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Ultrahigh strength and high ductility of bulk nanocrystalline copper

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We have synthesized artifact-free bulk nanocrystalline copper samples with a narrow grain size distribution (mean grain size of 23 nm) that exhibited tensile yield strength about 11 times higher than that of conventional coarse-grained copper, while retaining a 14% uniform tensile elongation. *In situ* dynamic straining transmission electron microscope observations of the nanocrystalline copper are also reported, which showed individual dislocation motion and dislocation pile-ups. This suggests a dislocation-controlled deformation mechanism that allows for the high strain hardening observed. Trapped dislocations are observed in the individual nanograins. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2034122]

Nanocrystalline (nc) metals—with grain sizes of less than 100 nm—exhibit extremely high strength and hardness. However, it has been generally observed that the ductilities of nanostructured metals are disappointingly low—typically less than 2% elongation to failure for most metals with grain size <25 nm,[1] where for the same coarse-grained metals the ductilities are usually large, up to 40%–70% elongation. The factors that can limit the ductility of nanostructured materials include artifacts from processing, the mechanical instability in materials with little or no strain hardening capacity, and low toughness and resistance to crack initiation and propagation.[2,3] There is thus an express need to develop processes for producing high strength nano materials with good ductility.

Due to the lack of strain hardening and poor ductility of nc materials, it was suggested that the normal dislocation activity (the dominant plastic deformation mode of ductile coarse-grained materials) is suppressed in nc grains.[1–9] The high strength of nc materials may give rise to other plastic deformation mechanisms that are not seen in coarse-grained materials. Grain boundary sliding and/or grain rotation in small grain size (⩽10 nm) materials have been proposed by molecular dynamic simulations[5,8,9] and reported recently using *in situ* transmission electron microscopy (TEM) deformation.[10] Deformation twinning has also been observed in nc materials.[11,12] Despite the observations of these mechanisms, they did not contribute much to enhance the ductility of nc materials. In order to improve the ductility of nc materials, while retaining the extremely high strength, dislocation-mediated deformation is needed to allow the material to strain harden and stabilize the uniform tensile deformation. However, supporting experimental evidence of this concept has not been reported up to now.

Bulk nc Cu spheres (up to 8 mm in diameter) are synthesized in this work using a combination of liquid nitrogen temperature and room temperature milling. Details of the synthesis process are listed elsewhere.[13] Figure 1(a) is a typical bright-field TEM (BFTEM) image of the *in situ* consolidated nc Cu. The TEM observations in Fig. 1(a) indicate that the consolidated Cu consists of equiaxed nano grains oriented randomly, as can be seen from the corresponding selected area diffraction pattern (SADP) included in the upper left inset in Fig. 1(a). Statistical analysis of several dark field images reveals a monotonic lognormal grain size distribution with an average grain size of 23 nm [Fig. 1(b)]. Density measurements, scanning electron microscopy of the polished

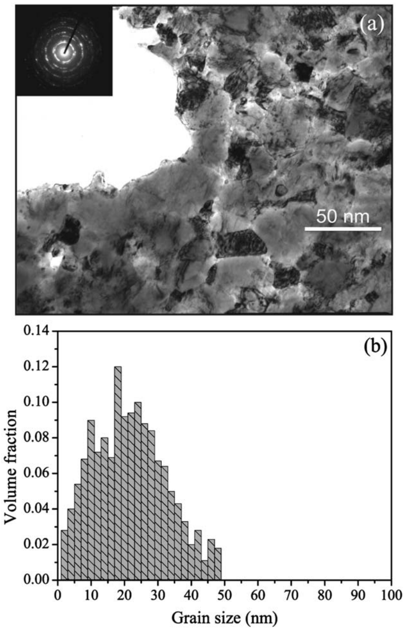

FIG. 1. TEM observations of the typical microstructure in the *in situ* consolidated nanocrystalline Cu. The bright-field TEM micrograph (a) and the SADP [the upper left inset in (a)] show roughly equiaxed grains with random orientations. The statistical distribution of grain size (b) was obtained from multiple dark-field TEM images of the same sample.

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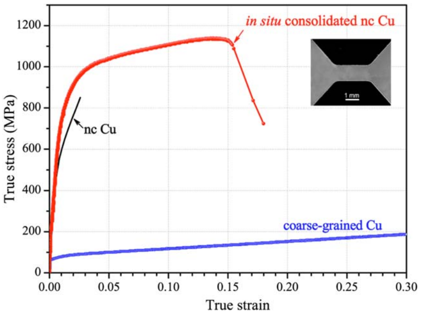

FIG. 2. A typical tensile stress-strain curve for the bulk *in situ* consolidated nanocrystalline Cu sample in comparison with that of a coarse-grained polycrystalline Cu sample (an average grain size larger than 80 μm) and a nanocrystalline Cu sample prepared by an inert-gas condensation and compaction technique (Ref. 17) (with a mean grain size of 26 nm).

and fracture sample surfaces,[13] and TEM analysis show that no porosity or other processing defects are introduced during the *in situ* consolidation of nc Cu.

The formation mechanism of this artifact-free nc Cu is not fully understood yet. However, our experimental observations indicate that milling at liquid nitrogen temperature allows for a higher dislocation density than can be obtained during milling at room temperature and also suppresses dynamic recovery and recrystallization. Accordingly, nanoscale grain sizes can be reached in a relatively shorter time, which minimizes contamination during milling. The average grain size determined using x-ray line broadening from five Bragg reflection peaks (Williamson and Hall equation[14]) after cryo milling for 3 h is about 20 nm with lattice strain of 1%. This relatively high lattice strain is an indication of the high dislocation density at this stage. Further milling at room temperature allows *in situ* consolidation of the Cu sample into fully dense spheres. X-ray diffraction analysis of the consolidated Cu spheres shows a drop in the lattice strain to 0.1%, which is one order of magnitude lower than that in the cryo milled sample. The relatively high temperature along with the existence of nano grains during room temperature milling can enhance the self-diffusivity of Cu, which in turn would facilitate closing the pores and maintaining good bonding by cold welding.

A comparison of the mechanical behavior during tensile testing reveals that nc Cu exhibits extremely high yield and ultimate tensile strengths (Fig. 2). The 0.2% offset yield strength (σ_y) and the ultimate tensile strength (σ_u) were 791 ± 12 MPa and 1120 ± 29 MPa, respectively. This σ_y value is at least one order of magnitude higher than that of coarse-grained (grain size >80 μm) pure Cu samples and σ_u is about five times higher (Fig. 2). The value of σ_y is higher than those reported previously for nc Cu in tensile tests.[15–17] The hardness (H_v) value of milled nc Cu is measured to be 2.3 GPa, and hence obeys the Tabor relation, $H_v \approx 3\sigma_y$. Therefore, the high value of σ_y (or H_v) appears to be due to the small grain size (23 nm).[13,17] In addition to these extraordinarily high strengths, the nc Cu sample shows a significant tensile ductility, with 14% uniform elongation and 15.5% elongation-to-failure (Fig. 2). This ductility is much larger than that reported for previous nc Cu samples either with conventional microstructure (i.e., nano grains with high angle grain boundaries), which show ductility as low as ~2% (Refs. 15 and 17–20) or nanotwinned Cu films [i.e., 1-μm sized grains containing a high density of growth twins with nanoscale lamellar spacings and coherent twin boundaries, which showed a uniform elongation of about 10% (Ref. 21)]. Another important feature of Fig. 2 is the large strain hardening that appears during plastic deformation. This indicates a high lattice dislocation accumulation during the plastic straining until failure. In previous studies, strain hardening was very limited in nc materials.[22,23] This lack of strain hardening was attributed to the absence of dislocation activity during deformation. Theoretical predictions suggest that it is impossible for dislocations to pile-up in $\leqslant$20-nm grains because of image forces and interactions within grain boundaries.[24]

To understand the origin of the ultrahigh strength, improved ductility, and the deformation mechanism, the nc Cu samples were deformed by *in situ* TEM tensile straining. The subsize, dog-bone-shaped tensile specimens were incrementally strained in discrete steps until a crack is formed. The crack advances perpendicular to the loading direction and the region ahead of the crack-tip was monitored. Upon straining, bright-field TEM observations showed rapid changes in contrast that take place continuously in almost all the grains. Similar observations have been identified previously as evidence of dislocation activity.[25–27] Figure 3 shows BFTEM micrographs of a single nano grain (~23 nm width) that was incrementally strained at the crack tip (the loading and crack growth directions are indicated by black arrows). At a given strain, the nano grain appears to have a significant number of dislocations [Fig. 3(a)]. With increasing the strain [Fig. 3(b)], more dislocations are generated from the grain boundary, glide through the grain, and pile-up all the way to the center of the grain (white arrows). Further straining shows also the dislocation pile-up at the grain boundary [Fig. 3(c)]. Fewer dislocations are seen in Fig. 3(c) than that in Fig. 3(b), which could be attributed to contrast variations during straining and/or annihilation of some dislocations. The dislocation pile-up exists in the grain interior even after the nano grain failed upon further straining [Fig. 3(d)]. Yamakov *et al.*[28] suggested that the trapped dislocations may only exist inside a nano grain under very high external or internal stress and that the removal of the stress will lead to reversible reabsorption of the dislocations at the grain boundary source. Our experimental results counter this assumption and show the existence of dislocation pile-up and glide activity during straining of nano grains and also after releasing of the stress [Figs. 3(a)–3(d)]. These findings are consistent with dislocation-controlled work hardening and stabilization of the uniform tensile elongation to large plastic strains (Fig. 2). Several simulation studies have shown that grain boundaries act as dislocation sources in nc materials.[5,29,30] Figure 4 shows the BFTEM image of another nano grain (~8-nm wide and 15-nm long) away from the crack tip. This grain also contains trapped dislocations (white arrows). This indicates that even very small nano grains can deform by dislocation motion and that effect is not confined to the crack tip region. Two recent studies have detected the presence of trapped dislocations in nc nickel while under stress,[31,32] although this was for larger grains (20 and 26 nm).

Artifact free bulk nc Cu can be synthesized by an *in situ* milling technique. This allows the intrinsic deformation behavior to be determined without failures induced by processing defects. Very high yield and ultimate tensile strengths can be achieved combined with much larger ductility than has previously been reported for elemental nc materials with

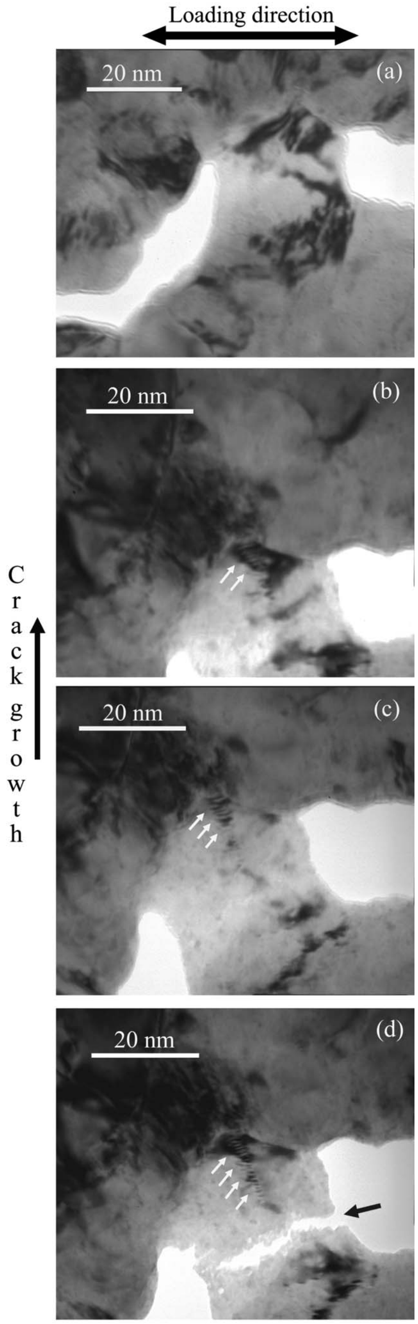

FIG. 3. BFTEM micrographs show the dislocation activity of a nanocrystalline Cu grain during *in situ* TEM deformation. The loading and crack growth directions are shown at the upper and left sides of the figure, respectively. (a) The nano grain at certain straining, which shows dislocations inside the nano grain. (b) Dislocation generation and pile-up on the grain boundary upon further straining (white arrows). (c) More straining of the nano grain showing also the dislocations pile-up. (d) Further straining initiates a crack in the nano grain (black arrow), while the piled-up dislocations still exist.

grain size on the order of 20 nm. TEM reveals dislocation plasticity that might be responsible for producing the strain hardening effect observed. These results are not necessarily limited to copper; other bulk nc metals and alloys can be produced free of artifacts and should exhibit such behavior. Current research in our laboratory is being extended to these materials.

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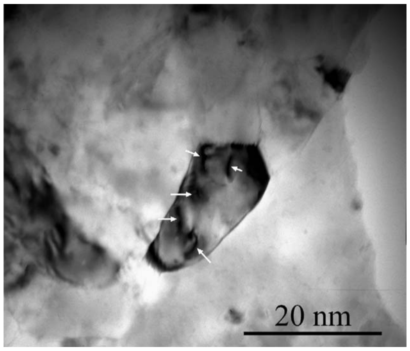

FIG. 4. A typical BFTEM micrograph of trapped dislocations in a Cu nanograin formed during *in situ* TEM deformation.

[1] C. C. Koch, D. G. Morris, K. Lu, and A. Inoue, MRS Bull. **24**, 54 (1999).
[2] J. R. Weertman, D. Farkas, K. Hemker, H. Kung, M. Mayo, R. Mitra, and H. Swygenhoven, MRS Bull. **24**, 44 (1999).
[3] C. C. Koch, J. Metastable and Nano. Mater. **18**, 9 (2003).
[4] H. Van Swygenhoven, Science **296**, 66 (2002).
[5] J. Schiotz, F. D. DiTolla, and K. W. Jacobson, Nature (London) **391**, 561 (1998).
[6] S. Yip, Nature (London) **391**, 532 (1998).
[7] J. R. Weertman, in *Nanostructured Materials: Processing, Properties, and Applications*, edited by C. C. Koch (William Andrews Publishing, Norwich, New York, 2002), pp. 397–421.
[8] J. Schiotz and K. W. Jacobson, Science **301**, 1357 (2003).
[9] V. Yamakov, D. Wolf, S. R. Phillpot, A. K. Mukherjee, and H. Gleiter, Nature Meter. **3**, 43 (2004).
[10] Z. Shan, E. A. Stach, J. M. K. Wiezorek, J. A. Knapp, D. M. Follstaedt, and S. X. Mao, Science **305**, 654 (2004).
[11] J. Y. Huang, Y. K. Wu, and H. Q. Ye, Acta Mater. **44**, 1211 (1996).
[12] M. Chen, E. Ma, K. J. Hemker, H. Sheng, Y. Wang, and X. Cheng, Science **300**, 1275 (2003).
[13] K. M. Youssef, R. O. Scattergood, K. L. Murty, and C. C. Koch, Appl. Phys. Lett. **85**, 929 (2004).
[14] G. K. Williamson and W. H. Hall, Acta Mater. **1**, 22 (1953).
[15] P. G. Sanders, J. A. Eastman, and J. R. Weertman, Acta Mater. **45**, 4019 (1997).
[16] Y. Wang, M. Chen, F. Zhou, and E. Ma, Nature (London) **419**, 912 (2002).
[17] M. Legros, B. R. Elliott, M. N. Rittner, J. R. Weertman, and K. J. Hemker, Philos. Mag. A **80**, 1017 (2000).
[18] B. Günther, A. Baalmann, and H. Weiss, Mater. Res. Soc. Symp. Proc. **195**, 611 (1990).
[19] G. W. Nieman, J. R. Weertman, and R. W. Siegel, Nanostruct. Mater. **1**, 185 (1992).
[20] P. G. Sanders, C. J. Youngdahl, and J. R. Weertman, Mater. Sci. Eng., A **234–236**, 77 (1997).
[21] L. Lu, Y. Shen, X. Chen, L. Qian, and K. Lu, Science **304**, 422 (2004).
[22] D. Jia, Y. M. Wang, K. T. Ramesh, E. Ma, Y. T. Zhu, and R. Z. Valiev, Appl. Phys. Lett. **79**, 611 (2001).
[23] Y. M. Wang, E. Ma, and M. W. Chen, Appl. Phys. Lett. **80**, 2395 (2002).
[24] N. Wang, Z. Wang, K. T. Aust, and U. Erb, Mater. Sci. Eng., A **237**, 150 (1997).
[25] C. J. Youngdahl, J. R. Weertman, R. C. Hugo, and H. H. Kung, Scr. Mater. **44**, 1475 (2001).
[26] K. S. Kumar, S. Suresh, M. F. Chilsholm, J. A. Horton, and P. Wang, Acta Mater. **51**, 387 (2003).
[27] R. C. Hugo, H. Kung, J. R. Weertman, R. Mitra, J. A. Knapp, and D. M. Follstaedt, Acta Mater. **51**, 1937 (2003).
[28] V. Yamakov, D. Wolf, M. Salazar, S. R. Phillpot, and H. Gleiter, Acta Mater. **49**, 2713 (2001).
[29] H. Van Swygenhoven, P. M. Derlet, and A. Hasnaoui, Phys. Rev. B **66**, 024101 (2002).
[30] V. Yamakov, D. Wolf, S. R. Phillpot, A. K. Mukherjee, and H. Gleiter, Nat. Mater. **1**, 45 (2002).
[31] R. Mitra, W.-A. Chiou, and J. R. Weertman, J. Mater. Res. **19**, 1029 (2004).
[32] Z. Budrovic, H. Van Swygenhoven, P. M. Derlet, S. V. Petegem, and B. Schmitt, Science **304**, 273 (2004).