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Five-fold twin and surface groove-induced abnormal size- and temperature-dependent yielding in Ag nanowires

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Molecular dynamics simulations are used to investigate the influence of pre-existing five-fold twins and surface grooves on the yielding of Ag nanowires under uniaxial deformation. While a five-fold twin together with a surface groove generally lead to strengthening in Ag nanowires under tension, abnormal weakening effects are observed under compression at low temperatures when the nanowire diameter is increased. The peculiar size and temperature effects can be attributed to the toggling of dislocation nucleation between various preferential sites under different loading conditions.

Keywords: Molecular dynamics; Nanowires; Five-fold twin; Surface groove

Recent state-of-the-art in situ nanomechanical tests [1,2] and molecular dynamics (MD) simulations [3] have been largely devoted to the mechanical characterization of one-dimensional nanostructures. One ultimate goal is to achieve a predictive understanding of the yielding mechanisms in metal nanowires (NWs) relating to their sample sizes, surface features and internal microstructural defects. Five-fold-twinned (FT) crystal structures [2,4–7] are amongst the most widely investigated structural defects by both MD [8–12] and experimental studies [2,4–7], yet the detailed yielding mechanisms in FT NWs have not been fully elucidated. One long-standing puzzle is that, based on lattice crystallography, the theoretical angle between adjacent {1 1 1} twin boundaries (TBs) in FT NWs is 70.53°, which will result in substantial internal strain in the NWs, or otherwise generate a 7.53° angular deficiency [13]. Such angular deficiency, however, has rarely been observed experimentally, though very recently Zhang et al. [7] found surface re-entrant grooves in FT Ag NWs.

It is well known from classical mechanics that structural defects, such as microcracks and sharp edges, are stress concentrations that lead to early failure of engineering materials. For example, under uniaxial tension and compression [14,15], single-crystalline (SC) fcc NWs will fail by nucleation of Shockley partial dislocations from the free surfaces. However, by introducing internal structural defects such as parallel coherent TBs and surface facets in fcc NWs [3], the yielding mechanisms can change from surface-dominated to site-specific dislocation nucleation. It is thus expected that FT structures and surface grooves in fcc metal NWs may also serve as dislocation nucleation sites and potentially affect their mechanical properties when deformed.

The aim of this work is to elucidate the yielding processes of FT Ag NWs with re-entrant surface grooves subjected to uniaxial tensile and compressive deformation by MD simulations. A comparative study of the atomistic insight into the yielding of SC Ag NW, FT Ag NW and FT Ag NW with surface grooves is presented.

The simulations were performed using LAMMPS [16] with a timestep of 5 fs. The interatomic interactions were characterized by an embedded-atom method potential developed for Ag [17]. All Ag NWs were cylindrical with a length of 50 nm and oriented along the [1 1 0] direction (Fig. 1). Two different radii, R, equal to 5 and 10 nm, respectively, were simulated for each type of Ag NWs. Periodic boundary conditions were applied along the NW axis while other directions were kept free. According to Zhang et al. [7], a gap (surface groove)

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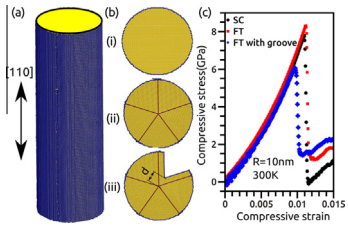

Figure 1. (a) Schematic model of Ag nanowire (NW) oriented along [1 1 0] direction. (b) Atomistic configuration of the cross-section of: (i) single-crystalline (SC) Ag NW; (ii) five-fold-twinned (FT) Ag NW; and (iii) FT Ag NW with surface groove (FT with groove). The groove size d is defined as the distance between the NW axis and groove edge. Atom colors correspond to local lattice orientation. (c) Representative compressive stress–strain curves of Ag NWs of radius $R = 10$ nm at 300 K.

with two {1 1 1} surfaces was constructed in the center of one grain of the five subunits (Fig. 1b). The two edge surfaces of the groove were parallel to the TBs and the groove size d was fixed at 2.5 nm. System temperatures ranging from 10 to 800 K were considered and a Nosé–Hoover thermostat was used for all simulations.

All NWs were initially relaxed for 100 ps under zero pressure under NPT. After that, uniaxial deformation was performed under NVT at a constant strain rate of $10^8\ s^{-1}$. The corresponding stress–strain curves in all Ag NWs showed a common sharp yielding phenomenon; an example is shown in Figure 1c for Ag NWs of $R = 10$ nm under compression at 300 K.

Under both tension and compression, the yield stress in this work was defined as the maximum stress on the stress–strain curves. Figure 2 is the plot of yield stress as a function of temperature for all NWs. It was first noted that the yield stresses were significantly higher under compression than under tension. This is consistent with past work reporting that under tension and compression, partial dislocations of different Schmid factors will be nucleated upon yielding [15]. Secondly, peculiar size effects were found in FT Ag NWs under compression. Size effects have been widely observed in one-dimensional nanostructures [1]. In particular, in situ tensile tests of pristine Cu nanopillars [1,18,19] confirmed that the sample size effects of "smaller is stronger" were intrinsic properties of metal NWs and did not rely on the pre-existing dislocations that may also lead to size-dependent plasticity in metal NWs, e.g. from "dislocation starvation" [1]. It was found from MD that the size-dependent yielding in pristine NWs was caused by

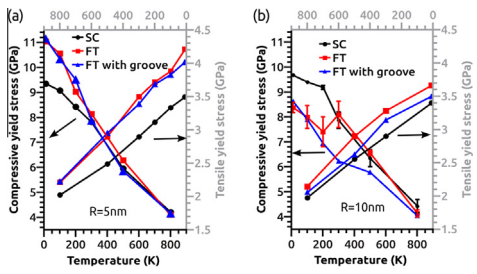

Figure 2. Plot of compressive and tensile yield stress as a function of temperature in various Ag NWs of (a) $R = 5$ nm and (b) $R = 10$ nm.

the change of internal stress when the NW diameter varied [15]. Due to the high surface-to-volume ratio, free-standing fcc metal NWs were generally in strong compressive state in order to balance the substantial surface tension, and the smaller the NW diameter, the stronger the compression of the interior of the NW [14,15]. As a result, the yield stress of SC NWs increased during uniaxial tension and decreased during uniaxial compression when the NW diameter decreased [15]. However, whereas the tensile yield stresses increased as the diameter of FT Ag NWs decreased, the compressive yield stresses also increased when the NW radius changed from 10 nm (Fig. 2b) to 5 nm (Fig. 2a). Such unusual size effects contradict the findings of previous studies regarding SC fcc NWs and should strongly correlate to the presence of FT structures.

Furthermore, it was surprising to find out that FT Ag NWs were stronger than SC Ag NWs of $R = 5$ nm under both tension and compression, e.g. at $T < 300$ K. By analyzing the initial stress state prior to any deformation at 10 K, it was found that the intrinsic interior compressive stress was higher in FT Ag NWs than in SC Ag NWs. It was thus natural to expect strengthening effects under tension but weakening effects under compression induced by five-fold TBs, which was contradictory to the observations in Figure 2a. In addition, it was shown that the surface groove had dramatically different effects on the yielding of FT Ag NWs when the NW size changed. For example, when $R = 5$ nm, the surface groove had only negligible effects (Fig. 2a). However, when $R = 10$ nm, the surface groove severely lowered the yield stress especially under compression, e.g. at 300 K, in comparison with FT Ag NWs with no surface groove (Fig. 2b).

The most striking finding from Figure 2, however, was the non-monotonic temperature dependence of yield stress in FT Ag NW under compression; an abnormal sharp drop in the compressive yield stress was observed when temperature changed from 300 to 200 K. This trend was unusual as it has been widely reported from past MD simulations that the lower the temperature, the higher the yield stress in NWs under uniaxial deformation [5,11,20,21]. Moreover, while FT Ag NWs were found to be significantly stronger than SC Ag NWs of $R = 5$ nm under compression at low temperatures, e.g. $T < 300$ K, the trend was inverted when the radius increased to $R = 10$ nm; the SC NW became the strongest among all the NWs simulated at $T < 300$ K under compression. To confirm such seemingly peculiar temperature-dependent compressive yielding behavior, three more independent simulations were carried out in both SC and FT Ag NWs of $R = 10$ nm. Although the yield stresses in FT Ag NWs showed a moderate scattering among different simulations, the overall trend remained unchanged.

In order to understand the complicated size- and temperature-dependent yielding phenomenon in Ag NWs, the atomistic configurations of each NW at the yield points were analyzed and summarized in Figure 3 (under tension) and Figure 4 (under compression), respectively. It was found that by varying the loading conditions, three different yielding modes can be toggled respectively under either compression or tension.

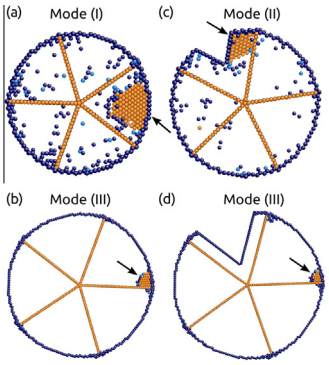

Figure 3. Different modes of yielding in Ag NWs under tension. (a) Surface-dominated dislocation nucleation and (b) site-specific dislocation nucleation from twin-surface intersection in five-fold-twinned Ag NWs; (c) surface groove dominated dislocation nucleation and (d) site-specific dislocation nucleation from twin–surface intersection in five-fold-twinned Ag NWs with surface groove. Atom colors correspond to local lattice structure and perfect fcc atoms have been removed for clarity. The dislocation nucleation sites at yield points are indicated by arrows.

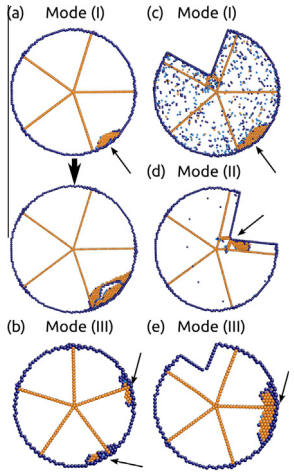

Figure 4. Different modes of yielding in Ag NWs under compression. (a) Surface-dominated dislocation nucleation followed by the emission of a second partial dislocation and (b) site-specific dislocation nucleation from twin–surface intersection in five-fold-twinned Ag NWs; (c) surface-dominated dislocation nucleation; (d) dislocation nucleation from surface groove; and (e) site-specific dislocation nucleation from twin–surface intersection in five-fold-twinned Ag NWs with surface groove. Atom colors correspond to local lattice structure and perfect fcc atoms have been removed for clarity. The dislocation nucleation sites are indicated by arrows.

Under uniaxial tension, mode I (Fig. 3a) refers to yielding via surface-dominated nucleation of Shockley partial dislocations. Mode II (Fig. 3c) refers to yielding via dislocation nucleation from the junction between the free surface and groove edge. Mode III (Fig. 3b and d), in contrast, refers to the yielding by dislocation nucleation at the junction between the free surface and TB. Site-specific dislocation nucleation at the intersection between free surface and TB has been previously reported in the yielding of fcc NWs containing parallel TBs under tension [22]. The tensile yielding modes under different loading conditions are summarized in Table 1.

Table 1. Yielding modes in Ag nanowires under uniaxial tension.

Tension				
Mode	Nucleation site	Nanowire type	R (nm)	T (K)
I	Free surface	SC	All	All
		FT	5	$\geqslant$300
II	Groove edge	FT with groove	5	All
			10	$\geqslant$300 K
III	Twin–surface junction	FT	5	<300 K
			10	All
		FT with groove	10	<300 K

It should be mentioned that only mode I yielding mechanism has been found by Gao et al. [13], who studied the tensile deformation of perfect FT Ag NW of diameter equal to 7.5 nm at T = 10 K by MD.

Under uniaxial compression, mode I (Fig. 4a and c) corresponds to yielding via surface nucleation of Shockley partial dislocations. However, it was found that prior to the yielding, partial dislocations can nucleate from the sharp edge of the surface groove in FT Ag NWs of $R = 10$ nm (Fig. 4c) without causing significant drop of the loading stress. Following the emission of the first partial dislocation, a second partial dislocation would follow and combine with the previous one to form a full dislocation, as shown in the subsequent frame of Figure 4a. This mechanism was consistent with past MD simulations of fcc NWs under uniaxial compression [15,23]. Mode II yielding (Fig. 4d), on the other hand, corresponds to surface nucleation of partial dislocations from the sharp edge of the surface groove. Lastly, mode III yielding (Fig. 4b and e) refers to site-specific dislocation nucleation from the junction between the TB and the free surface. The compressive yielding modes under different loading conditions are summarized in Table 2.

The peculiar size and temperature dependence of compressive yielding behavior in FT Ag NW as shown in Figure 2 can now be understood. For FT Ag NWs of $R = 5$ nm under compression at all temperatures, the yielding occurred via the same mechanisms of mode III (Fig. 4b, site-specific dislocation nucleation), therefore a monotonic change of compressive yield stress as a function of temperature was observed. In contrast, for FT Ag NWs of $R = 10$ nm under compression, as the temperature changed from 300 to 200 K, the yielding mechanisms changed from mode III (Fig. 4b, site-specific dislocation nucleation) to mode I (Fig. 4a, surface-dominated dislocation nucleation), causing the

Table 2. Yielding modes in Ag nanowires under uniaxial compression.

Compression				
Mode	Nucleation site	Nanowire type	R (nm)	T (K)
I	Free surface	SC	All	All
		FT	10	<300
		FT with groove	10	$\geqslant$500
II	Groove edge	FT with groove	10	$\leqslant$300
III	Twin-surface junction	FT	5	All
			10	$\geqslant$300
		FT with groove	5	All

yield stress to drop. Furthermore, the yielding mechanism in FT Ag NWs with a surface groove of $R = 5$ nm under compression was the same as that in FT Ag NWs with no surface groove (mode III), which explains why the compressive yield stresses in these two types of NWs were almost the same at all temperatures. Nevertheless, when the NW radius increased to $R = 10$ nm, the yielding in FT Ag NWs with surface groove at $T \leqslant 300$ K occurred via mode II (Fig. 4d, dislocation nucleation from the sharp groove edge). It thus required considerably lower external stress to nucleate dislocations than in SC Ag NWs because of the high stress concentration at the sharp groove edge. As a result, the compressive yield stresses were the highest in SC Ag NWs at temperatures lower than 300 K when $R = 10$ nm.

It is important to mention that the angular deficiency of FT structures can be compensated in various ways besides the formation of a surface groove. For example, possible effects from stacking faults (SFs) in FT Ag NWs have been studied by Gao et al. [13] and Cao and Wei [9]. It was found that while SF lowered the energy of the FT Ag NW, it had little effect on the yielding of FT Ag NWs. In addition, it has been reported in Ref. [10] that the FT structure in boron carbide NWs can be relaxed via the formation of a star-disclination core and a stress-relieving small-angle grain boundary (SAGB) in one of the sub-units augmented by a set of intersecting microtwins. Angular mismatch accommodated by multiple SAGBs was also observed in FT Si nanoparticles [24]. Furthermore, Gryaznov et al. [25] reported other types of channels of elastic relaxation in FT crystal structures, including origination of structural dislocations, origination of a negative disclination with a system of SFs in one of the tetrahedra, decomposition of the disclination into two others linked by a "disclinational" stacking fault, formation of a region without a disclination inside the FT structure, and shifting of the NW axis towards the periphery. A comprehensive comparison of the effects on the mechanical properties of FT Ag NWs among the aforementioned relaxation methods would be beyond the scope of this study and warrants a separate study. However, we have studied the disclination effects in FT Ag NWs by constructing a gap at the TB and varying the sizes of the surface groove. Firstly it was observed that the opening of 7.53° at the TB was unstable, gradually disappeared during the initial relaxation of the Ag NW and eventually formed a closed FT structure. It thus confirmed the experimental observations that an opening can only form in the middle of one sub-unit of the FT structure as shown in Figure 1b, which was similar to the structure of branched FT Si nanoparticles when the size increased [24]. Secondly, a relatively smaller surface groove ($d = 5$ nm, as defined in Fig. 1b(iii)) was constructed in Ag NW of $R = 10$ nm. It was found that the FT Ag NWs with different groove sizes would yield via the same mechanisms. Nevertheless, size effects from the surface groove were observed: the bigger the surface groove, the more relaxed the FT structure and the stronger the influence of the groove.

In summary, MD simulation of uniaxial deformation was performed to investigate the influence of five-fold TBs and surface grooves on the yielding of Ag NWs. It was found that the five-fold TBs and surface grooves can cause dramatically different temperature-dependent yielding behavior at different sample sizes. The seemingly peculiar size and temperature effects can be well explained by the toggling of different yielding modes, e.g. dislocation nucleation from different preferential sites, at different temperatures, sample sizes and loading conditions.

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