Simultaneously Increasing the Ductility and Strength of Ultra-Fine-Grained Pure Copper**

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Bulk ultra-fine-grained (UFG) materials produced by severe plastic deformation (SPD) usually have high strength but relatively low ductility at ambient temperatures. This low ductility is attributed to insufficient strain hardening due to an inability to accumulate dislocations. For a single-phase UFG material where dislocation slip is the primary deformation mechanism, a long-standing fundamental question concerns the feasibility of developing microstructures that offer high ductility without sacrificing strength. The answer appears to be positive because there are some isolated examples where excellent mechanical behavior has been observed. Nevertheless, the structural features contributing to high strength and good ductility remain undefined, and this lack of understanding has hindered the search for effective procedures to simultaneously improve the strength and ductility of UFG materials. Here, we report a new process in which high ductility is achieved without sacrificing strength by plastically deforming UFG Cu in liquid nitrogen. The enhanced ductility is attributed primarily to the presence of a high density of pre-existing deformation twins (PDTs) and also possibly to a large fraction of high-angle grain boundaries (HAGBs) formed during cryogenic processing. We conclude that this procedure provides a new strategy for increasing the ductility of UFG materials without any concurrent loss in strength.

Strength and ductility are often mutually exclusive, i.e., materials may be strong or ductile but are rarely both. This also applies to bulk UFG materials. The low ductility of UFG materials has invariably limited their practical application and, accordingly, much attention has been paid to the development of strategies for improving this poor ductility. In practice, however, a bimodal grain size distribution has been hindered because the evidence suggests that PDTs occur only in electrodeposited thin films of nanostructured Cu, and in nanocrystalline Cu by inert-gas condensation (IGC) followed by compaction. However, the ductility of IGC-prepared nanocrystalline Cu is very low.

The objectives of this study were twofold: First, to develop a procedure for increasing the ductility of large bulk UFG Cu without incurring any significant loss in strength. Second, to evaluate the mechanism contributing to high ductility in UFG Cu. A pure Cu (99.99 %) bar was initially processed by equal-channel angular pressing (ECAP) to produce a UFG structure (hereafter designated the UFGECAP sample), then cryodrawn (D) to a reduction in area of ca. 95 %, followed by cryorolling (R) with a reduction in thickness of ca. 96 % (hereafter designated the UFGECAP+D+R sample).

Figure 1a shows that the UFGECAP+D+R sample has superior mechanical properties compared to the UFGECAP sample. The UFGECAP Cu sample has a 0.2 % yield strength of ca. 410 MPa (0.002 %), which is significantly higher than the value of ca. 40 MPa in coarse-grained (CG) Cu. In addition, necking occurs rapidly after the stress reaches a maximum value, yielding a uniform elongation of only ca. 1.3 % and an elongation to failure of only ca. 5.9 % in the UFGECAP sample. By contrast, the yield strength is increased to ca. 500 MPa in the UFGECAP+D+R sample, and, more importantly, this sample undergoes strain hardening, giving a uniform elongation of

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ca. 3.5% and a subsequent elongation to failure of ca. 11.8%. These uniform elongations were determined using the Considère criterion,

\[ \frac{\partial r}{\partial e} \leq r \]  

where \( r \) is true stress and \( e \) is true strain. The limit of uniform elongation is marked on every curve. Calculations showed that the Hart criterion,

which includes a consideration of the strain-rate sensitivity, yields a slightly higher uniform elongation value of ca. 3.7% for the UFGECAP+D+R sample, but little difference for the UFGECAP sample. The strain-rate sensitivity (\( m \)) of the UFGECAP+D+R sample was measured as \( m \approx 0.018 \) at a true strain of 2%. It is important to note the large elongation occurring after the onset of necking in the UFGECAP+D+R sample, which is due to the presence of continuous strain hardening as shown in the true stress–strain curve.

Figure 1b demonstrates that the UFGECAP+D+R sample displays positive strain hardening to significant strains whereas, by contrast, the stress in the UFGECAP sample decreases after a small plastic strain. As shown later, this stress decrease was partially caused by strain softening. A similar strain softening was observed in many other SPD processed UFG metals and alloys.[27,28] Also, the strain-rate sensitivity of the UFGECAP+D+R sample is close to the values reported for UFG Cu processed for 8–12 passes in ECAP.[29] Therefore, the higher ductility of the UFGECAP+D+R sample is caused primarily by its higher strain-hardening rate. It is instructive to note that these experiments used tensile samples with a thickness of 0.1 mm, and work currently in progress suggests that thicker samples exhibit even higher ductilities due to a size effect (see Supporting Information, Fig. S1).

The mechanical properties of bulk solids are controlled by their microstructure. Investigations by transmission electron microscopy (TEM) indicate that the UFGECAP sample contains a large fraction of low-angle grain boundaries (LAGBs), and the subsequent cryodeformation forms numerous HAGBs and deformation twins in the UFGECAP+D+R sample. Figure 2a and b shows typical bright-field TEM images of the UFGECAP and UFGECAP+D+R samples, respectively. In Figure 2a, the slight contrast difference is caused by small orientation variations among the grains/subgrains. Careful examination of Figure 2a shows that most of the GBs are wavy, diffuse, and ill-defined in the UFGECAP sample, and these boundaries are primarily in a non-equilibrium state with extrinsic (non-geometrically necessary) dislocations or other interface defects.[30] The wavy and diffuse GB features are more clearly visible in high-resolution TEM images (Fig. S2). By comparison, the GBs in the UFGECAP+D+R sample are sharp, clear, and relatively straight (Fig. 2b), and the contrasts between neighboring grains are larger, thereby suggesting higher misorientation angles between the adjacent grains. By tilting
some grains to a <110> zone axis and checking the angle differences between neighboring grains/subgrains, it was found that UFGECAP+D+R Cu contains a higher fraction of HAGBs than UFG ECAP Cu. The grain size distributions measured from the TEM images are shown in Figure 2c and d. Both of these distributions are similar, but the average grain sizes are ca. 230 nm for UFGECAP+D+R Cu and ca. 290 nm for UFGECAP Cu.

Statistical observations by TEM show that many grains in the UFGECAP+D+R sample contain high densities of deformation twins, as typically shown in Figure 3a. These deformation twins have thicknesses ranging from several nanometers to ca. 85 nm and lengths in the 50–500 nm range (Fig. S3). Electron diffraction patterns of the twinned areas (inset in Fig. 3a) show that some diffraction spots are arc-shaped, indicating that the misorientations across the twin boundaries deviate slightly from 60°. Moreover, some twin boundaries are not straight (as denoted by the arrows in Fig. 3a), and this may be caused by the interactions between the twins and the dislocations during the cryodeformation. High-resolution TEM revealed sessile Frank partial dislocations (Burger’s vector, $h = 1/3[111]$, as shown in the inset of Fig. 3b by T) and glissile Shockley partials ($b = 1/6[211]$) on the twin boundaries, which may be formed by the dissociation of a full dislocation at the twin boundary through the following reaction: $1/2[101] \rightarrow 1/6[211] + 1/3[111]$. By contrast, TEM revealed no evidence for any twin in the UFGECAP sample.

Quantitative electron backscatter diffraction (EBSD) analysis was used to obtain information on the distributions of the GB misorientations (Fig. 4). It is assumed that the peak occurring near 60° for UFGECAP+D+R Cu is probably formed during the cryoprocessing, since it is known that low-temperature processing may introduce a large number of twin boundaries with misorientation angles of 60°. In addition, the UFGECAP+D+R sample has a high fraction (ca. 58%) of HAGBs with misorientations > 15°, whereas in the UFGECAP sample the fraction of HAGBs is only ca. 32%. More specifically, the fraction of boundaries with misorientations in the 50°–62.8° range is ca. 23% (which includes both deformation twins and general HAGBs), and the fraction of general HAGBs with misorientations of 15°–50° is ca. 35%. By contrast, for the UFGECAP sample, the fractions of HAGBs in the above two ranges are ca. 9% and ca. 24%, respectively. These results indicate that the UFGECAP+D+R sample contains larger fractions of both twin boundaries as well as general HAGBs than the UFGECAP sample, in agreement with the TEM observations. Subsequent cryorolling and the accompanying grain reorientation from the cryoprocessing in the UFGECAP+D+R sample produces the observed deviation from the initial twin misorientation of 60° shown in Figure 4. Because the fundamental zone is very small for misorientations approaching the maximal value for cubic symmetry of 62.8°, the misorientation distribution becomes predominantly skewed towards lower values, as observed experimentally.

To evaluate the mechanism controlling the strain-hardening rate, the UFGECAP+D+R Cu and UFGECAP Cu samples were analyzed by X-ray diffraction (XRD) before and after the ten-


Figure S3. Moreover, XRD patterns show the UFGECAP has qualitative agreement with the TEM observations recorded in strength and ductility by PDTs,\[^{37}\] and forming rate as the PGTs. However, it is probable that the PDTs should play a similar role in improving the strain-hardening rate, but most likely to a lesser extent. It is known that pure Ni subjected to cold-roll-
uid nitrogen to cool the specimen. The EBSD samples were first polished using a diamond lapping film (particle diameter 1 μm) and then electropolished in a solution of 66% H3PO4 and 34% H2O at 2 V. EBSD scans were performed using a TSL OIM system on a Philips XL30 FEG TEM apparatus with step sizes of 100 or 130 nm.

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