the value of k for the flow stress data on conventional grain size Cu of Ref. 11. Two Ag samples tested, including one of the samples which was tested in tension, are comparatively large-grained and show little increase in microhardness over that for a coarse-grained sample. The hardness of the nanocrystalline samples is about 0.5 GPa, compared to 0.4 GPa for a coarse-grained sample.

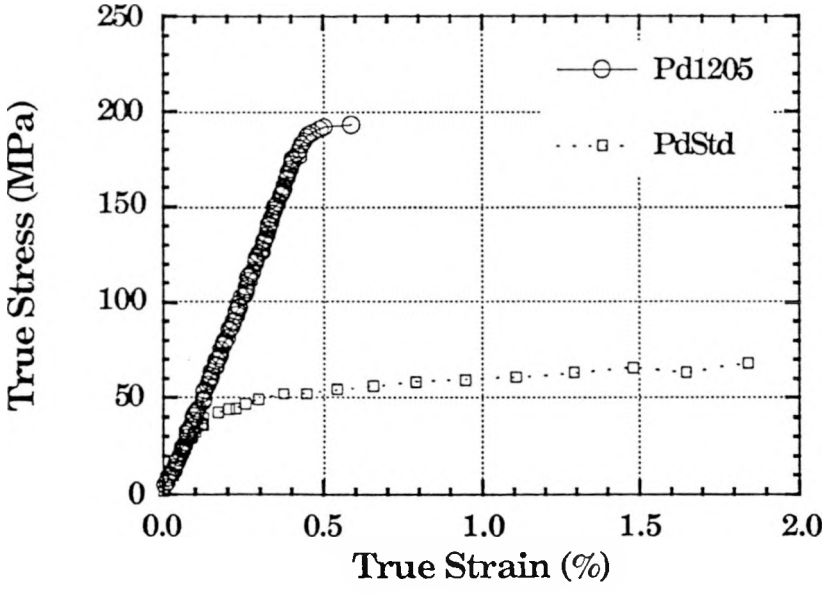

Fig. 1. Stress-strain curves for samples of nanocrystalline and annealed coarse-grained Pd.

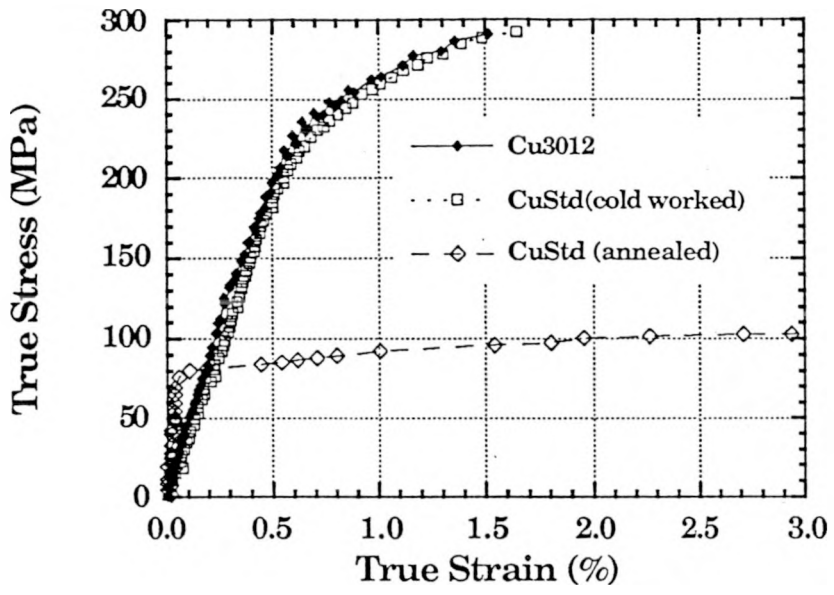

Fig. 2. *Stress-strain curves for samples of nanocrystalline, cold-worked coarse-grained, and annealed coarse-grained Cu.*

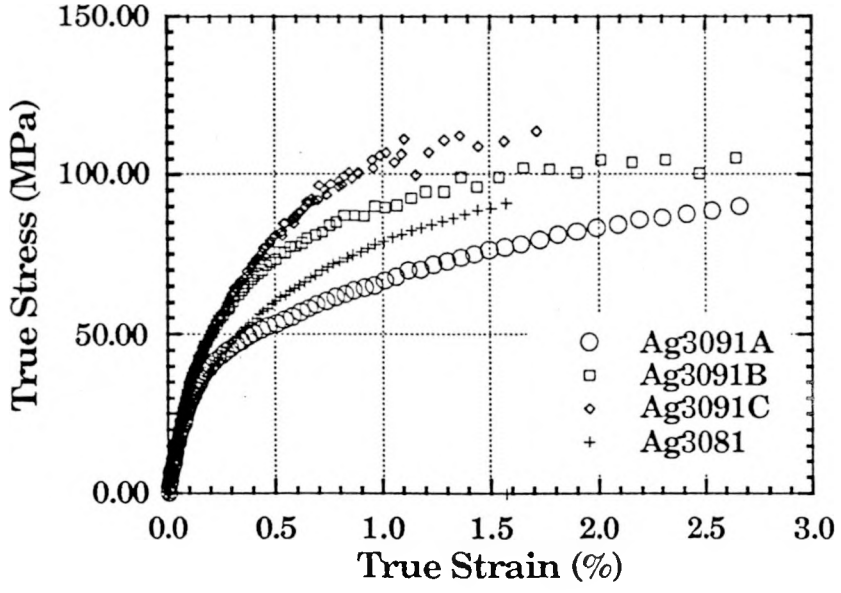

Fig. 3. *Stress-strain curves for two samples of nanocrystalline Ag, showing strain-hardening in sample Ag2091. After Ref. 8. Test order = A, B, C.*

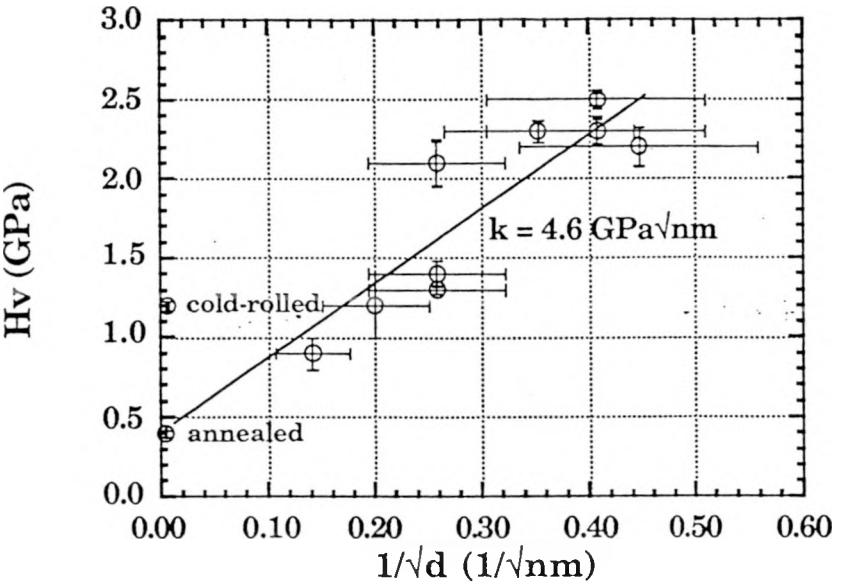

Fig. 4. Mean Vickers microhardness vs. (grain size)$^{-1/2}$ for nanocrystalline, cold-worked, and annealed Cu samples.

Hardness shows considerable spatial variation for a given Pd specimen, with the Cu and Ag samples displaying much more uniform hardness from point to point on the sample surface (4,5). This has been interpreted in conjunction with density measurements, microscopy observations and tensile test observations as indicating the presence of a distribution of flaws that are much larger than the grain size. The brittle behavior displayed by the nanocrystalline Cu and Pd in the tensile tests is partially explainable based on these indications of flaws. Any flaw that can propagate at or below the yield stress may cause catastrophic failure at low plastic strains.

Room temperature creep tests were performed on several nanocrystalline Cu and Pd samples (3,6) to determine whether the ultrafine grain size and possibly enhanced diffusivity (12) result in creep at abnormally low temperatures. These data are compiled in Table 2. 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 annealed 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.

High Resolution Electron Microscopy

Samples of consolidated and unconsolidated nanocrystalline Cu were studied by high resolution electron microscopy (HREM) to obtain information

about the detailed nanostructure resulting from the deformation that accompanied consolidation. All observations were made on the Hitachi H9000 microscope at Northwestern University, which operates at 300 kV. The consolidated samples were prepared by mechanical polishing, followed by jet polishing in a solution of 70% H_2O and 30% H_3PO_4 at approximately 5 °C, using 10 V and ≥ 100 mA. The samples were viewed with the electron beam direction nearly parallel to the axis of compression during sample consolidation. The unconsolidated samples were deposited on a carbon-formvar-coated grid after ultrasonic vibration in acetone.

Bright field and dark field micrographs of an example of unconsolidated Cu are shown in Fig. 5. The example shows the high degree of agglomeration typical of these ultrafine grain materials due to the large surface energies of the small particles. The shapes of the particles are nearly equiaxed and not faceted, although the degree of agglomeration greatly restricts observation of grain boundaries in bright field images. Twins are apparently not abundant. The dark field image shows better the shape of several grains. Contrast changes are often not symmetrical with the apparent grain edges, as would be expected if due to thickness changes only, and are likely modified by inhomogeneous strains (cf., 13) and overlap of grains.

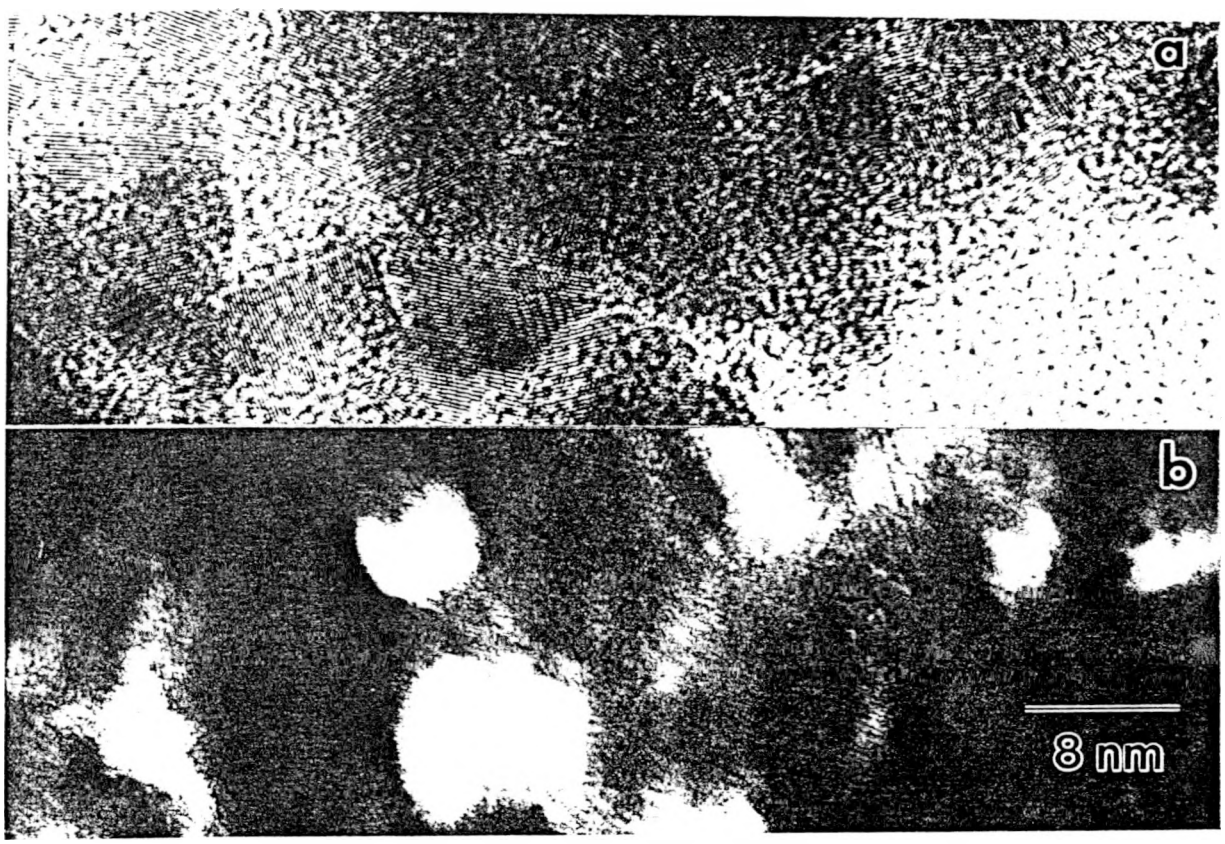

Fig. 5. Bright field (a) and dark field (b) HREM images of unconsolidated nanocrystalline Cu.

The bright field high resolution image in Fig. 6 shows features typical of the as-consolidated samples of Cu. Lattice fringe contrast is disrupted over short distances due to overlapping of crystals, grain boundaries, twin boundaries and localized strains. Foil thickness variations that could be influenced by relic fine scale porosity also contribute to contrast variations, since HREM contrast is a very sensitive function of crystal thickness. Single and multiple twin boundaries are abundant in the as-consolidated samples. Dislocations are rarely seen, but this may be due to the stringent conditions needed for their observation in HREM (14). Many of these same nanostructural features have been observed in nanocrystalline Pd produced by IGC (15). Grain sizes observed by HREM are in the range of the grain size estimates made by XRD for different diffraction conditions and by different XRD methods (10).

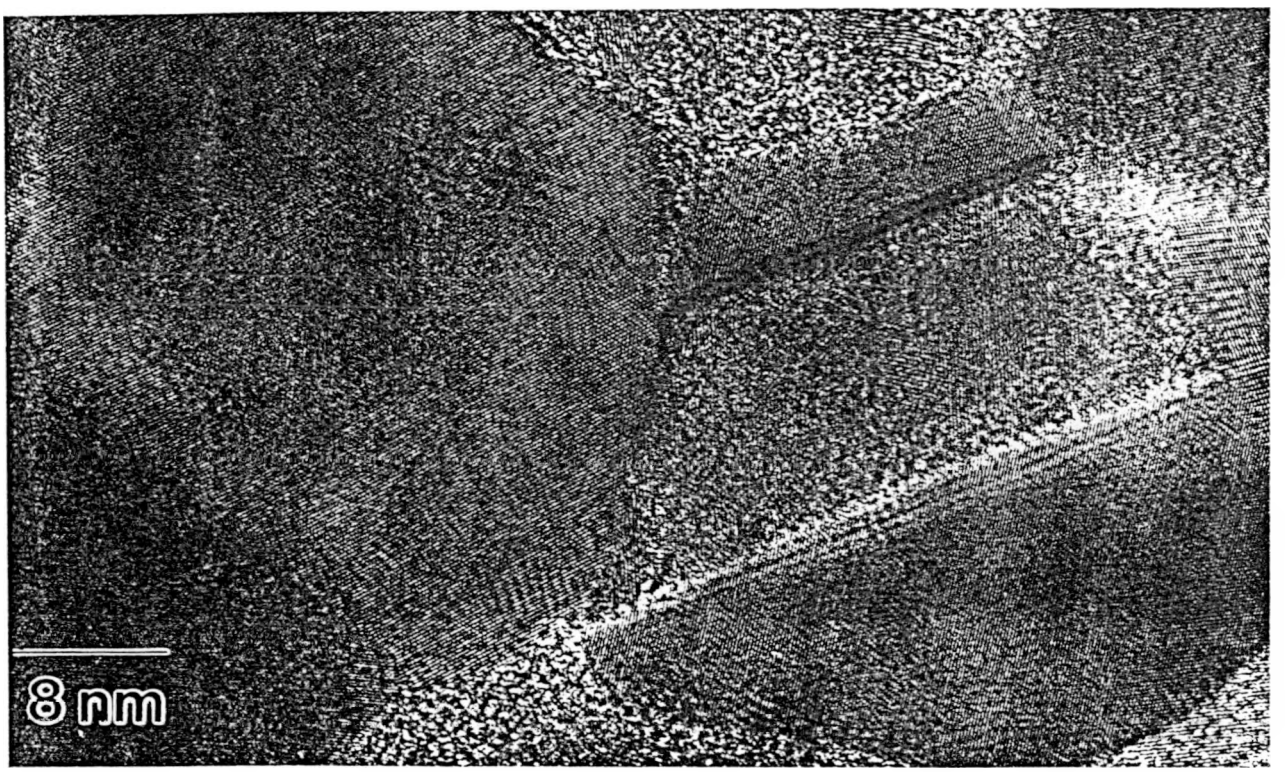

Fig. 6. *HREM image of consolidated nanocrystalline Cu. Mean grain size determined by XRD is 15 nm and mean lattice strain is* 12×10^{-3}.

Discussion and Conclusions

The data presented here characterize the mechanical behavior of a small number of nanocrystalline Cu, Pd and Ag samples with well-determined mean grain sizes, as evaluated by uniaxial tensile tests, Vickers microhardness measurements, and room temperature creep measurements. The results of these experiments are consistent and therefore offer some insight into the possible effects of ultrafine grain size on the mechanical behavior of nanocrystalline metals. Most importantly, the results demonstrate that ultrafine grain metals show a grain size dependent increase in strength into the 5-15 nm mean grain size range at room temperature. The rate of strengthening in nanocrystalline Cu, given by the slope of compressive microhardness H_v or tensile yield stress σ_y vs $1/\sqrt{d}$, is lower in the nanometer range than is seen at ordinary grain sizes. Other workers have noticed a decreasing hardening rate beginning at about 1 μm (16), or even softening (17). No evidence of diffusional creep at room temperatures, which would weaken nanocrystalline metals, could be found in nanocrystalline Cu or Pd. This is in contrast to the results of Ref. 16.

Strength increases significantly with decreasing grain size despite the presence of processing flaws that are much larger than the nanocrystalline grain size. These processing-induced features are not yet well characterized but include micrometer-scale porosity and cracks observable by optical and electron microscopy. These types of flaws could be present at nanometer scales as well. Broader grain size distributions, indicated by XRD data (9,10) and/or impurity concentrations could also influence mechanical properties strongly in ways not yet appreciated. For example, a small number of relatively large grains may take up a large proportion of strain at small total strains, relieving stress concentrations at grain boundaries of smaller grains. A sample of Cu which reached 6% true strain appears to have a relatively broad grain size distribution and contains abundant annealing twins.

The strengthening as a function of grain size observed in the present results must be interpreted cautiously, since knowledge of the mechanical properties in nanocrystalline materials is still very limited. By analogy with coarse grain materials, one can tentatively attribute much of the observed mechanical behavior to restrictions on dislocation activity (both generation and mobility) imposed by small grain size, as suggested by a simple calculation of the stress (σ_a) to activate a Frank-Reed source ($\sigma_a = 2Gb/d$; G = shear modulus, b = Burgers vector, $d \approx$ source length $\leq$ grain size). Ashby (18) recognized the significance of geometrical constraints on mechanical behavior in fine-grained polycrystalline materials. He proposed a theoretical basis for Hall-Petch behavior at small strains and small grain size that included dislocations which are geometrically necessary to accommodate deformation. Armstrong (16) has suggested that a smaller strengthening rate occurs at very small grain sizes than at large grain sizes due to the influence of small inclusions. Mathematical models based on dislocation pile-ups or stress/strain

concentrations at grain boundaries have also been developed to explain the small slopes at sub-micrometer grain sizes (19-23). Li (21) has shown that cracks can be nucleated at tilt grain boundaries. These cracks, or cracks which develop from trapped porosity can develop through Griffith crack behavior (e.g. 23) to account for the small strains prior to brittle fracture observed in the nanocrystalline samples. The current results suggest that the critical stress to initiate twinning or to propagate cracks may be reached in grain boundary-rich nanocrystalline metals at stresses where dislocation motion and generation is difficult.

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