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Atomic-scale studies on the effect of boundary coherency on stability in twinned Cu

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The stored energy and hardness of nanotwinned (NT) Cu are related to interaction between dislocations and {111}-twin boundaries (TBs) studied at atomic scales by high-angle annular dark-field scanning transmission electron microscope. Lack of mobile dislocations at coherent TBs (CTBs) provides as-deposited NT Cu a rare combination of stability and hardness. The introduction of numerous incoherent TBs (ITBs) reduces both the stability and hardness. While storing more energy in their ITBs than in the CTBs, deformed NT Cu also exhibits high dislocation density and TB mobility and therefore has increased the driving force for recovery, coarsening, and recrystallization. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4861610]

It has been experimentally established that the presence of a high density of nanoscale growth twins played crucial roles in materials performance.[1–8] 330 stainless steel with {111}-textured nanotwins (NT) had considerable thermal stability,[7] and the average twin spacing and orientation of twin interfaces remained unchanged after annealing up to 500 °C. NT Cu with high density (99%) of coherent twin boundaries (CTBs) exhibited much more stability than nanocrystalline (NC) Cu with random high-angle grain boundaries by maintaining the original nanotwin structure and hardness value during long-term ambience aging.[9] In interface dominant NT materials, TBs act as sources, sinks, barriers, and storage sites for dislocations. Therefore, the properties of TBs affect most of defects-related processes. TBs are special high-angle grain boundaries which have significantly lower energies than the random boundaries. These boundaries only exist at particular misorientations and boundary planes, which allow the two adjoining lattices to fit together with relatively little distortion of the interatomic bonds. If the twin boundary is parallel to the twinning plane the atoms in the boundary fit perfectly into both grains, the result is a CTB. The atoms in the boundary are essentially in undistorted positions, and the energy of CTBs is significantly lower than that of random high-angle boundaries. As a result of the orientation dependence of twin boundary energy, it is energetically favorable for TBs to align themselves parallel to the twinning plane.[10] If, however, the boundary is constrained to follow a macroscopic plane that is near but not exactly parallel to the twinning plane, the boundary will usually develop a stepped appearance with large coherent low-energy facets and small incoherent high-energy risers. It is therefore curious whether the losing of coherency will affect the stability and to what extent. Accordingly, it is of scientific interest and practical importance to understand the influence of coherency of TBs on the stability in NT materials.

High purity Cu foils ($50 \times 10 \times 0.1$–0.2 mm^3 in size) with high density (99%) of CTBs were synthesized by a pulsed electro-deposition technique in the cupric sulphate electrolyte. The details of preparation were described in Ref. 11. The deposited Cu foils were removed from the substrates after deposition. Some of them were deformed in plain-strain conditions by cold-rolling. Part of the deformation energy remained in the crystal lattice as stored energy. Differential Scanning Calorimeter (DSC) is a powerful tool for measuring stored energy that can be related directly to the microstructure evolution such as recrystallization and grain growth.[5,12–19] The thermal stability of NT Cu was assessed by a Shimadzu DSC-60. The samples were sealed in an aluminum pan and heated from ambient temperature to 350 °C in argon atmosphere at a constant heating rate of 5 °C/min. The baseline for DSC curves was determined by reheating the sample at the same heating rate. Both the temperature and the energy of the calorimeter were calibrated by pure Indium (99.999 wt. %) and Tin (99.999 wt. %). The stored energy in this work was determined by measuring the areas under peaks on the DSC curves. For rolled Cu, DSC analyses were conducted immediately after the rolling deformation. Micro-hardness tests were performed on substrate sides of Cu foil. The hardness of rolled samples was tested right after rolling. 50 g load was used and time duration was 10 s. The microstructures were characterized using scanning electron microscope (SEM), transmission electron microscope (TEM, JOEL-2011), and sub-angstrom TEM/STEM (scanning transmission electron microscope, JEM, ARM200F) on cross sections. The cross-section TEM (XTEM) samples were prepared by twin jet electro-polishing with a solution of 33% phosphoric acid in water at 5.5 V and 24 °C. Detailed preparation approaches can be found in a separate paper.[20]

Figure 1(a) summarizes the strain dependent thermal reaction temperatures in NT Cu. In as-deposited Cu, no evident exothermic or endothermic reaction can be observed upon heating until 308 ± 5 °C (the peak temperature, hereafter the reaction temperature refers the peak temperature on DSC curve). The subsequent microstructure examination (Figure 1(b)) revealed twin coarsening after DSC tests. The electron backscatter diffraction (EBSD) analysis indicated the same orientation with the original one, i.e., ⟨110⟩. Hence, the exothermic reaction at 308 °C was caused by twin coarsening. After deformation, the thermal reaction peak shifted downwards. At 287 ± 5 °C, All deformed samples showed an exothermic peak. After DSC tests, the hardness of rolled

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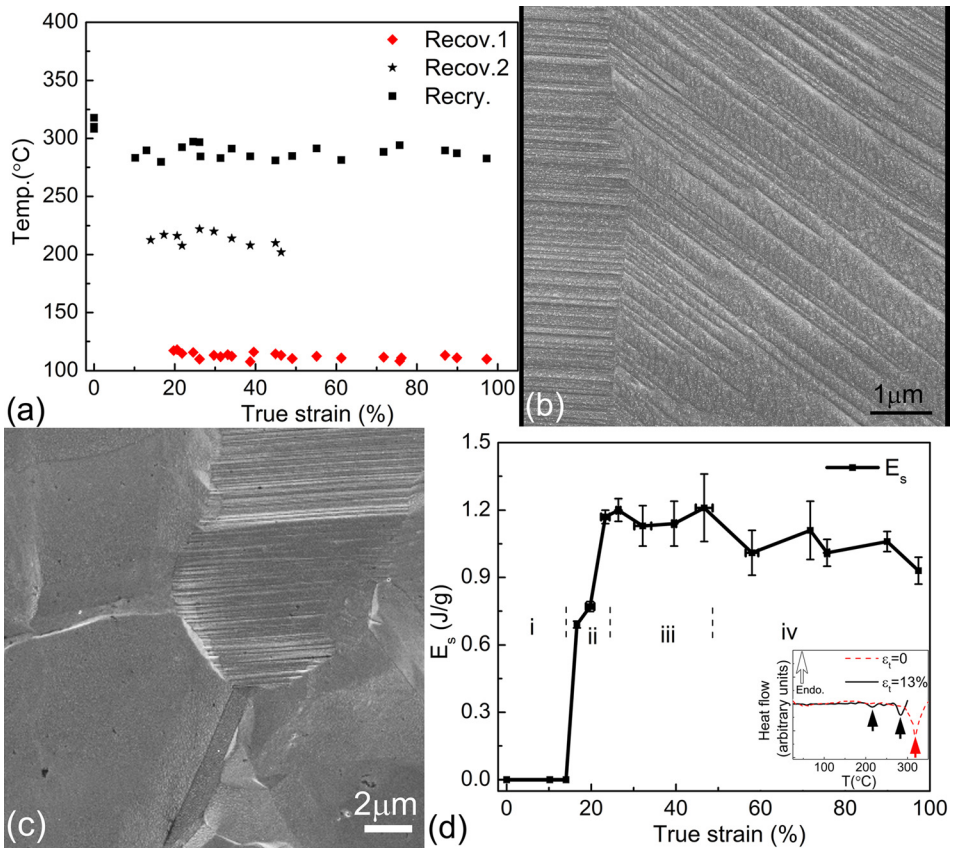

FIG. 1. (a) Strain dependence of recovery and recrystallization temperature in NT Cu obtained from DSC measurement. "Recov.1, Recov.2, and Recry." mean recovery at around 113 °C and 212 °C, and recrystallization, respectively; (b) twin coarsening and recrystallization after DSC tests; (d) stored energy for recovery as a function of deformation strain (an inset shows two typical DSC curves of as-deposited (dashed line) and as-rolled (solid line) samples with recovery (arrow at about 212 °C) and recrystallization peaks (arrows at about 308 °C and 287 °C, respectively)).

NT Cu dropped to 0.57 ± 0.03 GPa, which was close to the property of coarse-grained Cu with grain size larger than 80 μm. The corresponding microstructure showed in Figure 1(c) indicates the formation of new strain free grains, though some fine twins can still be seen. Apparently, recrystallization resulted in the exothermic reactions in deformed NT Cu at about 287 ± 5 °C. Meanwhile, prior to the recrystallization, recovery came to appear. In NT Cu with true strain of 13%–15%, there was a recovery at around 212 ± 4 °C. With true strain of 15% ~ 55%, another visible recovery occurred at about 113 ± 3 °C, apart from the one at around 212 ± 4 °C. While with further increase of strain, the number of exothermic reactions reduced down to two again, i.e., a recovery peak at around 113 ± 3 °C and a recrystallization peak at 287 ± 5 °C. The recovery at around 212 °C became very weak and difficult to be detected. The recovery at about 113 °C is attributed to the dislocation migration and annihilation, and the one at about 212 °C is a result of rearrangement of dislocations into stable arrays. On the other hand, since Cu is susceptible to be oxidization, it is necessary to know the influence of oxidation on DSC data.[21] DSC runs were carried out on coarse-grained Cu samples through 350 °C. Thermal effect was detectable at around 311 °C, which matches exothermic peaks of as-deposited and deformed Cu at this temperature range. After DSC tests, surfaces of coarse-grained Cu changed color, so did the NT Cu. Apparently, Cu begin to be oxidized at around 308 °C. Therefore, the exothermic reaction of twin coarsening and recrystallization in NT Cu becomes complicated by oxidation, and the corresponding stored energy is hardly separated from the oxidation peak. Because the recovery happens at a relatively low temperature and the oxidation signal could not detectable in our system, the recovery energy could be determined accurately.

Figure 1(d) illustrates the effect of strain on the total stored energy for recovery at both 113 °C and 212 °C in NT Cu. The kinetics can be subdivided into four stages. In stage (i), no recovery peak is detectable in as-deposited Cu and rolled Cu with strain less than 13%. In stage (ii), there is a sharp increase of stored energy for recovery with increasing strain in the strain range of 13%–22%. The average stored energies reach 0.69 ± 0.01 J/g and 1.17 ± 0.03 J/g in Cu with true strain of 16% and 22%, respectively. In stage (iii) ($22\% < \varepsilon_t < 50\%$), the stored energy for recovery becomes saturated and independent of strain. Saturation energy is 1.16 ± 0.09 J/g. The increased strain value makes no more contribution to the stored energy for recovery. In stage (iv), $60\% < \varepsilon_t < 92\%$, the stored energy for recovery appears to be reduced slightly with further increasing of strain. The stored energy of Cu with 92% reduces to 0.94 J/g, which is 19% lower than that of samples with strain of 22%. From these curves, it is deduced that the stored energy does not always increase with the rolling strain. Dynamic recovery during rolling deformation could consume some of the mechanical energy.

The effect of strain on the rate of recovery counterbalances the positive effect of strain on the strength of the metal. Figure 2(a) is a plot of the hardness as a function of the logarithm of annealing time at 100 °C with various strains ($\varepsilon_t = 0\%$, 15%, 20%, 25%, 39%, and 62%). Cold deformation increases the hardness of NT Cu provided that the hardness measurement is undertaken immediately after the cold work. Similar results were reported before.[22] However, the recovery rate at 100 °C also increases with strain. In the

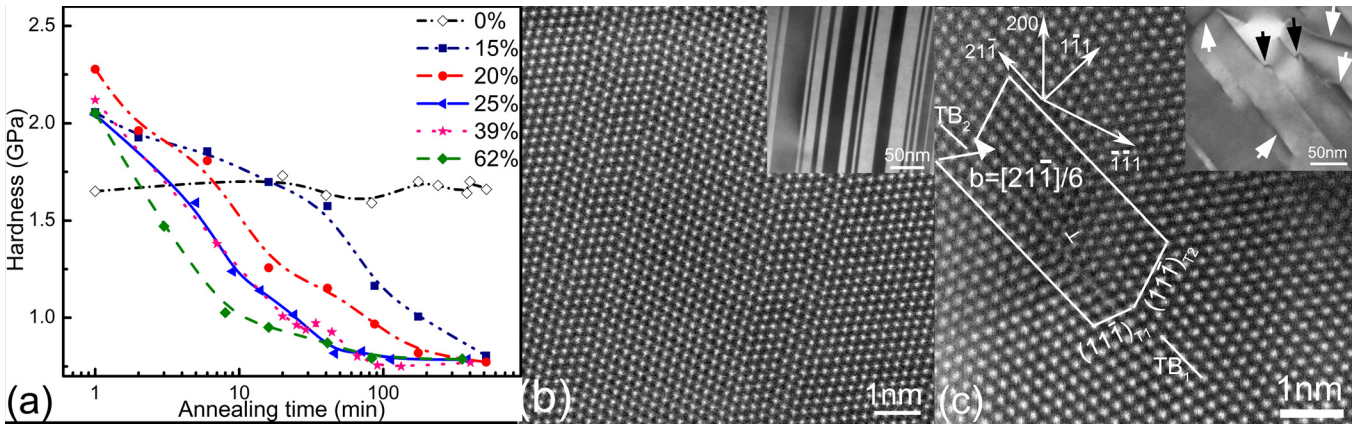

FIG. 2. (a) Strain vs. hardness with the heat treatment at 100 °C. (b) STEM images showing CTBs at atomic and micro (inset) scales with the incident beam along [011]. STEM image (c) showing partial dislocations at TBs identified by the Burgers circuit after rolling, and the inset exhibits ITBs (marked by black arrows) and dislocations (white arrows).

initial several minutes, the hardness drops sharply and then becomes slow at the end. The hardness of Cu foils with true strain 62% was reduced from 2.05 GPa to 1.47 GPa after 3 min annealing at 100 °C. It took 345 min for the hardness to lower to 0.79 GPa. By contrast, for the Cu foils at a strain of 15%, the hardness remains as high as 1.71 GPa even after 16 min annealing. This value is even much higher than that of the Cu deformed to a strain of 62% and then annealed for 3 min. Although the softening rates are influenced strongly by fabrication parameters, over the annealing time range studied, the hardness values of all deformed samples are converged to a same level (about 0.7 GPa). In deformed Cu, the recovery is fast and advances at relatively low temperatures, suggesting that large strain deformation cannot strengthen NT Cu alone. What worthy of pointing out is that the hardness of the as-deposited NT Cu foils showed no evident loss even after 72 h aging at 100 °C. This stability is consistent with the DSC observation of no recovery process at this temperature.

Previous work showed that the as-deposited NT Cu foils had a colony structure consisted of high density (99%) of CTBs among the entire boundaries.[9] The average twin spacing was 25 nm. To identify the exact location of the CTB and their associated defects, atomic-resolution STEM was used in combination with conventional HRTEM. Figure 2(b) reveals the atoms in the TBs fit perfectly into both grains and are essentially in undistorted positions. These {111}-TBs were engineered to grow parallel to foil surfaces. Cold deformation gave rise to the distortion of atoms arrays in TBs, and TBs do not lie exactly parallel to the twinning planes any more. As revealed in Figure 2(c), a glissile Shockley partial (1/6<211>) was identified with Burgers vector parallel to the CTB plane and its core was in the vicinity of CTB plane, constructing an incoherent TBs (ITBs). The gliding of partial dislocation along the twin plane from one side to the other within a grain results in the moving of the CTB by one atomic layer. Continuous nucleation and motion of the associated partial dislocations at TBs lead to TBs migration and formation of TB ledges/steps (the inset in Figure 2(c)). Associating with the existence of many TB steps on both sides, the initial continuous lamellae are broken into several fragments.

The predominant CTBs structure and the low incoherent defects density (<1%) play a dominant role on the stability in as-deposited Cu. The energy of a CTB is much lower than that of a random high-angle boundary.[10] The low CTB energy (0.15 J/g^9) provides system insufficient driving force for the instability upon heating until around 308 °C. The recrystallization temperature in deformed NT Cu is noticed much lower than that was reported. The thermal stability of sputter-deposited NT Cu was investigated by annealing up to 800 °C for 1 h and discovered that the average twin thickness merely increases to 20 nm from 4 nm.[6] Neither recovery nor recrystallization was reported in sputter-deposited NT Cu at such high temperature. As also indicates the superior stability of CTBs. The difference in recrystallization between our measured results and the literature data might be attributed to the difference in the impurity content and the time of heat-treatment. Inductively coupled plasma mass spectrometry (ICP-MS) analysis revealed our NT Cu very pure, and the elements with the highest (i.e., Ba, Pb, and Cr) concentration are still at the ppm level. In the above sputter-deposited NT Cu, the Fe content is about 0.5 at. %. Fe precipitates or segregation add a Zener drag force on the grain boundary, thereby may impede grain growth upon heating.[6] TBs movement needs more energy and time to overcome the obstacles.

In analyzing the recovery rate of NT Cu rolled to medium and high strains in the present work, we observed that the recovery rate increased with strain and rapid microstructural coarsening. The high recovery rate at large strain has its cause in the characteristics of the deformation microstructure. At the initial of rolling deformation, the twin spacing shrinks and dislocation density rises slightly. Most of the TBs remain coherent. At this strain level, the recovery process upon heating was too weak to be detected. With more dislocations accumulated at TBs, those dislocations reacted with CTBs, and gradually resulted in the transition from CTBs to ITBs. The energy of a twin boundary is very sensitive to the orientation of the boundary plane. The free energy of ITBs is 498 mJ/m^2,[10] which is about 24 times of the energy of CTBs. As a result, the system energy was increased with the generation of numerous ITBs, which contributed to the steep increase of stored energy as found in stage (ii) of Figure 1(d). This continued until a strain level

was reached when the stored energy reached saturated, and dislocations density became maximized. The saturation is a result of a balance reached between an increase in dislocation density due to dislocation multiplication with further deformation and a decrease in dislocation density and boundary density, for example, by twin coarsening or dynamic recovery. In this condition, dislocations created by multiplication in shrunk thin twins would escape to sinks before interacting with other dislocations. In case that twin spacing becomes even smaller than the average distance between twin boundaries, dislocations glide before creating another, the multiplication process itself ceases altogether. Any further deformation will lead to dislocation annihilation and twin coarsening (or detwinning named by other groups[23]). Thus, structures of higher stored energy generally had lower recovery or recrystallization temperature. However, this structure did not lead to a further reduction in recovery or recrystallization temperature on continuingly increasing strains once saturated stored energy was attained. When the balance was interrupted, the dislocation annihilation became to dominate the microstructure evolution, i.e., dynamic recovery or recrystallization intervenes so as to lower the stored energy, as the stage (iv) in Figure 1(d). The effect of strain on the rate of recovery counterbalanced the positive effect of strain on the strength of the metal.

In summary, as-deposited NT Cu shows atoms in the TBs fitting perfectly into both grains in undistorted positions so that the twin boundary is parallel to twin planes. These {111}-CTBs are stable until 308 °C above which twin coarsening occurs. Cold deformation introduces partial dislocations with core in the vicinity of the twin boundaries. Introduction of a true strain between 13% and 16% results in a recovery at around 212 °C with store energy up to 0.69 ± 0.01 J/g. When strain reaches 22% and above, the stored energy is saturated to 1.17 ± 0.03 J/g because of dynamic recovery. The low interfacial energy of CTBs contributes to the stability in NT Cu with high density of CTBs. By contrast, with generation of numerous ITBs accompanied by dislocations in deformed NT Cu, the stored energy is rapidly increased, which facilitates the recovery process, lowering the stability. Ways of stabilizing the deformation structure must therefore be investigated. These findings form the basis for a discussion of the stability of NT structure of both scientific and applied interest.

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