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The role of nanotwin lamellae in enhancing thermal stability of nanostructured materials is examined. Nanostructured copper with varying densities of twins was generated by controlling the deformation strain rate during severe plastic deformation at cryogenic temperatures. While the nanostructured materials produced under cryogenic conditions are characteristically unstable even at room temperatures, their stability is markedly improved when a dense dispersion of nanotwins is introduced. Observations of the role of nanotwins in pinning grain and subgrain structures suggest an interfacial engineering approach to enhancing the stability of nanostructured alloys. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3072595]

Future generations of thermostructural materials will have to satisfy a diverse set of capabilities requiring unique property combinations of strength, toughness, and thermal stability. Nanostructured alloys, with nominal grain size of 10–1000 nm, offer an emerging opportunity in this regard. However, such materials are subject to large driving forces for coarsening owing to the high interfacial energy of their nanostructures.[1] When exposed to thermal agitation, these materials spontaneously transform to the coarse-grained low-strength state, often limiting their application to low homologous temperatures. This stability challenge has been generally addressed by using second-phase particles, including pores and solutes, to reduce grain boundary (GB) mobility.[2,3] This has been particularly effective in enabling retention of the submicron microstructures to $0.7T_m$.[4] However, kinematic stabilization of this type is generally limited to nanostructured systems that form thermally stable second phase particles.[5] Furthermore, this generic strategy is incompatible with nanocrystalline single-phase metals, which lack a structural route to kinetic stabilization and must rely on the action of impurities or solute atoms to suppress grain growth.[6,7]

In contrast to the traditional approaches to stabilization, the drag induced by mutual pinning at GB intersections and triple junctions (TJs) offers an intriguing alternative for achieving thermal stability in fine-grained systems, which have a characteristically high TJ density. This is founded upon direct observations and molecular dynamics (MD) simulations of boundary migration, which suggest that TJs limit coarsening by imposing a drag on GB motion.[8–12] This effect has been found to be especially prominent for TJs formed by the intersection of high coincident site lattice (CSL) boundaries, as TJs comprised of low $\sum$ boundaries are particularly effective at retarding GB migration.[10,12] Furthermore, *in situ* observations of electromigration have shown a similar stabilizing behavior by high-CSL junctions wherein motion of GBs occurred by boundary ledge growth.[13] Irrespective of which of these mechanisms is dominant, nanostructured materials, specifically those with a sufficient density of high-CSL boundaries, can be envisaged for achieving thermal stability, wherein the drag induced by the high number of low-mobility TJs on GB migration limits coarsening.

Stability of such nanostructures was observed in severe plastic deformation (SPD) of oxygen-free high conductivity copper carried out at liquid nitrogen temperature (77 K), wherein highly nonequilibrium grain and subgrain structures were intersected by varying densities of high-CSL, $\sum 3$ coherent twin boundaries (TBs). The copper was of 99.99% purity with an initial grain size of 101 ± 40 μm and hardness of 77 ± 5 kg/mm^2. Machining at controlled strain rates was used to impose shear strains of approximately three in a single deformation pass at 77 K (cryo-SPD) and 298 K (RT-SPD). Control of twin density was realized by controlling the strain rate, which was measured using particle tracking techniques.[14] Strain rates of ~ 1/s and $\sim 10^3$/s were imposed under both SPD conditions. Thermal stability of the resulting copper microstructures at room temperature (298 K) was characterized by microindentation, transmission electron microscopy (TEM), and high-resolution electron microscopy (HREM). TEM and HREM samples were prepared by electrolytic jet thinning and ion milling, and characterized using a JEOL 2000FX operating at 200 kV and a Titan 80/300 operating at 300 kV.

Besides increasing the likelihood of twin formation, cryogenic deformation delays recovery and recrystallization by retarding dislocation climb and cross slip.[8] This results in a heavily defected microstructure of high strength that is inherently metastable; the strength degrading significantly over time even at room temperature.[15,16] The annealing behavior at 298 K of the cryo-SPD sample created at a strain rate of 1/s is consistent with this expectation, as an initial hardness of 188 ± 4 kg/mm^2 decreased gradually to 113 ± 14 kg/mm^2 after 350 h at 298 K (Fig. 1). Intriguingly, the cryo-SPD samples generated at the higher strain rate of 10^3/s possessed an initial hardness of 178 ± 5 kg/mm^2 that remained stable well beyond 350 h at 298 K, at variance with the usual notion of instability in materials created by low temperature deformation. For reference, the hardness of the

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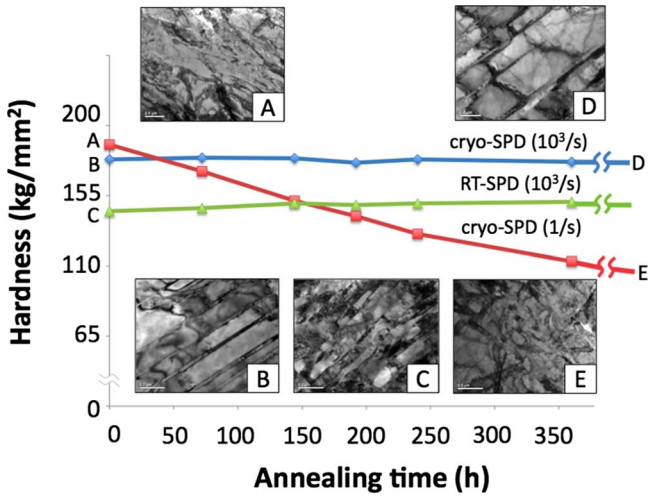

FIG. 1. (Color online) Variation in hardness with annealing time at 298 K for the RT- and the cryo-SPD samples created at 1/s and $10^3/s$. Also shown are the microstructures immediately after the SPD (<1 h) (A, B, C) and after 1460 h (D, E) of annealing. Inset A—sporadic twinning (cryo-SPD, 1/s), inset B—uniform dense twinning (cryo-SPD, $10^3/s$), inset C—absence of twinning (RT-SPD, $10^3/s$), inset D—dense twinning (cryo-SPD, $10^3/s$), and inset E—absence of twinning (cryo-SPD, 1/s).

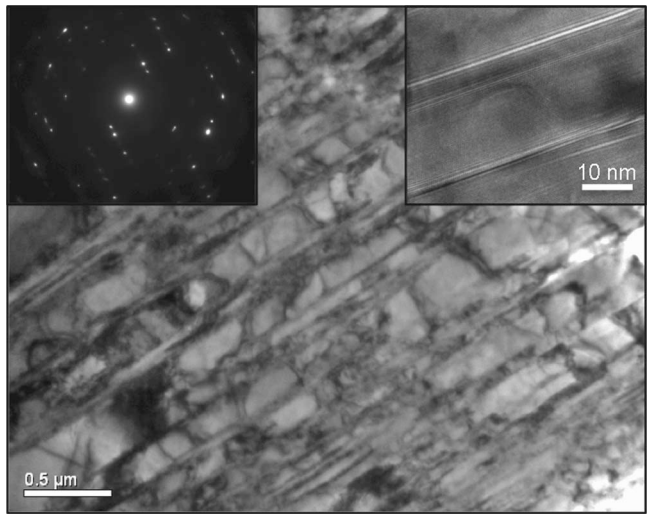

FIG. 3. TEM micrographs of copper created by the high-strain rate cryo-SPD showing a uniform nanotwinned region superimposed onto a nanostructured region. Top right inset shows ⟨001⟩ HREM micrograph of the copper. SAD pattern (inset top left) exhibits twin reflections.

copper after RT-SPD at 1/s and $10^3/s$ was stable at 149 ± 2 and 150 ± 4 kg/mm^2, respectively.

To understand the thermal stability characteristics of the samples, the microstructures were characterized shortly after the deformation and after extended periods at 298 K. The RT-SPD at both strain rates resulted in a microstructure devoid of twin interfaces, consistent with prior observations. At the lower strain rate, the cryo-SPD resulted in a nanostructured copper with a mix of heavily dislocated grains and subgrains and regions of sporadic twinning (Fig. 2). The selected-area diffraction (SAD) pattern (inset) confirms these observations, with twin reflections directly observed. While similar nanoscale grain and subgrain structures were generated by the cryo-SPD at the higher strain rate, the unique feature of this microstructure was a uniform very fine distribution of twin lamellae that was additionally introduced among the nanostructures (Fig. 3). HREM enabled direct observation of the TBs, seen in the inset to be clean, dislocation-free, and coherent with approximately 20 nm spacing. The twin densities in the microstructures of the low and high strain rate cryo-SPD samples were estimated to be 25% and 60%, respectively, using a point counting method.[17] When the cryo-SPD microstructures were examined after 1460 h at 298 K, the low strain rate sample was distinctively coarser and devoid of twins (Fig. 1). In contrast, the high strain rate sample was seen to retain the uniform twinning, with twins intersecting the retained grain or subgrain boundaries (Fig. 4). The retention of these defect structures in the form of intersecting networks with the twins is indicative of the stabilizing effect of the dense twin distribution.

The enhanced thermal stability of the more heavily twinned microstructure can be understood by considering the role of TBs in reducing the migration rate of GBs and TJs; minimization of either promotes stability by lowering the overall coarsening rate. Regarding GB migration, the $\Sigma 3$ coherent TB is well known to be immobile in response to thermal agitation[3] due to the restricted diffusion of impurities imposed by the high order in the boundary plane.[18] The sta-

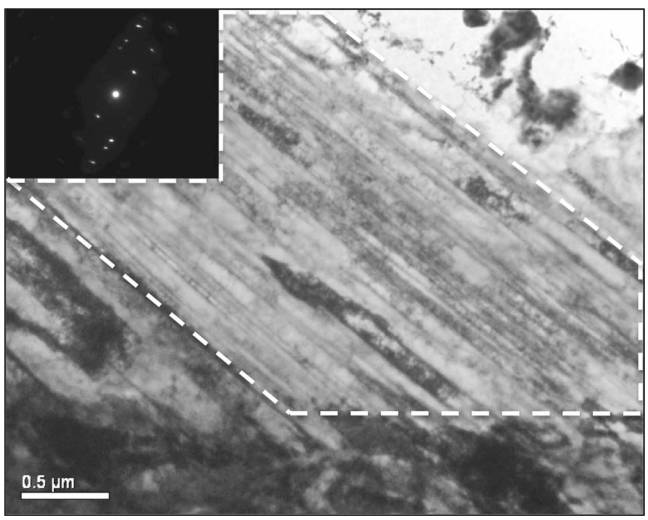

FIG. 2. TEM micrograph of copper created by cryo-SPD at 1/s showing discrete nanostructured regions and a nanotwinned region (demarcated by dashed line). SAD pattern (inset) confirms the nanotwinning.

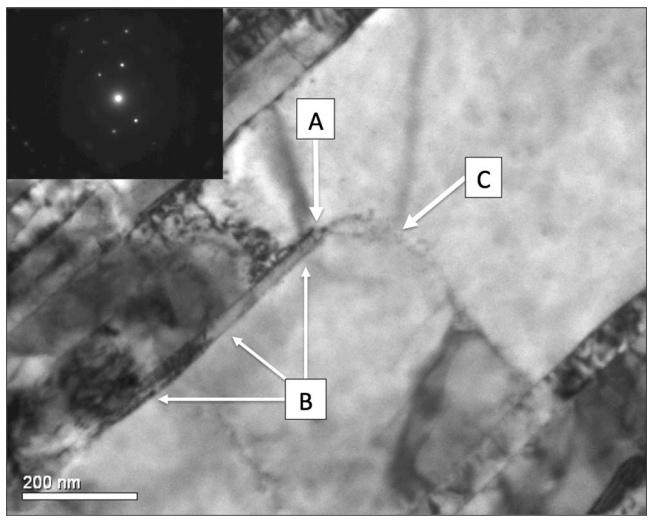

FIG. 4. Intersection (a) of a deformation twin (b) with a growing subgrain boundary (c) in the high strain rate cryo-SPD sample after 1460 h of annealing.

bility observed in the high strain rate cryo-SPD sample may then at least partially be attributed to the high density of sessile $\Sigma 3$ coherent TBs. However, the GB migration rate does not entirely describe growth kinetics, as TJs also hinder boundary migration due to their finite mobility. This is particularly relevant to microstructures incorporating twinned interfaces, as TJs incorporating $\Sigma 3$ coherent TBs have been observed to stabilize thermally activated GB motion in microcrystalline systems.[19,20] We now consider the mechanisms by which TJs can inhibit GB migration in the context of the nanotwinned copper.

An obvious framework to describe the stabilizing effect of TJs is the curvature-driven boundary migration model of Gottstein and Shvindlerman.[9–12] In this model, drag is generally facilitated by the low TJ migration rates that are associated with highly nonequilibrium dihedral boundary configurations. Intriguingly, direct observations and MD simulations of bicrystal growth have shown that such nonequilibrium conditions are more prevalent in TJs comprised of high-CSL boundaries.[10,12] While a mechanistic explanation of this has yet to be developed, the results suggest that high-CSL junctions are more likely to exhibit TJ drag. When also taking into account the microstructural observations in Fig. 4, this may prompt the inference that TJ drag, as prescribed by this framework, is operative in the current study. However, this conclusion is somewhat tenuous as anisotropic boundary systems, specifically those incorporating $\Sigma 3$ coherent twins, are able to adopt a range of equilibrium dihedral arrangements that act to suppress boundary curvature.[21,22] Considering that GB curvature is a key feature of this model, its applicability to twinned microstructures is then uncertain.

A more plausible explanation for TJ drag in nanotwinned systems is to be found in atomistic theories of boundary migration. These more "unconventional" explanations of drag are based on a renewed consideration of the role of TJs in GB migration by ledge growth[23] and GB dislocation accommodation.[24,25] With regard to the former, recent *in situ* observations of GB migration by kink motion and ledge growth in nanotwinned copper have indicated that kink motion is stagnated at TB-GB TJs due to a low nucleation rate of kinks and ledges at the TJ.[13] The more compact atomic arrangement of the $\Sigma 3$ coherent twin TJ presents a significant energy barrier to kink nucleation, whereas open boundary and junction structures can be envisaged to have a smaller barrier. Thus, considering the high density of coherent twin TJs in the heavily nanotwinned copper, the observed stability could certainly be a consequence of low kink nucleation rates that hinder thermally activated GB motion. While this mechanism presents the most plausible explanation for the TJ drag in the present study, it is worthwhile to also briefly consider the role of TJs in extrinsic grain boundary dislocation (EGBD) accommodation. Generally, the loss of EGBDs results in GB migration and grain growth by the coalescence of neighboring grains during grain/subgrain rotation.[24] The rate-controlling mechanism for boundary migration in this regard is GB dislocation climb, which is linearly dependent on the vacancy flux at the TJ.[25] Consequently, TJs with low diffusivity can be envisaged to have a stabilizing effect on GBs by limiting the vacancy flux needed to drive boundary migration. As the $\Sigma 3$ coherent TB is a rather poor diffusion path,[18] it is entirely probable that vacancy diffusion is arrested at TB-GB TJs, thereby providing an alternate route by which the TJs in nanotwinned materials can stabilize boundary migration. Ongoing and planned *in situ* HREM will likely reveal which, if any, of these TJ drag mechanisms are active and dominant in the nanotwinned copper.

Regardless of the exact nature of the underlying mechanisms, our observations have physically linked mechanical stability in nanostructured copper to twin density. When a high density of twins intersects GBs, the microstructure may inevitably be kinematically constrained by the low migration rates of the $\Sigma 3$ coherent TBs and/or their TJs. While the relative contributions of these factors to coarsening kinetics has not yet been isolated, the use of sessile TBs to stabilize GB motion suggests an important stabilization route for nanostructured metals that does not require second-phase particles or appreciable solute content. This is especially interesting in light of recent investigations that found heavily nanotwinned structures to have special properties, e.g., high ductility and superior strength,[26,27] presenting exciting opportunities to combine ductility with stability and strength.

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