

Do Twin Boundaries Always Strengthen Metal Nanowires?

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Abstract It has been widely reported that twin boundaries strengthen nanowires regardless of their morphology—that is, the strength of nanowires goes up as twin spacing goes down. This article shows that twin boundaries do not always strengthen nanowires. Using classical molecular dynamics simulations, the authors show that whether twin boundaries strengthen nanowires depends on the necessary stress for dislocation nucleation, which in turn depends on surface morphologies. When nanowires are circular cylindrical, the necessary stress of dislocation nucleation is high and the presence of twin boundaries lowers this stress; twin boundaries soften nanowires. In contrast, when nanowires are square cylindrical, the necessary stress of dislocation nucleation is low, and a higher stress is required for dislocations to penetrate twin boundaries; they strengthen nanowires.

Keywords Nanowire · Twin · Strengthening · Dislocation · Simulation

Introduction

Metallic nanowires [1] have been a focus of concerted efforts in last decade. Being sensitive to physical stimuli such as force and electricity and being capable of operating under high frequencies, metallic nanowires have found applications in nanoelectromechanical systems [2]. Metallic nanowires are also useful in scanning tunneling microscope (STM) and atomic force microscope (AFM) for

nanoscale tip–sample interactions [3]. Common in these applications are mechanical deformations of the nanowires, which affect their functionalities. Therefore, it is important to understand how nanowires respond to mechanical loading to realize their future applications in nanotechnology. Because of the large surface area, metallic nanowires exhibit a range of unique mechanical properties, including size-dependent elastic moduli [4], size-dependent yield strength [5], tension–compression asymmetry of yield strength [6], and shape memory [7, 8]. Twin boundaries, as high symmetry planar defects, form during both synthesis [9, 10] and mechanical deformation [11]. The presence of twin boundaries further expands the range of unique properties.

Twin boundaries interrupt glide of dislocations. For example, dislocations usually glide on {111} planes in face-centered-cubic (FCC) metals such as Cu. On encountering a twin boundary in a $\langle 111 \rangle$ nanowire, a dislocation may glide on {100} plane after penetrating the twin boundaries [12]. The penetration requires a high stress, leading to increased stress for glide; that is, twin boundaries can strengthen nanowires. Experimental investigations show that fivefold twin boundaries in silver nanowires lead to increase of strength [13]. In a somewhat different configuration—nano-twinned thin film—the twin boundaries demonstrate similar strengthening effects [14]. Therefore, it is not surprising when molecular dynamics simulations on metallic nanowires, such as Cu [15] and Au [16], also show such strengthening. Because the simulation results appear to agree with known experiments, one would think that the simulation results are true. Are they really true? It is interesting to note that the Cu nanowires have square cross-sections, while Au nanowires have circular cross-sections. In contradiction to Ref. [16], another molecular dynamics simulation on Au [17] shows that the

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existence of planar defects such as stacking faults or twin boundaries may slightly soften nanowires.

To address this contradiction, we perform molecular dynamics simulations on nano-twinned FCC copper nanowires with both square and circular cross-sections. The results show that twin boundaries do not always strengthen nanowires. Further, we show that whether twin boundaries strengthen nanowires depends on the necessary stress required for dislocation nucleation, which in turn depends on surface morphologies. In addition, we demonstrate that the contradiction of literature reports on strengthening is the result of artificial boundary conditions in the simulations.

Simulation Method

We describe the simulation method in terms of interatomic potential, setup of simulation cells, application of strain, and defect identification. The Mishin potential has been calibrated according to ab initio results of stacking fault and twin formation energies, and is therefore our choice for this study [18]. As shown in Fig. 1a, a simulation cell contains a $\langle 111 \rangle$ nanowire that has either a circular or a square cross-section. For the case of square cross-section, the side surfaces are of $\{110\}$ and $\{112\}$ to minimize their energy. The axial dimension is $L = 31$ nm, and periodic boundary condition applies along this direction. The lateral dimension h —side length for square cross-section or diameter for circular cross-section—is 8 nm. The twin spacing d varies from 15.75 to 1.05 nm. Before applying strain, the simulation cells are first relaxed using the conjugate gradient method [19, 20] and then equilibrated at 300 K using the Nose–Hoover thermostat [21, 22] for 5,000 integration steps; the integration step is 5 fs. It takes 1,000 steps to reach 300 K. In applying strain, the axial dimension is uniformly decreased by 0.1% of the original length every 2,500 steps. The corresponding (engineering) strain rate is 8×10^7 /s. After each strain application, the average virial stress is calculated for the last 500 steps. To identify dislocations, we use the bond pair analysis [23] to classify atoms into three categories: those that are in FCC structure, those in hexagonal-close-packed (HCP) structure, and others. Twin boundaries are outlined by one layer of HCP atoms, stacking fault by two layers of HCP atoms, and dislocations by the “others”.

Results and Discussions

In presenting the results, we first look at the overall behavior and then examine the atomic mechanism in details. Shown in Fig. 1b is the average virial stress along

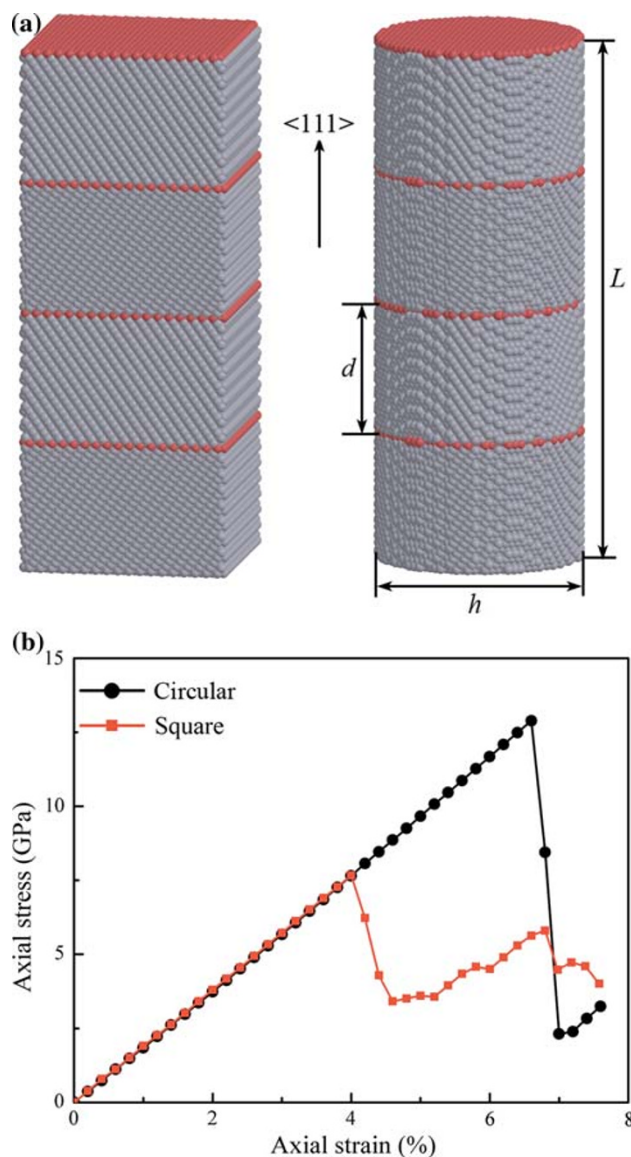


Fig. 1 (Color online) **a** Schematic of twinned nanowires with square (left) and circular (right) cross-sections; gray spheres represent atoms in FCC structure and red spheres those in HCP structure. **b** Stress-strain curve for nanowires with twin spacing of 5.25 nm

the nanowire axis as a function of engineering strain. The stress first linearly increases with strain before a sudden drop, which indicates yielding of nanowires. The Young’s modulus estimated from the initial proportional part is about 190 GPa, in agreement with results in the literature [15]. The stress at yielding σ_y is the maximum stress in the figure. The stress at which a dislocation nucleates σ_n is smaller than the yield strength and the dislocation nucleation is identifiable through the bond pair analysis. Shown in Fig. 2 are σ_y and σ_n as functions of twin spacing d . Indeed, twins do not always strengthen nanowires. For the nanowires of square cross-sections, the σ_y for twinned nanowires is larger than that of the non-twinned FCC

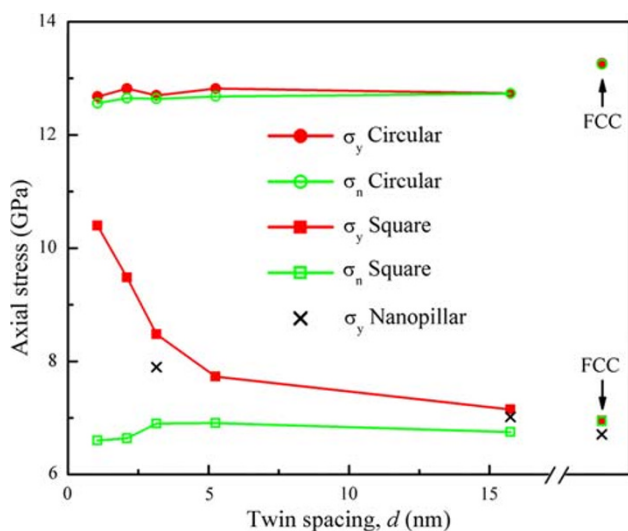


Fig. 2 (Color Online) Yield stress σ_y and nucleation stress σ_n of nanowires with square and circular cross-sections, as functions of twin spacing

nanowire and it increases as twin spacing decreases; this is in agreement with previous reports [15, 16]. In contrast, the σ_y for twinned nanowires of circular cross-sections is smaller than that of the non-twinned FCC nanowire, as reported in literature [17], and it varies little with twin spacing except some fluctuations. For both types of nanowires, the stress for dislocation nucleation σ_n varies little with twin spacing; and it is much higher for nanowires with circular cross-sections than with square cross-sections. We thus postulate that strengthening or softening depends on the necessary stress for dislocation nucleation. The following analyses of stress, magnitude of atomic vibration, and dislocation dynamics support this postulation.

First, we analyze the necessary stress for dislocation nucleation at surfaces versus that for dislocation penetration of twin boundaries, the latter being stress for yielding. According to Zhu et al. [24], dislocation nucleation stress or activation volume depends on surface conditions. With square cross-sections, the stress for dislocation nucleation is low, and additional stress is necessary for dislocations to penetrate twin boundaries. Therefore, the presence of twin boundaries leads to increase of yield stress, as shown in Fig. 2. With circular cross-sections, the stress for dislocation nucleation is high, and this stress suffices for yielding also. Therefore the presence of twin boundaries leads no increase of yield stress. In addition, this presence introduces intersections of twin boundaries and surfaces and thereby reduces the necessary stress for dislocation nucleation; this necessary stress is the highest for non-twinned nanowire.

By searching for evidences that support our postulation, we determine the vibration amplitude of each atom [25], averaged over 20,000 integration steps at 300 K and no

external strain. According to Ref. [25] and [26], the larger vibration amplitude corresponds to higher likelihood of dislocation nucleation. As shown in Fig. 3 for a square cross-section, atoms along the sharp edges have large amplitude of vibration (up to 0.121 nm), independent of their proximity to twin boundaries. In contrast, for a circular cross-section the largest amplitude of vibration is only 0.045 nm, which occurs near intersections of twin boundaries and surfaces. The differences in vibration amplitudes, and thereby differences in dislocation nucleation stresses, for circular and square cross-sections are in consistency with our postulation of strengthening conditions.

Searching for one more piece of evidence to our postulation, we have also examined the dislocation dynamics in the yielding process. With a square cross-section, a Shockley partial dislocation nucleates either away or near a twin boundary, from the sharp edges where the atoms have the largest vibration amplitude (Fig. 4a). Before it penetrates the twin boundary, the trailing partial dislocation also arrives to form a complete dislocation (Fig. 4b). The penetration occurs at a higher stress (or strain) (Fig. 4c). In comparison, the strain at nucleation is 3.5%, and that at penetration is 4.2%. In passing, we also note that a

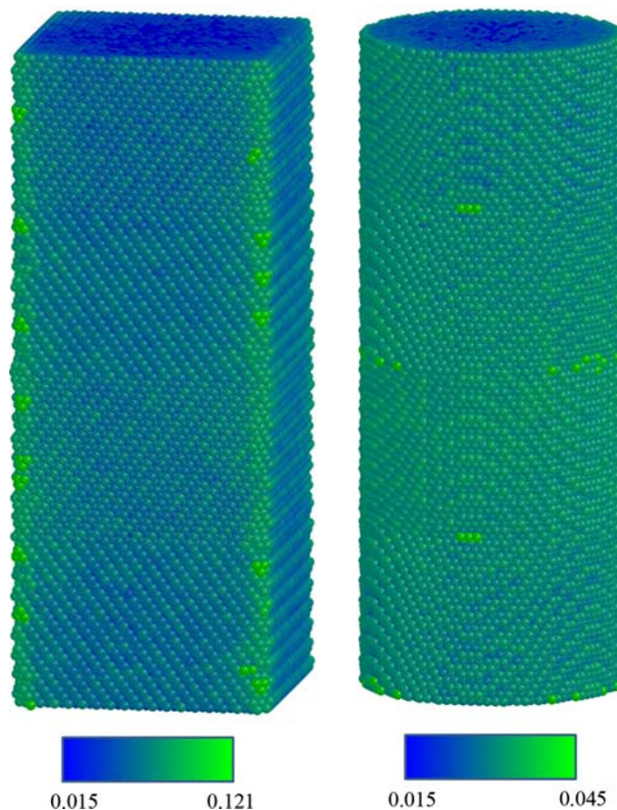


Fig. 3 (Color Online) Atomic vibration amplitude (in unit of nm) of nanowires with square (left) and circular (right) cross-sections; the twin spacing is 5.25 nm

Fig. 4 (Color Online) Atomic configurations of a nanowire with square cross-section under **a** 3.6%, **b** 4.0%, and **c** 4.2% compressive strain; the twin spacing is 5.25 nm. Red spheres represent atoms in HCP structure, and purple spheres other atoms; FCC atoms are not shown in the figure for clarity

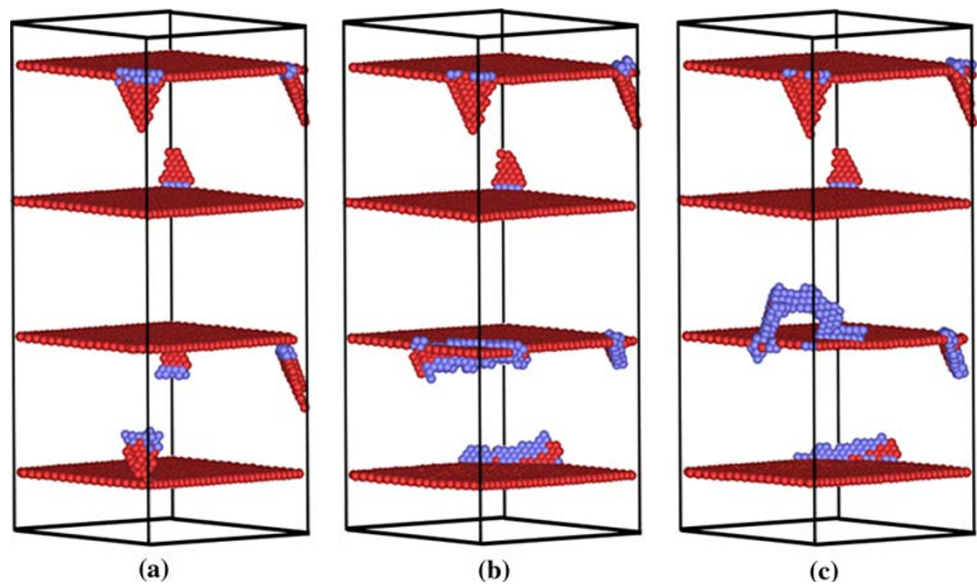
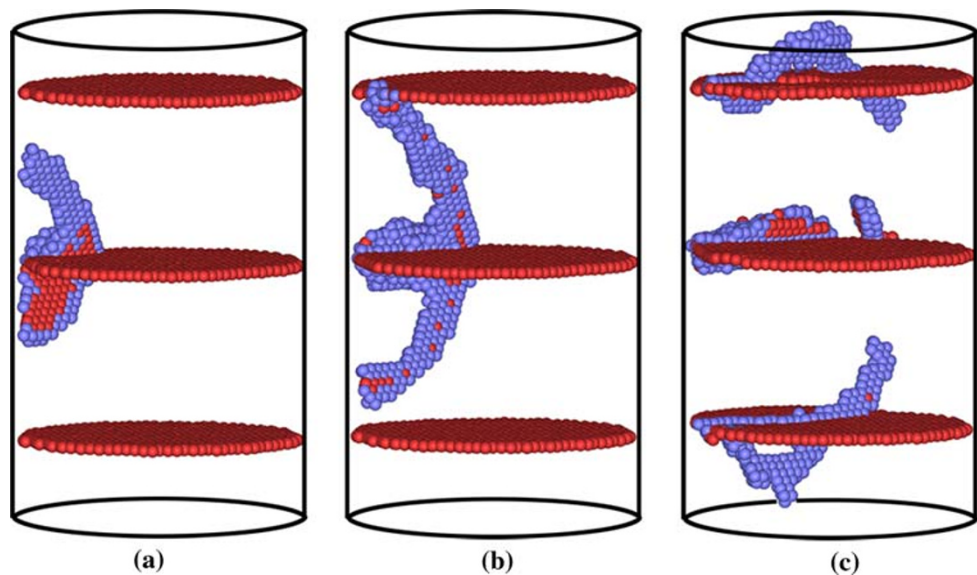


Fig. 5 (Color Online) Atomic configurations of a nanowire with circular cross-section under 6.6% compressive strain for **a** 1.0, **b** 2.0, and **c** 5.0 ps; the twin spacing is 5.25 nm. Red spheres represent atoms in HCP structure, and purple spheres other atoms; FCC atoms are not shown in the figure for clarity



Shockley partial dislocation does not propagate further through the twin boundary, when its trailing dislocation does not catch up because the stacking fault is not wide enough [27] (top section of Fig. 4a–c). With a circular cross-section, two dislocations nucleated near a twin boundary (Fig. 5a). These two dislocations propagate toward nearby twin boundaries (Fig. 5b). They penetrate the twin boundaries without additional stress (Fig. 5c). In comparison, the strain at nucleation is 6.6%, and that at penetration is the same.

It is worth reconciling our results with previous reports. In contrast to our results, previous reports show that twin boundaries strengthen nanowires [16], even with circular cross-sections. In Ref. [16], fixed boundary condition is applied, which may cause stress concentration and make

dislocation nucleation artificially easier. When the nucleation is easier, stress for dislocation penetration of twin boundaries becomes dependent on twin spacing. To confirm this point, we have used the same boundary condition as in Ref. [16], and indeed have found the artificial strengthening effects (as shown by the cross symbols (labeled as nanopillars) in Fig. 2).

Conclusion

In conclusion, molecular dynamics simulations on nano-twin copper nanowires reveal that twin boundaries do not always strengthen metallic nanowires. For nanowires with square cross-sections, strength increases as twin

spacing decreases. In contrast, strength varies little with twin spacing for nanowires with circular cross-sections; the strength with a twin boundaries is slightly lower than that in single crystals. Whether twin boundaries strengthening metallic nanowires depends on the necessary stress required for dislocation nucleation, which in turn depends on the surface morphology of the nanowires. For nanowires with square cross-sections, the existence of sharp edges makes dislocation nucleation feasible at a lower stress than that needed for dislocation penetration through the twin boundaries, leading to a twin-spacing dependence of strength. For nanowires with circular cross-sections, the necessary stress for dislocation nucleation is high, so penetration requires no additional increase of stress. At the same time, the presence of intersections of twin boundaries and surfaces facilitates dislocation nucleation, leading to slight softening because twin boundaries are present.

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