Engineering twin boundaries at the nanometer scale is regarded as an effective approach to achieve high strength while maintaining a substantial work-hardening ability. In this paper, the effects of twin thickness, grain size as well as strain rate on the work-hardening behavior of polycrystalline pure Cu with nanoscale twins are analyzed. The contribution of four possible work-hardening components (Types I–IV) to the hardening and softening process of nanotwinned Cu is also discussed.

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1. Introduction

The main motivation for nanostructural engineering stems from the promise of being able to obtain simultaneously high strength and high ductility. The former is expected from the empirical Hall–Petch relationship that predicts a continuous increase in strength with decreasing grain size \(d\) \([1,2]\), and the latter is strongly affected by deformation mechanisms which may prevail when the characteristic length scale of microstructure decreases down to the nanometer regime \([3–5]\). Experimental data accumulated so far indicate that for grain sizes below 30 nm the strength is 5–10 times higher than that of conventional coarse-grained (CG) counterparts \([6]\), but ductility, particularly uniform elongation in tension, is rather limited \([5]\). The reduced ductility of nanograin metals is associated with the drastically diminished work hardening in very small grains \([5]\), which is distinct from the obvious work hardening found in CG structures.

Recently, engineering coherent twin boundaries (TBs) at the nanoscale has been regarded as an effective way to achieve high strength while maintaining substantial ductility \([7–10]\). High-density nanoscale twins embedded in ultrafine-grained Cu, which are strong barriers to dislocation motion, lead to a significant strengthening, similar to that induced by grain refinement into the nanometer regime \([8,9]\). Moreover, remarkable work-hardening rates at high stress levels and consequent high tensile ductility indicate that nanotwinned Cu (nt-Cu) possesses a larger capacity for dislocation storage compared with nanograin Cu with conventional grain boundaries (GBs). Specifically, both ductility and work hardening increase with decreasing twin thickness \(\lambda\) \([11]\), suggesting a fundamental difference between TBs and GBs in controlling work hardening and plastic deformation as the length scale is significantly reduced.

In spite of extensive studies of TB strengthening mechanisms, including experiments \([7–15]\), plastic modeling \([16–18]\) and simulations \([19–23]\), the work-hardening behavior of nanotwinned structures is still not well understood. In this paper, the plastic deformation mechanism and work-hardening behavior of pure Cu samples with nanoscale growth twins under uniaxial tensile tests will be analyzed. The influences of twin thickness, grain size as well as strain rate on the work-hardening behavior, including work-hardening coefficients, work-hardening rates, and strain-softening processes related to dislocation recovery, in the nt-Cu will be discussed.

2. Deformation and work-hardening mechanism

The plastic deformation and work-hardening behavior of nt-Cu are intimately correlated with its microstructural features (including grain size, grain morphology, twin thickness, TB orientation, etc.) and loading conditions (strain rate and temperature). In contrast to forest dislocation interactions generally observed in CG metals, the plastic deformation of metals with nanoscale twins is dominated by TB-mediated...
processes. In Cu with equiaxed grains containing nanoscale twins randomly oriented with respect to the tensile direction, coherent TBs act as effective barriers for blocking dislocation slip-transfer due to the small scale, analogous to the behavior predicted by the Hall–Petch relationship based on the dislocation pile-up model [7,8]. Interactions between dislocations and TBs result in dislocation trapping and absorption along TBs. Molecular dynamics (MD) simulations clearly demonstrated at the atomistic level that when an edge dislocation impinges on a TB, it may either dissociate into two Shockley partials propagating along the TB in opposite directions, or transfer directly through the TB into the adjoining twin accompanied by emission of an additional partial dislocation along the TB or by leaving behind a long stacking fault ribbon in the twin or some sessile locks at the TB, depending on the nature of the incoming dislocations and applied stress [19,20].

Interestingly, the strength of nt-Cu firstly increases as \( \dot{\lambda} \) decreases, reaching a maximum strength at a critical \( \dot{\lambda} \) of about 15 nm, and then decreases as \( \dot{\lambda} \) is further reduced [9]. However, below this critical value, both ductility and work hardening increase with a further reduction in twin spacing [9]. This maximum strengthening can be explained by the deformation mechanism transition from the Hall–Petch type of strengthening due to dislocation pile-up and cutting through TBs to a dislocation nucleation controlled mechanism involving nucleation and motion of twinning partial dislocations parallel to the twin planes [9,23]. The partial dislocation nucleation occurs primarily at the GB/TB intersections and fewer dislocation/TB interactions occur at very small \( \dot{\lambda} \). MD simulations also indicate that the critical twin thickness is dependent on the grain size: the smaller the grain size, the smaller the critical twin thickness [23].

Another kind of nanotwinned structure with preferentially oriented nanoscale twins embedded in columnar grains has also been synthesized [14,15,24]. The detailed microstructures of equiaxial-grained nt-Cu and columnar-grained nt-Cu have been described elsewhere [8,24]. When the tensile direction is parallel to the preferentially oriented TBs in columnar-grained nt-Cu, deformation is dominated by a different mechanism, and thus dislocation slip-transfer across TBs in equiaxial-grained nt-Cu with randomly oriented twins no longer plays a dominating role. Instead, dislocations with the slip direction parallel to TBs but with the slip plane inclined to TBs are preferentially activated and individually glide in the lamellar channels confined by neighboring TBs [24]. This phenomenon bears much resemblance to the hairpin threading dislocations observed in nanoscale thin films and multilayer materials [25,26].

Based on these observations, strengthening and work hardening of nanotwinned Cu are principally attributed to the presence of high-density TBs interfering with or obstructing dislocation propagations. The work-hardening capacity in nt-Cu primarily originates from the possible work-hardening components as schematically shown in Figure 1, including glissile Shockley partial dislocations at TBs (Type I), sessile dislocation locks at TBs (Type II), extended stacking faults terminated at TBs (Type III), and threading dislocations in the twin/matrix lamellae (Type IV). Among the above work-hardening components, Shockley partial dislocations at TBs and threading dislocations within twin/matrix layers (Types I and IV) are mobile dislocations whose gliding contributes primarily to the plastic strain, while stacking faults as well as dislocation locks associated with dislocation/TB reactions (type II and III) are immobile and dominate the work hardening. In the following, the twin thickness, grain size as well as the strain-rate effect on the work-hardening behavior of polycrystalline pure Cu with nanoscale twins will be analyzed in terms of these four work-hardening components.

3. Twin thickness effect

In order to quantitatively analyze the twin thickness effect on work hardening, the work-hardening coefficients were computed from the uniform straining stages in the uniaxial tensile curves according to the Hollomon–Ludwik power law [27,28], \( \sigma = K_1 + K_2\varepsilon^n \) where \( K_1 \) is the initial yielding stress, \( K_2 \) represents the strength increment due to work hardening at \( \varepsilon = 1 \), and \( n \) is the work-hardening exponent. As shown in

![Figure 1. Schematic illustration of work-hardening components in fcc metals with nanoscale twins: (I) Shockley partial dislocations located at TBs; (II) stacking faults associated with TBs; (III) dislocation locks at TBs; (IV) threading dislocations moving parallel to TBs and confined within twin/matrix layers. Here \( \dot{\lambda} \) is the average grain size, \( \dot{\lambda} \) is twin thickness, \( T \) is twin and \( M \) is matrix. GB indicates grain boundary.](image)

![Figure 2. Effect of twin lamellar thickness (\( \dot{\lambda} \)) on work-hardening coefficient (\( n \)) of the equiaxial-grained nt-Cu with various twin thicknesses. Red solid squares and the black solid diamond are from samples with average grain sizes of 500 and 1500 nm, respectively [9]. For comparison, \( n \) values for nc-Cu and CG-Cu (blue solid circles) are also plotted as a function of grain size (\( \dot{\lambda} \)) [6,29]. Here \( n \) is determined according to the Hollomon–Ludwik power law, \( \sigma = K_1 + K_2\varepsilon^n \), where \( K_1 \) represents the initial yield stress, and \( K_2 \) the increment in strength at \( \varepsilon = 1 \). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image)
Figure 2, the value of $n$ for twin-free Cu with $d \approx 500$ nm is about 0.26, smaller than that of CG-Cu (0.35) [29]. For the equiaxial-grained nt-Cu samples with $d \approx 500$ nm, incorporating nanoscale twins in the grains only slightly affects $n$, as the $n$ value increases from 0.22 to 0.30 as $\lambda$ decreases from 90 to 20 nm (the calculated errors of $n$ is about ±0.03). Such $n$ values of equiaxial-grained nt-Cu are somewhat close to that of nanoscale Cu–Nb multilayers ($n = 0.25$) [29] but much larger than that obtained in nanocrystalline (nc)-Cu with $d = 80$ nm at low strain rates ($5 \times 10^{-6}$ s$^{-1}$) ($n = 0$) [30]. However, when $\lambda$ further decreases below 15 nm, $n$ increases and exceeds the value for CG-Cu, finally reaching a value of 0.66 at $\lambda = 4$ nm. Note that twin refinement induces a monotonic elevation in $n$, which is in opposite to the general observation in ultrafine-grained and nc materials where the $n$ value continuously decreases with decreasing $d$, as shown in Figure 2.

It is also standard practice to examine work-hardening behavior by plotting the instantaneous work-hardening rate ($\Theta = \Delta \sigma / \Delta \varepsilon$) vs. the flow stress increase ($\sigma - \sigma_y$) [31]. All curves in Figure 3 display an initially steep decrease in $\Theta$ for strains of less than ~1%, which corresponds to the elastic–plastic transition. After that, there is an approximately linear decrease of $\Theta$ as the flow stress increases, analogous to the conventional stage III hardening described by the Kocks–Mecking model [31], $\Theta = \Theta_0 - K \sigma$, where $\Theta_0$ is a constant hardening term related to dislocation storage, and the slope of the linear segment in $\Theta - \sigma$ plot, $K = \Delta \Theta / \Delta \sigma$, quantitatively characterizes the thermally activated work-softening process during deformation, which is related to the dynamic recovery of stored dislocations and is a function of both strain rate and temperature. Obviously, the decreasing rate of $\Theta$ appears to be intimately correlated with the twin thickness and grain size of the nt-Cu. For equiaxial-grained nt-Cu, the $K$ value decreases with decreasing twin thickness (Fig. 3a), whereas in columnar-grained nt-Cu, a reduction in $K$ value with increasing twin thickness and grain size was observed (Fig. 3b). To investigate work-hardening behavior, the two competitive processes, namely hardening caused by dislocation multiplication and accumulation, and softening induced by dynamic recovery of dislocations, should be considered. In the following, the hardening and softening mechanisms for the equiaxial-grained nt-Cu and columnar-grained nt-Cu will be discussed, respectively.

3.1. Equiaxial-grained nt-Cu

Remarkable work-hardening rates over an increasingly wider range of flow stress as twin spacing decreases from 90 to 4 nm are displayed in Figure 3a, manifesting a larger capacity to store dislocations in equiaxial-grained nt-Cu as twin spacing is refined. The high dislocation storage originates from the intense interactions and reactions between dislocations and TBs, which result in massive glissile dislocations (Type I at TBs) and sessile dislocations (Type II at TBs and Type III in the matrix/twin layers). The sessile Type II and III dislocations can serve as strong barriers to impede the motion of other dislocations and thus contribute significantly to work hardening; mobile Type I dislocations, however, although presenting relatively weak barriers may glide away along TB easily to accommodate other dislocations at TBs. Transmission electron microscopy (TEM) observations indeed verified that dislocations, primarily Types I and III as seen in Figure 4c in Ref. [9], with a density as high as $10^{16}$ m$^{-2}$, can be accumulated at TBs in equiaxial-grained nt-Cu with $\lambda = 4$ nm after deformation [9]. This is distinctly different from that of conventional GBs in nc metals. In this sense, TBs are unique strengthening agencies which can not only restrict dislocation motions, but also provide plenty of space for storing dislocations and thereby controlling the work hardening.

Furthermore, cyclic stress relaxation tests demonstrated that an increase in twin density (or a decrease in twin thickness) can lower the exhaustion rate of mobile dislocations in nt-Cu, which is also correlated with the work-hardening behavior [32]. The mobile dislocations are mainly the aforementioned Type I dislocations,
resulting from dislocation/TB interactions. When the twin thickness is less than the critical value, more Type I Shockley partial dislocations nucleate at the GB/TB intersections [9,23]. On the other hand, interfacial dislocations in columnar-grained nt-Cu can be explained by different dislocation behaviors. When tensile direction is parallel to the preferentially oriented TBs in columnar-grained nt-Cu, threading dislocations (Type IV) propagating individually through the channels confined by neighboring TBs dominate the plastic deformation. The accumulations of mobile threading dislocations in the matrix/twin lamellae and the trailing dislocations left behind at TBs upon their propagation lead to work hardening. However, since dislocation slip-transfer across TBs is largely suppressed in this case, the immobile dislocations (Type II and III) are rarely seen and contribute little to work hardening, unlike the situation in the equiaxial-grained counterpart. Therefore, only as a result of mobile Type IV threading dislocations was a relatively lower Θ found in the columnar-grained nt-Cu samples, as shown in Figure 3b.

It is noted in Figure 3b that reducing twin thickness in columnar-grained nt-Cu leads to Θ reducing at a higher rate [24]. For instance, the K value increases from 11 to 24 as the twin thickness decreases from 74 nm (sample B) to 40 nm (sample C) for samples with a similar grain size. This trend is different to that observed in equiaxial-grained nt-Cu.

The softening mechanism of the columnar-grained nt-Cu may be dominated by simple interactions of threading dislocations (Type IV) confined by twin layers (as shown in Fig. 1) and inhomogeneous plastic deformation at the GB regimes (which will be discussed in the next section). Increased dynamic recovery of threading dislocations with decreasing twin thickness in columnar-grained nt-Cu is similar to that with reducing layer thickness in Cu/Ag multilayers [35] and with reducing grain size in polycrystalline metals as well. More dynamic recovery and softening would occur when the localized dislocation density is higher and the length scale is reduced.

4. Grain size effect

Since twin lamellae are embedded within the grains in the nt-Cu samples, the twin structure inherently has two microstructural dimensions: the dimension in the direction perpendicular to TBs (λ) and the dimension parallel to them, which corresponds to the grain size. Tensile tests indicated that grain size also plays an important role in the ductility and work hardening of nt-Cu samples [36]. For example, with an increased grain size from 500 to 1500 nm, while keeping λ fixed at about 60 nm in equiaxial-grained nt-Cu, both ductility and work hardening of the nt-Cu are effectively elevated, but strengthening is not sacrificed to a notable degree [36]. The n value increases from 0.21 to 0.39 (Fig. 2) while the K value decreases from 126 to about 25 when the grain size increases from 500 to 1500 nm. This suggests that the larger grain size would suppress more softening and dislocation recovery during plastic deformation. A similar grain size effect on work-hardening behavior was also found in...
columnar-grained nt-Cu. When the grain size increases from 3 to 4.3 μm with a similar twin thickness of ~40 nm (from sample A to B in Fig. 3b), the K value decreases from about 37 to 25 \[24\]. The K value can be further decreased to about 4 in a columnar-grained nt-Cu sample with a grain size as large as 18 μm and a twin thickness of about 70 nm (sample D).

In addition to high-density TBs, GBs, especially GB/TB intersections, also serve as important dislocation sources and sinks during plastic deformation of nt-Cu samples. On the one hand, TEM observations on deformed nt-Cu reveal that the distribution of stored dislocations is not spatially uniform with a higher density of dislocations accumulated adjacent to GBs [8,37]. On the other hand, the stored dislocations in the vicinity of GBs are more likely to recover and annihilate when the local dislocation density is quite high, because GB/TB intersections could serve as regenerative dislocation sources for Type I partial dislocations in equiaxial-grained nt-Cu and for Type IV threading dislocations in columnar-grained nt-Cu. The reactions of these two types of dislocations with other stored dislocations lead to dislocation annihilation and promote dynamic recovery. This can be justified by the observations of well-developed dislocation cells in GB regions [11]. Since the volume fraction of GB affected regions is inversely proportional to the grain size, the influence of enhanced GB recovery on work hardening becomes more important as grain size decreases. This explains the larger K value and recovery rate for nt-Cu with \(d = 500\) nm compared with that for \(d = 1500\) nm.

Compared with equiaxial-grained nt-Cu, the columnar-grained nt-Cu seems to suffer a more significant inhomogeneous plastic deformation: GB regimes can sustain larger plastic strain than that sustained by grain interiors \[24\]. A high density of tangled dislocations gradually evolves into dislocation cells or subgrains as strain increases, as shown in Figure 7 in Ref. [24]. In certain places, even detwinning-induced elimination or thickening of growth twins was observed in the vicinity of GBs \[24\]. These substantially recovered substructures consequently reduce the work-hardening ability. Such GB-associated strain softening would be more serious in samples with small grain size and twin thickness, which accounts for the fact that the work hardening and uniform tensile ductility in columnar-grained nt-Cu with submicron grains is rather limited \[14,15,24\].

5. Strain-rate effect

The strain-rate sensitivity of nt-Cu has been investigated in a series of experiments \[17,37,38\]. Increased strain-rate sensitivity and reduced activation volume with decreasing twin thickness were found to be associated with TB-mediated slip transfer of propagating dislocations \[21\]. The flow stress increment caused by strain-rate sensitivity, coupled with those from dislocation accumulation, may render a strain-rate dependence of work-hardening behavior in nt-Cu. Figure 5 shows the \(\dot{\theta} - \dot{\sigma}\) plot for an equiaxial-grained nt-Cu with \(\lambda = 15\) nm tensioned at strain rates ranging from \(6 \times 10^{-4}\) to \(6 \times 10^{-2}\) s\(^{-1}\). Obviously, the K value decreases with increasing strain rate. The strain-rate sensitivity calculated in terms of saturated flow stress \(\sigma_v\) (flow stress extrapolated to \(\dot{\theta} = 0\)) is about 0.025, in good agreement with former investigations \[37,38\], which proves that the reduced K value here at high strain-rate tension is only caused by increased flow stress due to the strain-rate sensitivity effect. This phenomenon is analogous to conventional CG metals but is more pronounced here due to the larger strain-rate sensitivity in nt-Cu.

However, decreasing deformation temperature from 300 to 77 K results in enhanced strength and uniform ductility in equiaxial-grained nt-Cu samples \[39\]. This is mainly caused by suppressed dynamic recovery of stored dislocations and hence an improved work-hardening rate at 77 K. Furthermore, at these cryogenic temperatures, Shockley partial dislocations (Type I) appear to be more favorable in comparison with full dislocations due to the lower critical shear stress for partial dislocation activities. Type I dislocations gliding on TBs may lead to TB migration and variation in average twin thickness, as verified by the cold-rolling and in situ tension at cryogenic temperatures [40,41], which could also influence the work hardening. Similarly, significantly enhanced work hardening is expected if the strain rate is increased up to the dynamic deformation regime, higher than \(~10^3\) s\(^{-1}\), because increasing strain rate should have a similar effect on suppressing dynamic recovery as decreasing the deformation temperature.

6. Concluding remarks and perspective

The work-hardening behavior of nanotwinned metals is strongly dependent on their microstructures (twin thickness and grain size, as well as TB orientation with respect to loading directions) and loading conditions (strain rate and temperature). Four work-hardening components, including Shockley partial dislocations (Type I), sessile dislocation locks (Type II), stacking faults (Type III) and threading dislocations (Type IV), are summarized in order to explain the work-hardening behavior in nt-Cu. For equiaxial-grained nt-Cu, the interaction products between dislocations and TBs, i.e. Type I, II and III dislocations, control the hardening process, while the reactions between Type I and Type II/III dominate its softening process. The multiplications and
interactions of Type IV threading dislocations dominate the work hardening in columnar-grained nt-Cu.

Our study suggests that decreasing twin thickness or increasing grain size, increasing strain rate or decreasing deformation temperature may enhance work-hardening ability, resulting in enhanced mechanical performance, such as strength, uniform ductility and fracture toughness of nt-metals. Understanding of the work-hardening mechanism of the nt-metals can potentially benefit the possible applications for metals with lower stacking fault energies in which fine-scale twins can preferentially form.

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