Work hardening of ultrafine-grained copper with nanoscale twins

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Work hardening, relevant to the processing and use of materials, is one of the most important factors in the evaluation of plastic deformation. The deformability, ductility and toughness of materials are intimately linked to the work hardening capacity [1].

Polycrystalline face-centered cubic (fcc) metals with coarse grains (sizes greater than 1 μm; CG) exhibit obvious work hardening originating from the large grains supplying enough space for forest dislocation storage. Nevertheless, ultrafine-grained (ufg) metals with a grain size of 100 nm–1 μm and nanocrystalline (nc) metals with a grain size below 100 nm have been widely observed to show a very limited work hardening at room temperature (RT) [2,3]. Although significant strengthening is obtained, ufg/nc fcc metals exhibit drastically diminished work hardening with a few percent uniform plastic strain in uniaxial tension (usually less than 3–5%), distinct from the high ductility of conventional CG counterparts [3–5].

The work hardening coefficient (n) provides direct and conclusive evidence for the work hardening ability in metals. According to the Hollomon equation (σ = Kε^n) [1], the work hardening coefficient should be numerically equal to the true uniform strain from the tensile stress–strain curves. However, such experimental data are difficult to obtain in most ufg and/ or nc metals because of their limited tensile ductility owing to the early onset of necking and low plastic instability [2]. The work hardening rate at small strain levels is therefore usually used to estimate work hardening capacity for metals which become necked shortly after the onset of plastic flow [6,7]. Both the work hardening rate and its coefficient are necessary simultaneously to judge the work hardening capacity of metals, especially for the metals an with ultrafine or nanoscale microstructure.

Recent studies have indicated that pulse-electrodeposited (PED) ufg-Cu containing controlled densities of nanoscale growth twins (nt-Cu) possesses a high tensile strength and an impressive uniform plastic strain, both of which increase with increasing twin density [8–10]. Moreover, very high work hardening rates at high flow stress levels indicate that the Cu samples with nano-twin structures possess a larger capacity for dislocation storage compared with conventional nc Cu with high-angle GBs [11]. Former investigations have suggested that the nanoscale growth twin boundaries (TBs) could not only act as effective obstacles to the motion of dislocations like conventional GBs, but also absorb dislocations. In view of the above considerations, nano-twinned Cu, with a sufficiently large uniform plastic strain, offers a possible method of exploring the work hardening rate and work hardening coefficient simultaneously through direct tensile tests. Our results from uniaxial tensile and loading–unloading tensile tests on ufg-Cu with different twin densities demonstrate that the twinned structure enhances the work hardening rates significantly but has no obvious effect on the work hardening coefficient.

High-purity Cu sheets with nanoscale growth twins were synthesized by using pulse electrodeposition from a CuSO₄ electrolyte. The twin density was controlled by adjusting the physical and chemical parameters, such as the pH value, the current density and the temperature.
A ufg-Cu sample with a similar grain size but without growth twins (ufg-Cu) was also prepared from the same electrolyte by direct current electrodeposition. Further details about the preparation procedure and specimen characterizations can be found elsewhere [8–10].

To investigate the effect of nanoscale growth twins on strength, ductility and work hardening of Cu samples, two independent types of tensile tests were performed on a Tytron 250 Microforce Testing System at RT: (1) continuous uniaxial tensile tests at a constant strain rate of \(6 \times 10^{-4} \text{s}^{-1}\) were performed; (2) loading–unloading tests were carried out by instantaneously releasing the tension load to zero at a constant true strain (such as 2.4%). Subsequently, the specimens were reloaded and the plastic deformations were carried to a certain strain (4.4%), then unloaded to zero again. Finally, the Cu specimens were reloaded and strained to failure. The strain rate for the loading process was \(6 \times 10^{-4} \text{s}^{-1}\), while for the unloading process it was \(2 \times 10^{-4} \text{s}^{-1}\).

Dog-bone-shaped tensile specimens with a gauge length of 4 mm and a width of 1.7 mm were prepared by electrodischarging from the Cu foils. The final tensile samples which close to the substrate have a thickness of about 25 ± 5 µm after electropolishing. Microstructural characterizations of Cu specimens in their as-deposited state and after tensile testing were carried on a transmission electron microscope (TEM; JEM2010) operated at 200 kV.

Figure 1 presents the plan-view TEM micrographs of three as-deposited nt-Cu with different TB densities (a–c) and a ufg-Cu sample (d), respectively. The nt-Cu samples consist of roughly equiaxed grains with an average grain size of 400–500 nm. The high density of sharp boundaries inside each grain was determined to be \{111\}/\{112\} TBs, as seen by the selected area electron diffraction shown in the inset in Figure 1a. Most of growth twins are coherent Σ3 boundaries. Statistical measurements of the spacing of TBs along the \{110\} beam direction from TEM observations showed that the average twin lamellae spacings are approximate 20 ± 4 nm (hereafter referred to as nt-Cu-20), 36 ± 7 nm (nt-Cu-36) and 90 ± 26 nm (nt-Cu-90), respectively, as shown in Figure 1a–c. For comparison, the microstructure of ufg-Cu with essentially the same grain size is shown in Figure 1d. No evident growth twin is observed in as-deposited ufg-Cu, whereas distinct dislocations are present in grain interiors and in the vicinity of GBs.

Figure 2 displays continuous uniaxial tensile and loading–unloading tensile true stress–strain curves for the three nt-Cu specimens and the ufg-Cu specimen. It is obvious that the continuous and the loading–unloading tensile curves overlap completely. The clear effects of twin spacing (or twin density) on the mechanical properties are seen from this plot. First, the yield strength and tensile strength increase with decreasing twin spacing. For nt-Cu-20, yield strength (\(\sigma_y\)) is about 833 MPa, which is about two times higher than that of nt-Cu-90 and about 3.5 times higher than that of ufg-Cu. Second, the ductility increases significantly with increasing the twin density. For instance, for nt-Cu-90, the tensile strain-to-failure is only 3%, which is one-quarter of that of nt-Cu-20 (~10.9%).

A quantitative summary of the loading–unloading tensile results for each sample, including grain size, twin spacing, yield strength, flow strength at certain strains and tensile elongation-to-failure, is provided in Table 1. Also included are the flow strength increments between 2.4% and 0.2% strain, denoted by the term \(\Delta \sigma_f = \sigma_{2.4} - \sigma_y\). The increments of flow strength of nt-Cu are found to depend prominently on twin density: with increasing twin density, \(\Delta \sigma_f\) increases monotonically. A small \(\Delta \sigma_f\) of 46 MPa is measured for ufg-Cu, which is slightly smaller than that of nt-Cu-90. On the other hand, for nt-Cu-20, \(\Delta \sigma_f\) can be as high as 142 MPa. The evident flow strength increases for nt-Cu are contrasted by the absence of flow strength increment observed in loading–unloading tests made on electrodeposited nc Ni [7].

Figure 1. Plan-view bright field TEM images of the as-deposited Cu with different twin densities: (a) nt-Cu-20, (b) nt-Cu-36, (c) nt-Cu-90 and (d) ufg-Cu.

Figure 2. True stress–strain curves of nt-Cu specimens with different twin densities and a ufg-Cu specimen. The continuous tensile deformation is indicated as solid lines and the loading–unloading cycle deformation runs are indicated as open circles.
increment on the true stress (a) and true strain (b) for three nt-Cu specimens and a ufg-Cu specimen. According to the criterion for localized necking for sheet specimens, the uniform strains for the four Cu samples are evaluated, as indicated by crosses in (b). As seen in Figure 3b, the $\Theta$ of nt-Cu-20 remains remarkably high over a range of strains, while that of nt-Cu-90 reduces rapidly. When comparing the $\Theta$ values of the three nt-Cu specimens, it is clear that introducing nanoscale twins into ufg grains enhances $\Theta$ appreciably. At 2% strain, the work hardening rate for nt-Cu-90 is 1155 MPa; however the $\Theta$ value of nt-Cu-20 is 5135 MPa, which is about five times higher than that of ufg-Cu. In order to further quantify the work hardening response, the uniform plastic deformation stage in uniaxial tensile curve was fitted by the equation:

$$\sigma = K_1 + K_2 \varepsilon^n,$$

where $K_1$ represents the initial $\sigma_y$, which is especially important for the materials with high $\sigma_y$, $n$ is the work hardening coefficient and $K_2$, the strength coefficient, represents the increment in strength due to work hardening with $\varepsilon = 1$ [1,12]. The fitting results for nt-Cu are listed in Table 2. It can be seen that $K_2$ is intimately dependent on twin density, as is $\Theta$. When reducing the twin spacing from 90 to 20 nm, $K_2$ increases from 285 to 578 MPa. The larger values of $K_2$ and $\Theta$ for nt-Cu-20 suggest that a higher twin density leads to a higher strength increment following work hardening to unit strain, coincident with $\Delta \sigma_y$ in Table 1.

For ufg-Cu, the estimated $n$ is about 0.26, which is smaller than that of CG Cu (~0.35) [1,12]. However, it is interesting to find that incorporating twins in the crystals affects $n$ only slightly. The $n$ value increases slightly from 0.22 to 0.30 with increasing twin density in nt-Cu specimens, in view of the calculated errors of $n$ being about ±0.03. Such $n$ values of nt-Cu are somewhat similar to that of nanoscale Cu-Nb multilayer ($n = 0.25$) [12] and much higher than that obtained in nc Cu with a grain size of 80 nm at low strain rates ($5 \times 10^{-6}$ s$^{-1}$) ($n = 0$) [13].

Figure 4a and b presents the typical TEM micrographs after tensile testing for nt-Cu-20 and nt-Cu-90, respectively. In contrast to the clear and sharp coherent TBs in the as-deposited state, TBs in the deformed nt-Cu, with copious dislocations and debris, are much strained and stepped (or even curved), while the grain size does not change and the grains remain almost equiaxed with high-angle GBs. Plenty of dislocations and dislocation tangles are stored inside the wider twins, in contrast with the rather clean interior of the grains and twins before deforming. The separation spacing between dislocations at the TBs can be as small as several nanometers, suggesting that the TBs may serve as efficient sites for dislocation accumulation. Note that the dislocation cell/wall structures, normally forming in CG Cu submitted to plastic straining, are hardly observed at all in nt-Cu.

![Figure 3. Work hardening rate (calculated by $\Theta = (\frac{\sigma}{C_1})$ plotted vs. true stress (a) and true strain (b) for three nt-Cu specimens and a ufg-Cu specimen. According to the criterion for localized necking for sheet samples, $\Theta < \sigma/2$ [12], the uniform strains for the four Cu samples are evaluated, as indicated by crosses in (b).](Image 345x67 to 506x178)

![Figure 4. TEM micrographs showing the microstructures of tension-deformed nt-Cu-20 (a) and nt-Cu-90 (b), respectively.](Image 44x481 to 280x624)

### Table 1. Detailed summary of loading–unloading tensile results, such as flow strength ($\sigma_{0.2}$, $\sigma_{2,4}$, $\sigma_{4,4}$), ultimate tensile strength ($\sigma_{UTS}$), strength increment ($\sigma_{2,4} - \sigma_{0,2}$) and elongation-to-failure ($e_f$), and including details of grain size and twin lamellar spacing of nt-Cu samples and ufg-Cu

<table>
<thead>
<tr>
<th>Sample</th>
<th>Grain size (nm)</th>
<th>Twin spacing (nm)</th>
<th>$\sigma_{0.2}$ (MPa)</th>
<th>$\sigma_{2,4}$ (MPa)</th>
<th>$\sigma_{4,4}$ (MPa)</th>
<th>$\sigma_{0.2} - \sigma_{2,4}$ (MPa)</th>
<th>$\sigma_{UTS}$ (MPa)</th>
<th>$e_f$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>nt-Cu-20</td>
<td>400–500</td>
<td>20 ± 4</td>
<td>833 ± 60</td>
<td>975 ± 70</td>
<td>2.46</td>
<td>1006 ± 75</td>
<td>142 ± 10</td>
<td>10.9 ± 1.0</td>
</tr>
<tr>
<td>nt-Cu-16</td>
<td>400–500</td>
<td>36 ± 7</td>
<td>674 ± 60</td>
<td>778 ± 70</td>
<td>2.45</td>
<td>815 ± 70</td>
<td>104 ± 10</td>
<td>5.5 ± 0.6</td>
</tr>
<tr>
<td>nt-Cu-90</td>
<td>400–500</td>
<td>90 ± 36</td>
<td>445 ± 40</td>
<td>502 ± 50</td>
<td>2.45</td>
<td>–</td>
<td>57 ± 5</td>
<td>3.2 ± 0.3</td>
</tr>
<tr>
<td>ufg-Cu</td>
<td>400–500</td>
<td>–</td>
<td>256 ± 20</td>
<td>302 ± 30</td>
<td>2.42</td>
<td>328 ± 30</td>
<td>46 ± 5</td>
<td>10.5 ± 0.9</td>
</tr>
</tbody>
</table>

### Table 2. Work hardening parameters calculated by fitting the uniaxial tensile stress–strain curves with a power-law hardening equation of the form $\sigma = K_1 + K_2 \varepsilon^n$ for nt-Cu specimens

<table>
<thead>
<tr>
<th>Sample</th>
<th>$K_1$ (MPa)</th>
<th>$K_2$ (MPa)</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>nt-Cu-20</td>
<td>833</td>
<td>578</td>
<td>0.30 ± 0.03</td>
</tr>
<tr>
<td>nt-Cu-36</td>
<td>674</td>
<td>410</td>
<td>0.27 ± 0.03</td>
</tr>
<tr>
<td>nt-Cu-90</td>
<td>445</td>
<td>285</td>
<td>0.22 ± 0.03</td>
</tr>
<tr>
<td>ufg-Cu</td>
<td>256</td>
<td>254</td>
<td>0.26 ± 0.03</td>
</tr>
<tr>
<td>CG [12]</td>
<td>0</td>
<td>353</td>
<td>0.35</td>
</tr>
</tbody>
</table>
One phenomenon observed from the present results is that with increasing twin density, $\Theta$ of the nt-Cu samples increased, as observed in the ufg/nc metals [2, 6, 7]. It is conceivable that the strengthening effect of coherent TBs is analogous to that of conventional GBs [8–11, 14], and the origin of high $\Theta$ of nt-Cu also comes from the high density of TBs and their effective strengthening effect.

However, different from the effect of twin spacing on work hardening rates of nt-Cu, $n$ values of nt-Cu samples are insensitive to the twin density and comparable to that of ufg-Cu. That means that the introduction of high density nanoscale growth twins could block dislocation motions like conventional GBs but cannot promote the work hardening, because of the limit capability for trapping more dislocations inside ufg grains. Considering the lack of dislocation cell/wall structures in the deformed nt-Cu samples, the conventional work hardening mechanism of forest dislocations for CG fcc metals is not likely to be the dominate mechanism due to the thin twin lamellar structures, so another new work hardening mechanism should be sought.

One of the major reasons for the limited work hardening ability in nc materials relates to their small grain size, which cannot effectively store dislocations to increase defect density, as is normally possible in CG metals [2, 3]. Molecular dynamics computer simulations reveal that GBs might strengthen nc metals by generating and absorbing lattice dislocations, but there is no additional dislocation debris left inside the crystal that could contribute to work hardening [15]. Both experimental results from in situ X-ray diffraction [16] and post-deformation TEM observations [17] on the nc Ni support this point. Comparing the TEM micrographs of the nt-Cu before and after tensile tests (Figs. 1 and 4), it is clear that many defects (dislocations) are stored at TBs, a distinctive characteristic of nc metals. This is because that the initial dislocation-free conditions of nt-Cu (Fig. 1a–c) offer much room for dislocation storage during straining and dislocation debris can build up, starting from quite low levels. The relatively large grain size (400–500 nm) may naturally provide enough space for plastic deformation, as seen in ufg-Cu. Additionally, dislocation cell structures are unlikely to form since the twin spacing is as small as tens of nanometers, which increases the difficulty of dynamically recovering dislocations, as observed in ufg-Cu [18]. The rates of dislocation annihilation in recovery could be reduced further at 77 K, and the $\Theta$ of nt-Cu at 77 K is much higher even than that obtained at RT [11]. The above possible factors which are favorable for dislocation accumulation contribute to the work hardening capacity and play a critical role in the considerable $n$ values (0.22–0.30) measured for nt-Cu.

However, introducing a high density of TBs inside the crystal does not seem to enhance dislocation locks significantly compared with those of the ufg-Cu without twins. This may be due to following factors: (1) The twin lamellar structure is coherently two-dimension, which limits the dislocation interactions in three dimensions and consequently leads to the absence of dislocation locks in the lattice and TBs. (2) Considering the interaction between dislocation slips and TBs, there are two possible crystallographic orientations between them: dislocation slips parallel to the TBs and slips inclined to TBs by 70.5°. Although the former case can only happen with favorable initial slip systems, the dislocation interactions from multi-slip systems would not occur extensively due to the grain size (400–500 nm) confinement and the confinement from conjoint GBs or nearby TBs. (3) For the latter case, the stress concentration would result in a dislocation dissociation reaction at TBs. However, those reactant Shockleys, which could be left at the TBs and lead to TB migration (as seen in Fig. 5b in Ref. [10]), do not contribute to the work hardening significantly.

Note that the $n$ value in conventional CG metals is generally stated as the necking instability condition. However, the present study indicates that this is not the case in Cu with nanoscale twins. Usually based on $\sigma = K_n$, the $n$ value is expected to correlate with a material’s resistance to necking (uniform plastic strain). However, as we noted, nt-Cu samples with different twin densities have similar $n$ values but exhibit obvious differences in uniform plastic strain. The main reason for these differences may be derived from the equation $\sigma = K_1 + K_2 n$, used in the present analysis, which separated out the high initial yield strength of the nt-Cu specimens from the work hardening.

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