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Fivefold twin formation during annealing of nanocrystalline Cu

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Contrary to the common belief that many-fold twins in nanophase materials are due to the action of significant external stresses, we report molecular dynamics simulations of 5 nm grain size Cu samples annealed at 800 K showing the formation of fivefold twins with no external pressure. The structure of the many-fold twins is remarkably similar to those we have found to occur under uniaxial shock loading in nanocrystalline NiW. The formation mechanism of the many-fold twins is discussed.

Keywords: Molecular dynamics; Nanocrystalline materials; Twinning

Nanocrystalline (nc) materials are being intensively studied in part due to their potential in applications requiring high strength. This strength is directly related to the unique plastic behaviour of nc metals. From both experiments [1] and molecular dynamics simulations [2–4], there is strong evidence that many nc materials deform by emitting partial dislocations from grain boundaries (GBs) which are absorbed in the opposing GBs. These mechanisms based on partial dislocations might then lead to twinning, which in fact has been observed in nc materials that at the coarser microscale do not twin [5].

Multi-twin junctions have been seen in electrodeposited Ni [6] and NiMn [7]. Regarding nanocrystals, they have been observed in ball-milled nc [8] and high-pressure torsion nc materials [9–11]. Recently Liao et al. reported the observation of fivefold deformation twinning in nc Cu (10–20 nm) at room temperature and at low strain rates, under high-pressure torsion [10]. Their work strongly suggests that partial dislocation emission is responsible for twinning, and confirms, as stated in numerous other works, that the Hall–Petch effect observed for micron-sized grains seems to break down at the nanoscale. A mechanism for star twin formation by sequential twinning via emission of Shockley partials from neighboring GBs was later proposed [11]. Since the angle between <1 1 1> planes is ~70.5° in a face-centered cubic (fcc) metal and a fivefold twin leaves a gap of ~7.3°, these authors propose that such a gap could be accommodated by elastic strain. The two key ingredients that are identified as essential for star twin formation are (a) large shear stress to drive multiple partial emissions from GBs and (b) variation in stress orientation such that several sets of partials with different orientations can sequentially be emitted. Both ball milling and high-pressure torsion processing provide such conditions. Correspondingly, it was first claimed that molecular dynamics (MD) simulations, generally carried out with uniaxial stress conditions, would not lead to many-fold twins [11,12]. More recently, Cao and Wei [13] reported the formation of fivefold twins in MD simulations under tensile loading at a strain rate of $10^9\ s^{-1}$.

In this work, we report on relatively long MD simulations of grain growth at zero external pressure, and high temperature to accelerate the dynamics, where we observe star twin formation. Our sample is created with a Voronoi construction scheme and contains 15 grains (approximately 500,000 atoms), with a mean grain size of 5 nm. We used the Voter–Chen Cu embedded-atom method (EAM) potential [14], which predicts a stacking fault energy [15] of 37 mJ m^{-2}. We first relaxed the as-created nanostructure at $T = 300$ K and $p = 0$ bar for 30 ps; then raised the temperature to 800 K at zero pressure for 0.5 ns. The details of the induced grain growth and formation of regular annealing twins have been discussed elsewhere [16]. Here, we concentrate on the observation and mechanisms of formation of many-fold twins such as the one shown in Figure 1. This figure displays a time sequence detailing the process of formation of a fivefold twin. The centrosymmetry parameter [17] is used to identify twins and GB regions. The observed

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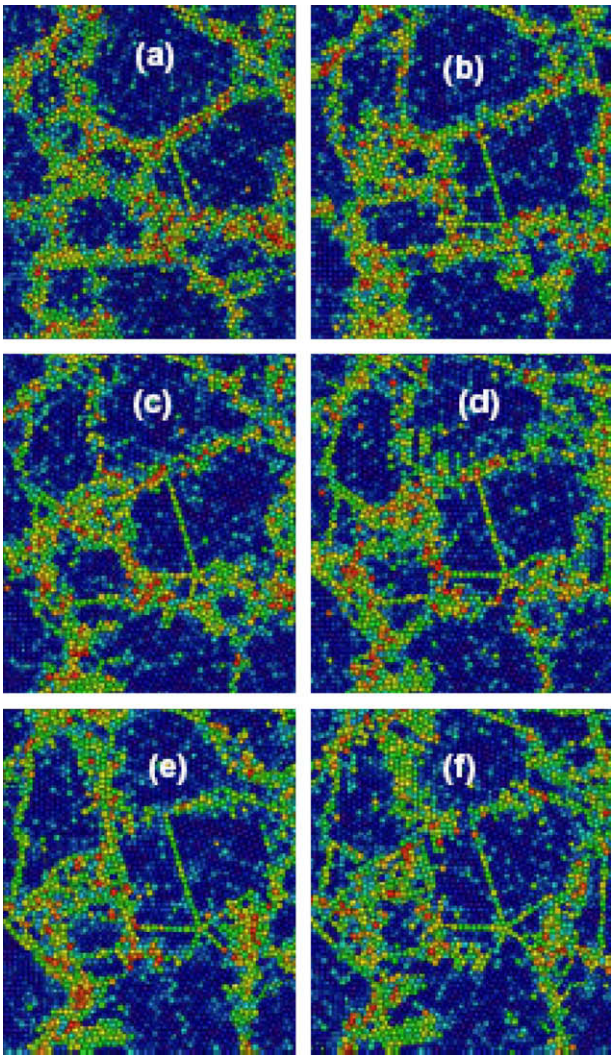

Figure 1. (a)–(f) Time sequence showing the formation of the fivefold twin (30, 90, 150, 210, 420 and 450 ps). Centrosymmetry parameter color scale to distinguish perfect fcc from defective material.

evolution matches the proposed mechanism of Zhu and Liao [12]. The sequential emission of Shockley partials creates various twins from sites along the GB. The dislocations travel across the grains to neighboring GBs. The various twins constituting the fivefold configuration appear sequentially in time and in a counterclockwise order in our example. Note that the complete formation and stabilization of the fivefold twin takes ~0.2–0.4 ns at the relatively high temperature of 800 K. Figure 2 shows the corresponding angles of the twin boundaries. The ideal twin angle of ~70.5 would leave a gap when closing the 360°; as expected, this gap produces large elastic strains, as suggested by Zhu et al. [12]. It is also interesting to note that by the end of the process a complete region of GB has disappeared. The nanometer scale in the grains here is very important in the viability of this mechanism since for larger grains the elastic strains necessary to close this gap would be much larger. As a matter of fact, regular twins are indeed known to result from standard annealing treatments in fcc materials and are known as annealing twins [18].

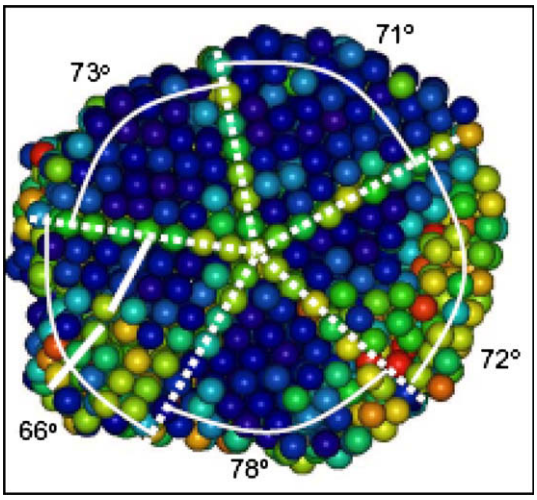

Figure 2. Close up of the frame in Figure 1f, showing the twin angles. The thick solid lines show one example of strained planes, with a misorientation of 12° to accommodate the fivefold twin.

Zhu et al. proposed that the trigger to form the many-fold twin is a very large stress [11,12]. What our results show is that the large stress is already present in the sample due to its nanoscale GB structure, without the necessity of an external contribution. It is this internal stress that drives the fast grain growth observed in nc materials even at room temperature.

A key observation extracted from our simulations of nanocrystals is that there is no need for a variation of the direction of the external stress, nor external stress at all, as previously proposed; internal stress in nanophase materials is so high that it suffices to activate this mechanism. A simple estimate of the stress, σ, inside a nanograin gives $\sigma \sim 2\gamma/d$, where γ is the GB surface energy and d is the grain size. Using $\gamma = 1\ \mathrm{J\ m^{-2}}$ and $d = 5$ nm, one obtains a GB-induced stress of ~0.4 GPa, enough to set dislocations in motion in this material.

The internal local stresses at particular points in the GB can be much larger than the estimate above, activating the Shockley partials creation mechanisms. Figure 3 shows the local stresses in the region where the fivefold twin appears; stress localization in the boundary can reach several GPa [19]. The GB structures in our samples have been fully relaxed and annealed, indicating that these high local stresses are an intrinsic feature of the GBs and are not an artifact of the way the sample is created. The total stress on the boundary is a result of the combination of these high local compressive and tensile loadings and is overall balanced out. Note that there is a clear correlation between the relatively large centrosymmetry parameter and high local stress. High local stresses are also observed in MD simulations using uniaxial loading, explaining the observation by Cao and Wei of many-fold twin formation in simulations under uniaxial external stress [13]. We note that the region of highest local stress in the left of Figure 3 is exactly where the center of the many-fold twin develops.

To confirm that uniaxial loading can actually lead to formation of many-fold twins and to compare the detailed structure of these twins to those found in our

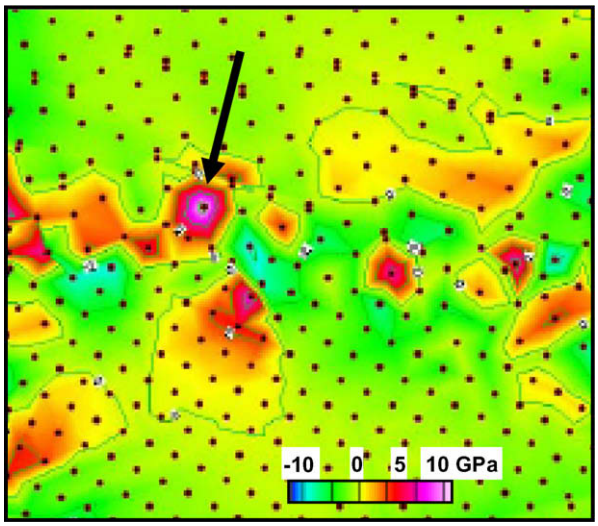

Figure 3. Shear stress calculated for our nc sample at 25 ps, before the first twin formation. The global stress was zero, but the local stress at the GBs was immense.

annealing simulations, we have carried out planar shock-loading experiments, which provide an alternative way to reach very high shear stress levels in a material. Shock waves typically involve uniaxial loading at very high strain rates (>107 s-1), which leads to plastic deformation and twinning [20]. We note that behind the shock front a nearly steady-state region is reached: the pressure is roughly hydrostatic and a considerable shear stress (the flow stress) is maintained during loading, inducing a strain rate much lower than at the shock front. This large shear stress applied for such "long" times is what would make multi-fold twinning possible in nc samples. MD simulations of shock loading in nc metals [21] capture the behavior of the flow stress and show single twin formation, but because they last 30–60 ps, they are not expected to show many-fold twin formation which takes ~200–400 ps. Here, we present experimental evidence of many-fold twins in recovered laser-shocked samples, as shown in Figure 4 for a four-fold twin. Loading was carried out at room temperature as previously described [22]. The loading pressure was estimated to be ~20 GPa at the surface, decreasing as the wave moves into the sample. In our MD simulations of shocks, this loading pressure induces a shear stress of up to several GPa. The sample was nc $Ni_{87}W_{13}$, with grain sizes of 5–30 nm, as described in Ref. [23]. The stacking fault energy of NiW is expected to be much lower than that of pure Ni [24], with a value close to the one in our simulations. Transmission electron microscopy samples were obtained 150 μm below the shock surface. The pre-shocked sample displays multiple growth twins that have a relatively large width of several nm, but no many-fold twins were seen in the multiple pre-shocked samples we examined. Note that the many-fold twin in Figure 4 shares many similarities with the one in Figure 1, suggesting that a similar mechanism is at work, independently of the source of high local stress.

In summary, here we present the observation of five-fold twins in atomistic simulations of annealing with zero applied stress. During these simulations the local shear stresses at some GB locations can reach up to several GPa and induce multiple emission of partial dislocations and therefore twin formation. Formation of multiple twins is accomplished in a multi-junction of GBs after ~0.4 ns at 800 K. Large local shear stress can also be produced by uniaxial shock loading, and we find similar many-fold twins in samples recovered from shock experiments for nc NiW with a grain size of ~5–30 nm and a peak pressure of 20 GPa. We conclude that the formation of star twins is a natural process in nanophase materials, where the small scale provides both the mechanisms to accommodate the closure gap via elastic/plastic distortion, and the high stresses needed for the emission of twins.

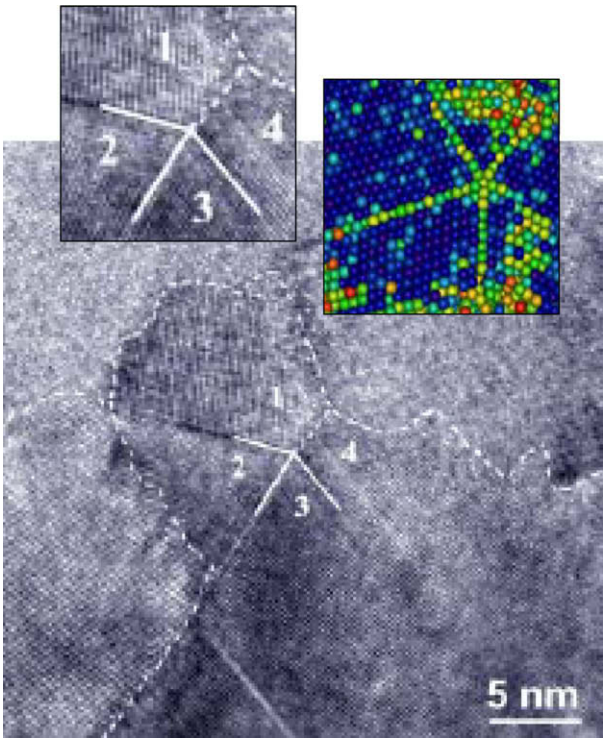

Figure 4. High-resolution transmission electron microscopy image of many-fold twin formation in nc NiW. Notice the similarities with Figure 1. The solid and dashed lines correspond to twin boundaries and GBs, respectively.

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