In situ atomic scale mechanical microscopy discovering the atomistic mechanisms of plasticity in nano-single crystals and grain rotation in polycrystalline metals

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\section*{1. Introduction}

A dynamic in situ atomic scale understanding of material deformation mechanisms under external stress and/or strain is important not only for materials scientists but also for physicists, metallurgists and others, and they are useful for developing new materials with controlled stability and easy processing [1,2]. Solving these problems has generally relied on theoretical models and molecular dynamics (MD) simulations [3-6], as direct experimentation has been difficult. Developing novel techniques for dynamic and in situ atomic scale elucidation of material deformation mechanisms under external stress and/or strain is necessary and urgent. Revolutionary Cs-corrected high resolution electron microscopy (HRTEM) technologies allow sub-angstrom scale direct observation [7-13]. With these and the recently developed in situ mechanical TEM-based microscopy techniques [14-23], the research field of in situ atomic scale experimental mechanics evaluation is emerging, and the opportunities are unprecedented.

In nano-sized single crystalline metallic materials, many important issues regarding the elastic-plastic transitions and the
plastic deformation mechanisms are unclear, and these properties are important in designing nano-electronic mechanical systems (NEMS) and micro-electronic mechanical systems (MEMS), as well as high-strength and high-ductility metals. In bulk face-centred cubic (FCC) metals, the plastic deformation is usually mediated by the slip of full dislocations, while deformation twins only occur under a high strain rate or low temperature conditions [24,25]. Because of this, deformation twinning has been rarely observed in FCC metals under regular deformation conditions [26,27]. When the size of these FCC metals decreases to the nanoscale, though, the mechanical behaviour may change. However, the atomic mechanisms that underlie these properties remain unclear.

For Pt polycrystalline metals, when the grain size (diameter \( G \)) is refined to the nanometre scale (\( G < 15 \) nm), grain boundary mediated plasticity may become active and even dominant, but many uncertainties exist. For example, when the intra-grain dislocation plasticity in nanocrystalline (NC) materials subsides, there is thus far no direct experimental evidence defining an alternative plasticity mechanism. Grain rotation, a well-known phenomenon in polycrystalline materials undergoing deformation at high temperatures [28,29], was proposed as a plastic deformation mechanism when the grain size is small [30,31], but there is no direct atomic-scale evidence on how the grain rotation accommodates the plasticity.

Here, using an in-lab developed deformation device, an in situ atomic-scale mechanical microscopy technique using a HRTEM and Cs-corrected HRTEM [7–13], the atomic-scale-time-resolved dynamic deformation processes of single and polycrystalline metals have been in situ recorded. We show (1) direct and quantitative evidence that when the single crystal size is below a certain value, approximately 100 nm, the full dislocation plastic deformation mode transitions to one of partial dislocations; (2) when these dislocation activities are suppressed in very small samples, 7.2% elasticity can be approached in tensile single crystalline Cu NWs; (3) for the nano-poly-crystalline case, we provide direct atomic-scale experimental evidence of the switching of the deformation mechanisms: at a critical \( d \) of \(< \) 6 nm, the classical intra-grain dislocation mechanism gives way to GB-mediated plasticity via grain rotation; and (4) the grain rotation is fully accounted for by the change in the density of dislocations in GBs. This GB dislocation mechanism dominates the low-temperature (room temperature) deformation in the absence of other diffusion and intragrain dislocation mechanisms.

2. Ultra-large elasticity of nano-metals

Conventional bulk crystalline metals normally yield at an elastic strain of only a fraction of 0.1%. This limit of the elastic zone is governed by the activation of pre-existing dislocations or other defects inside the material. For small-volume metals on the micro- and nano-scale, such as whiskers and NWs, in which the defect density can be significantly reduced, it was demonstrated that the apparent yield strength significantly increases, and the elastic strain correspondingly becomes much larger [32–34], approaching the ultimate elastic strain limit that can be sustained in a metal.

A tensile test was designed to determine the ultimate elastic strain limit that can be sustained in metals by a novel in-lab developed in situ TEM tensile device (see the sketch in Fig. 1a). The pulling force was provided by deformation actuators, which are made of metal strips that have differing thermal expansion coefficients [14–23]. Upon gradual heating (on a 3-mm-diameter copper-ring grid) in a TEM hot-stage holder (below \(<80\) °C), the two strips were oriented to bend slowly in opposite directions, actuating the pulling of the TEM specimens (such as thin films, NWs, or tubes) at a strain rate of \( \sim 10^{-4} \) s\(^{-1}\). A major advantage of this novel in situ testing device is that it retains the double-tilt capability, which allows the appropriate crystal orientation of TEM specimens to be obtained for atomic scale analysis during the loading process, as shown in Fig. 1b. This is important for measuring the lattice strains (see below) and the dislocation and defect dynamics in situ at the atomic scale. The real-time evolution of the atomic scale microstructures was captured in situ along with the deformation using a JEOL-2010F TEM and Cs-corrected JEM-2100F TEM operated at 200 kV.

Fig. 2a–c shows three atomic-resolution images showing the tensile process of a NW with a diameter of \( \sim 5.8 \) nm [16]. The NW is [001] direction oriented, and the pulling direction is indicated by the double-ended arrow. The inset in Fig. 2a shows a representative high-resolution image ([110] zone axis). The measured average value \( d_{001} = 3.62 \) Å (\( d \) is the lattice spacing), which is consistent with the [001] interplanar spacing for FCC Cu. After further pulling, the NW experienced clear deformation, as shown in Fig. 2b. Comparing the final gauge length \( L_f \) with \( L_0 \), the total elongation is \(<13\)%, with some of this elongation being plastic strain or permanent shape change. To accurately assess elastic deformation, the \( d_{001} \) spacing along the loading direction is mapped out again. The new \( d_{001} \) averages to 3.88 Å. In other words, the lattice has experienced a \(<7.2\% \) strain along the [001] tensile direction. To confirm that the strain measured from the lattice expansion is truly elastic, the NW was subjected to further pulling to fracture, as shown in Fig. 2c. At this point, the NW is no longer loaded, so the lattice spacing recovers. Indeed, as shown by the high-resolution images in Fig. 2c, the measured \( d_{001} \) spacing returns to the initial value of 3.62 Å. To confirm and quantify the size dependence of the elastic strain limit in Cu, systematic experiments were performed on samples of various sizes. Fig. 2d summarises the size-dependent elastic strain for Cu NWs and fibres with diameters ranging from 5.8 to 1400 nm, including previous experimental [33,35] and theoretical values [36,37] from the literature. The elastic strain clearly increases with decreasing sample diameter. At nanoscale wire sizes, the elastic strain rapidly approaches the theoretical elastic strain limit; the maximum elastic strain we observed (7.2%) is close to the theoretical elastic limit (\(<8\% \) ), which was predicted by MD simulations [36] and ab initio calculations [38–40]. The large elastic strain limit provides room for "elastic strain engineering" to observe new functional

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**Fig. 1.** (a) Schematic view of the in situ atomic-scale mechanical device. (b) With this novel in situ testing device, it enables to obtain atomic-scale images during the stress-loading process.
properties in metals when they sustain ultra-large elastic strain.

3. Full-partial dislocation transition in single crystal FCC metals

The plasticity of metallic NWs in response to mechanical stresses is an important aspect to be considered in designing NEMS and MEMS, in which metallic NWs serve as building blocks. In bulk FCC metals, plastic deformation is usually mediated by the slip of full dislocations. Stacking faults and deformation twinning normally occurs under high strain rate or low temperature conditions. However, these well-documented mechanical behaviours may change, when the characteristic size of these FCC metals is reduced.

Single crystalline Cu NWs with different sizes were fabricated using a focused ion beam technique. With our unique tensile test device, the atomic resolution images and electron diffraction patterns of the strained samples can be captured. This makes it possible to unambiguously identify the deformation twinning. These efforts, with the well-controlled geometry of the samples, also make it possible to quantify the contribution of partial dislocation and deformation twin mediated plasticity [17].

With our unique device, the samples with various $D$ ($D$ is the diameter of the NW) ranging from $\sim 70$ to $\sim 1200$ nm have been examined. Full dislocation slip was confirmed to be the dominant mode when the crystal size is large, as is well-known in bulk samples of Cu crystals. When $D$ is reduced to below $\sim 150$ nm, partial dislocations and deformation twins almost entirely replace full dislocation slip as the controlling plastic deformation process.

Fig. 3a and b shows two sequential images of a NW with $D$ $\sim 134$ nm during continuous straining along the [111] direction. Comparing $L_d$ with $L_0$, the blue framed region has experienced a $\sim 8.4\%$ total strain. Fig. 3c and d shows two enlarged TEM images demonstrating planar defects that are clearly deformation twins and stacking faults. The details can be found in Ref. [17].

With numerous experiments on samples of different sizes, a crossover deformation mechanism from ordinary full dislocation slip to partial dislocation mediated plasticity below a critical crystal size was demonstrated, as shown in Fig. 3e, which also includes previous experimental results from the literature [41–45]. The sample size dependence is consistent with a model prediction based on the competition between full dislocations and partial dislocation mediated plasticity [19,46]. The revelation of this size effect in single crystals also lends support to the previously claimed effect of nanoscale grain size on partial dislocation mediated plasticity in polycrystals [47].

4. Atomic mechanisms of grain rotation in NC FCC metals

NC materials are an important material family with high strength. Their plastic deformation mechanism and behaviours are critically important for advancing their properties and applications. However, the precise nature of the plastic deformation mechanism in NC materials is still not fully understood. As proposed by MD simulations, when the $G$ is less than approximately 15 nm, the dislocation activities subside and may completely give way to GB-mediated plasticity [3–6,30,31]. This phenomenon is often referred to as the inverse Hall–Petch effect, although the existence of this effect is under debate [1,48]. The plasticity mechanism under this grain size regime is unclear. Here, we prepared a thin film specimen with an average grain size in the range of $6–10$ nm. With our tensile device, we revealed the plasticity mechanism with atomic scale resolution and accuracy.

For larger grains ($G > \sim 10$ nm), upon loading we frequently observed movements and interactions of cross-grain dislocations [14,19,20]. Fig. 4a and b provides typical in situ HRTEM observations of full dislocation (marked with "T") nucleation and motion in a $\sim 11$ nm sized grain with a Burgers vector of $a[2011]$. Sometimes the interaction of two non-dissociated full dislocations on two intersecting slip planes will lead to Lomer dislocation (LD) formation. Fig. 4c shows a typical HRTEM image of a LD plane. For $G$ between 6 and 10 nm, full dislocations become much less frequent, and stacking faults resulting from the passage of partial dislocations become more frequent. Fig. 4d and e presents in situ HRTEM observations of partial dislocation (marked with arrows) nucleation in a $\sim 8$ nm sized grain. Fig. 4f shows the deformation twins that were observed in a $\sim 7$ nm sized grain. Large numbers of HRTEM observations were monitored during and at the end of the pulling. There is a clear trend with decreasing $G$ that the dislocations in action transit from full to partial inside the grains.

As proposed by many MD simulations, when the grain size is small, the deformation is controlled by GB-mediated plasticity. However, the atomic mechanisms of GB plasticity are unclear, although some progress has been made [1,3–6]. Here, we prepared a thin film specimen with a grain size population distribution in the range of $3–10$ nm with an average of 6 nm. With our tensile device, directly revealed the grain rotation details with atomic scale resolution [14].

Fig. 5 presents a series of HRTEM images showing the GB dislocation mediated grain rotation process at the atomic scale. We defined the in-plane motion about the axis parallel to the electron beam as "rotation" and the out-of-plane rotation around an axis in
the film plane as “tilt”. $G_{ij}$ is the GB between grains $G_i$ and $G_j$. Fig. 5a highlights six grains ($G_i$ = 5 nm, marked as “1” to “6”) separated by high-angle GBs. The GB angles are 12.1°, 15.1° and 35.1° for $G_{1-2}$, $G_{1-3}$ and $G_{3-4}$, respectively. The double-ended arrow in Fig. 5b indicates the loading axis. During the straining, $G_3$ and $G_4$ exhibit no obvious fringe change, indicating that there is no global tilt and shift of the specimen. As shown in Fig. 5b–f, during the in situ straining, the number of dislocations at $G_{1-3}$ decreases, and the average spacing of the GB dislocations increases from 0.9 to 1.7 nm. This corresponds to a reduced misorientation angle at $G_{1-3}$, decreasing from 15.1° to 1.9°. Fig. 5e and f shows that GB dislocations have climbed toward the triple junction (TJ) points, and the dislocation annihilation/absorption in the TJ (or other GBs) is the reason for the decrease in the number of GB dislocations. For other inter-grain rotations, the GB angle’s changes can be tracked, such as $G_{1-2}$ from 12.1° to 21.6°, while that for $G_{3-4}$ decreased from 35.1° to 27.7°. No intra-grain dislocations were observed inside these tiny grains throughout the deformation process. As noted by the red squares in Fig. 6a, the partial dislocation activities in tensile Cu NW. ‘σ’ represents the tensile direction. (a) Initial morphology of the Cu NW, and (b) Cu NW with a large plastic strain. (c, d) In situ HRTEM images that shows that deformation twins and stacking faults is the dominant plasticity. (e) Sample size dependence of two plasticity mechanisms: relative contribution to the overall plastic strain experienced by the sample region under observation of perfect dislocation slip (blue symbols) and partial dislocation (red symbols) mediated processes. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
Fig. 4. The crossover plasticity mechanisms in NC metals. (a, b) In situ HRTEM observation of full dislocation (marked with “T”) nucleation and motion in a \( \sim \) 11 nm sized grain. (c) A typical HRTEM image of a Lomer dislocation formed by full dislocation interaction. (d, e) In situ HRTEM observation of partial dislocation (marked with arrows) nucleation in a \( \sim \) 8 nm sized grain. (f) The deformation twins were also observed in a \( \sim \) 7 nm sized grain.

Fig. 5. The collective multiple grain rotations in Pt NC thin films. (a) An array of dislocations (as marked with ‘T’) forms a wedge-shaped disclination at the GB. (b–e) During straining, the number of dislocations decreases, leading to a decreasing GB angle. (e, f) The decrease of dislocation number is caused by GB dislocations climbing into the TJs or other GBs.
Fig. 7a, we frequently observed movements and interactions of cross-grain dislocations in larger grains. For $G$ between 6 and 10 nm, full dislocations become much less frequent, and stacking faults resulting from the passage of partial dislocations become more frequent (as noted by black dots in Fig. 7a). When $G \sim 6$ nm, the grain rotation mediated by the climb and absorption/generation of Frank–Bilby dislocations in the GB dominate the plasticity, as noted by the blue triangles in Fig. 7a. The crossover from intragrain dislocation to grain boundary dislocation mediated grain rotation is depicted schematically in Fig. 7b and c.

In summary, an “in situ atomic scale mechanical experimental technique” was developed, and we demonstrated several examples of the investigation of material deformation dynamics at the atomic scale. Working with the revolutionary Cs-corrected imaging technologies [4–10], the strength of ASMET can be greatly enhanced, paving a new research direction for material deformation dynamics at the atomic scale. Integrating with Cs-corrected HRTEM imaging techniques and the atomic scale chemical element distinction ability, the in situ ASMET may provide unprecedented opportunities in the research field of atomic scale material deformation dynamics, not only on line and planar defect dynamics under stress and strains, but also in chemical element resolved and even single atom and atomic cluster resolved material deformation dynamics. These may be also helpful to develop novel materials with strength and high stability under regular and harsh service conditions.

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References