Ultratough nanocrystalline copper with a narrow grain size distribution

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(Received 19 April 2004; accepted 14 June 2004)

We report a unique way of using mechanical milling/*in situ* consolidation at both liquid-nitrogen and room temperature to produce artifact-free nanocrystalline Cu (23 nm) with a narrow grain size distribution. This nanocrystalline Cu exhibits an extraordinarily high yield strength (770 MPa), as predicted from a Hall–Petch extrapolation, along with good ductility (comparable with ~30% uniform tensile elongation). Possible factors leading to this excellent optimization of strength and ductility are discussed. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1779342]

Significant increases in hardness and strength have been documented for nanocrystalline metals[1–3] (grain size <100 nm). The yield strength of nanocrystalline Cu, for example, increased to a range of six to eight times higher than that of coarse-grained Cu.[1,2,4–8] However, ductility of nanocrystalline metals is very low—typically less than 2% elongation for most nanocrystalline metals with grain sizes <25 nm, whereas for the same conventional grain size metals the ductility is typically large—40%–60% elongation.[1,5] In some cases, the poor ductility may be attributed to porosity within the samples due to incomplete compaction of nanoparticles.[1,5] This poor ductility limits the applications of nanocrystalline metals. We believe that eliminating the effect of artifacts plays a major role in improving the strength and ductility of nanocrystalline Cu, which will have a significant effect on the utilization of nanocrystalline metals in various applications.

Nanocrystalline (nc) Cu is synthesized in this work by a special method of combining liquid-nitrogen (LN)-temperature (cryo) and room-temperature (RT) milling. After 3 h of cryo milling, the starting Cu powder is flattened and welded together to form thin small rounded flakes about 1 mm in diameter. Further combinations of RT and cryo milling up to 10 h induced *in situ* consolidation of these small flakes into fully dense and spherical-shaped balls with sizes up to 5–8 mm diameter. Density measurements and scanning electron microscopy (SEM) observations (micrographs are not included) show that our Cu spheres exhibit full density with no pores. After 10 h of combined milling, the average grain size determined from x-ray diffraction (XRD) analysis in terms of diffraction line broadening of five Bragg reflection peaks (using the Williamson and Hall equation)[9] is about 25 nm. The lattice strain in these milled Cu spheres also determined by XRD is about 0.1%. Figure 1(a) shows the transmission electron microscopy (TEM) dark-field micrograph and electron diffraction pattern for nc Cu after 10 h of combined milling. The grain size distribution [Fig. 1(b)] for this nc Cu based on a total grain count of 270 shows an average grain size of 23 nm, which is consistent with the XRD results. Another important feature of the Cu nanostructure is that the grain size distribution is monotonic and lies within a relatively narrow range, with no grain sizes >50 nm [Fig. 1(b)].

The mechanical behavior of the milled nc Cu is evaluated using microhardness measurements and the miniaturized disk bend test (MDBT). The MDBT was conducted at RT with a displacement rate of 8.5×10^{-3} mm/s, which corresponds to a strain rate of $2.8\times10^{-4}\,\mathrm{s}^{-1}$. Samples for MDBT were mechanically polished to mirrorlike images in order to eliminate the effect of surface flaws with final thicknesses of 326–330 μm. The standard deviation of thickness values, measured at different locations on the sample surface was typically 2–4 μm. The mechanical behavior of nc Cu is compared with that of microcrystalline (μc) pure Cu (~50 μm grain size) sample and a pure Cu block rolled at LN temperature (−150 °C) to a high plastic deformation (93%) followed by low-temperature (200 °C) annealing for 3 min. In the rest of our letter, we refer to the latter sample as LNRA. This LNRA Cu sample exhibits the best combination of strength and ductility for Cu reported so far.[10] Figure 2 shows the force versus normalized displacement curves of the selected specimens, which are averaged from three replicates. The scatter of the three replicates was negligible. Finite element analysis and previous experimental results show that a deviation of the force–displacement curve from linearity corresponds to the yield stress of the tested material.[11,12] Hence, yield stresses are calculated from the following equation:[12]

$$\sigma_y = \frac{3P}{2\pi t^2}\left\{(1-\nu)\ln\frac{a}{b} + \frac{1-\nu}{2}\left[1-\frac{b^2}{a^2}\right]\left(\frac{a^2}{R^2}\right)\right\}, \qquad (1)$$

where σ_y is the stress, P is the load in the units of Newton, t is the specimen thickness, v is Poisson's ratio of Cu, which is taken to be 0.35,[13] a is the radius of the support ring, b is the radius of the load ring, and R is the radius of the specimen. Normalized displacement (η) is expressed by w/t, where w is the displacement of the specimen up to failure. Although, normalized displacement is not a strain, it does give an indication of the specimen ductility given that all specimens have similar thicknesses (t).[14]

A comparison of the mechanical behavior during MDBT (Fig. 2) reveals that μc Cu (Curve A) exhibits a yield stress (σ_y) value of 56 MPa [calculated from Eq. (1)], which is a typical value for annealed conventional grain size Cu. The LNRA Cu specimen (Curve B) shows a dramatic increase in σ_y to about 327 MPa. A similar σ_y (330 MPa) for a Cu sample processed under the same conditions was first reported by Wang *et al.*[10] during tensile testing. The matching

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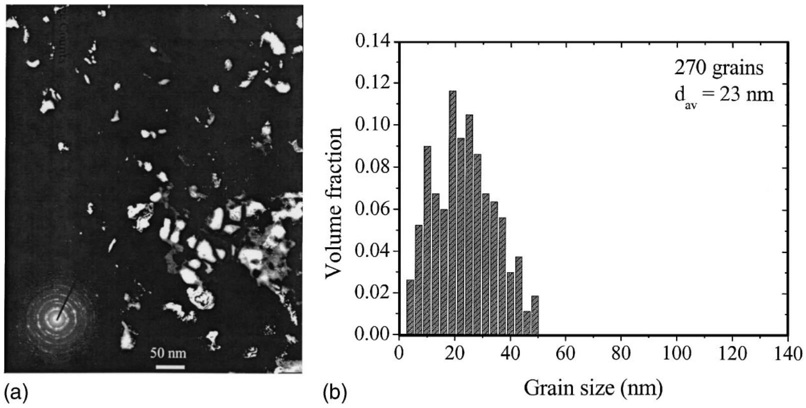

FIG. 1. TEM results showing: (a) a dark-field image of nc Cu after 10 h of combined cryo and RT milling; the lower left inset shows the electron diffraction pattern, and (b) grain size distribution of nc Cu based on a total grain count of 270.

of the σ_y values, obtained from MDBT and tensile test,[10] suggests that the MDBT yield strength is comparable to the tensile yield strength. As can be seen from Fig. 2 Curve C, a remarkable increase in the σ_y to 770 MPa was found for the milled nc Cu concurrent with ductile behavior. This extraordinarily high value of σ_y is about fourteen times higher than that of μc Cu and more than twice that obtained from the LNRA Cu sample (Fig. 2). In addition, the hardness (H_v) value of milled nc Cu is measured to be 2.3 GPa, and hence obeys the Tabor relation, $H_v = 3\sigma_y$. The high value of σ_y (or H_v) appears to be due to the small grain size (23 nm). This high value of σ_y is consistent with that measured by tensile testing (760 MPa) for a thin (11 μm) nc ($\sim$30 nm) Cu layer produced using ultrasonic high-energy shot peening.[15] Along with the high σ_y of this Cu layer, it was reported that fracture occurs very soon after yielding, accompanied with very low ductility ($\sim$2%). The nc Cu layer presumably survives to a σ_y of 760 MPa because of the absence of internal porosity; however, its ductility is still poor.[15]

The shape of the MDBT curves in Fig. 2 is typical of ductile materials.[16,17] All curves start with initial linear region after which yielding occurs. After initial yielding, plastic deformation propagates through the specimen thickness and radially from the area of contact between the punch and specimen. This is followed by a membrane-stretching regime and then maximum load is approached and fracture begins. Figure 3 shows the field emission SEM images of surface morphology of LNRA and nc Cu specimens after MDBT. The two specimens have a hat-shaped disk morphology, which is an indication of significant plastic deformation.[17] As can be seen from Figs. 3(a) and 3(b), the plastic deformation and the overall ductility up to failure of nc Cu are comparable to that for the LNRA Cu sample, which showed $\sim$30% uniform tensile elongation.[10] Figure 3(c) shows a higher magnification of the punched out hat without any indication of surface cracking. The fracture surface of nc Cu [Fig. 3(c) upper right inset] shows a dimpled rupture that extends thoroughly over the sample cross section with dimple size ranges from 100–400 nm. Therefore, our nc Cu exhibits good ductility along with an extraordinarily high yield strength (770 MPa, see Fig. 2).

All the results reported in literature showed brittle failures of nc Cu.[6,8,18–20] Explanations of this brittle behavior were attributed to artifacts (porosity and contamination) from processing, force instability in tension, and crack nucleation or propagation instability.[21,22] The only exceptions reported

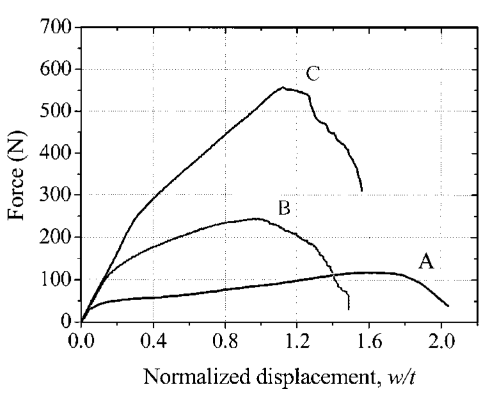

FIG. 2. Force vs normalized displacement for tested samples. Curve A, annealed, coarse-grained Cu; Curve B, LN-temperature rolled Cu to 93% plastic deformation followed by annealing at 200 °C for 3 min; Curve C, nc Cu after 10 h of combined cryo and RT milling.

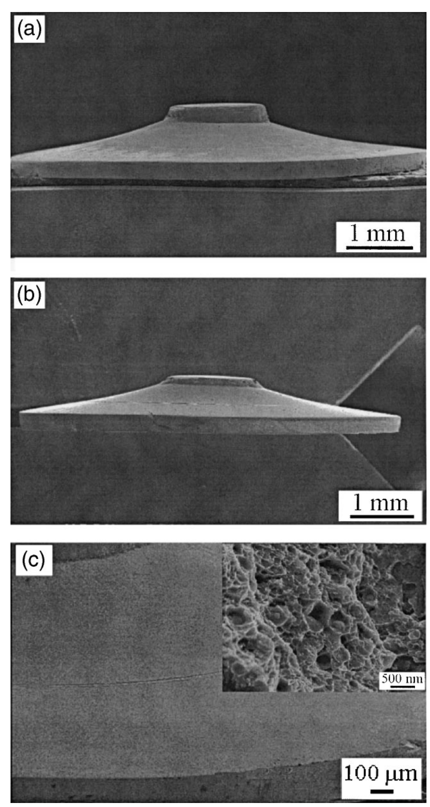

FIG. 3. Field emission scanning electron micrographs of selected Cu samples after MDBT. (a) LNRA Cu sample, (b) nc Cu sample, and (c) a higher magnification of the nc Cu sample near the fracture surface; the upper right inset shows the fracture surface of nc Cu sample.

of an improved tensile ductility were for Cu structures different from the typical nc structures of metals. The high ($\sim$30%) tensile ductility of an electrodeposited Cu sample had a structure that consisted of nanoscale subgrains with very low-angle boundaries, which results in a low σ_y of $\leqslant$100 MPa.[23] The impressive uniform tensile elongation (30%) obtained after thermomechanical processing of Cu was attributed to a bimodal structure consisting of micrometer-sized grains (1–3 μm) embedded in a nano/ultrafine-grained matrix.[10] The nanoscale/ultrafine grains in the bimodal structure provide the strengthening (σ_y =330 MPa) while the micron size grains allowed for significant strain hardening which prevents localized deformation and premature fracture.[10] However, our results indicate that nc Cu with a narrower grain size distribution (Fig. 1) can exhibit a substantial improvement in ductility along with high strength.

The strength of our nc Cu with a 23 nm average grain size corresponds very closely with values reported in literature for the same grain size range.[15,24] The unique feature of our work is the high strength accompanied by good ductility. In those few examples of nc Cu with similar small grain sizes to ours, the ductility was very low, of the order of $\sim$2%.[6,8,18–20] The three main reasons for limitations on ductility can be considered: (1) Artifacts—our nc Cu has no artifacts. Density measurements and SEM observations show that no porosity was introduced during *in situ* consolidation of nc Cu. Also, the contamination during milling has no effect on the ductility because the oxygen content only increased from 0.10 at. % in the starting Cu powder to 0.29 at. % in the final nc Cu. The measured iron contamination was negligible. Therefore, the artifacts effect is eliminated. (2) Mechanical instability—from the MDBT results (Fig. 2), it seems that we have strain hardening that prevents plastic instability during the membrane-stretching regime. This also implies that dislocations are responsible for the plastic deformation rather than other mechanisms (e.g., grain-boundary sliding). The ductile fracture surface of the nc Cu [Fig. 3(c)] is also an indication of dislocation-controlled plasticity. *In situ* TEM observations of nc Cu and Ni tensile specimens (30–40 nm) have revealed dislocation movement during the deformation process.[25] (3) Crack nucleation and propagation—the nanoscale grain size can inhibit these processes, as would be suggested from the effect of grain size on ductility in conventional grain size materials. Twinning is also an alternative mode of plastic deformation and it has been observed in nanostructured face-centered-cubic metals with relatively high stacking fault energies when deformed at cryogenic temperatures.[10,25,26]

In summary, our special way of producing artifact-free nc Cu with a narrow grain size distribution allows for improved mechanical properties and gives a remarkable high yield strength (770 MPa) along with good ductility (comparable to $\sim$30% uniform tensile elongation). A combination of high strength and good ductility has also been reported recently for artifact-free nc electrodeposited Co (Ref. 27) and Ni–Fe alloys (Ref. 28) with small nc grain sizes (10–20 nm). These observations are consistent with our results on nc Cu. We expect that these optimizations of strength and ductility will have implications in the development of tough nc Cu in several applications and will provide important input into understanding the deformation behavior of nanostructured materials.

Financial support by the Department of Energy under Grant No. (DE-FG02-02ER46003) is gratefully acknowledged.

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