Atomic-Scale In-situ TEM Investigation on Mechanical Deformation and Friction in

Nanocrystals

by

Xiang Wang

B.S., Nanjing University of Science and Technology, 2013

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SWANSON SCHOOL OF ENGINEERING

This dissertation was presented

by

Xiang Wang

It was defended on

January 18, 2022

and approved by

Scott X. Mao, Ph.D., Professor, Department of Mechanical Engineering and Materials Science

Wei Xiong, Ph.D., Assistant Professor, Department of Mechanical Engineering and Materials

Science

Guangyong Li, Ph.D., Associate Professor, Department of Electrical and Computer Engineering

Dissertation Director: Guofeng Wang, Ph.D., Professor, Department of Mechanical Engineering

and Materials Science

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Xiang Wang, PhD

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Revealing the deformation and friction mechanisms of nanomaterials at atomic scale, remains challenging due to the technology limitation. In this dissertation, in-situ transmission electron microscopy (TEM) experiments have been carried out to study the mechanical deformation of nanocrystals and friction between nanocrystals.

Twinning in body cubic centered (BCC) metals requires to be activated by extreme high stress due to its high activation energy barrier. The stability of the deformation twins remains largely elusive, which is crucial for employing twinning or twin structures to improve BCC metals' mechanical properties. Here, it is found that the twin stability in BCC W is strongly dependent on the type of twin boundary. A unique high-energy interface structure called the inclined twin boundary provides the driving force for spontaneous detwinning in BCC nanocrystals. On the other hand, it is well-known that materials follow a "smaller is strong" trend when the sample size is below submicron and nanoscale. But the ultrahigh surface-to-volume ratio in nanoscale materials can dramatically activate surface diffusion to mediate the plastic deformation, resulting in the softening of nanoscale materials. Here, it is found that the diffusion-assisted dislocation nucleation is responsible for the transition from "smaller is stronger" to " smaller is weaker" and diffusionmediated plastic deformation induces the decline of the flow stress in face-cubic centered (FCC) nanocrystals. Up to now, visualizing the friction process between nanocontacts to reveal the friction mechanism at the atomic scale is barely achieved. Here, by designing the nanocontact and performing relative motion between nanoscale asperities under high-resolution TEM, the real-time atomistic friction process is realized, revealing that atomic friction displays a discrete stick-slip behavior. Interface atoms exhibit an asynchronous motion, consistent with the non-uniform strain distribution in contact. This work proposes a new methodology to achieve in-situ atomic-friction research and sheds light on the fundamental mechanisms of friction at atomic-scale.

This dissertation gives insights into the mechanical behaviors of BCC and FCC nanocrystals and provides feasible nanotechnology to investigate the atomic friction in nanocrystals, which are of importance for advancing the understanding of nanomaterials degradation and extending the service life of nanodevices.

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Preface

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1.0 Introduction

Reducing energy consumption and controlling the emission of CO₂ are urgent challenges for the world. Artificial intelligence and intelligent manufacturing provide opportunities to save resources and improve production efficiency.¹ where micro/nano electro-mechanical system (M/NEMS) plays an essential role by being employed in manufacturing technologies². With the development of M/NEMS, the size of components/devices scales down to micro and nanoscale. The degradation of these small-sized materials constituting components, which is generally because of the plastic deformation and fracture, directly leads to the failure of M/NEMS. It is technically demanding, especially for the design and process of advanced materials in applications of M/NEMS to investigate their mechanical properties and deformation mechanisms at small scale³. What's more, many nanoscale materials exhibit excellent mechanical performances such as ultrahigh strength⁴, super-elongation⁵, and high elasticity⁶, which are widely applied in candidates of MEMS devices⁷. These outstanding properties are supposed to result from their unique deformation mechanisms which are size- and structure-dependent^{8, 9}. Transitions among different deformation mechanisms are expected to occur as the sample size decreases continuously, strongly affecting the mechanical performances of materials. For example, small-sized materials would lose their high strengths when the sample size reaches below a critical value, which is ascribed to the transition of the displacive deformation to diffusive deformation.^{10, 11} Unfortunately, previous studies about the deformation mechanisms of nanocrystals mainly relied on the atomic simulation, ^{12, 13, 14, 15} due to challenges on the preparation of the appropriate nanosized sample and atomic-scale observation. As seeing is believing, a great deal of solid

experimental evidences are required to unevil the authenic mechanisms that how nanoscale materials reponse to the external loading.

On the other hand, tribology issues are generally inevitable in numerous mechanical systems having moving components and contacts between them in modern industries. Near 23% of global energy output in transportation, utilities, and industrial applications lost originate from friction and wear.¹⁶ Understanding the atomic friction mechanisms is critical for improving the performances at all scales to reduce energy consumption. Additionally, M/NEMS devices like accelerators and resonators have been extendedly applied in the aerospace, automobile industry, and biomedical industry.7 As decreasing these devices' sizes to micro/nanoscale, atomic tribological phenomena normally occur in contact and then affect their properties. For instance, the continuous friction and wear between the silicon sidewall of MEMS device and the on-chip actuator under oscillation caused surface damage in MEMS devices.¹⁷ The friction and wear would lower the lifetime of the microactuators¹⁸ and the high stiction at the rotor-stator interface confines the operation repeatability in the electrostatic micromotors¹⁹. Thus, investigating the friction mechanism is critical to control the damage of devices and improve the feasibility and reliability of MEMS/NEMS. Furthermore, different from the bulk counterparts, surface in small-sized materials plays a more prominent role in governing the materials' properties and degradation, especially at the preliminary stage of the deformation and friction process. However, traditional ex-situ characterizations hinder the disclosure of the effect from the surface. Recent advances in in-situ mechanical testing techniques give rise to revealing the underlying deformation mechanisms of nanomaterials^{20, 21}, either at surface or in the interior of specimens. Notably, transmission electron microscopy (TEM)-based techniques^{22, 23, 24, 25} open up opportunities for achieving the observation on the dynamic deformation processes at micro or even atomic scale ²⁶,

providing direct evidence to understanding/uncovering possible deformation mechanisms of nanoscale materials.

In this dissertation, by performing in-situ mechanical loading including the compression, tension, and shear, the detwinning of deformation twins in BCC W nanocrystals, the dislocation nucleation and plastic flow in Ag and Pt nanowires, and the atomic friction between are captured. The relation of mechanical and friction behaviors with the microstructure and deformation mechanism in nanocrystals were explored at atomic scale. This thesis is organized as follows:

In chapter 2, the deformation twinning and detwinning in BCC metals, the strength-size dependences of nanocrystals, and the previous research about atomic friction are reviewed. Based on the background, the research motivation and objectives are proposed.

Chapter 3, the materials used in the experiment, experimental setup and procedures for insitu mechanical tests, and in-situ nanotechnology for atomic friction observation are introduced in detail.

Chapter 4, the stability of the deformation twins in BCC W nanocrystals is investigated by in-situ TEM observation. Followed by the formation of deformation twins with a large fraction of Moire Fringes (MF) in W nanocrystals through in-situ straining experiments, the spontaneous detwinning processes are captured. The mechanistic analysis indicated that the high-energy inclined twin boundary (MF region) makes the twin unstable and provides the driving force for detwinning. The proportion of the inclined twin boundary or MF determines the twin stability and its detwinning rate.

Chapter 5 focuses on the strength-size dependences of silver and platinum nanocrystals. By analyzing the dislocation nucleation in two nanocrystals, it discovers that the diffusion-assistant nucleation mechanism will lead to the reduction of the yielding strength of Ag nanowires, breaking down the classical "the smaller is stronger" law. Additionally, diffusion-mediated plastic deformation induces lowered plastic flow stress in Ag nanowires. The detailed diffusion-involved deformation mechanisms will be discussed.

In Chapter 6, one in-situ nanotechnology for investigating atomic friction is proposed. By using the developed method, the atomic friction between sing-asperity contacts under TEM has been studied. It is found that the friction between nanoscale W asperities displays a discrete stickslip behavior containing two slipping events in one sliding period. The interface atoms possed diverse sliding routes and the interface showed an inhomogeneous strain/stress distribution. The proposed methodology paves a pathway to establish the connection between the structure evolution of interface and friction at atomic scale.

Finally, the conclusions of this dissertation are summarized in Chapter 7, and perspective and potential research directions are discussed in Chapter 8.

2.0 Background

In this chapter, the deformation twinning and detwinning in body cubic-centered (BCC) metals will briefly be introduced. And the strength-size dependences in small-sized materials will be reviewed. Additionally, the pioneering research on atomic friction between single-asperity contacts will be introduced and discussed.

2.1 Deformation Twinning and Detwinning in BCC Metals

2.1.1 Twinning Mechanisms in BCC Metals

Twinning, as a common deformation model, plays an important role in the properties of materials. Compared to the dislocation-dominated plasticity, twinning provides an effective pathway to enhance the work-hardening capacity, as accommodating the plastic strain effectively and hindering the movement of dislocation impressively by the generated twin structures^{27, 28}. In general, the deformation twin is generated by sequence slipping of twinning partial dislocations on the parallel twinning planes under shear²⁹ or the overlap of stacking faults³⁰, as observed and probed a lot in face cubic centered (FCC) and hexagonal close-packed (HCP) metals by the previous research³¹. Stacking fault formed by slipping of single twinning partial on the twinning plane can act as the twin embryo and then the embryo is thickened by following slipping of twinning partials on neighboring parallel planes layer by layer, leading to the formation and growth of the deformation twin. Twins generated by this mechanism normally contain two types of twin

boundaries, namely the coherent twin boundary (CTB) parallel to the twinning plane and the incoherent twin boundary (ITB) composed of twinning partials.³² Different from FCC structures, however, BCC metals possess very high lattice friction and high stacking fault energy,^{33,34} making it hard to activate twinning except in some extreme conditions such as ultralow temperature³⁵ or ultrahigh stress³⁶. What's more, the screw dislocation in BCC metals has a dissociated core, causing complex twinning mechanisms in deformation.³⁷ The core of one perfect screw dislocation generally dissociates into three coaxial planes ³⁶ and could be regarded as the aggregation of three partials with a burgers vector 1/6 < 111 > 38. In addition, the mobility difference between edge and screw dislocations further affects the twinning dynamics.^{37, 39, 40}

Some theoretical models were proposed to explain the nucleation and growth of deformation twins in BCC metals. Akin to twinning in FCC metals, the Cotrell-Bilby pole mechanism was applied to explain the twinning nucleation in BCC metals.⁴¹ As shown in Figure 2.1, one full dislocation AO with burgers vector 1/2[111] dissociated into one sessile partial 1/3[112] OB and another partial dislocation $1/6[11\overline{1}]$ BDEO on the parent slip plane (112). Then, the screw partial OE can cross slip to the twinning plane ($\overline{1}21$), transforming into the twinning partial OF. Subsequently, this twinning partial repeatedly rotated around the pole dislocation OB, leading to the formation and growth of the twin layer by layer. However, this mechanism requires extremely high energy to activate, which is not supposed to operate in real BCC metals.⁴² Another classical theory called Sleeswyk's model was proposed for understanding the twin nucleation.³⁷ As shown in Figure 2.2, one full screw dislocation of 3-layer twin nuclei. This model has been indirectly verified by the experiment. Mahajan ⁴³ found the deformation twins were bounded by abundant parallel full screw and partial dislocations in BCC Mo-Rh alloys. Later, the twin

nucleation process following this model was captured in atomistic simulation in Fe.12 The subsequent growth of the twin can also be achieved by the dissociation model of full screw dislocations. Chen et al⁴⁴ proposed a slip-assisted double-cross-slip mechanism to explain the growth process of one individual twin in BCC Ta. The cross-slip and subsequent dissociation of screw dislocations on adjacent planes facilitated the twin growth by three layers. Dislocation sources in bulk BCC metals supplied required screw dislocations for the continuous twin growth. Furthermore, Jiang et al⁴⁵ captured self-thickening twinning mechanisms through in-situ TEM observation in Ta and Nb, in which the twin thickening was completed by repeatedly extruding and expanding of bulges on CTB. The evolution of bugles was concluded to result from repeated formation and dissociation of a complementary zonal dislocation by dislocation reactions at steps on CTB.45 Different from the double cross-slip mechanism, this growth mechanism did not demand a sustaining supply of screw dislocations. Besides the dislocation mechanisms responsible for twinning, people found the twinning in BCC metals can be mediated by consecutive phase transformation^{46, 47}. The ω phase, a simple hexagonal structure, acted as the intermediate phase during the twinning process in Mo, and the successive phase transformation was executed by atoms shuffle rather than slipping of twinning partials.⁴⁷

However, crystals suffer the lack of enough dislocation sources for twinning when the sample size decreases to nanoscale.^{39, 48, 49} MD simulation implied that twinning in BCC nanowires might be controlled by the surface dislocation nucleation.^{39, 50} Instead of the dislocation dissociation, twinning partials are directly nucleated at surface and then propagate through the crystal, leading to the twin growth layer by layer.^{39, 51} Nevertheless, the observed twinning process in BCC nanowires by atomistic simulation lacks direct experimental support. Recent in-situ TEM observation⁵² found that the twinning dominated the plastic deformation of BCC W nanocrystals,

and demonstrated that the twinning started at surface or the intersection of the grain boundary with the surface. The competition between the dislocation slip and twinning depends on the orientation of loading in nanocrystals.⁵³ However, the quick propagation process of twinning in nanoscale BCC metals makes it hard to capture the initial stage of the twin nucleation,⁵² rendering the detailed nucleation and growth mechanism in BCC metals remain elusive.



Figure 2.1 The pole mechanism for twinning in BCC metals.⁴¹



Figure 2.2 Sleeswyk's twin nucleation model.³⁷

2.1.2 Detwinning in BCC Metals

Twinning not only accommodates the plastic strain but also generates twinned structures contributing to the later plasticity. Coherent twin boundaries are normally considered as low energy interfaces,⁵⁴ even though the twin formation increases the system Gibbs free energy compared to the undeformed structure. Under the stress or thermal effect, the twin may become unstable, leading to detwinning consequently.^{55, 56} In general, the detwinning is mediated by the migration of CTB and ITB.^{31, 56, 57, 58, 59, 60, 61} For example, the slipping of one reversal twinning partial on CTB would lead to the thinning of the twin by one layer, as well as the migration of the dislocation with CTB^{55, 62} or nucleate from the intersection of CTB with GB²⁷. The collective movement of twining partials consisting of the ITB can also induce twinning.⁶⁴

Due to the high stacking fault energy, the twin structures in BCCmetals are deemed to be more unstable compared to those in most FCC metals. The high Gibbs energy of twins including the interfacial and strain energy provides the main driving for the detwinning in BCC metals. ^{58, 59, ⁶⁵ For instance, {332}⁶⁶<113> twins exhibited instability under thermal treatment in BCC Ti alloys.⁵⁸ The collective migration of the twin tip from GB in {332}<113> twin led to the detwinning, transforming the twin back into the original structure.⁵⁸ (Figure 2.3 a and b) Similar detwinning process was observed in BCC Ti Mo-Fe multilayered alloy.⁵⁹ Additionally, the authors found one supplementary detwinning mechanism as well as the transformation of ITB into a Σ 3 boundary before the migration of the twin tip.⁵⁹ Different from {332}<113> twins in BCC alloys, {112}<111> twin is a more common type of twins in pure BCC metals, especially for the deformation twins in BCC nanowires.⁴². Detwinning is generally induced by the reverse migration of CTB under unloading in BCC nanowires.^{50, 51, 52} As shown in Figure 2.3c-d, the twinned part in} a Mo nanowire reverts to the initial structure through reversible CTB migration under unloading.⁵¹ The twinning and detwinning under cyclic loading make BCC nanowires exhibit superelasticity⁵¹ and shape memory effect⁵⁰.

However, moire fringes are frequently observed in the deformation twins of BCC metals,^{44,}^{45, 52, 67} making the detailed twin structure elusive. Moreover, the sluggish movement and dissociated core of screw dislocations increase the complexity of deformation twins. To date, little effort has been made to elaborate the relation between twinning/detwinning mechanisms and the twin structure which is crucial for interpreting the stability of deformation twins in BCC metals.



Figure 2.3 Detwinning in BCC metals. (a, b) Detwinning induced by migration of the twin tip in {332}<113> twins.⁵⁸ (c, d) Detwinning induced by migration of CTB in {112}<111> twins under unloading.⁵¹

2.2 The Strength-Size Dependence in Small-Sized Materials

2.2.1 "Smaller is stronger"

The well-known Hall-Petch relation is generally used to describe the strength-grain size dependency in polycrystalline materials, that the strength of materials increases with decreasing the grain size.^{68, 69} This relation can be interpreted by the dislocation pile-up model that cumulate dislocations at GB improve the critical stress for the dislocation propagation.^{70, 71} A lot of efforts were devoted to improving materials strength through reducing the grain size to micro and even nanoscale.^{72, 73} As shown in Figure 2.4a, the yield strength of polycrystalline Ni is inversely proportional to the square root of the boundary spacing (grain size)⁷⁴. The dislocation pile-ups model, i.e GB strengthening, can empirically predict the yield strength-size dependence in many polycrystalline metals.⁷⁵

Akin to bulk polycrystalline materials, single crystals also exhibit a "smaller is stronger" trend.^{76, 77} For example, the yield strength of micro gold pillars exhibited a scaling law with the sample diameter.⁷⁸ (Figure 2.4b) However, unlike the dislocation pile-ups at GB, dislocations can easily annihilate at surface in small-sized single crystals and the Hall-Petch-like sample-size dependency is mainly attributed to the decrement of effective dislocation sources^{48, 77, 79, 80}. The yield strength of single crystals is dominated by dislocation nucleation. At microscale, the half-arm dislocation sources in bulk polycrystalline materials, half-arm dislocations are scarce because of the limited volume of crystals.⁸² One end of the half-arm dislocation is pinned and the other one is at surface. One new dislocation is generated by the propagation of the half-arm dislocation and its interaction with the surface,⁸² similar to the operation of Frank source in bulk
materials⁸³. As the sample size decreases to sub-micro and nanoscale, the surface dislocation nucleation controls the elastic instability of crystals.^{14, 76, 77} Assuming that the surface nucleation site such as corners or surface defects empirically decreases with the sample size, the surface nucleation model gives a weak strength-sample size dependency in nanoscale crystals.^{14, 84, 85} Compared to the size effect, the critical nucleation stress is supposed to be more sensitive to the temperature and strain.¹⁴ Moreover, the flow stress follows a similar "smaller is stronger" law, scaling with the sample size, due to the dislocation starvation.^{48, 77, 86} As dislocations emit from the surface, they quickly propagate through the whole crystal and annihilate at surface, causing the dislocation starvation. Consequently, the discrete emission of dislocations⁸⁷ dominates the plasticity in sub-micro and nanocrystals. However, the statistical nature of the half-arm dislocation source or nucleation site only provides an empirical prediction for the strength-size dependence. According to the surface nucleation model, the surface configuration should play a vital role in determining the critical stress for nucleation. However, the effect of surface configuration has been less investigated. The detailed dislocation dynamics still requires to be explored further.



Figure 2.4 "Smaller is stronger" in polycrystalline materials (a)⁷⁴ and single crystals (b)⁷⁸.

2.2.2 "Smaller is stronger" in Polycrystalline Materials

As the feature size is below a critical value, the Hall-Petch-like law in polycrystalline or single-crystal materials will be broken, i.e. inverse Hall-Petch relation or "smaller is weaker". As shown in Figure 2.5a,⁸⁸ after the Hall-Petch regime, the strengths of Ni and Ni-W alloys decreased when the grain size was below 11 nm. In nanocrystalline materials, the inverse Hall-Petch is normally supposed to result from GB-mediated plasticity.^{89, 90} When the grain size decreases to a threshold value, GB-accommodation mechanisms including GB diffusion (Coble creep⁹¹)⁹² and GB sliding⁹³ would take the place of dislocation slip to dominate the deformation of nanograins. The GB Coble creep can be expressed by⁹¹

$$\dot{\varepsilon} = A \frac{\sigma \Omega_D \delta_D D_{GB}}{k_B T \, d^3} \tag{2-1},$$

where σ is the stress, Ω_D is the activation volume, δ_D is the diffusional width, D_{GB} is the diffusion constant along GB, *d* is the grain size, k_B is Boltzmann constant, and *T* is the temperature. *A* is the proportionality constant related to the grain shape. The diffusion flow ($\delta_D D_{GB}$) along GB sustains the homogeneous plastic strain. This model describes the relation between stress and grain size at a certain strain rate. As the grain size decrease, the required stress for creep would decrease, leading to the inverse Hall-Petech relation in nanocrystalline materials. However, this GB diffusion is hard to be directly observed in experiments. Unlike the homogeneous deformation accommodated by Coble creep, the GB sliding can provide a supplementary way to accommodate the inhomogeneous strain at the local region.^{93, 94, 95, 96} The GB sliding process can be completed by the atomic shuffling and stress-assisted free-volume migration⁹³ or the motion of GB dislocations⁹⁷. Langdon⁹⁴ gave a creep-like equation

$$\dot{\varepsilon}_{gbs} = A' \frac{DGb}{k_B T} \left(\frac{b}{d} \right)^m \left(\frac{\sigma}{G} \right)^n \tag{2-2}$$

to describe the GB sliding, where $\dot{\varepsilon}_{gbs}$ is the strain rate from sliding, *D* is the diffusion constant, *G* is the shear modulus, b is the burgers vector, *A'* is a dimensionless constant and m and n are constants related to the grain size. This GB-deformation mechanism has been found in many ultrafine/nanograin metals^{98, 99, 100}.

As the sample size drops continuously to a smaller scale, the displacive plasticity is supposed to be activated that the surface diffusion participates in the deformation.^{101, 102} Sun et al found the surface diffusion mediated the plastic deformation of sub-10-nm Ag particles, leading to the pseudoelasticity under compression.¹⁰³ The capillary energy-driven surface diffusion dominated the shape change of Ag crystals while no evident dislocation activity was captured. Ag nanoparticles behaved like a liquid droplet but remained the initial crystalline structure. This diffusive plasticity induced by coble-like surface diffusion would lead to the transition from "smaller is stronger" to "smaller is weaker".^{10, 103} Unlike the liquid-like behavior of nanoparticles under compression, Tian et al¹⁰ reported the diffusion-induced softening under tension by in-situ TEM observation. The Coble creep mediated the fast elongation of the Sn nanoligament under low stresses, leading to a "smaller is much weaker".¹⁰ The switch from "smaller is stronger" to "smaller is weaker" was attributed to the competition between the dislocation slip and surface creep. It's worth noting that this competition also depends on extrinsic loading conditions such as temperature¹⁰ and strain rate⁵. Without regard to the diffusion activities in nanocrystals, Li et al¹⁵ proposed a surface dislocation nucleation-associated mechanism to explain the "smaller is weaker". (Figure 2.5b) The applied strain generated the surface stress and then increased the local maximum shear stress, which caused the declined stress required for surface dislocation nucleation. However, this mechanism strongly depends on the loading type that the softening or "

smaller is weaker" is supposed to only come up in nanowires under compression instead of tension¹⁵.

On the other hand, due to the timelapse of the diffusion activity, it is hard to track the diffusion trace in real-time. The detailed diffusion dynamics require more experimental evidence to support. Additionally, the interaction between displacive and diffusive plasticity remains elusive,⁵ especially for the effect of diffusion activity on the dislocation nucleation.



Figure 2.5 The breakdown of the Hall-Petch law. (a) Inverse Hall-Perth in nanocrystalline materials. ⁸⁸ (b) "Smaller is weaker" in single crystals.^{11,15}

2.3 Atomic Friction between Single-Asperity Contacts

2.3.1 Principles of Atomic Friction

As the macro friction can be regarded as the congregation of numerous atomic-scale friction, various atomic friction models were established to understand the friction behaviors at nano/atomic scale. In the 1920s, a simple one-dimension model, called as Prandtl-Tomlinson model was proposed to resolve the origin of atomic friction.¹⁰⁴ As illustrated in Figure 2.6, the

friction was assumed as the movement of a point-like tip driven by a spring with a body M on an atomically smooth surface. The tip was required to overcome the surface potential energy barriers between lattice atoms for sliding with a velocity v, and the stored total energy in this system can be simplified into¹⁰⁵

$$U_{tot}(\mathbf{x},t) = U_{eff}(\mathbf{x}) + \frac{1}{2}k(\mathbf{x} - \mathbf{v}t)^2$$
(2-3),

where $U_{eff}(x)$ is an interaction potential between the tip and surface, the right second part is the elastic energy stored in the spring, k is the effective spring constant ^{106, 107, 108}, and x represents the tip position at time t. Then, the lateral force, i.e the instantaneous friction force, can be expressed by¹⁰⁵

$$F_L = k(x-vt) = -\frac{2\pi U_0}{a} \sin \frac{2\pi x}{a}$$
(2-4),

and *a* is the lattice distance between two atoms and U_0 is the amplitude of the surface potential. This model provides a valuable insight into the energy dissipation originated from the friction at atomic scale. When the tip is located in the minimum potential well, the tip is trapped and exhibits the "stick" behavior. As the tip escapes from the potential well and overcomes the energy barrier of the surface potential corrugation, the tip jumps toward the next point and exhibits the "slip". This friction behavior is called stick-slip¹⁰⁹ that the friction force oscillates periodically with the sliding displacement of the tip.



Figure 2.6 Schematic of the Prandtl-Tomlinson model.¹¹⁰

Since the real contact surface on crystals has a two-dimension interaction potential, people extended the one-dimension P-T model to a two-dimension model^{111,112}. The interaction potential of the sample surface depends on the periodicity and symmetry of the sample structure and the similar relation between the interaction potential and movement of the tip can be built up by implanting suitable parameters.^{113, 114} Some simulations have successfully applied this twodimension model to study the atomic friction on many crystals.^{115, 116, 117} Based on the P-T model, the friction is expected to transit from the stick-slip to smooth sliding with ultralow friction by changing loading conditions and friction configuration.^{118, 119, 120, 121, 122, 123} The ultralow friction behavior is referred to as super-lubricity¹²⁴. Via changing the normal force¹²⁵ and the cantilever stiffness ¹¹⁰, superlubricity has been achieved in experimental observation. In addition, considering the tip size instead of the ideal point contact with the substrate, the P-T model was developed to Frenkel-Kontorova-Tomlinson (FKT) assuming the atoms in the tip were connected by harmonic springs¹²⁶. Due to taking into account the potential periodicity of the tip, this FKT model is capable of describing the transition between commensurate-incommensurate contacts where the friction exhibited distinct behaviors.^{126, 127}

2.3.2 Atomic Friction Studied by AFM-based Technology

As friction causes surface damage and the energy consumption in contact, people mainly care about the friction coefficient-the ratio of the normal force and the friction force which is used to evaluate the friction intensity. The basic issue in tribology research is to determine the magnitude of the friction force. However, the micro/nanoscale contact makes friction force hard to be detected. Inspired by the principle of atomic force microscopy (AFM), friction force microscopy or lateral force microscopy (Figure 2.7) was developed to determine the normal and friction forces between a rigid tip and the sample surface by measuring the vertical deflection and torsion of the cantilever^{128, 129}. The deflection of the cantilever is normally recorded by optical sensors¹³⁰ while the accuracy of the force detection can be improved by calibrating the spring constant of the cantilever and the relation between the deflection and its readout^{105, 128, 131}. The friction force microscopy gives rise to investigating the friction behaviors and associated mechanisms at atomic scale.





Numerous friction phenomena and the evolution of friction behaviors with various parameters have been revealed via the friction force microscopy observation. A typical atomic friction behavior, the stick-slip has been reported in many systems under vacuum^{120, 132, 133, 134}. For example, friction on the Cu (111) surface displayed stick-stip characters as the friction changed with sliding displacement along the ($1\overline{10}$) direction by a zigzag pattern¹³². (Figure 2.8a) The friction force increased with increasing the sliding velocity. (Figure 2.8b) Notably, AFM-based microscopy possesses the ability to capture the surface morphology of the substrate by the scanning of the tip but is unable to reveal the real contact scenario between the tip and substrate. The friction mechanism was mainly deducted from the friction force-displacement evolution coupled with the analytical models. The stick-slip friction was also found in two-dimensional (2D) materials such as graphene and molybdenum disulfide MoS₂.^{135, 136} Interestingly, researchers found that the friction force can be controlled by changing the sheet number of 2D materials^{136, 137}. The underlying mechanism of the friction-thickness dependence is attributed to the surface deformation and interlaminar interaction of 2D materials.

When changing the loading parameters and contact configuration, the stick-slip pattern would disappear. For instance, Hirano et al¹³⁸ reported an orientation-dependence friction behavior between two mica sheets. As the misfit angle between two sheets was 30 degrees, half of the symmetry angle, bringing two micas into incommensurate contact, friction exhibited an ultralow value i.e the superlubricity state.¹³⁸ While the misfit angle approached 0 or 60 degrees, the friction force significantly increased. The ultralow friction was contributed to the lattice misfit-induced weak interaction between contacting lattices.¹²⁴ This phenomenon was also found in graphite. As shown in Figure 2.8c, the friction force was nearly zero when the rotation angle between graphite flake and substrate was 20-40 °.¹³⁹ Moreover, lowering the normal loading can effectively lower

the friction coefficient.^{120, 125} Socoliuc et al¹²⁰ proposed a parameter η related to the normal loading and stiffnesses of asperities to assess the stick-slip instability. When $\eta < 1$, the stick-slip disappears and the movement between asperities is continuous with low friction. In addition, the thermal excitation can favor the tip to overcome energy barriers for sliding in friction, inducing the superlubricity¹⁴⁰. The tip with the aid of the thermal jump could move on the surface by confronting a very low energy barrier. Whereas if the thermal effect was negligible compared to the interaction between two asperities, the friction would transit back to a high-resistance regime.¹⁴¹ Achieving superlubricity is a pragmatic pathway to reduce energy consumption and prolong the service life of machines. However, the majority of AFM-based experimental research is incapbale of clearly outlining the relation of friction behaviors with interface structure in contact, due to the technology limitation. Thus, visualizing the interface in friction is an expectant breakthrough to explicate the friction mechanisms at atomic scale.



Figure 2.8 Typical friction behaviors. (a, b) Stick-slip friction in copper¹³². The zigzag sliding pattern in (a) and the friction-velocity dependency in (b). (c) Superlubricity in graphite¹³⁹.

2.3.3 In-situ TEM observation on atomic friction

How to set up the friction configuration under TEM observation is all through a challenge for atomic-friction research. The recent development of in-situ transmission electron microscopy (TEM) technologies gives rise to directly observing the atomic structure of materials in real-time. ^{21, 142, 143} Implanting the friction tests under TEM provides an idea to record the real-time friction process and inspect the interface structure between asperities. Referring to the design of scanning probe microscopy, Kizuka et al¹⁴⁴ successfully reached an atomic-scale observation on contact and scanning on gold surfaces in high-resolution TEM with a piezo-driven holder. With the aid of the moveable probe controlled by a low-velocity motor, they captured the formation and fracture of Au junction between the Au tip and substrate.¹⁴⁴ The real-time evolution of the cross-section of Au junction could be recorded by this technique ¹⁴⁴. However, the probe was confined to moving along one direction and the motion space was limited. Whereafter, an upgraded platform, the scanning tunneling microscopy-transmission electron microscopy (STM-TEM) holder, (Figure 2.9a) was designed with a flexible control system, making the probe able to advance in three dimensions¹⁴⁵, ¹⁴⁶. Using this platform, friction tests under TEM have been achieved with success^{145, 147}. For example, M'ndange-Pfupfu et al¹⁴⁷ directly observed the tribochemically-assisted wear on diamond-like carbon thin films using STM-TEM holder.

Although visualizing contact and dynamic sliding between friction asperities has been achieved, force detection is still imperative for atomic friction study. Inspired by atomic force microscopy allowing to measure tiny forces precisely, coupling AFM with TEM¹⁴⁸ provides a new pathway to determine the force during observation of the friction process. (Figure 2.9b) Jacobs et al provided direct experimental support for the validation of atom-by-atom wear via using AFM-TEM-coupled apparatus.¹⁴⁸ Based on the principle of detecting the force by the cantilever deflection, Sato et al designed a MEMS with two force sensors to measure the friction and normal forces under TEM, as shown in Figure 2.9c ^{149, 150}. There are two major parts in this MEMS device including suspended opposing tips and two-degree-of-freedom electrostatic actuators. By inputting

voltage, the actuators control the motion of tips. This MEMS device has been applied to study the nanofriction in single-asperity Ag contact¹⁵⁰ and nanoscale wear between diamond-like carbon films¹⁴⁹, revealing the friction force evolution in the shear of Ag junction¹⁵⁰ and slipping and rolling process of DLC-like wear particles¹⁴⁹. However, these studies focused on the deformation of the metal junction and the motion of wear debris. Visualization of friction process at atomic scale with the dynamic interface evolution has not been realized. Exploring the role of the well-defined interface structure in friction is still a challenge.



Figure 2.9 Platforms for in-situ friction observation under transmission electron microscopy. (a) Scanning tunneling microscopy-TEM platform.¹⁴⁶ (b) The AFM-TEM apparatus.¹⁴⁸ (c) Design of the MEMS device for force measurement under TEM observation.¹⁵⁰

2.4 Motivation and Research Objectives

A fundamental understanding of the deformation and friction mechanisms is significant in governing the nanomaterials' service life and application. Based on the above discussion, due to difficulties in preparing appropriate samples and conducting real-time observation during mechanical deformation and friction, most studies rely on atomistic simulations and theoretical prediction or postmortem characterization. Moreover, previous studies fall short in offering a window to observe the diffusion phenomenon, and obtaining the well-defined interface in friction at the atomic scale. On the other hand, the ultrahigh stress which is generally required for the deformation of BCC metals is hard to apply in in-situ study. The mechanical loading on nanocrystals under TEM observation provides opportunities to fill in these gaps. In this dissertation, in-situ mechanical deformation and friction testes under TEM observation will be employed to address the concerns in nanocrystals as follows:

- If the twinning dominates the plastic deformation of BCC nanocrystals, can the generated deformation twins keep stable? What factors do determine the stability of deformation twins in BCC metals?
- 2. What mechanisms are responsible for the softening of nanocrystals? How does surface diffusion involve in the deformation of nanocrystals? If diffusion contributes to the plastic deformation of nanocrystals, how does it affect the mechanical behaviors?
- 3. How to visualize the real-time friction process between single-asperity contacts at atomic scale?

Atomistic observation on mechanical behaviors of BCC and FCC nanocrystals and friction between nanoscale asperities will be gained by advanced in-situ TEM experiments, which uncover the underlying mechanisms determining materials' performance and degradation and provide new insights on nanoscale materials' design and application.

3.0 Materials and Experimental Procedures

In this chapter, the materials and experimental methods employed in the research will be described. High purity BCC tungsten (W) will be used for the study about the stability of deformation twins in BCC nanocrystals and atomic friction; high purity FCC silver (Ag) and platinum (Pt) polycrystalline rods are selected as the model metals to study the diffusion-involved plasticity in nanocrystals. An advanced method to prepare nanowires is applied to study the deformation of nanocrystals under TEM observation. In addition, a novel nanotechnology will be proposed to visualize the real-time friction process at atomic scale and further investigate the underlying friction mechanisms.

3.1 Materials

3.1.1 High Purity BCC W

Polycrystalline tungsten rods with a diameter of 0.013 inches (bought from ESPI Metal) were used in the in-situ observation of deformation of BCC nanocrystals and in-situ atomic friction. The metal purity is 99.98 wt.% and the impurity elements and corresponding concentrations are listed in Table 3.1. Before the experiment, the polycrystalline W rods were soaked into acetone for about 24 hours to remove surface grease and then air dry. The bulk rod was fractured to attain numerous nanosized tips which are used to prepare nanocrystals or nanowires through in-situ welding method⁵², as shown in Figure 3.1 and Figure 3.2. By

electrochemical etching method with NaOH solution, the W probe was obtained to act as the mobile end for applying the deformation/loading. Nanotips with appropriate orientations were used for the preparation of nanowires and nanoscale asperities in the study of twinning/detwinning in BCC W nanocrystals and atomic friction respectively.

| Element | Concentration, ppm | | |
|---------|--------------------|--|--|
| Fe | 20 | | |
| Cu | 20 | | |
| K | 20 | | |
| Cr | 10 | | |
| Ni | 130 | | |

Table 3.1 The impurities in the W rod.



Figure 3.1 Illustration of the in-situ welding.



Figure 3.2 The nanocrystals/nanowires preparation. (a) Nanotips at the fracture edge of the rod. (b) The nanocrystal/nanowire prepared by Joule-heating welding.

3.1.2 High Purity FCC Ag and Pt

Polycrystalline silver and platinum rods with purity 99.999% are used in the research of investigating the surface-diffusion mediated deformation of nanoscale metals. The impurities in silver and platinum rods are listed in Table 3.2 and Table 3.3 respectively. Before the in situ tensile tests, the Ag and Pt nano-tips were generated at the clean fracture surface of bulk metallic wires using a wire cutter and then loaded onto the static side of the TEM holder. The approach in this work produced nano-tips with clean surfaces, which were appropriate for studying surface diffusive phenomena in nanoscale metals. Plasma cleaning was conducted on the Ag and Pt nanotips before all in situ TEM tests to diminish the potential effects of carbon deposition on sample surface diffusion. Compared to Pt, Ag has a lower melting point and a higher surface diffusivity, making it possible to capture the surface diffusion activities at atomic scale.

| Element | Concentration, ppm |
|---------|--------------------|
| Bi | <0.5 |
| Cu | <0.5 |
| Fe | <0.5 |
| Ni | <0.5 |
| Pb | <0.5 |
| Pd | <0.5 |
| Те | <0.5 |

Table 3.3 The impurities in Pt wires.

| Element | Concentration, ppm |
|---------|--------------------|
| Ag | 3 |
| Al | <2 |
| Ca | 8 |
| Fe | <1 |
| Ir | <2 |
| Na | <1 |

3.2 Experimental Procedures

3.2.1 In-situ Experimental Configuration and Mechanical Tests

In-situ experiments were performed at Nanofactory STM-TEM platform shown in Figure 3.3 under aberration-corrected FEI Titan 80-300 kV TEM at Environmental Molecular Sciences Laboratory in Pacific Northwest National Laboratory and Themis G2 200 Probe Cs Corrected STEM at Petersen Institute of Nanoscience and Engineering in University of Pittsburgh. One end of the platform was designed to load the rod sample and the other one connecting with the piezo system acted as the mobile port for loading the STM probe. The piezo system controls the movement of the probe to apply the deformation such as tension, compression, and shear. The strain rate in deformation/sliding speed in friction is controlled by adjusting the displacement rate of the probe with a piezo-manipulator. The common strain rate in in-situ mechanical tests is about 10⁻³s⁻¹. In addition, this platform allows generating a bias between the sample and the probe, which provides the precondition for the Joule-heating welding¹⁵¹. (Figure 3.1)



Sample fixed side

Piezo tube

Figure 3.3 The Nanofactory TEM-STM platform.

3.2.2 Microstructure Observation and Strain/Stress Analysis

Aberration-corrected TEM allows imaging the atomic structure of samples under a highresolution (HR) TEM model. The contrast between the dark and bright dots provides information on the atom positions in nanocrystals, although it is generated by the interference of parallel electron beams.¹⁵² The defects such as twin, dislocation, and surface step can be detected from HRTEM images, as shown in Figure 3.4. The microstructure evolution including the birth of defects, interactions between defects, and the lattice distortion gives the clues of the deformation mechanisms. Additionally, the movement of the surface step serves as one signal of mass transportation as well as diffusion activities.



Figure 3.4 Defects in the crystal.

When the crystal suffers the deformation or loading, the spacing between atoms will change, generating the lattice strain. (Figure 3.5) The tensile/compression strains can be determined by calculating the lattice spacing change while the shear strain is obtained by

measuring the relative position change between two atoms. Interior stresses in nanocrystals are determined by timing the lattice strain with the crystal's modulus. Moduli of metals used in this dissertation are listed in Table 3.4. To reduce the measurement error, at least 7 parallel lattice planes were selected to detect the average lattice strain. The engineering strain of the sample in tension can be obtained by tracking the evolution of the nanowire's gauge length. In addition, the sliding distance of the probe compared to the substrate gives the relative displacement between asperities in friction.

| Material Orientation | W | Ag | Pt |
|-------------------------|-----|-------|--------|
| <100> | 389 | | |
| <110> | 389 | | |
| <112> | 389 | 83.61 | 185.01 |

Table 3.4 The modulus of W, Ag, and Pt. (Unit: GPa)



Figure 3.5 Lattice strain measurement of Ag NW under <112> tensile deformation. a, Lattice strain was obtained by measuring lattice expansion along the loading direction. The scale bar is 1 nm. b, Interplanar spacing over 20 atomic planes of the unstressed state. c, Interplanar spacing over 20 atomic planes of the deformed state. An elastic lattice strain of 2.56 % was obtained by comparing the difference in interplanar spacings.¹⁵³

3.3 Simulations Methods

All MD simulations to support the experimental observation and advance the understanding of the underlying mechanisms in the deformation of nanocrystals and atomic friction between single-asperity contact were completed by my collaborators. The simulation on the deformation of Ag and Pt nanocrystals in Chapter 5 was carried out by Prof. Shigenobu Ogata and Dr. Shuhei Shinzato in Osaka University. The simulation on the atomic friction between

nanoscale W asperities in Chapter 6 was conducted by Prof. Guofeng Wang and Dr. Zhenyu Liu in University of Pittsburgh.

3.3.1 MD Simulation on The Deformation of Ag and Pt Nanocrystals

MD simulations were performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) package¹⁵⁴. The embedded atom method (EAM) potentials for Ag developed by Wu and Trinkle¹⁵⁵ and for Pt by Sheng et al.¹⁵⁶ were used for interatomic interaction. To investigate the surface atomic diffusion on facets and the related dislocation nucleation events as observed in our experiments, the cross-sectional shapes of the samples in MD simulations were set to be rectangular. Given that surface diffusion is a rate-limiting process¹⁵⁷, the sample geometry could not change significantly during the observation period. Thin-film samples oriented along $[\overline{112}]$, [111] and $[1\overline{10}]$ directions with two different sizes were modeled. The $[1\overline{10}]$ and $[\overline{112}]$ directions were the viewing and loading direction in the experiments, respectively. The supercell size and gauge section length along $[\overline{112}]$ direction were 25nm and 9nm, respectively. The crosssection areas of the gauge section were 6×2 and 20×6.7 nm², respectively. A periodic boundary condition was applied along the loading direction. The energy of the models was minimized by the conjugate gradient method, and then relaxed for 100 ps under zero pressure using an NPT ensemble with a Nose-Hoover thermostat at 300, 500, and 800 K, respectively. Following relaxation, tensile deformation at the same temperature was carried out by stretching the simulation box along the $[\overline{112}]$ direction at a constant engineering strain rate in the NVT ensemble. Two different strain rates of 10⁵ and 10⁷ s⁻¹ were studied. The virial stress of the gauge section was calculated as the stress along the loading direction using the undeformed cross-section area at the gauge section. Atomic structures of nanofilm during deformation was studied in the OVITO¹⁵⁸

using common neighbor analysis (CNA) for the defect structure and the non-affine squared displacements $(D_{\min}^2)^{159}$ calculation for diffusivity of atoms. In the CNA study, the average atomic positions of 2ps MD run for each snapshot were used to reduce the noise due to thermal fluctuation. Notably, based on Wuffle construction theory, the equilibrium Ag crystals consist of {111} and {100} facets. Beyond the interested period investigated in our MD simulation, the cross-sectional shape of the samples changed from the initial rectangle to the polygon, and finally to the nearly-circular shape (hexagonal shape consisted of {111} and {100} planes).

3.3.2 MD Simulation on The Atomic Friction between W Single-Asperity Contact

The atomistic molecular dynamics (MD) simulations were performed using the LAMMPS code.¹⁵⁴ The interatomic potential within the embedded atom method (EAM)¹⁶⁰ formalism was employed in the simulations.¹⁶¹ All the MD simulations were performed in the canonical ensemble. The temperature of the system was set at 300K by applying a Nosé-Hoover thermostat.¹⁶² The equation of motion was integrated using the velocity Verlet algorithm with a time step of 1fs. Several vacancies were introduced to the top surface of the probe to ensure the friction event occurs at the interface, otherwise the shear would happen within the 2-3 layers of atoms in the probe-side crystal away from the interface. The positions of the atoms at the boundary zone containing three atom layers were fixed whereas all the other atoms were allowed to move. During the MD simulation, non-periodic boundary conditions were assumed along all dimensions. The friction process was modeled by two stages: (1) the W probe first approached the substrate at a speed of 0.01nm/ps in the direction normal to the surface. After every 0.025 nm step, the system was subject to a 15 ps equilibration to relax the structure; (2) at a desired vertical distance between the probe and the substrate, the probe slid parallelly at a controlled speed of 1 m/s. The force, virial stress

between the probe and the substrate, and the resulted structures were extracted for further analysis. In addition, the interface potential landscape at the given separation distance between the probe and substrate was plotted by evaluating the system energy after rigidly shifting the probe along the vectors parallel to the friction plane. During the simulation, only the position of the atoms along the normal direction of the interface was allowed to relax. The position of the atoms along the normal direction of the interface was allowed to relax.

4.0 The Stability of Deformation Twins in BCC W Nanocrystals

Twinning is commonly activated in plastic deformation of low stacking fault face-centered cubic (FCC) metals but rarely found in body-centered cubic (BCC) metals under room temperature and slow strain rates.⁴² Here, by conducting in situ transmission electron microscopy (TEM) at atomic scale, it was discovered that, in stark contrast to those in most Fcc metals, a majority of deformation twins in BCC metals were unstable and underwent spontaneously detwinning upon unloading. Such unexpected instability of BCC twins was found to be closely related to the prevalence of the inclined twin boundaries—a peculiar structure where twin boundaries are not parallel to the twinning plane, and the degree of instability was in direct proportion to the fraction of the inclined twin boundary. This work provided significant insights into the structure and stability of deformation twins in BCC metals.

4.1 Introduction

Twinning as a common deformation mode plays a significant role in the mechanical properties of materials.^{31, 42} Twin boundaries can not only act as an effective barrier to hinder dislocation motion but also provide the motion path and nucleation sites for dislocations, contributing to the excellent mechanical properties without the traditional trade-off between strength and ductility.^{27, 163, 164} An ideal coherent twin boundary with a coincidence interface is considered as a low energy boundary with excellent thermal stability^{27, 165}, which provides massive

space for property adjustments. Understanding the twinning ability and the stability of the twin structure is critical for engineering nanotwins toward advanced materials design.

BCC metals, such as ferritic steels, are widely used as structural materials and magnetic functional materials. Different from metals with closed-packed structures like FCC and HCP, BCC metals show poor twinning ability because of their high stacking faults energy^{166, 167}. As a consequence, dislocation plasticity normally dominates the plastic deformation of BCC metals, while deformation twinning is only activated under extreme conditions, *e.g.* high stress, high strain rate, and low temperatures.³⁶ Recently, twinning-dominated plasticity in nanoscale BCC metals was discovered by *in situ* TEM experiment,^{52, 67} opening up a good opportunity to directly study the twinning process and the thermodynamic stability of the twin that associates with the structures and energies of twin boundaries, which remains largely unclear in BCC metals.

Here, by performing atomistic *in-situ* TEM study, it is revealed that the twin stability and the detwinning process in BCC W strongly depend on the type of twin boundary. Specifically, it is found that the stability of deformation twins in BCC metals is controlled by a unique interface structure *i.e.* inclined twin boundary. Quantitative analysis demonstrates that the high energy of the inclined twin boundary contributes significantly to the driving force for detwinning and twins containing a high proportion of inclined twin boundaries show higher self-detwinning rates. This work reveals the underlying mechanism of spontaneous detwinning in BCC metals and provides a deep understanding of the (de)twinning behaviors, which is significant for the design and processing of twin structures in BCC metals. Moreover, the spontaneous detwinning associated with the unstable twin brings possibilities to develop advanced materials with prominent pseudoelasticity and self-healing effects.

4.2 Experimental Procedures

The nanocrystal preparation method is referred to in Reference [52] and Chapter 3, through welding two nano-tips together to form a nanocrystal bridge. As applying the tension or compression on nanocrystals, the deformation twins formed under loading. When fracture occurres on the boundary between the nanocrystal and the substrate as well as the connection site under continuous loading, there is only physic contact and no chemical bonding between the indenter and the nanocrystal. The strain rate is controlled by the displacement rate of the mobile probe connecting with a piezo-manipulator. A common strain rate used in in-situ deformation is about 10^{-3} s⁻¹.

4.3 Experimental Results

4.3.1 Spontaneous Detwinning

High energy twin boundaries are generally deemed to reduce the stability of deformation twins. When a W single crystal was loaded as shown in Figure 4.1a, one deformation twin was formed near the edge of the nanopillar. It is worth noting that a large portion of the twinned region was filled with Moiré fringes (MF) (Figure 4.1b and c). The Moiré fringe is formed by overlapping of the twinned and matrix lattices¹⁶⁸ as is proved by the diffraction analysis of the Moiré fringe pattern (Figure 4.2a), indicating that the twin has not fully propagated along the crystal thickness direction. Therefore, there should exist an inclined twin boundary that is nonparallel to the twinning plane between the twin and matrix in the overlapped region. This inclined twin boundary

is fundamentally different from the traditional twin boundary-coherent twin boundary (CTB) and the MF region should coincide with the projection of this inclined twin boundary in the current viewing direction. Finally, a deformation twin with ~70% MF region was generated after the fracture of the pillar, while no contact existed between two fractured crystals after 496s (Figure 4.1d), excluding any loading effect on the following structural changes. Subsequently, a peculiar phenomenon, spontaneous detwinning of this twin occurred and proceeded steadily, as shown in Figure 4.1e-1. The reduction of the MF region indicates the gradual retraction of the inclined twin boundary and the transformation from bulgy to flat-shaped twin boundaries is supposed to lower the interface energy. (Figure 4.1e-g). The length of the twin decreased quickly from 13.7 nm to 10.9 nm before 121s (Figure 4.1g) and then changed slowly when the size of the inclined twin boundary has decreased significantly (Figure 4.1h-j). The twin tip as the vertical front of the twin spontaneously retracted towards the bottom surface and the twin vanished quickly when the twin became very small and close to the surface (Figure 4.1k and I).



Figure 4.1 The spontaneous detwinning in the deformation twin containing ~70% Moiré Fringes region. (a-d) The formation of the deformation twin under tension. (e-l) Spontaneous detwinning process upon unloading. Scale bar 2 nm.¹⁶⁹



Figure 4.2 Fast Fourier Transform (FFT) pattern analysis of the Moiré Fringes region in deformation twins of tungsten. (a) FFT pattern analysis of the Moiré Fringes region in the deformation twin showed in Figure 4.1d along with [113] zone axis. (b) FFT pattern analysis of the Moiré Fringes region in the deformation twin shown in Figure 4.4a. (c) FFT pattern analysis of the Moiré Fringes in the deformation twin shown in Figure 4.4b.¹⁶⁹

Steps (marked in Figure 4.1e) were often found on the inclined twin boundaries, which were regarded as the trace of the gliding of twinning partials on the CTB⁶². These steps disappeared during the detwinning (Figure 4.1f), indicating that the reverse motion of twinning partials along CTB contributed partly to the self-detwinning process. Some parts of the inclined twin boundary moved relatively faster than others, as marked by the yellow arrow in Figure 4.1e, which may result from the structural inhomogeneity along the inclined twin boundary. The detwinning process eliminated the twinned structure and strain, recovering the twinned structure back to the perfect lattice (Figure 4.1l). Electron beam irradiation is suspected to affect the structures and migration of twin boundaries.^{170, 171} To exclude this effect, beam-blanked experiments were carried out (Figure 4.3). The retraction of the MF region still occurred and the twin disappeared after 40 minutes without the continuous electron beam exposure, implying that the observed detwinning is an intrinsic behavior. Abundant MD simulations show that the driving force for detwinning during

unloading in BCC nanowires is attributed to the large surface energy difference between the {110} and {100} facets.^{50, 172} Above experimental results indicate that the spontaneous detwinning discovered here was very likely driven by the high energy of the inclined twin boundary rather than external effects.



Figure 4.3 Spontaneous detwinning in the twin with a high proportion of the inclined twin boundary under beam-blank. (a) The deformation twin with a high proportion of Moiré Fringes. (b) The twin after 15 minutes under beam-blanked condition. (c) The twin after 35 minutes under beam-blanked condition. (d) The twin disappeared after 40 minutes under beam-blank. Scale bar 2 nm.¹⁶⁹

4.3.2 Profound Differences in The Structure of Twin Boundaries in BCC Tungsten and FCC Silver

Interestingly, the existence of inclined twin boundaries in deformation twins is a common phenomenon in tungsten. Figure 4.4 shows representative deformation twins in BCC (W) and FCC (Ag) metals when both of them were viewed along the <110> direction parallel to the twin plane (*i.e.* CTB). Compared to the sharp twin boundaries in Ag (Figure 4.4c), there exist a lot of inclined twin boundaries (see the Moiré fringe patterns, the corresponding diffraction analysis was shown in Figure 4.2b and c) near the coherent twin boundary and the twin tip in W (Figure 4.4a and b, respectively). Moiré fringe patterns usually formed during the twinning process and their profiles are usually flexuous and irregular, implying that the slope of the inclined twin boundary is

diversified. As a result, the detailed structure of this inclined interface cannot be determined directly by the projection view provided by the TEM image. The detailed 3D structure of the inclined twin boundary demands to be studied by future advanced experiments and simulations. However, as a non-coherent twin boundary, strong lattice distortion is deemed to exist near the inclined twin boundary, giving rise to higher strain energy compared to CTB. In addition, the shear strain within the matrix right in front of the twin tip provides an additional driving force for the detwinning.



Figure 4.4 Representative deformation twins in body-centered cubic metals and face-centered cubic metals. (a) Deformation twin with the moiré fringe near coherent twin boundary in tungsten. (b) Deformation twin with the Moiré Fringes near the incoherent twin boundary (the twin head) in tungsten. (c) Typical deformation twin in silver. Fast Fourier Transform patterns proving the twin structure are inserted in the Figure. (d) The sample percentage of the area fraction of the Moiré Fringes in deformation twins in tungsten and face-centered cubic metals (Ag, Pt, Au). Scale bar in Figs. a, b and c is 2 nm.¹⁶⁹

Statistical analysis shows that more than 90% of the twins found in BCC W possess inclined twin boundaries (Figure 4.4d). Moreover, the area fractions of MF region in deformation twins are also calculated (the method is illustrated in Figure 4.5). Most of the twins with over 90%

MF counted here were captured during loading. By contrast, the CTB of the deformation twins in Ag crystals is very sharp and no MF formed in there. In FCC metals, the twin tip is usually bounded by an incoherent twin boundary parallel to the {112} plane, where the periodic stacking of twinning partials could lead to zero macro-strain^{56, 173}, and thus remarkably reduce the extra energy cost over the CTB energy¹⁷⁴. Admittedly, some distorted twin boundaries with MF were occasionally found in FCC metals with low stacking fault energies, especially undergoing severe plastic deformation, which might be induced by the operation of the pole mechanism that is hardly activated in BCC metals.⁴²



Figure 4.5 Schematic of the calculation of the area fraction of Moiré Fringes (MF) region in the twin. (a) The three-dimension diagram of the twin with MF. (b) The projection of the twin with MF along the beam direction. (A2+A1) represents the projection area of the whole twin on the (110) plane ([110] is the view direction of TEM observation). A1 and A2 represent the projection areas of Moiré Fringes region and the twin part without Moiré Fringes on (1-10) plane. Due to the curved boundary of Moiré Fringes, the region could be subdivided into many small trapezoids with the same height value a. b1', b2', ..., bn' represent the base lengths (marked by red arrows in b) of trapezoids in the whole twin and b1, b2, ..., bn represent the base lengths (marked by green arrows in b) of trapezoids in Moiré Fringes region. The projection areas of the twin and Moiré Fringe region could be approximately calculated by the summation of all trapezoid areas respectively, as shown by inserted equations in the figure.¹⁶⁹

4.3.3 The Proportion of The Inclined Twin Boundary on Detwinning

The proportion of the inclined twin boundary plays an important role in the instability of deformation twins and detwinning in W and most captured spontaneous detwinning happened in twins with over 70% MF region. As shown in Figure 4.6a-d, detwinning proceeded quickly in the twin enriched in MFs, especially in the first 28 seconds, and completed after 62s. This trend was

also observed in Figure 4.1, where the detwinning rate (i.e., the rate of reduction in the twin area) kept decreasing with the shrinking of the MF (Figure 4.6e), implying that the instability of the twin in BCC metals is closely associated with the proportion of inclined twin boundaries. Note that the abnormal increase in the detwinning rate after 1681.5 s in Figure 4.6e can be attributed to the increasing imaging force⁸⁶ acting on the twinning dislocations as they approached the surface (Figure 4.1g and h). Similarly, detwinning could be facilitated when the twin was very small and near the surface, such as the self-detwinning processes observed in tiny twins as shown in Figure 4.7.


Figure 4.6 Dependence of the twin instability on the portion of the inclined twin boundary. (a-d) Detwinning in the twin with full Moiré Fringes and ~15 nm thickness. (e) Development of the twin and the area fraction of the Moiré Fringes with the detwinning time. (f) The dependence of the average detwinning rate on the area fraction of the Moiré Fringes region. Scale bar in Figs. a-d is 2 nm.¹⁶⁹

To further quantify the effect of inclined twin boundary on the stability of twins, the dependence of the average detwinning rate on the inclined twin boundary in twins with similar sizes (2-10 nm) was investigated, as shown in Figure 4.6f. Clearly, the detwinning rate increases with the MF area fraction. When the percentage of MF region is lower than ~60%, the deformation twins kept stable without obvious spontaneous detwinning after 30 minutes (Figure 4.8). This indicated the instability of the twin structure increases with the proportion of inclined twin

boundaries and the interface energy of the inclined twin boundary provides the main driving force for detwinning.



Figure 4.7 Spontaneous detwinning of a small twin near the surface of W nanocrystal. (a-c) The detwinning process of one small twin near the surface. (d-e) One small twin disappeared after 27 hours under beam-blanked condition. Scale bar 2 nm.¹⁶⁹



Figure 4.8 Stable twin with a low fraction of Moiré fringes (MF) region in W nanocrystal. (a) The deformation twin with a low fraction of MF. (b) The twin after 30 minutes under beam-blanked condition. Scale bar 2 nm.¹⁶⁹

4.4 Discussion

The thermodynamic instability of deformed structures is largely decided by the excess energy compared to the perfect structure. For deformation twins, the excess energy is mainly from the interface energy of twin boundaries and the shear strain induced by twinning. The shear strain also induces the reorientation of the single crystal leading to the surface energy difference between the pristine crystal and deformed counterpart.⁵⁰ These excess energies provide the driving force for detwinning. MD simulation indicated that high-energy interfaces rather than coherent twin boundaries could induce the detwinning in BCC nanowires during unloading,¹⁷² consistent with the experimental observation.

As shown in Figure 4.9, the formation of the inclined twin boundary in BCC metals is associated with the twinning process. There are two scenarios for the formation of the Moiré fringes. The first case: the formation of MF via the stacking of screw-type twinning partials, with the different propagation distances on multiple twinning planes, as shown in Figure 4.9a. The second case: mixed-type twinning partial, e.g. curved dislocation, as shown in Figure 4.9c. As shown in Figure 4.9a, some twinning dislocations (marked by broken orange lines) don't penetrate through the whole crystal, leading to the overlapping between the matrix and the twin along the electron beam direction (Figure 4.9b). However, for case 1, because the dislocation lines are parallel to the electron beam direction, it is not practically possible to determine the positions of twinning partials. Since the uncertainty of the propagation distance of twinning partials on different twinning planes, the inclined twin boundary cannot be evaluated directly. Furthermore, it is hard to develop one accurate analytical model to decide the critical condition for detwinning. Additionally, it is difficult to describe the relationship between the area fraction of MF f and the stacking of twinning partials. Based on the above difficulties associated with case 1, case 2 is selected for quantitative analysis. Based on our model shown in Figure 4.9c, the Moiré fringes could be formed by the stacking of one set of curved twinning dislocations on different parallel twinning planes similar to the result shown in Figure 4.1. As shown in Figure 4.9d, the electron beam would go through the matrix and the twin, leading to the captured MF under TEM observation. For the quantitative analysis, it is assumed that the geometry and the propagation distance of all dislocations on different twinning planes are the same. One possible reason for the formation of the inclined twin boundary is the proposed double-cross-slip assisted twinning process⁴⁴. In the current study, it is noted that the propagation of twinning partials is very slow, which could be another factor contributing to the formation of inclined twin boundaries. Compared to the high glide velocity of twinning partials in FCC metals¹⁷⁵, the lattice friction is very high for dislocation slip in BCC metals, especially for screw dislocations^{80, 176, 177}. Besides, the twinning partials are deemed to be formed by the dissociation of full screw dislocations³⁷ which move slowly through a kink-pair mechanism in BCC metals¹². And kinks like small steps in screw parts of the twinning partial may increase the lattice distortion near the inclined twin boundary and its complexity further. Moreover, twinning partials nucleated from the surface are subjected to higher resistance when propagating to the thicker region and thus demonstrated lower mobility,¹⁷⁸ which increases the probability to form the inclined twin boundary. In addition, previous simulation results^{39, 179} indicated that the Peierls stress of the screw partial is much higher than that of the edge partial. And the prominent mobility difference between screw and edge partials is supposed to contribute to the formation of the curvy dislocation lines on the inclined twin boundary.



Figure 4.9 The stacking of multiple twinning dislocations on different twinning planes. (a) The formation of MF via the stacking of multiple screw-type twinning partials. (b) The view of a along $[11\overline{1}]$ direction. (c) The formation of MF via the stacking of multiple mixed-type twinning partials, based on the proposed model. (d) The view of c along [112] direction. The twinning dislocations are marked by the orange lines on the twinning plane (112).¹⁶⁹

The instability of deformation twins and the high interface energy of the inclined twin boundary likely originate from the curved twinning partials in BCC crystals. A general model of the deformation twin with MF in BCC metals was illustrated in Figure 4.10. A group of curved twinning partials pile on parallel twinning planes (marked with (112)) in the nanocrystal due to the partial penetration of the partial dislocation, forming a 3D inclined twin boundary (the grey hook surface) (Figure 4.10a) and thus the corresponding MF region (the cyan region in Figure 4.10b) when viewed along the electron beam direction of $[1\overline{1}0]$. To understand the detwinning mechanism, we further analyzed the dynamic behavior of twinning partials quantitatively. Due to the complex morphology and the core structure of the curved twinning partial, one simplified model was developed, as schematically shown in Figure 4.9c and Figure 4.11a. Each 1/6[111] twinning partial was treated as a half-circle dislocation loop subject to four types of forces when external forces are absent, *i.e.* the restoring force $F_{restore}$ due to the curvature of the dislocation line, F_{SF} due to the stacking fault formation in crystals,⁶⁰ the positive and negative image forces, F_{image}^+ and F_{image}^- respectively, originating from the opposite surfaces, and the friction force F_{friciton} due to the lattice resistance, as shown in Figure 4.10c and Figure 4.11a. F_{restore} reflects the strain induced by the curvature of the dislocation line and thus the elevated energy of the inclined twin boundary, while F_{SF} for one individual twinning dislocation results from the existence of the stacking fault in the interior of the nanocrystal. Considering the formation of MF via the stacking of multiple twinning dislocation on different twinning planes, the drag force due to the existence of the twin with two twin boundaries is $2F_{twin fault}$ (the twin fault force).⁶⁰



Figure 4.10 Schematic of the inclined twin boundary (Moiré Fringes region) and associated-detwinning in the nanocrystal. (a) The three-dimension twin structure with the inclined twin boundary in the nanocrystal. The curved dislocation lines are marked by the orange line on the twinning plane (112) and the inclined twin boundary is marked by the grey hook surface. (b) The front view of MF along [110]. MF region-the projection of the inclined twin boundary region and the fully-grown twin are marked by the blue and red polygons respectively. (c) One selected twinning plane in the twin. One individual curved twinning partial on the twinning plane (112), mainly suffering four forces, the restoring force $F_{restore}$, the stacking fault force F_{SF} , the positive and negative image forces, F^+_{image} and F_{image} respectively, and the friction force $F_{friction}$ under unloading. The detwinning direction is indicated by the bold green arrow.¹⁶⁹



Figure 4.11 (a) Schematic of the force of one individual twinning partial on the (112) twinning plane. The dislocation line is marked by the red half-loop. (b) Schematic of the image force on the half-circle loop dislocation.¹⁶⁹

The restoring force $F_{restore}$ can be approximately expressed by the following equation¹⁸⁰:

$$F_{restore} = \frac{\alpha \mu b^2}{4\pi r} \tag{4-1},$$

where μ is the shear modulus, *r* is the radius of curvature and α is the coefficient (~2.1 for pure edge dislocation and ~6.3 for pure screw dislocation). Since F_{SF} is determined by the stacking fault energy, and it is estimated to be ~0.089 N m⁻¹.^{33, 34, 181} Image force for edge dislocation,¹⁸⁰

$$F_{image} = \frac{\mu b^2}{4\pi l(1-\nu)} \tag{4-2}.$$

Image force for screw dislocation,¹⁸⁰

$$F_{image} = \frac{\mu b^2}{4\pi l} \tag{4-3}.$$

For the half-circle dislocation loop, the image force as shown in Figure 4.11b is

$$F_{image} = \frac{\int_0^{\pi} (\mu b^{2} r d\theta \sin\theta) / 4\pi r \sin\theta (1-\nu) + \int_0^{\pi} (\mu b^{2} r d\theta \cos\theta) / 4\pi r \sin\theta}{\pi r}$$
(4-4)

where *l* is the distance from the surface, *v* is the Poisson ratio, *r* is the radius and θ is the angle. The total force *F_{total}* acting on the individual dislocation line on one twinning plane is expressed as:

$$F_{total} = F_{restore} + F_{image}^+ + F_{SF} - F_{friction} - F_{image}^-$$
(4-5).

Considering the stacking of multiple twinning dislocation on different twinning planes, the average net force for the twin with *N* layers can be expressed as:

$$\bar{F}_{total} = \frac{N(F_{restore} + F_{image}^{+} - F_{friction} - F_{image}^{-}) + 2F_{twin fault}}{N} = F_{restore} + F_{image}^{+} - F_{friction} - F_{image}^{-} + \frac{2F_{twin fault}}{N}$$

$$(4-6).$$

Two scenarios are considered in Figure 4.11a as follows:

Scenario 1: $0 < d \le \frac{B}{2}$. There is one assumption that the twinning partial keeps as a halfcircle loop to propagate, the area fraction of MF f = 100%. Scenario 2: $\frac{B}{2} < d \le 2B$ where the assumption that the dislocation would keep as the original half-circle loop to move forward is made and the area fraction of MF $f = \frac{B}{2d}$. As scenario 2 is developed, the balance ($\overline{F}_{total} =$ 0) can be reached and f_c is determined. Based on references^{39, 167}, it is assumed that the layer number of the twin $N \ge 6$.

Note that F is defined as the force applied per unit length of the dislocation line in our analysis. Based on the analytical model, there exists a critical area fraction of MF f_c above which the average net force \overline{F}_{total} on the twin is positive (Figure 4.12), providing the driving force for spontaneous detwinning. It is found that except in cases where twinning partials are located

extremely close to the surface (e.g. < 5 nm distance to the surface, as shown in Figure 4.13), the image force is trivial compared to the twin fault force or stacking fault force—the property that is intrinsic to materials, indicating that the detwinning phenomenon and mechanism observed in W nanocrystals could be inherent to BCC metals regardless of specimen size. Although the assumed geometry of the dislocation line is related to the sample size in the analytical model, the curvature of the dislocation line which determines the restoring force and influences the structure of the inclined twin boundary in the actual materials is closely associated with the mobility of dislocations, especially for Bcc materials. Given that in bulk materials, the driving force for detwinning is mainly determined by ($2F_{twin fault} + F_{restore} - F_{friction}$), the detwinning behavior in Bcc metals should be materials-dependent, and those with relatively high stacking-fault and twinboundary energies are more likely to demonstrate low stability in deformation twins.



Figure 4.12 The critical condition for detwinning. (a) Multiple twinning planes, N = 6. (b) Multiple twinning planes, N = 60. The average net force \overline{F}_{total} (blue line) on twinning dislocation line and the area fraction of the Moiré Fringes f (red line) to the propagation distance of the twining partial d. (B = 15 nm, $\mu = 188$ GPa in W) The solid line represents case 1 and the broken line represents case 2.¹⁶⁹



Figure 4.13 Functions of $2F_{twin\,fault}$ (F_{SF}) and the positive image force F^+_{image} with the propagation distance of the twinning partial d. (B = 15 nm).¹⁶⁹

The unstable twin structure can significantly influence the mechanical properties of BCC metals, especially in small-sized BCC metals where deformation twinning becomes a competing deformation mode against dislocation plasticity due to their comparable activation stresses. 52, 182, ¹⁸³ Massive inclined twin boundaries with high interface energy formed during deformation make it difficult to induce continuous and steady twinning networks in BCC metals. This also gives little chance to induce secondary twinning. Moreover, the inclined twin boundary as the high energy interface provides opportunities to accumulate the mechanical energy during plastic deformation and twinning, which, followed by subsequent self-detwinning, makes small-sized BCC metals potentially applicable for microdevices with the ability of storage and release of mechanical energy¹⁸⁴ with considerable conversion efficiency. Besides, the excellent pseudoelasticity enabled by unstable twin is different from that by phase transformation^{185, 186} or surface-diffusion^{103, 187}, which makes materials recoverable to the initial structure even they are deformed over the elastic limit ¹⁸⁸. In addition, self-detwinning in BCC metals helps remove the plastic strain and may heal the "wound" induced by twinning. Consecutive twinning and detwinning during cyclic loadings might provide the pathway to bear the fatigue deformation and improve the fatigue life of BCC metals¹⁸⁹. These findings assist in making BCC nanomaterials with magnificent properties applicable in MEMS.

4.5 Conclusions

In conclusion, unstable twin in Bcc nanocrystals was revealed by capturing atomic-scale self-detwinning process through in-situ TEM experiments. The intrinsic instability of deformation twins in BCC metals is related to the inclined twin boundary with high interfacial energy that

provides the driving force for spontaneous detwinning. The formation of inclined twin boundaries might be contributed to the low mobility of twinning partials in Bcc metals and the geometry of the twinning grain. The high proportion of inclined twin boundaries would facilitate complete detwinning. These findings offer new insights for understanding deformation twinning in BCC metals as well as guidelines for processing new structural and functional materials. For unstable twin structures, adding appropriate alloy elements may lower the interface energy and stabilize the twin and dislocation structure,¹⁹⁰ which provides possibilities to improve properties of BCC metals by implanting high-density nano-twins.

5.0 In-situ TEM Investigation on Surface-Diffusion-Induced Abnormal Softening in Nanoscale Metallic Crystals

In this chapter, the abnormal softening in nanoscale metallic crystals is revealed. Ultrahigh surface-to-volume ratio in nanoscale materials could dramatically facilitate mass transport, leading to surface-mediated diffusion similar to Coble-type creep¹⁹¹ in polycrystalline materials.¹⁰³ Unfortunately, the Coble creep is just a conceptual model, and the associated physical mechanisms of mass transport have never been revealed at atomic scale. Akin to the ambiguities in Coble creep, atomic surface diffusion in nanoscale crystals remains largely unclear, especially when mediating yielding and plastic flow. Here, by using in situ nanomechanical testing under high-resolution transmission electron microscope, it is found that the diffusion-assisted dislocation nucleation induces the transition from a normal to an inverse Hall-Petch-like relation of the strength-size dependence and the surface-creep leads to the abnormal softening in flow stress with the reduction in size of nanoscale silver, contrary to the classical "alternating dislocation starvation" behavior⁴⁹ in nanoscale platinum. This work provides insights into the atomic-scale mechanisms of diffusion-mediated deformation in nanoscale materials and guidelines on the design for ultrasmall-sized nanomechanical devices.

5.1 Introduction

Controlling mechanical properties in the design of new materials through the manipulation of microstructural length scale has attracted a great deal of interest in the field of materials science and engineering.^{72, 79, 164} As described by Hall–Petch strengthening rule, grain refinement leads to a strength increase in nanocrystalline (NC) metals, due to the reduction of dislocation-nucleation sources^{192, 193}. As the grain size decreases to a few nanometers (< 10 nm), intragrain dislocation activity gives way to GB-mediated mechanisms, including GB sliding¹⁹⁴, grain rotation¹⁹⁵, GB migration^{196, 197}, and diffusional creep^{92, 191}, which are candidate deformation mechanisms for inverse Hall-Petch relation^{90, 198}. Analogous to the impact of GBs on the plastic deformation of NC materials, free surface plays an essential role in mediating the plasticity of nanocrystals or nanowires (NWs) with ultrahigh surface-to-volume ratio⁸⁷.

On account of the scarcity of the effective dislocation sources inside NWs, free surface, an effective sink, and source of dislocations, governs yielding behavior, leading to the well-known 'smaller is stronger' in NWs^{15, 79, 84, 85}. Besides, akin to the role of GBs in Coble-type diffusion softening behaviors in bulk NC metals, free surface in nanostructured materials can serve as a highway for mass transport¹⁰. Coble creep presented a conceptual model to describe GB diffusion, but both the concomitant GB sliding and the complex GB structure make the concrete diffusion pathway elusive in polycrystalline materials^{92, 191}. Contrary to the conjectured diffusion process along grain boundary in the classical Coble creep model,¹⁹¹ the free surface provides a window to visualize the mass transport during creep. Previous studies suggested that as the sample sizes of silver crystals decreased below ~10 nm surface atom diffusion replaced displacive deformation as the dominant deformation mechanism resulting in 'smaller is much weaker'^{5, 103}, that, however, has not been corroborated by direct experimental evidence to date. Furthermore, the theory based on the Coble-creep model only gave a plausible description of the softening trend but was incapable of providing a consolidated criterion to reveal the inherent transition from a normal to an inverse Hall-Petch regime.¹⁰ Until very recently, Sun et al.^{199, 200} reported that displacive

mechanisms were still activated in the plastic deformation processes of sub-5 nm-diameter Ag NWs. In light of the discrepancy between the fundamentally different plasticity mechanisms activated in the nanostructured metals of comparable size, the validity of the mechanisms proposed in previous studies to account for the so-called inverse Hall–Petch-like effect remains questionable. In addition, Zhong et al.⁵ revealed that slip-activated surface diffusional creep gave rise to a self-healing mechanism, that prevented shear localization and the tendency of plastic instability, leading to super-elongation in Ag NWs. However, whether or not such surface diffusional creep contributed to plasticity and hence caused stress relaxation during plastic flow was not identified in their work. On account of some ambiguity in previous studies, leaps, not strides, need to be taken to bolster our understanding of the atomic-scale mechanism governing strength and plastic flow in small-sized metals, which are of importance not only for drawing a comprehensive mechanistic picture of size-dependent deformation but also for the mechanical reliability and stability of nanoelectronics.

Here, in situ high-resolution transmission electron microscopy (HRTEM) tensile testing technique complemented by MD simulations are performed to investigate the yielding and plastic flow behavior in nanoscale Ag and Pt. The physical creep processes of the surface mass transport are successfully captured. It is revealed that the yield strength-size relationship transits from 'smaller is stronger' to 'smaller is weaker' with the reduction of sample diameters of Ag crystals, while nanoscale Pt shows traditional Hall-Petch-like-strengthening, i.e., 'smaller is stronger'. Dislocation nucleation and plastic flow evolution involved by surface creep processes are further analyzed by both direct experimental evidence and complementary molecular dynamic simulation. Based on in situ observation on the physical creep process and mechanical behaviors of nanocrystals, the mechanisms proposed in this study catch sight of understanding diffusionmediated deformation in nanoscale metallic crystals.

5.2 Experimental Procedures

The sharp nano-tips of Ag and Pt oriented in the <110> zone axis were selected to be welded together with the probe side by applying a constant voltage of $\sim 1 \text{ V}^5$. When the nano-tip contacted with the probe side, the pre-applied potential could melt the nano-tip and then generate bridge-shaped single-crystal nanowires with controllable dimensions, which were epitaxially grown from one substrate and connected to either a tungsten probe or another substrate at the opposite side. The cross-section of the as-fabricated NW is nearly circular with equal width and thickness⁵². The middle segment of the single-crystalline nano-bridge had a smaller diameter compared to those at either end, serving as a gauge section. The strain rate of $\sim 10^{-2} \text{ s}^{-1}$ and $\sim 10^{-3} \text{ s}^{-1}$ during tensile loading were controlled by the movement speed of the piezo-manipulator of the STM holder. Besides, all in situ experiments were recorded in real-time by a charge-coupled device (CCD) camera at a rate of 0.5 s/frame.

5.3 Experimental Results

5.3.1 Strength-size Dependences in Nanoscale Ag and Pt

In situ HRTEM tensile tests were performed along <112>-orientation at room temperature under a strain rate of $\sim 10^{-3}$ s⁻¹ to investigate yield strength-size dependence in Ag and Pt NWs. The yield strength here is defined as the maximum elastic lattice stress that a defect-free crystal can withstand just before the first event of dislocation nucleation. As shown in Figure 5.1, the yield strength of Pt NWs increased with decreasing sample size following the classical Hall-Petch-like relationship, that is 'smaller is stronger', as previously reported in nanowhiskers²⁰¹ and nanopillars²⁰². In contrast, the yield strength-size relationship in Ag NWs changed from 'smaller is stronger' to 'smaller is weaker' as the sample diameter of Ag NWs decreased below a critical size of ~ 15 nm (the red line in Figure 5.1). Given that the strength of NWs is controlled by dislocation nucleation^{52, 87, 203}, these two distinct size effects are speculated to be associated with different nucleation behaviors.



Figure 5.1 Size dependence of yield strength in Ag NWs and Pt NWs. In situ tensile straining of <112>-oriented Ag NWs with different sample diameters were performed at strain rates of $\sim10^{-2}$ s⁻¹ (green points) and $\sim10^{-3}$ s⁻¹ (red points). Pt NWs were loaded along <112>-orientation at a strain rate of $\sim10^{-3}$ (blue points). The blue, red and green lines represent the tendency of the strength-size relationship in Pt NWs under a strain rate of $\sim10^{-3}$ s⁻¹ and Ag NWs under a strain rate of $\sim10^{-2}$ s⁻¹ and $\sim10^{-3}$ s⁻¹, respectively.¹⁵³

To uncover the underlying mechanisms governing different nucleation behaviors, atomicscale deformation processes of Ag and Pt NWs were systematically investigated, as shown in Figure 5.2 and Figure 5.3. Some blurry boundaries in the HRTEM images were attributed to the delocalization effect instead of surface contamination¹⁵². After fabrication, three surface defects (surface atomic steps) existed in the 6.6-nm-diameter Ag NW (Figure 5.2a). The lateral movements of surface atomic steps, arose from curvature- and stress-driven surface atom diffusion^{5, 103, 199}, occurred before surface dislocation nucleation. As shown in Figure 5.2b-d, steps 2 and 3 migrated to the right side, while step 1 migrated to the left side upon tensile loading. As step 3 migrated to the initial location of step 2 (indicated by a navy blue circle), a partial dislocation nucleated and propagated from this site, leaving behind a stacking fault (SF), as shown in Figure 5.2e-g. Subsequently, the SF was eliminated by a trailing partial at the same site, leaving behind a one-atomic-layer step at surface (step 4)^{87, 204}, as shown in Figure 5.2h. Instead, the eventual site of moving step 1 did not favor dislocation nucleation, which was associated with the different surface diffusional processes. Surface atom diffusion via the overlap of surface defects (steps 2 and 3) changed surface atomic configuration and thus lowered nucleation stress, that is, yield strength^{101, 157}. In contrast to Ag NWs, the migration of surface steps, namely, surface diffusion was not observed before dislocation nucleation in Pt NWs (Figure 5.3). This difference was attributed to the high activation energy barrier and low surface mobility for self-diffusion in Pt, compared to Ag (Table 5.1)^{5, 205}.



Figure 5.2 Dislocation nucleation assisted by surface diffusion in an Ag NW. a, TEM image of a pristine 6.6nm-diameter Ag NW under <112> tensile loading at room temperature and a strain rate of ~10⁻³ s⁻¹. b-f, Sequential TEM images showing the lateral migration of three atomic steps (surface atom diffusion) on the {111} surface of the Ag NW. The initial position of step 2 was marked by a navy blue circle. g, A partial dislocation activity observed at the overlapping position of steps 2 and 3. h, A one-layer surface step (step 4) formed by the elimination of a stacking fault. i-l, Sequential TEM images showing the plastic flow of the Ag NW with a small number of surface diffusion. All scale bars are 2 nm. Each surface step is tracked by an arrow of specific color. m, Lattice stress versus applied strain curve during tensile loading; points (a-l) indicate the states of deformation shown in the TEM images of a–l. The error bars represent the variations of the measured lattice stresses at different locations of the nanowire.¹⁵³

| | Ag NWs | Pt NWs |
|--|---------|--------|
| Young's modulus E (GPa) | 83.61 | 185.01 |
| Lattice constant a (nm) | 0.4079 | 0.3924 |
| Full dislocation burgers vector b (nm) | 0.2921 | 0.2810 |
| Activation energy barrier for diffusion (eV) | 0.064 | 0.171 |
| Surface mobility μ_s (m ² ·J ⁻¹ ·s ⁻¹) | 1.4*104 | 4.3 |
| Surface energy γ (J/m ²) | 1.17 | 2.3 |
| | | |

Table 5.1 Physical property parameters of Ag and Pt.¹⁵³



Figure 5.3 In situ TEM tensile testing shows pure displacive deformation in a Pt NW. a-f, A series of TEM images showing the plastic deformation process of a 5.9-nm-diameter under tensile loading along <112>- orientation at room temperature under a strain rate of ~10⁻³ s⁻¹. The plasticity of Pt NW is controlled by repeated nucleation and emission of full dislocations, and each full dislocation activity resulted in the surface steps thickened by one atomic layer (b, d, f). Obvious surface atom diffusion was not observed during tensile loading causing that surface steps remained immobile. All scale bars are 2 nm. g, Lattice stress versus applied strain curve during tensile loading; points (a-f) indicate the states of deformation shown in the TEM images of a–f. The error bars represent the variations of the measured lattice stresses at different locations of the nanowire.¹⁵³

In addition to the direct experimental observations, activation volume (Ω), that is an effective kinetic signature of deformation mechanism^{79, 102, 206, 207}, as well as activation free energy (ΔG) were determined to confirm the operation of surface-diffusion-assisted nucleation mechanism in Ag NWs (Appendix). The calculated Ω and ΔG for Ag NWs (<15 nm) are ~0.24 b^3 and ~0.063 eV, respectively, where *b* is the Burgers vector for a perfect dislocation. These values are of the same order as the theoretical values (~0.1 b^3 ⁷⁹ and 0.044-0.3 eV ^{205, 208, 209}) for surface diffusion in Ag. In contrast, the calculated Ω and ΔG for the Pt NWs (~1.02 b^3 and 0.316 eV) and the Ag NWs with diameters above 15 nm (~1 b^3 and 0.141 eV), are consistent with the theoretically

predicted values for surface dislocation nucleation without diffusional events, where Ω and ΔG are in the range of 1-10 b^3 and 0.16-0.34 eV^{14, 80}, respectively. Thus, it is plausible to conclude that the diffusional mechanism facilitates dislocation nucleation in Ag NWs (< 15 nm), whereas, conversely, dislocation nucleation in Ag NWs (> 15 nm) (Figure 5.4) and Pt NWs was not associated with diffusional deformation.



Figure 5.4 The surface dislocation nucleation in the Ag NW with 30 nm. Scale bar 2 nm. The slip-activated surface step was marked by the yellow arrow in e and f. The motion of the step was indicated by the blue arrow.¹⁵³

Considering that the diffusional deformation is sensitive to the strain rate, $^{91, 157, 206}$ to further probe the surface-diffusion-assisted nucleation, which is a rate-controlling process the yield strength-size dependence of Ag NWs at a higher strain rate of $\sim 10^{-2}$ s⁻¹ was investigated. As shown in Figure 5.1, the yield strength of Ag NWs increased with the applied strain rate, and the critical size for softening was smaller, which may be attributed to the less diffusional events before dislocation nucleation at a higher strain rate. Several lines of direct observational evidence and theoretical calculations mentioned above indicated that two distinct nucleation mechanisms were operative in Ag NWs, that is, surface dislocation nucleation and surface-diffusion-assisted dislocation nucleation. Analogous to GB in NC materials, free surface in NWs plays an increasingly important role in mediating plasticity with the reduction of sample size^{48, 207}. Surface dislocation nucleation and subsequent dislocation starvation governed the plasticity of nanoscale crystals.^{14, 84, 85, 210} Based on surface-dislocation-nucleation-theory^{14, 84}, the effective nucleation sites were reduced with decreasing sample size, resulting in the "smaller is stronger" observation in Pt NWs and Ag NWs (> 15 nm). Free surface, having reduced constraints and larger diffusivity, can also act as a highway for mass transport in NWs¹⁰. Since activation energy for atomic diffusion on a low-indexed surface is small, surface atom diffusion can be activated in the nanometer regime and becomes stronger with the reduction of sample size^{5, 103, 199, 211}. Consequently, surface diffusion served as a precursor mechanism for dislocation nucleation resulting in a "smaller is weaker" trend in Ag NWs (< 15 nm).

5.3.2 Atomic-Scale Mechanisms of Surface-Diffusion-Assisted Dislocation Nucleation

Albeit the inherent high strain rate in MD simulations make it difficult to compare deformation mechanisms in experiments and simulations, the temperature of 800 K and the strain rates of 10⁵ s⁻¹ and 10⁷ s⁻¹ were chosen in our simulations such that surface diffusion, if any, only occurred near free surface (Figure 5.5 and Figure 5.6), which is a salient characteristic of surface diffusion in nanocrystals at room temperature^{5, 103, 199, 204, 212}.



Figure 5.5 Atomic diffusion at the onset of plasticity in Ag NWs under <112> tensile loading at strain rates of 10^5 s^{-1} and 10^7 s^{-1} . a,b,c, 6-nm-diameter Ag NWs at the temperature of 300 K (a), 500 K (b) and 800 K (c). d, 20-nm-diameter Ag NWs at the temperature of 800 K. Non-affine squared displacement (D^2_{min}) was used to quantify diffusion in small samples²¹³. Each atom in the samples is colored according to its value of D^2_{min} , and the red atoms are diffusive.¹⁵³



Figure 5.6 Atomic diffusion at the onset of plasticity in 6-nm-diameter Pt NWs deformed along <112> tensile loading under strain rate of 10^5 s⁻¹ and at, a-c, the temperature of 300 K (a), 500 K (b), and 800 K (c), respectively. Non-affine squared displacement (D^2_{min}) was used to quantify diffusion in small samples²¹³. Each atom in the samples is colored according to its value of D^2_{min} and the red atoms are diffusive.¹⁵³

As shown in Figure 5.7a, (steps 1 and 2), formed by surface diffusion, appeared at the surface of a 6-nm-diameter Ag NW. With further loading, the moving step 2 overlapped step 1 forming a two-atomic-layer step, and then partial dislocations nucleated from the newly formed step (Figure 5.7b-d), similar to the experimental observations (Figure 5.2a-g). The increase in step height via the overlap of surface defects increased local stress concentration near the overlapping position^{204, 214, 215}, and thus lower nucleation stress, favoring dislocation nucleation from this site. Additionally, the computational results of 6-nm-diameter Ag NWs also showed that localized diffusion of individual atoms in a random and chaotic way turned initially smooth surfaces into

potholed surfaces, creating some mass-deficient defects, that significantly lower nucleation stress^{157, 214} (Figure 5.7e). It is energetically more favorable to nucleate a dislocation from the mass-deficient defects (Figure 5.7e). MD simulations of Ag nanowires here provide direct computational evidence that long-range and localized atomic diffusion at surface can lower nucleation stress and further cause the inverse Hall-Petch effect. In contrast, weak and nearly no surface diffusion occurred before dislocation nucleation in 20-nm-diameter Ag NW (Figure 5.7f) and 6-nm-diameter Pt NW (Figure 5.7g), respectively, in agreement with the experimental evidence that surface diffusion in NWs was size- and material-dependent (Figure 5.1 and Figure 5.3). In these nanoscale metals without surface diffusion, dislocations prefer to nucleate at the middle segment or the corners of the sample with higher stress compared to the other parts of sample²¹⁶, as shown in Figure 5.7f-g. With the decrease in the size of the sample without preconditioned by surface diffusion, the effective nucleation sites were reduced, resulting in "smaller is stronger"^{14, 84}. For all the Ag and Pt NWs, dislocation always nucleated in the gauge section, and surface diffusion, if any, remained confined to free surface during tensile loading. Besides, the yielding of 6-nm-diameter and 20-nm-diameter Ag NWs at a higher strain rate of 10⁷ s⁻¹ were also shown to be controlled by dislocation nucleation with and without being pre-conditioned by diffusional events, respectively (Figure 5.8), consistent with the size effect on yielding observed experimentally (Figure 5.1). Compared with surface dislocation nucleation, the surface-diffusionassisted nucleation mechanism led to obviously increased strain-rate sensitivity of nucleation stress owing to its small activation volume (Figure 5.9).



Figure 5.7 MD simulations of dislocation nucleation mechanism in metallic NWs under <112> tension at the temperature of 800 K and a strain rate of 10⁵ s⁻¹. a, Two atomic steps (steps 1 and 2) formed by surface diffusion in a 6-nm-diameter Ag NW. b, Surface-diffusion-assisted migration of atomic steps (steps 1 and 2) to the right side of NW. c, Overlap of surface defects. d, Nucleation and propagation of leading partial dislocations at the overlapping position of surface defects. e, Dislocation nucleation assisted by single-atom diffusion at the surface

of a 6-nm-diameter Ag NW in a random and chaotic way. f, Dislocation nucleation in a 20-nm-diameter Ag NW with weak surface diffusion. g, Dislocation nucleation in a 6-nm-diameter Pt NW with nearly no surface diffusion. h, No diffusional events during plastic flow in the Pt NW causing that surface steps remained immobile. Surface steps caused by full dislocation activities are colored by orange and yellow in g,h. The color coding corresponds to surface atoms in blue color, atoms in SFs in light green color, and atoms in perfect face-centered cubic (FCC) crystal arrangement in light blue.¹⁵³



Figure 5.8 MD simulations of dislocation nucleation mechanism in <112>-oriented Ag NWs at 800 K and a strain rate of 10⁷ s⁻¹. a, Sequential snapshots (from the left to right) showing dislocation nucleation in a 6-nmdiameter Ag NW, assisted by single-atom diffusion in a random and chaotic way. b, Snapshots showing atomic diffusion in the deformed Ag NWs corresponding to a. c, Sequential snapshots (from the left to right) showing dislocation nucleation in a 20-nm-diameter Ag NW where weak surface diffusion occurred. d, Snapshots showing atomic diffusion in the deformed Ag NWs corresponding to c. Non-affine squared displacement (D^2_{min}) was used to quantify diffusion in small samples²¹³. Each atom in the samples is colored according to its value of D^2_{min} , and the red atoms are diffusive.¹⁵³



Figure 5.9 Stress-strain curves obtained by MD simulations of tensile straining of Ag NWs at strain rates of 10⁵ s⁻¹ and 10⁷ s⁻¹. a, 6-nm-diameter Ag NWs. b, 20-nm-diameter Ag NWs. With the increase in strain rate, the nucleation stress controlled by surface-diffusion-assisted nucleation increased from 1.98 GPa to 2.73 GPa in 6-nm-diameter Ag NW, while the nucleation stress controlled by surface dislocation nucleation increased from 1.97 GPa to 2.15 GPa in 20-nm-diameter Ag NW. Surface-diffusion-assisted nucleation mechanism exhibit a higher strain-rate sensitivity of nucleation stress.¹⁵³

5.3.3 Surface-Atom-Diffusion-Induced Softening during Plastic Flow

To reveal the effect of surface diffusion on plastic flow, the lattice stress-applied strain relations and the corresponding mechanical behaviors in Ag NWs were investigated (Figure 5.2, Figure 5.10, and Figure 5.11). The applied strains were determined from the length variation of the gauge section which is chosen based on the geometry of samples. At the early stage of tensile deformation without detectable diffusional events, the lattice stress increased with the applied strain linearly (before point a in Figure 5.10m and Figure 5.11i). As the lattice stress increased to a yield point, plastic deformation occurred with dislocation nucleation, subsequent propagation across the NW and eventual annihilation at free surface. Such displacive deformation partly released elastic lattice stress inside NW and thus led to very precipitous stress drops (Figure 5.2g,

h, j, l, Figure 5.10b, i, l and Figure 5.11b, f, h), as reported previously^{49, 199}. The differences between the experimental and theoretical values of strain increments, that correspond to different stress drops, were generally less than 0.05%, verifying that the evaluation method for the stress-strain curves in this work is feasible and reliable. After the yielding of 13.1-nm-diameter Ag NW, two atomic steps, induced by full dislocation activities^{5, 87, 204}, formed at the surface (Figure 5.10b), and then continuously migrated to the right edge with further loading (Figure 5.10c-h), driven by the chemical potential difference between the middle thin regions and terminal thick regions^{5, 199}. Meanwhile, the flow stress-strain behavior when surface diffusional creep happened cannot be described well by a linear elastic relationship before the next plastic event (points b-h in Figure 5.10m), which was also observed in 30-nm-diameter Ag NW (points b-e in Figure 5.11i). In contrast, no obvious softening occurred during plastic flow with very limited surface diffusion (points i-k in Figure 5.10m, points f-g in Figure 5.11i, and points h-l in Figure 5.2m).



Figure 5.10 Surface atom diffusion induced abnormal softening during plastic flow in an Ag NW. a, Pristine Ag NW with a diameter of 13.1 nm as viewed along $[\overline{1}10]$ and loaded along $[\overline{1}\overline{1}2]$ -orientation at room temperature and a strain rate of ~10⁻³ s⁻¹. b, Two surface steps (steps 1 and 2) formed by full dislocation activities. c-h, Surface-diffusion-assisted migration of surface steps (steps 1 and 2) to the right side of the NW during tensile loading. i, Two new surface steps (steps 3 and 4) in NW formed by full dislocation activities. j-l, Sequential TEM images showing the plastic flow of the Ag NW with a small number of surface diffusion. All scale bars are 2 nm. Each surface step is tracked by an arrow of a specific color. m, Lattice stress versus applied strain curve during tensile loading corresponding to the sequence in a–l. The initial strains were nominalized by subtracting the plastic strain in the previous plastic deformation history. The error bars represent the variations of the measured lattice stresses at different locations of the nanowire.¹⁵³



Figure 5.11 Surface atom diffusion induced abnormal softening during plastic flow in an Ag NW. a, Pristine Ag NW with a diameter of 30 nm as viewed along [$\overline{1}10$] and loaded along [$\overline{1}\overline{1}2$]-orientation at room temperature and a strain rate of ~10⁻³ s⁻¹. b, One surface step (step 1) formed by a full dislocation activity. c-e, Continuous migration of step 1 to the right side of the NW during tensile loading. f, A new surface step (step 2) in NW formed by a full dislocation activity. g, No obvious surface diffusion during further loading. h, A new surface step (step 3) in NW formed by a full dislocation activity. All scale bars are 2 nm. Each surface step is tracked by an arrow of a specific color. i, Lattice stress versus applied strain curve during tensile loading; points (a-h) indicate the states of deformation shown in the TEM images of a–h. The initial strains were nominalized by subtracting the plastic strain in the previous plastic deformation history. The error bars represent the variations of the measured lattice stresses at different locations of the nanowire.¹⁵³

Different from the alternatively elastic rise and drop of the lattice stress in most NWs,^{48, 49} such an unusual softening behavior during plastic flow in Ag NWs is associated with surface diffusional creep. When slip-activated surface diffusional creep occurs, the increasing rate of flow stress $\dot{\sigma}$ at any given applied strain can be expressed as

$$\dot{\sigma} = \frac{E}{100} \cdot \frac{\dot{\varepsilon} \cdot \dot{\varepsilon}_{\text{diffusion}}}{\dot{\varepsilon}},\tag{5-1},$$

where $\dot{\varepsilon}$ is the applied strain rate, and $\dot{\varepsilon}_{diffusion}$ is the plastic strain rate accommodated by surface diffusion, which increases continually with lattice stress/strain²¹¹. Hence, $\dot{\varepsilon}_{diffusion}$ progressively

reduced the increasing rate of stress versus strain during tensile loading, in accordance with experimental evidence. The observed diffusional deformation could partly contribute to the plastic strain of NWs. (Figure 5.12) MD simulations also demonstrated that surface atoms could diffuse into the interior of NW, contributing to plastic strain (Figure 5.13 and Figure 5.14). In contrast to the experimental results, the stress-strain curve before yielding was linear in MD, despite a wealth of atomic diffusion occurred at surface. Such difference may be attributed to the fact that the strain rate in MD simulations (10^5 s^{-1}) is 8 orders of magnitude higher than that in our experiments (~10⁻ ³ s⁻¹). According to our experimental results, $\dot{\varepsilon}_{diffusion}$ was of the same order as the experimental strain rate, and thus was too small to influence the shape of the stress-strain curve in MD. Different from the coupled displacive-diffusive deformation process in Ag NWs, no migration of surface steps, namely, no obvious surface diffusion was observed during plastic flow in Pt NWs (Figure 5.3), which was also captured in MD simulations (Figure 5.7g, h). The plasticity in Pt NWs was mediated by a pure displacive mechanism where each full dislocation activity increased the step height by one atomic layer (Figure 5.3b, d, f)^{5, 87, 204}. Consequently, the stress-strain curve in Pt NW before dislocation nucleation (points a, c, and e in Figure 5.3g) was described well by linear elastic relationship, consistent with alternating dislocation starvation behavior in NWs ^{48, 49}. Surface diffusional creep, accommodating plastic strain, effectively delayed the progressive activation of the following dislocations and thus weakened the hardening effect resulted from dislocation starvation,48, 49, 79, 87, 203 leading to an abnormal softening during plastic flow. In addition to softening, surface creep, overwhelmingly dominating over displacive deformation, may raise the probability of stress concentration and premature necking, instead of superelongation benefiting from the compatible interplay of displacive and diffusive mechanism⁵.



Figure 5.12 The diffusion-contributed plastic strain during tension in Ag NWs. (a-b) Necking behavior in an Ag NW caused by surface atom diffusion under tensile test. (c-e) Non-surface diffusion. Surface steps activated by slipping were indicated by arrows. Steps 1 and T1(T means the twin part) were disappeared near the twin boundary at 92s in e. Scale bar, 2nm.¹⁵³



Figure 5.13 Surface diffusional creep in Ag NWs. a, Pristine Ag NW with a diameter of 6 nm as viewed along $[\overline{110}]$ and loaded along $[\overline{112}]$ -orientation at a temperature of 800 K and a strain rate of 10^5 s⁻¹. The atoms at surface and in the interior of NW is colored by red and grey, respectively. b, Some surface atoms diffused onto the $(\overline{110})$ surface of Ag NW. c, The diffused atoms moved on $(\overline{110})$ surface. d, Surface atom diffused into the interior of the NW.¹⁵³


Figure 5.14 Surface diffusional creep in Ag NWs deformed along <112> tensile loading at temperature of 800 K and a strain rate of 10⁵ s⁻¹. a, Pristine Ag NW with a diameter of 6 nm as viewed along [112]-orientation. The atoms at surface and in the interior of NW is colored by red and grey, respectively. b, Surface atoms diffused into the interior of NW during mechanical loading.¹⁵³

5.4 Discussion

The yield strength of nanoscale crystals, controlled by surface dislocation nucleation, can be expressed as¹⁴

$$\sigma = \hat{\sigma}_{ath} - \frac{k_B T}{\Omega} ln \left(\frac{k_B T \tilde{N} v_D}{E \dot{\epsilon} \Omega} \right), \qquad (5-2),$$

where k_B is the Boltzmann constant, v_D is the attempt frequency, $\hat{\sigma}_{ath}$ is athermal stress and \tilde{N} is the number of dislocation-nucleation sites. For the Pt and Ag NWs (> 15 nm), nucleation sites (\tilde{N}) decreased with size causing Hall-Petch-like-strengthening^{14, 15, 84}. Notably, the incipient plasticity, that is dislocation nucleation, was supposed to occur at sites where the relative interatomic displacements exceed the critical value^{84, 85}. Especially for Pt NWs with negligible diffusional activities, surface diffusion cannot create surface defects, favoring dislocation nucleation. The effective nucleation sites for dislocation in Pt NWs from the initial defect sites, which decrease with reducing sample size^{84, 85}, leading to the "smaller is stronger" trend. For the Ag NWs (< 15 nm), coupled displacive-diffusive mechanism leads to a 'smaller is weaker' trend, which is attributed to the following reasons. First, with decreasing size, diffusion of the individual atom becomes stronger^{5, 103, 199, 211}, and introduce more surface defects (Figure 5.7e), leading to an increase in the nucleation sites. The driving force for the surface diffusion and atom diffusivity would increase with the reduction of the sample size.^{10, 217} Second, the activation volume is reduced due to a mechanism transition from displacive deformation (1-10 b³) to diffusional deformation (~0.1 b³)⁷⁹. Third, the overlap of surface defects changed surface Figure 5.2e, f and Figure 5.7c), reducing the athermal nucleation stress ($\hat{\sigma}_{ath}$) directly^{101, 157, 215, 218}. Considering all the factors mentioned above, the yield strength of Ag NWs (< 15 nm), based on Eq. 5-2, decreases with size, causing the breakdown of the Hall-Petch-like relation. The relation of the melting point of metal particles with the size can be expressed by^{217, 219}

$$\frac{T_m(D)}{T_m(\infty)} = 1 - \frac{4}{\rho_s L} \left\{ \gamma_s - \gamma_l \left(\frac{\rho_s}{\rho_l}\right)^{2/3} \right\}_D^1,$$
(5-3),

where $T_m(\infty)$ is the bulk melting temperature, $T_m(r)$ is the melting temperature of the particle with a diameter *D*, *L* is the molar heat of fusion, ρ_s , ρ_l are the solid and liquid densities. Then, the relation of diffusivity with the melting temperature can be expressed by²¹⁷

$$D_D = D_m exp\left[-\Delta H(r)\left(\frac{1}{T} - \frac{1}{T_m(D)}\right)\right],\tag{5-4},$$

where D_m is the diffusion coefficient at the bulk melting temperature, D_D is the diffusion coefficient of the particle with a diameter D, ΔH is the activation enthalpy of diffusion, T is the temperature and D_0 is the prefactor. Based on equations (5-3) and (5-4), the surface diffusivity is inversely proportional to the sample size. The athermal nucleation stress with the surface step $\hat{\sigma}_{ath}$ can be expressed by

$$\hat{\sigma}_{ath} = (1 - \Delta \cdot \rho_D) \cdot \sigma_{ath}, \tag{5-5},$$

where Δ is the stress decrement due to the step,²¹⁵ and ρ_D is the probability function of the involvement of the step for the nucleation which is proportional to the surface diffusivity. The nucleation site number with the diffusion activities can be expressed by

$$\widetilde{N} = N + \frac{D_D \cdot t}{\pi \cdot D \cdot L},\tag{5-6},$$

where *N* is the nucleation site number without diffusion, *t* is the unit time. The critical size scale for the breakdown of Hall-Petch-type relation will decrease and even disappear with increasing applied strain rate or decreasing experimental temperature, since fewer diffusional events occur before dislocation nucleation^{10, 213}. Surface-diffusion-assisted nucleation mechanism should be highly sensitive to some intrinsic properties, e.g. sample size^{5, 103, 212}, surface configuration^{15, 157}, activation energy barrier for atomic diffusion^{205, 220}, as well as some extrinsic properties, e.g. loading conditions, strain rate, experimental temperature^{10, 221}. Given the complexity and uncertainty of diffusional deformation⁷⁹, the complex interplay among these factors should await systematic future research.

Previous studies suggested that as the size of Ag nanoparticles decreased below ~ 10 nm, plastic deformation should be controlled by surface atom diffusion without dislocation activity, which was expected to cause inverse Hall-Petch-like relation^{5, 103}. In contrast, this work painted a continuous picture of the size dependence of yield strength, and directly revealed that aside from pure diffusive mechanism, surface-diffusion-assisted dislocation nucleation, namely, coupled displacive-diffusive mechanism, truncated the 'smaller is stronger' trend and turned it into 'smaller is weaker'. A recent experimental study on pristine Pd NWs also demonstrated that coupled diffusive-displacive processes could govern plastic deformation instead of pure crystal slip or diffusional creep, causing that 'smaller is stronger' no longer holds¹⁰². The previous research showed that the interplay between compressive loading and tensile surface stress in nanocrystals could also cause 'smaller is weaker'.¹⁵ However, such loading-dependent properties did not reflect the intrinsic effect of size scale.¹⁵ Besides, the initial interior stress in the sample influenced the critical dislocation-nucleation stress.¹⁵ In this study, the pristine nanocrystals or NWs generated by Joule-heating welding⁵² weakens the interior stress effect from the defect debris. In addition to the scenario of softening, the surface oxidation and triaxial loading could suppress the diffusion and surface dislocation-nucleation and may lead to the size-independent strength plateau.²²² Given that free surfaces in nanocrystals have some similar features as GBs in NC metals when mediating displacive and diffusive deformation, small-volume single crystals can be regarded as isolated small grains in NC metals roughly. The coupled displacive-diffusive mechanism studied here may provide atomic-scale insights into interplays between intragranular crystal slip and GB-mediated diffusive processes in bulk NC metals, especially in metals with relatively low melting temperatures.

Coble creep is a classical model for describing the diffusional transport of atoms along GBs, which quantitatively interprets the plastic strain accommodated by diffusive processes in nanocrystalline metals at room temperature.¹⁹¹ Different from the driving force for Coble creep resulted from vacancy concentration gradient with applied stress¹⁹¹, the difference in chemical potential caused by curvature and stress drives atomic diffusion along free surface in nanoscale metals ^{5, 10, 103, 213}. The atoms at a surface step with high chemical potential tend to migrate towards the end of the NW with low chemical potential, following the pathway for surface atomic diffusion proposed by Zhong *et al.* ⁵. The atoms at the step edge on {111} planes sequentially hop along <112> direction to climb the surface step²²⁰, leading to the experimental observation of the continuous lateral movement of the surface steps (Figure 5.2 and Figure 5.10). Assuming the

diameter of the Ag NW is ~10 nm, the flux per second for surface step motion with an average velocity of 0.2-1 nm s⁻¹ was $0.4-1\times10^{-17}$ m²·s⁻¹, which was comparable in magnitude with the curvature-driven surface diffusivity in Ag nanoparticles (~5×10⁻¹⁷ m²·s⁻¹)^{5, 10}. Though TEM observation here fell short in capturing the localized random diffusion of individual atoms at surface directly, its diffusional pathway was supposed to be similar to that for surface step migration²⁰⁵. Considering that the direct observation of the process of mass flow along GBs is still lacking, this work gives insights into understanding the diffusional processes of the surface-assisted Coble-type creep¹⁰³ and the coupled diffusive–displacive deformation mechanism in nanoscale metals.

5.5 Conclusions

In conclusion, the combined in situ HRTEM tensile tests and MD simulations have presented the surface-mediated mass transport in nanoscale Ag, and revealed that the yield strength-size relationship changed from 'smaller is stronger' to 'smaller is weaker' with decreasing the sizes of Ag crystals, whereas nanoscale Pt showed traditional "Hall-Petch-like" behavior. Both direct experimental and computational results demonstrated that surface-diffusion-assisted dislocation nucleation was responsible for the inverse Hall-Petch-like effect. This work also unveiled that surface atom diffusion significantly lowered flow stress during mechanical loading in nanoscale Ag, which was quite different from the pure displacive plasticity in nanoscale Pt. Broadly, this work visualized the physical surface creep processes at atomic-scale and developed an integrated model to reveal the strength-size dependence of nanoscale materials, which sheds light on the atomistic mechanism of surface diffusion-involved displacive deformation in nanoscale materials.

6.0 Atomic-Scale Friction between Single-Asperity Contact under In-Situ TEM

In this chapter, one innovative in-situ nanotechnology is proposed to investigate the atomic friction under TEM. To date, visualizing the friction process between nanocontacts at an atomic scale is rarely accomplished. Here, through designing the nanocontact and performing controlled motion between asperities under high-resolution transmission electron microscopy (HRTEM), the real-time atomic-friction process is captured. Moreover, the interface dynamics and friction mechanism are illustrated by combining in-situ TEM observation with molecular dynamics simulation. For the first time under in-situ TEM, the atomic friction between single-asperity nanocontacts is revealed to display a discrete stick-slip behavior and an asynchronous process for the accumulation and dissipation of the strain energy together with the nonuniform motion of interface atoms. This work provides a study approach to realize in-situ atomic-friction research and attains a fundamental understanding of friction phenomena at atomic scale.

6.1 Introduction

The friction and wear are the major sources of the service failure of devices and unexpected energy dissipation in considerable mechanical applications.²²³ Unraveling the underlying friction mechanism at atomic scale is desired to reduce the energy consumption and elongate the devices' service life.^{142, 224} AFM-based technologies have already been applied to investigate the atomic friction processes. Atomic stick-slip friction, one typical case manifested by a periodic saw-tooth-like oscillation in the lateral force-displacement function, was first observed in the sliding of a

tungsten probe on a graphite surface under AFM.¹⁰⁹ Thereafter, similar atomic-friction behavior has been observed in ceramic²²⁵, metals^{132, 226}, and two-dimensional materials¹³⁶. Numerous atomic-friction mechanisms, especially on the transition between the stick-slip and superlubricity, have been proposed through investigating the friction dependence on contact configuration^{138, 225,} ²²⁷ and the scan conditions^{120, 132, 226}. However, the physical sliding scenario between the contacts and the buried surface/interface deformation during friction is still elusive due to the lack of direct interface observation in the AFM-based experiments. In-situ experiments, especially TEM observation, are thus preferable to directly view the actual atomic-friction processes. With the aid of in situ TEM, Merkle et al.²²⁸ found liquid-like tribological phenomena between a tungsten probe and gold surface. Sato et al.¹⁴⁹ directly observed the formation and motion of nano-sized wear particles between diamond-like carbon (DLC)-covered Si interfaces by combing electromechanical actuators and TEM. Moreover, Jacobs et al.¹⁴⁸ proposed a stress-assisted atom-byatom wear mechanism in nanocontacts based on in-situ TEM observation. Oviedo et al.²²⁹ captured the shear-induced interlayer sliding process in two-dimensional materials. Despite progress, visualizing the atomically-resolved friction process with a clear-cut interface has not been achieved yet. As a result, the relationship between the friction mechanisms and interface structure has not been fully understood. Recently advanced in-situ TEM platform with high resolution^{143,} ¹⁶⁹ permits us to image the interface structure between nanocontacts and further investigate the dynamic atomic-friction processes. Complementarily, MD simulation can render insights into interface dynamics during atomic friction, such as the dynamic evolution of surface morphology in the silicon tip-graphene friction¹³⁷ and the evolvement of interacting atoms during friction process²³⁰.

Here, by designing nanocontact and in-situ counter-motion driven by piezo actuators between W asperities, the real-time single-asperity atomic friction with explicit interface evolution was successfully visualized under HRTEM. Moreover, the sliding pathway of interface atoms and the dynamic strain/stress evolution on the interface has been elaborated by combining the in-situ HRTEM observation with MD simulations. Importantly, the materials processes underlying the observed unique sliding behavior and the abnormal interface dynamics of this atomic friction have been investigated by examining the interface structure and the scanning conditions between asperities, to attain a fundamental understanding of the atomic-friction mechanism.

6.2 Experimental Procedures

For atomic friction research, one nanosized crystal with [001] zone axis was selected as the asperity candidate in the in-situ TEM experiment. A bias was applied between the selected nanocrystal (the asperity as the substrate) surface and the prepared W probe (the asperity as the mobile tip) after making them contact and the substrate and the tip would weld together due to the Joule heating. These two asperities, the sample side-substrate and the probe side-tip, slid with each other and were then separated by controlling the lateral and longitudinal movement of the probe driven by the STM-holder piezo-system. Repeat the contact, welding, slide, and separation process to obtain the final substrate and tip with a perfectly smooth surface. The lattice constant of tungsten is 3.16 Å and its melting point is ~3422 °C. The comparable stiffness between the tip and substrate (same materials) can effectively prevent the severe deformation of one asperity.

6.3 Experimental Results

6.3.1 Discrete Stick-slip Behavior between Single-Asperity Nanocontacts

To visualize the single-asperity atomic-friction processes, a face-to-face nanocontact and subsequent counter-motion were performed between a mobile W tip controlled by the piezo-actuator and a stiff W substrate under HRTEM. In the experiment set-up, multiple nano-teeth of a fractured surface in a cut-off W rod⁵³ served as the stiff substrate with desired orientations (Figure 6.1a) and one electrochemically-etched W tip acted as the mobile asperity. (Figure 6.1b) Further precisely tuning the separation distance and the alignment between the tip and the substrate, the nanocontact was acquired to form the friction pair. Thus, the atomic-friction process was visualized during a controlled counter-motion between the two tungsten asperities. In addition, the measurement of the lattice strain/stress from HRTEM images provides an effective method to estimate the shear and compression forces,¹⁹⁹ avoiding the complex calibration for lateral force in AFM-based technology¹²⁸.



Figure 6.1 Nanoscale crystals acting as the substrate (a) and mobile tip (b) in friction. Scale bar 2 nm.

As shown in Figure 6.2a, the atomic friction displayed typical stick-slip behavior¹⁰⁹ that the shear force (friction force) fluctuated periodically with the sliding displacement. It is found that there exist two distinct slipping events, marked by slip1 and slip2, within one lattice period (theoretical value 4.46Å along [110] direction on $(1\bar{1}0)$ plane), suggesting a discrete stick-slip behavior²³¹ (Figure 6.2a) rather than a consecutive slipping described by Prandtl–Tomlinson (P-T) model²³² in the cases of the tungsten tip on Cu (111) plane¹³² and the silicon tip on NaCl (100) surface¹²⁰. The sequential friction process marked by the letters in Figure 6.2a was shown in Figure 6.2b-f. Flat substrate and tip contacted with each other face-to-face along [1 $\bar{1}0$] and a wellarranged interface was presented without the diffusion interference from soft metals¹⁵⁰. (Figure 6.2b) The normal force was controlled by adjusting the asperity separation distance (~2.14Å, lower than the plane spacing of 2.23Å) and the counter-motion was set up along [110]. (Figure 6.2b) The starting point b possessed a negative shear force due to the lattice distortion induced by the interplay between asperities²³³ or caused by the existence of defects such as vacancies formed after in-situ melting¹⁵¹. As the tip moved horizontally, the shear force increased gradually to reach the first peak (Figure 6.2c). Then slip1 occurred and the shear force dropped dramatically as the tip had shifted by ~3.3Å. (Figure 6.2d) Similar to the first stick-slip, the shear force climbed to the second stick point and subsequently descended after slip2. (Figure 6.2e-f) The total sliding displacement of the tip was ~5.4 Å, close to the lattice distance along [110]. Period 2 showed an analogous pattern as period 1. The slipping of the tungsten tip was inferred to follow the zigzag route divided into two steps within one period. This abnormal zigzag path was first reported in friction on mica surface²²⁵ and then was further demonstrated by Hölscher et al. on graphite¹¹⁴. However, the slipping route detected by scanning of the AFM tip in these previous studies lacked the direct inspection of interface atom movement. Advancing from these works, the results presented here provided explicit movement traces of interface atoms.



Figure 6.2 In situ atomic observation of stick-slip behavior between single-tungsten asperity nanocontacts. (a) The function of the shear force with the sliding displacement of the tip. The error bars represent the vibration of the shear force. (b-f) Serial images of the friction process at one period. The relative displacement of the tip was indicated by the white arrow. The top layer of the tip and the reference layer of the substrate were marked by the red and blue solid circles (Fig. 6.2b) and short dotted lines (in c-f) respectively and numbered by 1~7 and 1'~7'. The bottom layer in the substrate was marked by the broken circles. Two atom columns, indicated by the red and yellow vertical lines in the substrate and tip respectively, were served as the reference coordination to determine the relative displacement between the asperities. The absolute distance between the referred layer and the interface layer along [110] was pointed out by yellow numbers in the figure and the relative displacement between the substrate and the tip was noted by white numbers. Scale bar 1 nm.

Interestingly, it is discovered that the movement of the top layer was inconsistent with the sliding of the tip. The atoms on one immovable layer with negligible deformation in the substrate (marked by the blue circles, numbered by 1-7) were selected as the reference to evaluate the relative motion of the atoms (red circles, numbers 1' and 7') on the top layer. (Figure 6.2b) The horizontal distances between the atoms 1 and 1' and atoms 7 and 7' were initially -0.54Å and 0.18Å respectively (Figure 6.2b) and then increased to 0.14 Å and 0.44 Å (Figure 6.2c) with the slide of the tip. Relative displacements of these two atoms (1' and 7') with respect to the atoms 1 and 7 were only 0.68 Å and 0.26 Å, lower than the relative sliding displacement (1.0 Å) of the whole tip, which indicated a hysteretic motion of the top layer compared to the whole tip. The later process exhibited similar phenomena that the displacement of the top layer (2.14 Å for atom 1' and 2.81 Å for atom 7') was still less than that of the tip (~3.3 Å) after slip1. (Figure 6.2d-f) These results pointed out that the displacement within the tip was progressively transmitted from the bottom (drive-end) to the top, consistent with the assumption treating the nanoscale tip as the spring in the classical model^{107, 232}. It should be noted that this nonuniform displacement transmission process cannot be directly discerned by single scanning displacement in AFM experiments^{109, 114}, but be clearly revealed in our HRTEM observation

To gain insights into the observed discrete stick-slip process, MD simulation was carried out to simulate our experiments (Figure 6.3). As shown in Figure 6.4a, the predicted lateral force (friction force)-displacement curve also exhibited two peak-valley features (marked by numbers 3-7) within one lattice period of relative motion. The first reduction of the lateral force (points 2-3) was found to be induced by the abrupt fluctuation of the normal force (Figure 6.5) without generating a noticeable structure change. (Figure 6.4b, c.) The lateral force reached the first stick point (point 4) and then dropped sharply after slipping1 (point5). (Figure 6.4a) The second stick-

slip followed a similar routine. (points 5-7 in Figure 6.4a) Notably, the first slip did not lead to the dramatic drop of the lateral force, which was supposed to be attributed to the undulation of forces along other directions.^{132, 231} The slight deviations in the lateral force-displacement curve between the experiment and MD results (Figure 6.2a and Figure 6.4a) possibly resulted from the statistical discrepancy between the two-dimensional lattice measurement by TEM images and/or the algorithm for the average stress/force used in MD simulation²³⁴. The sequential movement traces of interface atoms (the top layer of the tip) were presented in Figure 6.4b-h corresponding to points 1-7 in Figure 6.4a. The bottom layer in the substrate (cyan atoms) served as the reference for the movement of atoms (deep-blue) in the top layer of the tip. Some vacancies were included in the atomistic structure (Figure 6.4b) used in MD simulations (in MD methods). As shown in Figure 6.4c-f, the interface atoms first shifted forward along [110] and then some of them slipped into the hollow sites along [111] (The "hollow site" and "shoulder" in the lattice are indicated in Figure 6.4k, the interface potential landscape.), while the rest stayed at their previous positions during slipping. For slip2, the majority of atoms moved further along [111] rather than [110] to complete the remaining movement of one period, (Figure 6.4g, h) which confirmed the conjectural slipping route in the experiment. As illustrated in Figure 6.4i, the discrete stick-slip can be divided into two steps along <111> direction (atoms jump to the hollow circles in the figure) to accomplish one entire period counter-motion between asperities, consistent with the proposed pathway in copper,²³¹ platinum/gold system²³⁵ and dislocation-assisted slip²³⁶. Moreover, it is remarkable that the MD simulation also showed that the motion of atoms in the same layer was nonuniform. For instance, the five atoms, marked in different colors, showed different movement routes marked by the circles in Figure 6.4j. Compared to the red and gray atoms walking through one complete route (Figure 6.4b-h), the black and yellow atoms just finished a half journey along $[11\overline{1}]$ and [111]

directions respectively. (Figure 6.4f- h). In contrast, the green atom only shifted a little near the initial position. The variety in the slipping pathways of these four atoms was in stark contrast to the uniform motion of the interface atoms predicted in the simulation of Pt/Au system²³⁵. MD results further confirmed that the tip experienced a continuous elastic deformation like a spring without severe plastic deformation (Figure 6.6).



Figure 6.3 Model set-up of molecular dynamics simulation.



Figure 6.4 Discrete stick-slip behavior between tungsten asperities revealed by molecular dynamics (MD) simulation. (a) The function of the lateral force with the sliding displacement of the tip. (b-h) The snapshots of the dynamic movement of atoms in the top layer of the tip with respect to the substrate. (i) Schematic of the discrete stick-slip mechanism between two tungsten asperities. The dark blue and cyan balls represent the atoms in the top layer of the substrate respectively. Five selected atoms were colored in yellow, green, red, dark, and gray respectively. (j) The motion traces of the selected five atoms marked by the circles within one friction period. (k) The interface potential landscape, showing the potential variation with the interface structure. The red and blue regions correspond to the atom site and the hollow site, respectively.



Figure 6.5 Predicted evolution of normal force and shear force as a function of lateral displacement during atomic friction in MD simulation.

Additionally, the average friction force and normal force can be calculated by $\frac{\int_0^x F_f dx}{x}$ and $\frac{\int_0^x F_h dx}{x}$ respectively. Then the friction coefficient can be estimated as $\mu_{ex} = \frac{F_f}{F_h}$. Based on the above equations, the friction coefficients from the experiment and MD were ~0.39 and ~0.21 respectively, which are comparable to the values reported in single-asperity stick-slip friction like copper (~0.8)¹³² and MoS₂ (~0.2)¹³⁶. Similar results showing the discrete stick-slip friction have been found in the scenario with eleven contact atoms. (Figure 6.7) As the tip slid over 4.65 Å almost one period, the shear force experienced two raise-drops, implying there existed two separate slipping events. Moreover, the movement of interface atoms was asynchronous, as indicated by the yellow numbers in Figure 6.7b-f, which is consistent with the results shown in Figure 6.2. The corresponding MD simulation verified similar phenomena. (Figure 6.8) There existed two stickslips in one sliding period (Figure 6.8a) and the interface atoms showed different sliding routes (Figure 6.8b-i). However, it is worth noting that its slipping showed a higher friction force

compared to the case in Figure 6.7 and Figure 6.8. For example, the detected maximum shear force is 76.14 nN and the average friction force is 32.16 nN in the case with 11 contact atoms, (Figure 6.7) higher than those in the case with 7 contact atoms in Figure 6.2. The difference of the friction force in these two cases should be ascribed to the difference in the contact area²³⁰ and normal load¹²⁰, which will be discussed later.



Figure 6.6 The friction process within one period in MD simulation. (a-g) The structure evolution of the single asperity W-W contact during friction, corresponding to the points of numbers 1-7 in Fig. 6.4a.



Figure 6.7 In-situ TEM observation of atomic friction. (a) Variation of shear force with the sliding displacement of the tip. (b-f) Serial images of the friction process at one period. The relative displacement of the tip was indicated by the white arrow. The top layer of the tip and the reference layer of the substrate were marked by the red and blue solid circles in (b) and short dotted lines in c-f respectively. The bottom layer in the substrate was marked by broken circles. Two atom columns, indicated by the red and yellow vertical lines in the substrate and tip respectively, were served as the reference coordination to determine the relative displacement between the asperities. The absolute distance between the referred layer and the interface layer along [110] was pointed out by yellow numbers in the figure and the relative displacement between the substrate and the tip was noted by white numbers. Scale bar 1 nm.



Figure 6.8 Discrete stick-slip behavior between tungsten asperities revealed by molecular dynamics (MD) simulation (The width of the contact region is 11 atoms' space). (a) The function of the lateral force with the sliding displacement of the tip. (b-h) The snapshots of the dynamic movement of atoms in the top layer of the tip with respect to the substrate. The cyan balls represent the atoms at the bottom of the substrate. Four selected atoms were colored in yellow, orange, red, dark respectively. (i) The motion traces of the selected four atoms marked by broken circles within one friction period.

6.3.2 Asynchronous Accumulation and Dissipation of Strain Energy

Furthermore, the dynamic evolution of lattice strain on the interface was surveyed as shown in Figure 6.9. The shear strain on the top layer (layer2, red atoms) was analyzed by determining the position changes of seven atoms (marked by numbers 1-7) relative to the neighboring layer (layer1, blue atoms), as shown in Figure 6.9a. The geometry centers of the atoms (intensity profile centers of these atoms on TEM images) were marked by the orange and blue short lines for layer2 and layer1 respectively. Generally, the interface plane-strain distribution in friction is predicted by contact mechanics^{237,238}, or relies on indirect tools such as Raman spectra²³⁹ for a rough estimation. In this study, the accurate lattice strain could be directly measured from HRTEM images. The initial strain showed an inhomogeneous distribution with opposite shear strains, pointed out by the red (positive) and blue (negative) arrows in Figure 6.9a. As the friction went on, the accumulated elastic strain increased gradually (Figure 6.9b-c) to one maximum value for activating the consequent slipping (Figure 6.9d). All shear strain switched to positive and the distribution inhomogeneity in the magnitude and direction of strain was alleviated. (Figure 6.9d) Whereafter, the accumulated strain was only partly released after slipping and exhibited an inhomogeneous distribution again. (Figure 6.9e) This indicated that the accumulation and release of strain energy during friction are asynchronous, consistent with what predicted by the modified Frenkel-Kontorova-Tomlinson (FKT) model²³⁵, but in stark contrast to the uniform process described by the P-T model¹⁰⁷. The shear strains measured from two selected atoms (atoms 1 and 7) confirmed this character, where the magnitude and direction of the shear strain for atom 1 differed from those for atom 7 during the friction process, and these two atoms displayed incompatible strain evolutions. (Figure 6.10) The out-of-step movement paces of these two atoms were in accordance with the phenomenon shown in Figure 6.4, which implied the dynamic diversity of interface atoms.



Figure 6.9 Strain evolution on the top layer of the tip during friction. (a-f) The sequential images of the top layer during one friction period and the corresponding intensity profile. The selected top layer and referred-neighboring sublayer are marked with red lines 2 and 1 respectively. The atoms for accounting the strain are indicated by the numbers 1-7. Geometry centers of atoms on the top layer and referred-neighboring sublayer are indicated by the orange and blue lines respectively. Here, the positive and negative shear strains are indicated by red arrows and blue arrows respectively.



Figure 6.10 The shear strain evolutions measured from two selected atoms marked by numbers 1 and 7 in Fig. 6.9 during friction within one period.

To further verify the asynchronous accumulation and dissipation of strain energy, the stress evolution on the interface during the friction process was investigated via MD simulations. According to the force equilibrium between the substrate and tip during the friction process, the dynamic evolution of the shear stress field in the bottom layer of the substrate was analyzed as shown in Figure 6.11a-e (the lateral shear stress- σ_{xy} and the vertical shear stress- σ_{zy} , the corresponding sequences were indicated by Roman numbers in Figure 6.4a). The central region in the stress field figure can almost be identified with the contact area. σ_{xy} initially displayed a relatively homogeneous distribution with little area holding negative stress, compared to the inhomogeneous σ_{zy} field. (Figure 6.11a) As the friction progressed, the negative stress dominated the σ_{xy} field with the local region preserving high positive values while σ_{zy} experienced little change. (Figure 6.11b). σ_{xy} and σ_{zy} both exhibited severely inhomogeneous distribution in the magnitude and direction of stress and such a high inhomogeneity in stress distribution is expected in incommensurate contacts²³⁵. Over the maximum point (III Figure 6.4a), σ_{xy} displayed an inhomogeneity along [110]-the counter-motion direction, instead of disordered distribution as

before. (Figure 6.11c) This implied that the atoms in the deep-blue region with high stress (Figure 6.11c) would first slide followed by the motion of the rest of the atoms, showing the non-uniform movement of the interface atoms, which was consistent with experimental results and the reported simulation results²³¹. Most of the σ_{xy} field held the negative value, in contrast to the homogeneous σ_{zy} field with high positive stress. (Figure 6.11c) As the tip moved further, two stress fields both switched to the strongly inhomogeneous distribution that the positive or negative dominated the right side and vice versa after the first slip (Figure 6.11d) and the coupled stress was in consistent with the second slipping direction along [111] (Figure 6.4). The dynamic evolution of the inhomogeneous stress distribution further demonstrated the asynchronous evolution of strain energy in atomic friction, which would possibly occur in friction hypothesized with multipledislocation-cooperated slip²⁴⁰. The inhomogeneous stress distribution was also observed when using eleven contact atoms in the MD simulation. (Figure 6.12) oxy and ozy both experienced the transition from homogeneous to inhomogeneous distribution over one sliding period. (Figure 6.12) Especially, they showed noticeably inhomogeneous stress distribution along the sliding direction after the second slipping. (Figure 6.12e)



Figure 6.11 Dynamic evolution of shear stress field on the bottom layer of the substrate in MD simulation. (ae) The evolution of σ_{xy} (σ_{zy}) distribution on the bottom layer of the substrate and the corresponding sequences are indicated by red Roman numbers in Fig. 6.4a. The color scale is in units of bar × Å³. This virial stress is defined to account for the effects of momentum change of both mechanical forces and mass transport and has units of pressure × volume (bar × Å³) where the volume is that of an individual atom.²³⁵



Figure 6.12 Dynamic evolution of shear stress field on the bottom layer of the substrate in MD simulation. (ae) The evolution of σ_{xy} (σ_{zy}) distribution on the bottom layer of the substrate and the corresponding sequences are indicated by red Roman numbers in Fig. 6.8a. The color scale is in units of bar × Å³.

6.4 Discussion

In-situ HRTEM observation combined with MD simulation presented a dynamic diagram of atomic friction in nanocontacts. Atomic friction between W asperities exhibited a discrete stickslip behavior that the nanoscale asperity tends to choose a zigzag sliding route containing multiple steps with low energy barriers rather than the rigid slip along a given scanning direction. This abnormal sliding behavior is supposed to be mainly attributed to the contact structure and sliding conditions between asperities. For BCC W, the easy-glide direction of dislocations is <111> in preference to $<110>^{241}$ - the pre-set scanning direction on the $\{110\}$ plane in friction. Furthermore, the atoms of the tip encounter the two-dimensional interaction potential landscape in contact Figure 6.4k) instead of the energy barrier along a single direction.¹⁰⁷ The interface atoms tend to pass through the "shoulder" between atoms to the "hollow sites" (marked in Figure 6.4k), following a zigzag route, rather than directly going over the atoms (red regions, the potential peak sites in Figure 6.4k) to complete the relative motion between asperities. Another factor leading to discrete slipping is the alignment condition between the asperities.²³⁵ As designed in our experiment, the substrate and the tip were aligned with little misorientation, which allows imaging the contact of two asperities in a joint zone axis with atomic-scale resolution by TEM and avoids the incommensurate registry and the destruction of the surface potential periodicity^{138, 235}. The periodic symmetry of the interface potential with the diversity in sliding directions such as on the closely-packed contact surface in FCC, 231, 235 BCC, and Hexagonal-structured materials, 114, 225 gives rise to the discrete stick-slip. The breakdown of this potential symmetry via alternating alignment and scanning conditions between asperities, or in amorphous materials is expected to suppress this sliding behavior. In addition, the scanning velocity of the tip (~0.01 nm/s used in the in-situ experiment), which is much lower than the parameters in AFM-based experiments (normally, several nanometers/s)¹³², provided adequate time for the discrete stick-slip by allowing the atoms to move collectively to stable sites. Notably, this discrete stick-slip is supposed to generate moderate frictions by increasing discontinuous stick points²³¹, whereas it is less likely to be observed in macro contacts due to the imperceptible pinning effect²³¹ and irregular asperity geometry²²⁵.

Meanwhile, the convoluted surface potential and complex sliding pathway of the tip jointly raise the possibility that slipping paces of the atoms become inconsonant. Tailoring the orientation relationship between asperities can switch the stick-slip to the structural lubricity via destroying the periodicity of surface potential and inducing the incommensurate sliding.^{138, 231, 235} This incommensurate sliding should belong to an asynchronous process containing a divided stress field with alternative negative and positive regions²³⁵, which suggested that the degree of strain incompatibility or the movement discordance of interface atoms plays a critical role in the amplitude change of the friction force and the transition between superlubricity and stick-slip. The nonuniform movement of interface atoms and the inhomogeneity of stress distribution can be effectively promoted by adjusting the initial interface structure and stress state. Implanting interface defects such as vacancies or interstitial atoms are believed to enhance the inhomogeneity of the surface structure and strain field²⁴². In addition, presetting in-plane strain can be a practical approach to reduce the net friction force²³⁹ by changing the surface or interaction potential corrugation. Nevertheless, it should be noted that the inhomogeneous in-plane stress field in flat contacts is different from the stress corrugation in models composed of the round tip-flat substate couple^{238, 239}. This in-plane strain inhomogeneity accompanied by atomic discreteness within the interface differs from the strain-induced atomic-scale roughness derived from the continuum contact mechanics^{230, 238}. Moreover, the structure disparity between two asperities such as the difference of lattice periodicity would also give rise to strain incompatibility during the friction process. The dynamic diversity of interface atoms calls for modifying the one-dimensional FKT model²³⁵ to consider in-plane interplays among the atoms. Additionally, the hysteretic transmission of the strain/displacement within the nanoscale asperity regarded as a spring¹⁰⁷ may further facilitate the inhomogeneous stress distribution and non-uniform movement, which may directly

cause energy dissipation by the irregular emission of phonon¹¹⁰. The local interface structure and atom dynamics play an important part in the atomic friction and may further induce the breakdown of linear friction behaviors^{230, 243}. Notably, the friction between nanoscale W asperities did not exhibit the liquid-like or diffusion-mediated sliding reported in soft metal friction systems^{150, 228, 244}. This is supposed to be attributed to the high thermal stability of W. The cohesive energy and melting point of W²⁴⁵ are much higher than those of Au and Ag²⁴⁶. Furthermore, compared to Au and Ag⁵, the high diffusion barrier of W^{205, 247} makes it hard to activate the surface diffusion at room temperature. The ultralow sliding velocity is ultralow (~0.1nm/s) only contributes little to the sliding-induced heating rather than the linear friction welding²⁴⁸.

In this study, two main sets of experiments and simulations were conducted with different contact areas as well as the cases with 7 and 11 contact atoms. They both showed the discrete stickslip friction and asynchronous accumulation and dissipation of strain energy but different friction amplitude. The case with 11 contact atoms has ~ 2.35 times the contact area as compared to the case with 7 contact atoms while its average friction force is ~1.98 times higher than the latter in experiments. On the other hand, the normal load in the case with 11 contact atoms is more than three times of the latter. (Figure 6.13 and Figure 6.14) Moreover, the contact area in our experiments was decided by the size of the sliding tip instead of depending on the normal load described in contact area in the atomically-flat contact, compared to the classical tip-sample model. The contact area did not change appreciably in the whole friction process. (Figure 6.2 and Figure 6.7) Notably, the shear force only experienced a little change when the normal load dramatically decreased. (Figure 6.2a and Figure 6.13) The detected normal load also did not evolve periodically with the friction force as predicted by the simulation²³¹. Admittedly, there existed uncertainty in the measurement of the shear force and normal force, which might hide the actual load-dependency in our experiments. Nevertheless, these results still indicated that the contact area plays a more important role in deciding the magnitude of friction force compared to the normal load^{230, 250}. Meanwhile, the low surface corrugation²³⁸ and adhesive effect^{125, 230, 251} between W asperities might make the friction force insensitive to the normal load. Account of the high vacuum under TEM, the passivation effect from absorption on the W surface is limited. In addition, the loadindependence friction can also be understood by thermolubricity in Krylov's model.¹⁴¹ In contrast, our results showed a typical stick-slip with high friction rather than ultralow friction. Thus, the thermolubricity cannot explain the observed results here. Further studies are necessary to clarify the load-dependence in atomic friction between single-asperity contact in future.



Figure 6.13 Variation of normal force with the displacement of the tip in the experiment. The error bars represent the vibration of the normal force.



Figure 6.14 Variation of normal force with the displacement of the tip in the case with 11 contact atoms. The error bars represent the vibration of the normal force.

The single-asperity friction was designed here to perform on {110} plane, which is a common slip plane in BCC metals,²⁴¹ between two separate tungsten crystals with the same orientation. The atomic friction proceeds along <111> direction in a zigzag fashion. Similarly, the resistance encountered in the slipping within a BCC crystal gives the criteria to evaluate the materials' strength. For instance, the ideal strength of a BCC metal can be evaluated under simple shear on {110} plane inducing the elastic instability in the single crystal.²⁴¹ (Figure 6.15a) The deformation in most materials containing defects is generally mediated by the shear-driven slipping of dislocations.²⁵² (Figure 6.15b) The strengths such as the yield strength can be assessed through measuring critical stresses for the motion of dislocations leading to the permanent plastic deformation (Figure 6.15c). Either the simple shear or the dislocation slipping can be regarded as a fractional counter-motion between two parts of the crystal rather than the overall rigid movement in the friction process or under simple shear. If misfit dislocation-mediated the shearing in the

interface layer, the movement of interlayer atoms should follow the slipping traces of $1/1[11\overline{1}]$ or [111] dislocation along $[11\overline{1}]$ or [111] on $(1\overline{1}0)$ plane. Considering the stress state influences the critical stress for dislocation slip, the applied compression force in contact is supposed to increase the threshold value activating the dislocation nucleation in friction.²³¹ The maximum resolve shear stress could provide the driving force for the dislocation nucleation, but the dislocation-assisted slipping in the friction process is expected to exist in a large contact region where the dislocation could stably nucleate and pile up.^{236, 240} The range of contact radius for the single-dislocationassisted slip in friction is normally within 10 nm-10 µm.²³⁶ When the contact area is lower than the critical value, the friction force is supposed to be the order of the ideal shear strength,^{236, 253} consistent with our experimental results (the contact area is only 1.54-5.24 nm² in the experiment). Strengths of tungsten defined under various loading conditions were collected in Table 6.1. It is found that the maximum shear stress encountered (~12.9 and ~10.1 GPa for cases with 7 and 11 contact atoms respectively in the experiment and ~16.4 and ~18.2 GPa for two cases respectively in MD) in friction studied here was close to the ideal strength (~16.5 GPa), much higher than values for the dislocation slipping (~2.5 GPa for screw and ~0.06 GPa for edge), which exemplified that the local fractional shear mediated by the defect motion is much easy in real crystals²⁴¹. This also suggested that the discrete stick-slip may not be easily explained by the dislocation-assisted slip model^{235, 236}. The design in atomic-friction between the same crystals without misorientation may be employed to estimate the ideal strength or lattice friction in the bulk crystal when considering the comparability between the atom interaction within the crystal and the contact-surfaces interlay in friction under compression.

It is worth noting that the shear strength did not change appreciably when the normal load increased. This implies that the shear strength is not sensitive to the normal load while the contact

area mainly influences the friction amplitude. Compared to the experimental results, MD simulations showed an extra force-drop in one sliding period. (Figure 6.3 and Figure 6.8). To investigate whether this force undulation is related to the boundary conditions employed, a new MD simulation with a different boundary condition has been carried out. (Figure 6.16) When the displacement restriction along y is relieved, the first force-drop disappears. (Figure 6.16a) However, unexpectedly, it is found that the real friction or the relative sliding did not occur in contact between the top layer of the tip and bottom layer of the substrate but between the top layer and sublayer of the tip or/and between the sublayer and the next layer of the tip (indicated in Figure 6.16d and e), which is quite different from our experimental observation. On the other hand, it is noted that the heights of the two peaks obtained from the MD simulations have a large difference, (Figure 6.3a and Figure 6.8a), while the two peaks in experiments are much closer in values (Figure 6.2a and Figure 6.7a) The second "lower peak" in the simulation is supposed to induced by the relaxation of the mechanical stress along z-direction.²³¹ (Figure 6.17) Overall, experiments and simulations here both demonstrated the discrete stick-slip behavior with non-uniform strain distribution in atomic friction although there exist some differences between them.



Figure 6.15 The material strengths defined under different models. (a) The simple shear. (b) The dislocation slip under the shear. (c) The friction. (d) The cleavage fracture under tension.



Figure 6.16 The effect of boundary conditions in simulation for the case with 11 contact atoms. (a) The shear forcedisplacement evolution in simulation with restriction along directions y and z. (b) The shear forcedisplacement evolution in simulation with restriction along direction z but relaxation along y. (c-e) Sequential snapshots of the friction in b. Compared to the initial boundary condition where the normal direction (y) and another shear direction (z) are fixed, the displacement restriction along y is relieved in the new simulation and then the first force-drop disappears in (a). Unexpectedly, the real friction or the relative sliding in this simulation did not occur in contact between the top layer of the tip and bottom layer of the substrate but between the top layer and sublayer of the tip or/and between the sublayer and the next layer of the tip (indicated in d and e). This case is quite different from our experimental observation. Thus, this simulation method was not employed in our study, even though this simulation with clear two peaks seemed to agree better with the experimental results from the numerical aspect.


Figure 6.17 Three force components of the interface atoms in MD simulation with 7 contact atoms. When the interface atoms completed the second slipping along the zig-zag route, the accumulated stress along z-direction in the first slipping would release, leading to the drop of the friction force. In experiments, since the shear force was obtained by measuring shear strains of seven/eleven atoms along x-direction in contact, the effect from the stress release along z-direction on the friction force might not be noticed.

| Definition | Loading condition | Reference Value (GPa) | |
|---|---|------------------------------------|------------------------------|
| Ideal strength | Simple shear ²⁴¹ | {110}<110> 16.54 | {110}<111> 16.5 |
| Critical stress for the dislocation slip | Uniaxial loading | Edge ²⁵⁴ 0.056-0.075 | Screw ²⁵⁵ ~2.5 |
| Maximum shear stress Experiment | Friction under compression The case with 7 contact atoms | {110}<110> ~18.9 | {110}<111> ~12.9 |
| | The case with 11 contact atoms | ~14.7 | ~10.1 |
| Maximum shear stress MD simulation | Friction under compression The case with 7 contact atoms | {110}<110> ~20.1 | {110}<111> ~16.4 |
| | The case with 11 contact atoms | ~22.3 | ~18.2 |

Table 6.1 The strengths defined under different conditions for W single crystal.

6.5 Conclusions

This work demonstrates a practical approach to visualizing the real-time friction at an atomic scale by designing single-asperity nanocontacts and performing controlled counter-motion between asperities. The nanoscale tip was found to adopt a zigzag pathway through two slipping steps along <111> to complete one full-period friction along <110> on $\{1\overline{1}0\}$ contact surface, displaying a discrete stick-slip behavior, and showed a spring-like behavior that the sliding displacement within the tip was discontinuously transmitted. The accumulation and release of strain energy on the friction interface underwent an asynchronous evolution, accompanied by the inhomogeneous strain/stress distribution and a non-uniform movement of interface atoms during the friction process. These unique behaviors mainly resulted from the interface structure and sliding conditions of the asperities. The detailed motion trace and strain analysis of the interface atoms constructed an informative paradigm to clarify the dynamic diversity in real atomic friction, contributing to interpreting the friction mechanisms at the atomic scale. In addition, different from the normal load, the contact area may play a more important role in atomic friction. Compared to the shear-driven deformation in crystals, the friction process between the two same crystals investigated here provided new insights into the understanding of the lattice friction and strength of crystals.

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7.0 Summary and Conclusions

Understanding the deformation and friction mechanisms in nanoscale materials is imperative to lessen the materials' damage and prolong their service life. In this dissertation, insitu atomic-scale TEM observation was employed to investigate the deformation processes of BCC and FCC nanocrystals, revealing the stability of deformation twins in BCC metals and the strengthsize dependency of FCC nanocrystals. Further inspired by in-situ mechanical tests under TEM, an innovative in-situ methodology was proposed to study the real-time atomic friction in singleasperity contact.

Twinning dominated the plastic deformation of BCC W nanocrystals, but the generated deformation twins were generally unstable. The stability of deformation twins in BCC nanocrystals was strongly dependent on the fraction of inclined twin boundary presented as Moire Fringes in TEM images. Based on the force analysis suffered by the twin, the critical condition for spontaneous detwinning was determined. As the area friction of MF was above the critical value, the twin became unstable and then detwinning spontaneously proceed. Moreover, contrary to deformation twins in FCC metals, the inclined twin boundary was frequently formed during the twinning process in BCC nanocrystals. Its formation was supposed to ascribe to the mobility difference between edge and screw dislocations in BCC metals. These discoveries advance the understanding of deformation twinning and twin structures in BCC metals and provide guidelines for the processing and service of BCC metals under loading.

"Smaller is stronger" has been verified in many small-sized materials. However, this trend would be broken, namely "smaller is weaker", when the diffusive activities participated in the deformation of nanocrystals. It was discovered that the surface diffusion-assisted dislocation nucleation induced the decline of the yield strength in silver nanowires by increasing the potential nucleation sites and generating surface with a lowered critical stress for nucleation via surface diffusion. The calculation of the cumulative probability of dislocation nucleation in silver nanowires verified the diffusion-assisted nucleation mechanism that the activation parameters of Ag nanowires below 15nm were approximate to those of diffusion in Ag nanocrystals. Moreover, the diffusion activities lowered the flow stress of nanowires because of the creep-induced tardy rising of flow stress for the next dislocation emission. The intensity of diffusion was highly associated with the sample size. As the sample size decreases continuously, the diffusion probability is exacerbated and surface curvature and stress provide the required driving force. In contrast to Ag, Pt nanowires followed a traditional Hall-Petch law due to negligible diffusion activities. These findings provide a new sight to understanding the softening in small-sized materials through establishing a connection between diffusion and dislocation nucleation and are significant for the failure analysis and application of nanoscale metals.

Besides the deformation-induced failure of materials, friction is another common route to cause the degradation of materials. Fabricating appropriate nanoscale asperities and adopting proper loading modes in in-situ mechanical tests, in-situ friction configuration was built up under high-resolution TEM observation to study the atomic friction in W single-asperity contact. The proposed methodology successfully achieved the visualization of the well-defined interface in friction at atomic scale which is a major deficiency in previous atomic friction research. By inspecting the dynamic evolution of the interface during the friction process, it was found that the friction between nanoscale W asperities exhibited a discrete stick-slip containing two slip events in one period. The interface atoms followed a zigzag route to complete the sliding along <110> on the {110} plane. Moreover, the movement of interface atoms was not uniform and they showed

various sliding pathways. The nanoscale W probe also behaved like a string where the displacement was gradually transmitted from the driven-end. In addition, the distribution of strain/stress in contact was inhomogeneous, verified by corresponding MD simulation. This work provides an applicable in-situ technology to investigate the atomic friction and clarify the interface dynamics in discrete stick-slip friction, advancing the understanding of friction mechanisms in metal contacts.

In summary, this dissertation provides insights into the mechanical deformation and friction in nanocrystals and develops an in-situ methodology to investigate the tribological problems in metals at atomic scale, which is of importance for the design and failure analysis of nanostructured materials.

8.0 Outlook

As the degradation of nanoscale components in MEMS mainly results from their plastic deformation and surface friction/wear, this dissertation was focused on the investigation of deformation and friction mechanisms by in-situ TEM observation. Apart from the dislocation slip and twinning in metals, phase transformation also plays an important role in plastic deformation.^{256, 257} The stress-induced phase transformation directly alters the material's structure, leading to the transition of their physical and chemical functions or even the immature failure of the device. For example, deformation-induced phase transformation has a dramatic effect on the mechanical properties of materials ^{258, 259, 260, 261, 262, 263}. Martensite transformation, a common deformation-induced transformation, enables materials the shape-memory effect^{264, 265} and enhances the elastic/plastic limits of materials at nanoscale ^{261, 263, 266}. The deformation-induced phase transformation provides a pathway for materials to overcome the trade-off of strength-ductility. ^{259, 262, 267}

Omega (ω) phase-one hexagonal structure, having multiple variants ²⁶⁸, is usually observed in various BCC transition metals ^{36, 46, 269} during the solidification process ²⁷⁰. The formation of ω phase easily renders some metals especially alloys brittle ^{269, 271}. The mechanically-driven solid phase transformation from the body-centered cubic phase (β phase) to the hexagonal phase (ω) was normally activated under harsh conditions such as high-pressure and high strain rates ^{272, 273, ²⁷⁴. Chen et al⁴⁶ reported this phase transformation in bulk nanocrystalline molybdenum (Mo) prepared by severe plastic deformation accompanying the deformation twinning. The extra TEM inspections indicated that the omega phase transformation might act as the middle pathway in the twinning process. Wu et al⁴⁷ found that ω phase islands were inserted into the deformation twin in} Ti alloys. However, the dynamic process of the ω phase-mediated twinning was not verified experimentally in BCC metals. The in-situ TEM method employed in this dissertation provides a possibility to reveal the dynamic ω phase transformation in BCC metals by interpreting the atomic structures on TEM/STEM images. In addition, in-situ mechanical tests under TEM pave a pathway to investigate the competition among different deformation models which determines the materials' performances, via changing the sample size, loading orientation, and strain rate so on.

The study about diffusion-induced abnormal softening in nanocrystals in Chapter 5 implies that the diffusion is expected to be activated when the sample size is below a critical value. The diffusion-involved friction has been reported in many systems, especially for soft metal asperities.^{150, 228, 231, 275} Presented results in this dissertation about the deformation of nanocrystals zoomed in the microstructural evolution and more efforts are expected to be put in the quantitative analysis about the strain-stress response in future research. The methodology applied in the friction gives enlightenment to realize the quantitative measurement in the mechanical tests for deformation of nanoscale materials under TEM observation. However, as atoms become mobile at room temperature and shift dynamically through diffusion, the stress measurement by evaluating the lattice stress in in-situ friction becomes unreliable, leading to large uncertainty in lattice stresses. This simulates us to seek a more decent method to detect the friction force under TEM observation. Recently, He et al²⁷⁶ proposed a methodology via combing the in-situ TEM and AFM to achieve the atomic observation on friction and detection of the friction force simultaneously. Under tensile stress, a loosely-packed interfacial layer was formed due to the diffusion of Au atoms to the W side, which effectively lowered the friction force.²⁷⁶ Notable, the shear force within the loosely-packed layer can not be evaluated by the lattice strain in crystalline structures.²⁷⁷ When the separation distance between Au and W asperities increased and the normal loading became

compressive, this loosely-packed layer transited into an ordered layer, leading to ascending friction.²⁷⁶ The dynamic friction process mediated by diffusion within this interfacial layer and the transformation of the interfacial structure with the separation distance were visualized by in-situ TEM, while the friction and normal force were assessed by recording the deflection of the AFM cantilever. Nevertheless, it is required to note that these two forces were separately obtained at two testes. The connection between the normal and friction forces was indirectly built by the interfacial structure, where the normal force and interfacial structure both depended on the separation distance between two asperities. This indirect measurement naturally introduced the uncertainty of the force magnitude, which demands a more appropriate way to detect normal and friction forces synchronously. To design a platform containing force sensors along two directions is a target for future research at atomic friction. On the other hand, a majority of research attention is paid to the single-asperity friction under vacuum and thus the environmental factors are hardly taken into account in the study, especially for the in-situ experiments. In practice, the absorption of gas on the surface of asperities directly influences the friction behaviors.^{278, 279, 280, 281, 282} Different interactions between the absorbed molecules and asperities could dramatically tune the friction magnitude. For instance, the strong interlocking between the absorbed molecules and the metal surface would increase the friction while the weak interaction might lead to the decline of the friction.²⁷⁸ Gas atoms such as hydrogen could even change the bonding of asperity' surface and then cause the surface passivation, leading to a superlubricity.²⁸³ Recent advancements in the environment TEM²⁸⁴ provide a possibility to study the friction involving the anticipation of the atmosphere or gas. Studying the effect of the gas environment on friction is a promising direction for atomic-friction research.

Appendix Deformation of The Activation Parameters in Nanowires

According to the transition state theory (TST), the rate of dislocation nucleation is expressed as

$$\nu = N \nu_0 \exp\left(-\frac{\Delta G(\sigma, T)}{k_{\rm B}T}\right) \tag{A-1},$$

where *N* is the number of equivalent nucleation sites v_0 is the attempt frequency, $\Delta G(\sigma, T)$ is the activation free energy, σ is the applied stress, k_B is the Boltzmann constant, *T* is the experimental temperature. The activation free energy for dislocation nucleation is given by ^{102, 285}

$$\Delta G\left(\sigma, T\right) = \Delta U(T)(1 - \frac{\sigma}{\sigma_{\text{ath}}}) \tag{A-2},$$

where $\Delta U(T)$ is the Helmholtz free energy of activation, σ_{ath} is the athermal nucleation strength. The activation free energy ($\Delta G(\sigma, T)$) can also be expressed as

$$\Delta G\left(\sigma,T\right) = \Delta U(T) - \Omega\sigma \tag{A-3}.$$

where Ω is the activation volume defined as the derivative of activation energy with stress $(\Omega = \frac{\Delta U(T)}{\sigma_{ath}})^{14}$. Combining Eqs. (S1) and (S3), the rate of dislocation nucleation can be expressed as

$$v = N v_0 \exp\left(-\frac{\Delta U(T)}{k_B T}\right) \exp\left(\frac{E \dot{\epsilon} t \Omega}{k_B T}\right)$$
(A-4),

in which we assume $\sigma = E\dot{\epsilon}t$, where *E* is Young's modulus of the NWs, $\dot{\epsilon}$ is the strain rate (~10⁻³ in this work) and *t* is the loading time. Recasting Eq. (S4) into the following expression for the cumulative distribution function (CDF)²⁸⁶

$$F(t)=1-\exp(-\int v(t)dt)$$
(A-5).

The cumulative probability of dislocation nucleation related to the stress can be obtained and expressed as

$$F(\boldsymbol{\sigma}) = 1 - \exp\left\{\frac{N\nu_0 k_B T}{E \varepsilon \Omega} \left[\exp\left(-\frac{\Delta U(T)}{k_B T}\right) - \exp\left(\frac{E \varepsilon t \Omega - \Delta U(T)}{k_B T}\right) \right] \right\}$$
(A-6).

Bibliography

- 1. Zhong RY, Xu X, Klotz E, Newman ST. Intelligent manufacturing in the context of industry 4.0: a review. *Engineering* **3**, 616-630 (2017).
- 2. Faudzi AAM, Sabzehmeidani Y, Suzumori K. Application of micro-electro-mechanical systems (MEMS) as sensors: a review. *Journal of Robotics and Mechatronics* **32**, 281-288 (2020).
- 3. Van Spengen WM. MEMS reliability from a failure mechanisms perspective. *Microelectronics Reliability* **43**, 1049-1060 (2003).
- 4. Uchic MD, Dimiduk DM, Florando JN, Nix WD. Sample dimensions influence strength and crystal plasticity. *Science* **305**, 986-989 (2004).
- 5. Zhong L, Sansoz F, He Y, Wang C, Zhang Z, Mao SX. Slip-activated surface creep with room-temperature super-elongation in metallic nanocrystals. *Nature materials* **16**, 439-445 (2017).
- 6. Banerjee A, *et al.* Ultralarge elastic deformation of nanoscale diamond. *Science* **360**, 300-302 (2018).
- 7. Pattanaik P, Ojha M. Review on challenges in MEMS technology. *Materials Today: Proceedings*, (2021).
- 8. Zhu Y, *et al.* Size effects on elasticity, yielding, and fracture of silver nanowires:In situexperiments. *Physical Review B* **85**, (2012).
- 9. Kumar K, Van Swygenhoven H, Suresh S. Mechanical behavior of nanocrystalline metals and alloys1. *Acta Materialia* **51**, 5743-5774 (2003).
- 10. Tian L, Li J, Sun J, Ma E, Shan Z-W. Visualizing size-dependent deformation mechanism transition in Sn. *Scientific reports* **3**, 2113 (2013).
- 11. Li Q-J, Ma E. When 'smaller is stronger' no longer holds. *Materials Research Letters* **6**, 283-292 (2018).
- 12. Marian J, Cai W, Bulatov VV. Dynamic transitions from smooth to rough to twinning in dislocation motion. *Nature materials* **3**, 158-163 (2004).
- 13. Cao AJ, Wei YG, Mao SX. Deformation mechanisms of face-centered-cubic metal nanowires with twin boundaries. *Applied Physics Letters* **90**, 151909 (2007).

- 14. Zhu T, Li J, Samanta A, Leach A, Gall K. Temperature and Strain-Rate Dependence of Surface Dislocation Nucleation. *Physical Review Letters* **100**, (2008).
- 15. Li Q-J, Xu B, Hara S, Li J, Ma E. Sample-size-dependent surface dislocation nucleation in nanoscale crystals. *Acta Materialia* **145**, 19-29 (2018).
- 16. Holmberg K, Erdemir A. Influence of tribology on global energy consumption, costs and emissions. *Friction* **5**, 263-284 (2017).
- 17. Asay DB, Dugger MT, Ohlhausen JA, Kim SH. Macro-to nanoscale wear prevention via molecular adsorption. *Langmuir* **24**, 155-159 (2008).
- 18. Patton S, Zabinski J. Failure mechanisms of a MEMS actuator in very high vacuum. *Tribology International* **35**, 373-379 (2002).
- 19. Tai Y-C, Fan L-S, Muller RS. IC-processed micro-motors: Design, technology, and testing. In: *IEEE Micro Electro Mechanical Systems, Proceedings, 'An Investigation of Micro Structures, Sensors, Actuators, Machines and Robots'*). IEEE (1989).
- 20. Zhu Y. Mechanics of Crystalline Nanowires: An Experimental Perspective. *Applied Mechanics Reviews* 69, 010802 (2017).
- 21. Wang X, Zhong L, Mao S. Advances in understanding atomic-scale deformation of smallsized face-centered cubic metals with in situ transmission electron microscopy. *Materials Today Nano* **2**, 58-69 (2018).
- 22. Ramachandramoorthy R, Bernal R, Espinosa HD. Pushing the envelope of in situ transmission electron microscopy. *ACS nano* **9**, 4675-4685 (2015).
- 23. Legros M, Gianola D, Motz C. Quantitative in situ mechanical testing in electron microscopes. *MRS bulletin* **35**, 354-360 (2010).
- 24. Xu T, Sun L. Dynamic In Situ Experimentation on Nanomaterials at the Atomic Scale. *Small* **11**, 3247-3262 (2015).
- 25. Zhu Y. In Situ Nanomechanical Testing of Crystalline Nanowires in Electron Microscopes. *Jom* **68**, 84-93 (2016).
- 26. Wang J, Mao SX. Atomistic perspective on in situ nanomechanics. *Extreme Mechanics Letters* **8**, 127-139 (2016).
- 27. Lu K, Lu L, Suresh S. Strengthening materials by engineering coherent internal boundaries at the nanoscale. *science* **324**, 349-352 (2009).
- 28. Bouaziz O, Guelton NJMS, A E. Modelling of TWIP effect on work-hardening. **319**, 246-249 (2001).

- 29. Zhu YT, Liao XZ, Srinivasan SG, Lavernia EJ. Nucleation of deformation twins in nanocrystalline face-centered-cubic metals processed by severe plastic deformation. **98**, 034319 (2005).
- 30. Liao XZ, Zhao YH, Srinivasan SG, Zhu YT, Valiev RZ, Gunderov DV. Deformation twinning in nanocrystalline copper at room temperature and low strain rate. *Applied Physics Letters* **84**, 592-594 (2004).
- 31. Zhu Y, Liao X, Wu X. Deformation twinning in nanocrystalline materials. *Progress in Materials Science* 57, 1-62 (2012).
- 32. Sennour M, Lartigue-Korinek S, Champion Y, Hÿtch† MJ. HRTEM study of defects in twin boundaries of ultra-fine grained copper. **87**, 1465-1486 (2007).
- 33. Vitek V. Multilayer stacking faults and twins on {211} planes in bcc metals. *Scripta Metallurgica* **4**, 725-732 (1970).
- 34. Wasilewski R. BCC stacking fault energies. *Scripta Metallurgica* **1**, 45-47 (1967).
- 35. Mahajan S. Nucleation and growth of deformation twins in Mo-35 at.% Re alloy. *Philosophical Magazine* **26**, 161-171 (1972).
- 36. Hsiung L, Lassila D. Shock-induced deformation twinning and omega transformation in tantalum and tantalum–tungsten alloys. *Acta materialia* **48**, 4851-4865 (2000).
- 37. Sleeswyk A. ¹/₂< 111> screw dislocations and the nucleation of {112}< 111> twins in the bcc lattice. *Philosophical Magazine* **8**, 1467-1486 (1963).
- 38. Vitek V, Perrin R, Bowen DJPM. The core structure of ½ (111) screw dislocations in bcc crystals. **21**, 1049-1073 (1970).
- Ogata S, Li J, Yip S. Twinning pathway in BCC molybdenum. *EPL (Europhysics Letters)* 68, 405 (2004).
- 40. Ogawa K. Edge dislocations dissociated in {112} planes and twinning mechanism of bcc metals. *Philosophical Magazine* **11**, 217-233 (1965).
- 41. Cottrell A, Bilby B. LX. A mechanism for the growth of deformation twins in crystals. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science* **42**, 573-581 (1951).
- 42. Christian JW, Mahajan S. Deformation twinning. *Progress in Materials Science* **39**, 1-157 (1995).

- 43. Mahajan S, Chin GJAm. Formation of deformation twins in fcc crystals. **21**, 1353-1363 (1973).
- 44. Chen C, Florando J, Kumar M, Ramesh K, Hemker K. Incipient deformation twinning in dynamically sheared bcc tantalum. *Acta materialia* **69**, 114-125 (2014).
- 45. Jiang B, *et al.* Direct observation of deformation twinning under stress gradient in bodycentered cubic metals. *Acta Materialia*, (2018).
- 46. Cheng G, Yuan H, Jian W, Xu W, Millett P, Zhu Y. Deformation-induced ω phase in nanocrystalline Mo. *Scripta Materialia* **68**, 130-133 (2013).
- 47. Wu S, et al. $\{1 \ 1 \ 2\} < 1 \ 1 \ 1>$ Twinning during ω to body-centered cubic transition. Acta Materialia **62**, 122-128 (2014).
- 48. Shan Z, Mishra RK, Asif SS, Warren OL, Minor AM. Mechanical annealing and sourcelimited deformation in submicrometre-diameter Ni crystals. *Nature materials* 7, 115 (2008).
- 49. Cao A, Wei Y, Mao SX. Alternating starvation of dislocations during plastic yielding in metallic nanowires. *Scripta Materialia* **59**, 219-222 (2008).
- 50. Cao A. Shape memory effects and pseudoelasticity in bcc metallic nanowires. *Journal of Applied Physics* **108**, 113531 (2010).
- 51. Li S, *et al.* Superelasticity in bcc nanowires by a reversible twinning mechanism. **82**, 205435 (2010).
- 52. Wang J, Zeng Z, Weinberger CR, Zhang Z, Zhu T, Mao SX. In situ atomic-scale observation of twinning-dominated deformation in nanoscale body-centred cubic tungsten. *Nature materials* **14**, 594 (2015).
- 53. Wang J, Wang Y, Cai W, Li J, Zhang Z, Mao SX. Discrete shear band plasticity through dislocation activities in body-centered cubic tungsten nanowires. *Scientific Reports* **8**, (2018).
- 54. Sutton AP, Balluffi RW. Overview no. 61 On geometric criteria for low interfacial energy. *Acta Metallurgica* **35**, 2177-2201 (1987).
- 55. Cao Y, *et al.* De-twinning via secondary twinning in face-centered cubic alloys. *Materials Science & Engineering A* **578**, 110-114 (2013).
- 56. Wang J, *et al.* Detwinning mechanisms for growth twins in face-centered cubic metals. *Acta Materialia* **58**, 2262-2270 (2010).

- 57. Zhu Y, Liao X, Wu X, Narayan J. Grain size effect on deformation twinning and detwinning. *Journal of Materials Science* **48**, 4467-4475 (2013).
- 58. Qu L, et al. A detwinning process of {3 3 2}< 1 1 3> twins in beta titanium alloys. Scripta materialia 69, 389-392 (2013).
- 59. Gutierrez-Urrutia I, Li C, Emura S, Tsuchiya K. Twinning and detwinning mechanisms in a BCC Ti Mo-Fe multilayered alloy. In: *IOP Conference Series: Materials Science and Engineering*). IOP Publishing (2017).
- 60. Li BQ, Sui ML, Li B, ., Ma E, ., Mao SX. Reversible twinning in pure aluminum. *Physical Review Letters* **102**, 205504 (2009).
- 61. Szczerba M, Kopacz S, Szczerba M. Experimental studies on detwinning of face-centered cubic deformation twins. *Acta Materialia* **104**, 52-61 (2016).
- 62. Zhu Y, Wu X, Liao X, Narayan J, Kecskes L, Mathaudhu S. Dislocation-twin interactions in nanocrystalline fcc metals. *Acta Materialia* **59**, 812-821 (2011).
- 63. Liu L, Wang J, Gong S, Mao S. High resolution transmission electron microscope observation of zero-strain deformation twinning mechanisms in Ag. *Physical review letters* **106**, 175504 (2011).
- 64. Zhang JY, Zhang P, Wang RH, Liu G, Zhang GJ, Sun J. Grain-size-dependent zero-strain mechanism for twinning in copper. *Physical Review B* **86**, 064110 (2012).
- 65. Lai M, Tasan CC, Raabe DJAM. On the mechanism of $\{332\}$ twinning in metastable β titanium alloys. **111**, 173-186 (2016).
- 66. Yamaguchi M, Vitek VJPM. Twin boundaries and incoherent steps on twin boundaries in body-centered-cubic metals. **34**, 1-11 (1976).
- 67. Wei S, Wang Q, Wei H, Wang JJMRL. Bending-induced deformation twinning in bodycentered cubic tungsten nanowires. 7, 210-216 (2019).
- 68. Hall EO. The Deformation and Ageing of Mild Steel: III Discussion of Results. *Proceedings of the Physical Society Section B* **64**, 747-753 (1951).
- 69. Petch N. The cleavage strength of polycrystals. *Journal of the Iron and Steel Institute* **174**, 25-28 (1953).
- 70. Chokshi AH, Rosen A, Karch J, Gleiter H. On the validity of the hall-petch relationship in nanocrystalline materials. *Scripta Metallurgica* **23**, 1679-1683 (1989).
- 71. Lian J, Baudelet B, Nazarov A. Model for the prediction of the mechanical behaviour of nanocrystalline materials. *Materials Science and Engineering: A* **172**, 23-29 (1993).

- 72. Valiev RZ, Islamgaliev RK, Alexandrov IV. Bulk nanostructured materials from severe plastic deformation. *Progress in materials science* **45**, 103-189 (2000).
- 73. Ovid'Ko IA, Valiev RZ, Zhu YT. Review on superior strength and enhanced ductility of metallic nanomaterials. *Progress in Materials Science* **94**, 462-540 (2018).
- 74. Hansen N. Hall–Petch relation and boundary strengthening. *Scripta Materialia* **51**, 801-806 (2004).
- 75. Masumura RA, Hazzledine PM, Pande CS. Yield stress of fine grained materials. *Acta Materialia* **46**, 4527-4534 (1998).
- 76. Uchic MD, Shade PA, Dimiduk DM. Plasticity of micrometer-scale single crystals in compression. *Annual Review of Materials Research* **39**, 361-386 (2009).
- 77. Greer JR, De Hosson JTM. Plasticity in small-sized metallic systems: Intrinsic versus extrinsic size effect. *Progress in Materials Science* **56**, 654-724 (2011).
- 78. Greer JR, Oliver WC, Nix WD. Size dependence of mechanical properties of gold at the micron scale in the absence of strain gradients. *Acta Materialia* **53**, 1821-1830 (2005).
- 79. Zhu T, Li J. Ultra-strength materials. *Progress in Materials Science* 55, 710-757 (2010).
- 80. Weinberger CR, Jennings AT, Kang K, Greer JR. Atomistic simulations and continuum modeling of dislocation nucleation and strength in gold nanowires. *Journal of the Mechanics and Physics of Solids* **60**, 84-103 (2012).
- 81. Oh SH, Legros M, Kiener D, Dehm G. In situ observation of dislocation nucleation and escape in a submicrometre aluminium single crystal. *Nature materials* **8**, 95 (2009).
- 82. Parthasarathy TA, Rao SI, Dimiduk DM, Uchic MD, Trinkle DR. Contribution to size effect of yield strength from the stochastics of dislocation source lengths in finite samples. *Scripta Materialia* **56**, 313-316 (2007).
- 83. Frank FC. The Frank—Read source. *Proceedings of the Royal Society of London A Mathematical and Physical Sciences* **371**, 136-138 (1980).
- 84. Zuo L, Ngan A. Molecular dynamics study on compressive yield strength in Ni3Al micropillars. *Philosophical magazine letters* **86**, 355-365 (2006).
- 85. Ngan A, Zuo L, Wo P. Size dependence and stochastic nature of yield strength of micronsized crystals: a case study on Ni3Al. *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences* **462**, 1661-1681 (2006).

- 86. Weinberger CR, Cai W. Surface-controlled dislocation multiplication in metal micropillars. *Proceedings of the National Academy of Sciences*, (2008).
- 87. Zheng H, et al. Discrete plasticity in sub-10-nm-sized gold crystals. *Nature Communications* 1, : 144. (2010).
- 88. Giga A, Kimoto Y, Takigawa Y, Higashi K. Demonstration of an inverse Hall–Petch relationship in electrodeposited nanocrystalline Ni–W alloys through tensile testing. *Scripta Materialia* **55**, 143-146 (2006).
- 89. Takeuchi S. The mechanism of the inverse Hall-Petch relation of nanocrystals. *Scripta materialia* **8**, 1483-1487 (2001).
- 90. Van Swygenhoven H. Grain boundaries and dislocations. *Science* **296**, 66-67 (2002).
- 91. Coble RL. A Model for Boundary Diffusion Controlled Creep in Polycrystalline Materials. *Journal of Applied Physics* **34**, 1679-1682 (1963).
- 92. Yamakov V, Wolf D, Phillpot S, Gleiter H. Grain-boundary diffusion creep in nanocrystalline palladium by molecular-dynamics simulation. *Acta Materialia* **50**, 61-73 (2002).
- 93. Van Swygenhoven H, Derlet P. Grain-boundary sliding in nanocrystalline fcc metals. *Physical review B* **64**, 224105 (2001).
- 94. Langdon TG. Grain boundary sliding revisited: Developments in sliding over four decades. *Journal of Materials Science* **41**, 597-609 (2006).
- 95. Mara NA, Sergueeva AV, Mara TD, McFadden SX, Mukherjee AK. Superplasticity and cooperative grain boundary sliding in nanocrystalline Ni3Al. *Materials Science and Engineering: A* 463, 238-244 (2007).
- 96. Valiev RZ, Murashkin MY, Kilmametov A, Straumal B, Chinh NQ, Langdon TG. Unusual super-ductility at room temperature in an ultrafine-grained aluminum alloy. *Journal of Materials Science* **45**, 4718-4724 (2010).
- 97. Gutkin M, Ovid'ko I. *Plastic deformation in nanocrystalline materials*. Springer Science & Business Media (2013).
- 98. Valiev RZ, Sergueeva AV, Mukherjee AK. The effect of annealing on tensile deformation behavior of nanostructured SPD titanium. *Scripta Materialia* **49**, 669-674 (2003).
- 99. Sergueeva AV, Mara NA, Krasilnikov NA, Valiev RZ, Mukherjee AK. Cooperative grain boundary sliding in nanocrystalline materials. *Philosophical Magazine* **86**, 5797-5804 (2006).

- Kumar P, Kawasaki M, Langdon TG. Review: Overcoming the paradox of strength and ductility in ultrafine-grained materials at low temperatures. *Journal of Materials Science* 51, 7-18 (2016).
- 101. Li J. Diffusive origins. *Nature Materials* 14, 656-657 (2015).
- 102. Chen LY, He M-R, Shin J, Richter G, Gianola DS. Measuring surface dislocation nucleation in defect-scarce nanostructures. *Nature Materials* 14, 707-713 (2015).
- 103. Sun J, et al. Liquid-like pseudoelasticity of sub-10-nm crystalline silver particles. *Nature materials* **13**, 1007-1012 (2014).
- 104. Tomlinson GJTL, Edinburgh,, magazine Dp, science jo. CVI. A molecular theory of friction. 7, 905-939 (1929).
- 105. Gnecco E, Meyer E. Fundamentals of Friction and Wear on the Nanoscale. Springer (2015).
- 106. Lantz M, O'shea S, Hoole A, Welland MJApl. Lateral stiffness of the tip and tip-sample contact in frictional force microscopy. **70**, 970-972 (1997).
- 107. Hölscher H, Schirmeisen A, Schwarz UD. Principles of atomic friction: from sticking atoms to superlubric sliding. *Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences* **366**, 1383-1404 (2008).
- 108. Hölscher H, Ebeling D, Schwarz UD. Friction at atomic-scale surface steps: experiment and theory. *Physical review letters* **101**, 246105 (2008).
- 109. Mate CM, McClelland GM, Erlandsson R, Chiang S. Atomic-scale friction of a tungsten tip on a graphite surface. In: *Scanning Tunneling Microscopy*). Springer (1987).
- 110. Wang Z-J, Ma T-B, Hu Y-Z, Xu L, Wang H. Energy dissipation of atomic-scale friction based on one-dimensional Prandtl-Tomlinson model. *Friction* **3**, 170-182 (2015).
- 111. Steiner P, *et al.* Two-dimensional simulation of superlubricity on NaCl and highly oriented pyrolytic graphite. **79**, 045414 (2009).
- 112. Gyalog T, Bammerlin M, Lüthi R, Meyer E, Thomas H. Mechanism of atomic friction. *EPL (Europhysics Letters)* **31**, 269 (1995).
- 113. Hölscher H, Schwarz U, Wiesendanger R. Modelling of the scan process in lateral force microscopy. *Surface science* **375**, 395-402 (1997).
- 114. Hölscher H, Schwarz U, Zwörner O, Wiesendanger R. Consequences of the stick-slip movement for the scanning force microscopy imaging of graphite. *Physical Review B* **57**, 2477 (1998).

- 115. Sasaki N, Kobayashi K, Tsukada M. Atomic-scale friction image of graphite in atomicforce microscopy. *Physical Review B* **54**, 2138 (1996).
- 116. Hölscher H, Schwarz UD, Wiesendanger R. Simulation of a scanned tip on a NaF(001) surface in friction force microscopy. *Europhysics Letters (EPL)* **36**, 19-24 (1996).
- 117. Lüthi R, *et al.* Friction on the atomic scale: An ultrahigh vacuum atomic force microscopy study on ionic crystals. *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures Processing, Measurement, and Phenomena* 14, 1280-1284 (1996).
- 118. Braun O, Röder J. Transition from stick-slip to smooth sliding: an earthquakelike model. *Physical review letters* **88**, 096102 (2002).
- 119. Gourdon D, Israelachvili JN. Transitions between smooth and complex stick-slip sliding of surfaces. *Physical Review E* **68**, 021602 (2003).
- 120. Socoliuc A, Bennewitz R, Gnecco E, Meyer E. Transition from stick-slip to continuous sliding in atomic friction: entering a new regime of ultralow friction. *Physical review letters* **92**, 134301 (2004).
- 121. Braun O, Peyrard M, Bortolani V, Franchini A, Vanossi A. Transition from smooth sliding to stick-slip motion in a single frictional contact. *Physical Review E* **72**, 056116 (2005).
- 122. Socoliuc A, *et al.* Atomic-scale control of friction by actuation of nanometer-sized contacts. **313**, 207-210 (2006).
- 123. Breki A, Nosonovsky M. Ultraslow frictional sliding and the stick-slip transition. *Applied Physics Letters* **113**, 241602 (2018).
- 124. Hirano M, Shinjo KJPRB. Atomistic locking and friction. 41, 11837 (1990).
- 125. Gosvami NN, Filleter T, Egberts P, Bennewitz R. Microscopic friction studies on metal surfaces. *Tribology letters* **39**, 19-24 (2010).
- 126. Weiss M, Elmer F-J. Dry friction in the Frenkel-Kontorova-Tomlinson model: Static properties. *Physical review B* **53**, 7539 (1996).
- 127. Gyalog T, Thomas H. Friction between atomically flat surfaces. *EPL (Europhysics Letters)* 37, 195 (1997).
- 128. Liu E, Blanpain B, Celis J-PJW. Calibration procedures for frictional measurements with a lateral force microscope. **192**, 141-150 (1996).

- 129. Cannara RJ, Eglin M, Carpick RW. Lateral force calibration in atomic force microscopy: A new lateral force calibration method and general guidelines for optimization. *Review of Scientific Instruments* **77**, 053701 (2006).
- 130. Zijlstra T, et al. Fabrication of a novel scanning probe device for quantitative nanotribology. Sensors and Actuators A: Physical 84, 18-24 (2000).
- 131. Stiernstedt J, Rutland MW, Attard P. A novel technique for the in situ calibration and measurement of friction with the atomic force microscope. *Review of Scientific Instruments* **76**, 083710 (2005).
- 132. Bennewitz R, Gyalog T, Guggisberg M, Bammerlin M, Meyer E, Güntherodt HJ. Atomicscale stick-slip processes on Cu(111). *Physical Review B* **60**, R11301-R11304 (1999).
- 133. Müser MH. Velocity dependence of kinetic friction in the Prandtl-Tomlinson model. *Physical Review B* 84, 125419 (2011).
- 134. Li M, Shi J, Liu L, Yu P, Xi N, Wang Y. Experimental study and modeling of atomic-scale friction in zigzag and armchair lattice orientations of MoS2. *Science and Technology of advanced MaTerials* **17**, 189-199 (2016).
- 135. Zhang S, Ma T, Erdemir A, Li Q. Tribology of two-dimensional materials: From mechanisms to modulating strategies. *Materials Today* **26**, 67-86 (2019).
- 136. Lee C, et al. Frictional characteristics of atomically thin sheets. **328**, 76-80 (2010).
- 137. Li S, *et al.* The evolving quality of frictional contact with graphene. *Nature* **539**, 541-545 (2016).
- 138. Hirano M, Shinjo K, Kaneko R, Murata Y. Anisotropy of frictional forces in muscovite mica. *Physical review letters* **67**, 2642 (1991).
- 139. Dienwiebel M, Verhoeven GS, Pradeep N, Frenken JW, Heimberg JA, Zandbergen HW. Superlubricity of graphite. *Physical review letters* **92**, 126101 (2004).
- 140. Krylov SY, Jinesh K, Valk H, Dienwiebel M, Frenken J. Thermally induced suppression of friction at the atomic scale. *Physical Review E* **71**, 065101 (2005).
- 141. Krylov SY, Frenken JW. Thermal contact delocalization in atomic scale friction: a multitude of friction regimes. *New Journal of Physics* **9**, 398 (2007).
- 142. Jacobs TDB, Greiner C, Wahl KJ, Carpick RW. Insights into tribology from in situ nanoscale experiments. *MRS Bulletin* **44**, 478-486 (2019).
- 143. Minor AM, Dehm G. Advances in in situ nanomechanical testing. *MRS Bulletin* **44**, 438-442 (2019).

- 144. Kizuka T, Yamada K, Deguchi S, Naruse M, Tanaka NJPRB. Cross-sectional timeresolved high-resolution transmission electron microscopy of atomic-scale contact and noncontact-type scannings on gold surfaces. **55**, R7398 (1997).
- 145. Nafari A, Karlen D, Rusu C, Svensson K, Olin H, Enoksson PJJoms. MEMS sensor for in situ TEM atomic force microscopy. **17**, 328-333 (2008).
- 146. Golberg D, Costa PM, Mitome M, Bando Y. Nanotubes in a gradient electric field as revealed by STM TEM technique. *Nano Research* **1**, 166-175 (2008).
- 147. M'ndange-Pfupfu A, Ciston J, Eryilmaz O, Erdemir A, Marks LJTL. Direct observation of tribochemically assisted wear on diamond-like carbon thin films. **49**, 351-356 (2013).
- 148. Jacobs TD, Carpick RW. Nanoscale wear as a stress-assisted chemical reaction. *Nature nanotechnology* **8**, 108-112 (2013).
- 149. Sato T, Nabeya S, Menon V, Ishida T, Kometani R, Fujita H. Real-time observation of slipping and rolling events in DLC wear nanoparticles. *Nanotechnology* **29**, 325707 (2018).
- 150. Sato T, Ishida T, Jalabert L, Fujita H. Real-time transmission electron microscope observation of nanofriction at a single Ag asperity. *Nanotechnology* **23**, 505701 (2012).
- 151. Zhong L, Wang J, Sheng H, Zhang Z, Mao SX. Formation of monatomic metallic glasses through ultrafast liquid quenching. *Nature* **512**, 177-180 (2014).
- 152. Williams DB, Carter CB. The transmission electron microscope. In: *Transmission electron microscopy*). Springer (1996).
- 153. Wang X, *et al.* Atomistic processes of surface-diffusion-induced abnormal softening in nanoscale metallic crystals. *Nature Communications* **12**, 5237 (2021).
- 154. Plimpton S. Fast parallel algorithms for short-range molecular dynamics. *Journal of computational physics* **117**, 1-19 (1995).
- 155. Wu HH, Trinkle DR. Cu/Ag EAM potential optimized for heteroepitaxial diffusion from ab initio data. *Computational Materials Science* **47**, 577-583 (2009).
- 156. Sheng H, Kramer M, Cadien A, Fujita T, Chen M. Highly optimized embedded-atommethod potentials for fourteen fcc metals. *Physical Review B* **83**, 134118 (2011).
- 157. Li J, Sarkar S, Cox WT, Lenosky TJ, Bitzek E, Wang Y. Diffusive molecular dynamics and its application to nanoindentation and sintering. **84**, (2011).

- 158. Stukowski A, Albe K. Extracting dislocations and non-dislocation crystal defects from atomistic simulation data. *Modelling and Simulation in Materials Science and Engineering* **18**, 085001 (2010).
- 159. Falk ML, Langer JS. Dynamics of viscoplastic deformation in amorphous solids. *Physical Review E* 57, 7192 (1998).
- 160. Daw MS, Baskes MI. Embedded-atom method: Derivation and application to impurities, surfaces, and other defects in metals. *Physical Review B* **29**, 6443 (1984).
- 161. Ding Z, Zhou S, Zhao Y. Hardness and fracture toughness of brittle materials: a density functional theory study. *Physical Review B* **70**, 184117 (2004).
- 162. Hoover WG. Canonical dynamics: Equilibrium phase-space distributions. *Physical review* A **31**, 1695 (1985).
- 163. Lei L, Yongfeng S, Xianhua C, Lihua Q, Lu K, . Ultrahigh strength and high electrical conductivity in copper. *Science* **304**, 422-426 (2004).
- 164. Lu L, Chen X, Huang X, Lu K. Revealing the maximum strength in nanotwinned copper. *Science* **323**, 607-610 (2009).
- 165. Zhang X, Misra A. Superior thermal stability of coherent twin boundaries in nanotwinned metals. *Scripta Materialia* **66**, 860-865 (2012).
- Vítek V. Intrinsic stacking faults in body-centred cubic crystals. *Philosophical Magazine* 18, 773-786 (1968).
- Ogata S, Li J, Yip SJPRB. Energy landscape of deformation twinning in bcc and fcc metals. 71, 224102 (2005).
- Meadows D, Johnson W, Allen JJAO. Generation of surface contours by moiré patterns. 9, 942-947 (1970).
- 169. Wang X, Wang J, He Y, Wang C, Zhong L, Mao SX. Unstable twin in body-centered cubic tungsten nanocrystals. *Nature Communications* **11**, 1-7 (2020).
- 170. Song D, Li X, Xue J, Duan H, Jin ZJPML. Irradiation-enhanced twin boundary migration in BCC Fe. **94**, 361-369 (2014).
- 171. Li N, Wang J, Wang Y, Serruys Y, Nastasi M, Misra A. Incoherent twin boundary migration induced by ion irradiation in Cu. *Journal of Applied Physics* **113**, 023508 (2013).
- 172. Yang Y, Li S, Ding X, Sun J, Salje EKJAFM. Interface Driven Pseudo Elasticity in a Fe Nanowires. **26**, 760-767 (2016).

- 173. Wang J, Anderoglu O, Hirth JP, Misra A, Zhang X. Dislocation structures of $\Sigma 3$ {112} twin boundaries in face centered cubic metals. *Applied Physics Letters* **95**, 021908-021908-021903 (2009).
- 174. Schmidt C, Finnis M, Ernst F, Vitek VJPMA. Theoretical and experimental investigations of structures and energies of $\Sigma = 3$,[112] tilt grain boundaries in copper. 77, 1161-1184 (1998).
- 175. Kibey S, Liu JB, Johnson DD, Sehitoglu H. Predicting twinning stress in fcc metals: Linking twin-energy pathways to twin nucleation. *Acta Materialia* **55**, 6843-6851 (2007).
- 176. Weinberger CR, Tucker GJ, Foiles SM. Peierls potential of screw dislocations in bcc transition metals: Predictions from density functional theory. *Physical Review B* **87**, 054114 (2013).
- 177. Greer JR, Weinberger CR, Cai W. Comparing the strength of fcc and bcc sub-micrometer pillars: Compression experiments and dislocation dynamics simulations. *Materials Science and Engineering: A* **493**, 21-25 (2008).
- 178. Dutta A, Bhattacharya M, Barat P, Mukherjee P, Gayathri N, Das GJPrl. Lattice resistance to dislocation motion at the nanoscale. **101**, 115506 (2008).
- 179. Ostapovets A, Paidar V. Evaluation of the Peierls stress for boundary dislocations. **111**, 229-235 (2011).
- 180. Hirth JP, Lothe J. Theory of dislocations. (1982).
- 181. Smith D, Bowkett K. The analysis of field-ion micrographs: Stacking faults in tungsten. *Philosophical Magazine* **18**, 1219-1233 (1968).
- 182. Chen M, Ma E, Hemker KJ, Sheng H, Wang Y, Cheng X. Deformation twinning in nanocrystalline aluminum. *Science* **300**, 1275-1277 (2003).
- 183. Zhu YT, *et al.* Nucleation and growth of deformation twins in nanocrystalline aluminum. *Applied Physics Letters* **85**, 5049-5051 (2004).
- 184. Li S, Ding X, Li J, Ren X, Sun J, Ma E. High-efficiency mechanical energy storage and retrieval using interfaces in nanowires. *Nano letters* **10**, 1774-1779 (2010).
- 185. Otsuka K, Sakamoto H, Shimizu K. Successive stress-induced martensitic transformations and associated transformation pseudoelasticity in Cu-Al-Ni alloys. *Acta Metallurgica* 27, 585-601 (1979).
- 186. Miyazaki S, Ohmi Y, Otsuka K, Suzuki YJLJdPC. Characteristics of deformation and transformation pseudoelasticity in Ti-Ni alloys. **43**, C4-255-C254-260 (1982).

- 187. Gu XW, Hanson LA, Eisler CN, Koc MA, Alivisatos APJPrl. Pseudoelasticity at Large Strains in Au Nanocrystals. **121**, 056102 (2018).
- 188. Delaey L, Krishnan R, Tas H, Warlimont HJJoMS. Thermoelasticity, pseudoelasticity and the memory effects associated with martensitic transformations. **9**, 1521-1535 (1974).
- 189. Pan Q, Zhou H, Lu Q, Gao H, Lu LJN. History-independent cyclic response of nanotwinned metals. **551**, 214 (2017).
- 190. Nie J, Zhu Y, Liu J, Fang X. Periodic segregation of solute atoms in fully coherent twin boundaries. *Science* **340**, 957-960 (2013).
- 191. Coble R. A model for boundary diffusion controlled creep in polycrystalline materials. *Journal of applied physics* **34**, 1679-1682 (1963).
- 192. Yamakov V, Wolf D, Phillpot S, Mukherjee A, Gleiter H. Deformation-mechanism map for nanocrystalline metals by molecular-dynamics simulation. *Nature materials* **3**, 43 (2004).
- 193. Hu J, Shi YN, Sauvage X, Sha G, Lu K. Grain boundary stability governs hardening and softening in extremely fine nanograined metals. *Science* **355**, 1292-1296 (2017).
- 194. Shan Z, Stach E, Wiezorek J, Knapp J, Follstaedt D, Mao S. Grain boundary-mediated plasticity in nanocrystalline nickel. *Science* **305**, 654-657 (2004).
- 195. Wang L, *et al.* Grain rotation mediated by grain boundary dislocations in nanocrystalline platinum. *Nature communications* **5**, 1-7 (2014).
- 196. Rupert T, Gianola D, Gan Y, Hemker K. Experimental observations of stress-driven grain boundary migration. *Science* **326**, 1686-1690 (2009).
- 197. Zheng S-X, Luo X-M, Zhang G-P. Cumulative shear strain-induced preferential orientation during abnormal grain growth near fatigue crack tips of nanocrystalline Au films. *Journal of Materials Research* **35**, 372-379 (2020).
- 198. Pande CS, Cooper KP. Nanomechanics of Hall–Petch relationship in nanocrystalline materials. *Progress in Materials Science* **54**, 689-706 (2009).
- 199. Sun S, *et al.* Atomistic Mechanism of Stress-Induced Combined Slip and Diffusion in Sub-5 Nanometer-Sized Ag Nanowires. *ACS nano* **13**, 8708-8716 (2019).
- Sun X, Ariza M, Ortiz M, Wang K. Atomistic modeling and analysis of hydride phase transformation in palladium nanoparticles. *Journal of the Mechanics and Physics of Solids* 125, 360-383 (2019).

- 201. Richter G, Hillerich K, Gianola DS, Monig R, Kraft O, Volkert CA. Ultrahigh strength single crystalline nanowhiskers grown by physical vapor deposition. *Nano Letters* **9**, 3048-3052 (2009).
- 202. Jennings AT, Burek MJ, Greer JR. Microstructure versus size: mechanical properties of electroplated single crystalline Cu nanopillars. *Physical review letters* **104**, 135503 (2010).
- 203. Lu Y, Song J, Huang JY, Lou J. Surface dislocation nucleation mediated deformation and ultrahigh strength in sub-10-nm gold nanowires. *Nano Research* **4**, 1261-1267 (2011).
- 204. Cao G, *et al.* Superplasticity in gold nanowires through the operation of multiple slip systems. *Advanced Functional Materials* **28**, 1805258 (2018).
- 205. Kim SY, Lee I-H, Jun S. Transition-pathway models of atomic diffusion on fcc metal surfaces. I. Flat surfaces. *Physical Review B* **76**, 245407 (2007).
- 206. Wei Q, Cheng S, Ramesh KT, Ma E. Effect of nanocrystalline and ultrafine grain sizes on the strain rate sensitivity and activation volume: fcc versus bcc metals. **381**, 71-79 (2004).
- 207. Dao M, Lu L, Asaro R, De Hosson JTM, Ma E. Toward a quantitative understanding of mechanical behavior of nanocrystalline metals. *Acta Materialia* **55**, 4041-4065 (2007).
- 208. Ala-Nissila T, Ferrando R, Ying SJAiP. Collective and single particle diffusion on surfaces. **51**, 949-1078 (2002).
- 209. Hummel R, Geier H. Activation energy for electrotransport in thin silver and gold films. *Thin Solid Films* **25**, 335-342 (1975).
- 210. Weinberger CR, Cai W. Plasticity of metal nanowires. *Journal of Materials Chemistry* **22**, 3277 (2012).
- 211. Torres JA, *et al.* The puzzling stability of monatomic gold wires. *Surface Science* **426**, L441-L446 (1999).
- 212. Kong D, *et al.* Surface energy driven liquid-drop-like pseudoelastic behaviors and in situ atomistic mechanisms of small-sized face-centered-cubic metals. *Nano letters* **19**, 292-298 (2018).
- 213. Guo W, Wang Z, Li J. Diffusive versus displacive contact plasticity of nanoscale asperities: temperature-and velocity-dependent strongest size. *Nano letters* **15**, 6582-6585 (2015).
- 214. Brochard S, Hirel P, Pizzagalli L, Godet J. Elastic limit for surface step dislocation nucleation in face-centered cubic metals: Temperature and step height dependence. *Acta Materialia* **58**, 4182-4190 (2010).

- 215. Li C, Xu G. Critical conditions for dislocation nucleation at surface steps. *Philosophical Magazine* **86**, 2957-2970 (2006).
- 216. Amodeo J, Begau C, Bitzek E. Atomistic simulations of compression tests on Ni3Al nanocubes. *Materials Research Letters* **2**, 140-145 (2014).
- 217. Dick K, Dhanasekaran T, Zhang Z, Meisel D. Size-dependent melting of silicaencapsulated gold nanoparticles. *Journal of the American Chemical Society* **124**, 2312-2317 (2002).
- 218. Bishop CM, Tang M, Cannon RM, Carter WC. Continuum modelling and representations of interfaces and their transitions in materials. *Materials Science and Engineering: A* **422**, 102-114 (2006).
- 219. Buffat P, Borel JP. Size effect on the melting temperature of gold particles. *Physical review* A 13, 2287 (1976).
- 220. Kim SY, Lee I-H, Jun S. Transition-pathway models of atomic diffusion on fcc metal surfaces. II. Stepped surfaces. *Physical Review B* **76**, 245408 (2007).
- 221. Yue Y, *et al.* Crystalline liquid and rubber-like behavior in Cu nanowires. *Nano letters* **13**, 3812-3816 (2013).
- 222. Han WZ, *et al.* From "Smaller is Stronger" to "Size Independent Strength Plateau" : Towards Measuring the Ideal Strength of Iron. *Advanced Materials* **27**, 3385-3390 (2015).
- 223. Achanta S, Celis J-P. Nanotribology of mems/nems. In: *Fundamentals of Friction and Wear on the Nanoscale*). Springer (2015).
- 224. Park JY, Salmeron M. Fundamental aspects of energy dissipation in friction. *Chemical reviews* **114**, 677-711 (2014).
- 225. Fujisawa S, Sugawara Y, Ito S, Mishima S, Okada T, Morita S. The two-dimensional stickslip phenomenon with atomic resolution. *Nanotechnology* **4**, 138 (1993).
- 226. Liu X-Z, Ye Z, Dong Y, Egberts P, Carpick RW, Martini A. Dynamics of atomic stick-slip friction examined with atomic force microscopy and atomistic simulations at overlapping speeds. *Physical Review Letters* **114**, 146102 (2015).
- 227. Li Q, Dong Y, Martini A, Carpick RW. Atomic friction modulation on the reconstructed Au (111) surface. *Tribology Letters* **43**, 369 (2011).
- 228. Merkle AP, Marks LD. Liquid-like tribology of gold studied by in situ TEM. *Wear* **265**, 1864-1869 (2008).

- 229. Oviedo JP, *et al.* In situ TEM characterization of shear-stress-induced interlayer sliding in the cross section view of molybdenum disulfide. **9**, 1543-1551 (2014).
- 230. Mo Y, Turner KT, Szlufarska I. Friction laws at the nanoscale. *Nature* **457**, 1116 (2009).
- 231. So M, Jacobsen KW, Stoltze P. Simulations of atomic-scale sliding friction. *Physical Review B* 53, 2101 (1996).
- 232. Dong Y, Vadakkepatt A, Martini A. Analytical models for atomic friction. *Tribology Letters* 44, 367 (2011).
- 233. Sørensen MR, Brandbyge M, Jacobsen KW. Mechanical deformation of atomic-scale metallic contacts: Structure and mechanisms. **57**, 3283-3294 (1998).
- 234. Subramaniyan AK, Sun C. Continuum interpretation of virial stress in molecular simulations. *International Journal of Solids and Structures* **45**, 4340-4346 (2008).
- 235. Dong Y, Li Q, Wu J, Martini A. Friction, slip and structural inhomogeneity of the buried interface. *Modelling and Simulation in Materials Science and Engineering* **19**, 065003 (2011).
- 236. Hurtado JA, Kim KS. Scale effects in friction of single-asperity contacts. I. From concurrent slip to single-dislocation-assisted slip. *Proceedings of the Royal Society of London Series A: Mathematical, Physical and Engineering Sciences* **455**, 3363-3384 (1999).
- 237. Maugis D. Adhesion of spheres: the JKR-DMT transition using a Dugdale model. *Journal* of colloid and interface science **150**, 243-269 (1992).
- 238. Luan B, Robbins MO. The breakdown of continuum models for mechanical contacts. *Nature* **435**, 929-932 (2005).
- 239. Zhang S, et al. Tuning friction to a superlubric state via in-plane straining. Proceedings of the National Academy of Sciences **116**, 24452-24456 (2019).
- 240. Hurtado JA, Kim KS. Scale effects in friction of single-asperity contacts. II. Multipledislocation-cooperated slip. *Proceedings of the Royal Society of London Series A: Mathematical, Physical and Engineering Sciences* **455**, 3385-3400 (1999).
- 241. Krenn C, Roundy D, Morris Jr J, Cohen ML. Ideal strengths of bcc metals. *Materials Science and Engineering: A* **319**, 111-114 (2001).
- 242. Trevethan T, Latham CD, Heggie MI, Briddon PR, Rayson MJ. Vacancy diffusion and coalescence in graphene directed by defect strain fields. *Nanoscale* **6**, 2978-2986 (2014).

- 243. Urbakh M, Klafter J, Gourdon D, Israelachvili J. The nonlinear nature of friction. *Nature* **430**, 525-528 (2004).
- 244. Cross G, Schirmeisen A, Stalder A, Grütter P, Tschudy M, Dürig U. Adhesion interaction between atomically defined tip and sample. *Physical review letters* **80**, 4685 (1998).
- 245. Bylander D, Kleinman L. Self-consistent relativistic calculation of the energy bands and cohesive energy of W. *Physical Review B* **29**, 1534 (1984).
- 246. Ambrosetti A, Silvestrelli PL. Cohesive properties of noble metals by van der Waalscorrected density functional theory: Au, Ag, and Cu as case studies. *Physical Review B* **94**, 045124 (2016).
- 247. Ehrlich G, Stolt K. Surface diffusion. *Annual Review of Physical Chemistry* **31**, 603-637 (1980).
- 248. Vairis A, Frost M. High frequency linear friction welding of a titanium alloy. *Wear* **217**, 117-131 (1998).
- 249. Schwarz UD. A generalized analytical model for the elastic deformation of an adhesive contact between a sphere and a flat surface. *Journal of Colloid and Interface Science* **261**, 99-106 (2003).
- 250. Gao G, Cannara RJ, Carpick RW, Harrison JA. Atomic-scale friction on diamond: a comparison of different sliding directions on (001) and (111) surfaces using MD and AFM. *Langmuir* **23**, 5394-5405 (2007).
- 251. Ruths M, Alcantar N, Israelachvili J. Boundary friction of aromatic silane self-assembled monolayers measured with the surface forces apparatus and friction force microscopy. *The Journal of Physical Chemistry B* **107**, 11149-11157 (2003).
- 252. Hill R, Milstein F. Principles of stability analysis of ideal crystals. *Physical Review B* **15**, 3087 (1977).
- 253. Carpick R, Agrait N, Ogletree D, Salmeron M. Variation of the interfacial shear strength and adhesion of a nanometer-sized contact. *Langmuir* **12**, 3334-3340 (1996).
- 254. Liu X, Golubov SI, Woo CH, Huang H. Glide of edge dislocations in tungsten and molybdenum. **365**, 96-100 (2004).
- 255. Srivastava K, Gröger R, Weygand D, Gumbsch P. Dislocation motion in tungsten: atomistic input to discrete dislocation simulations. *International Journal of Plasticity* **47**, 126-142 (2013).
- 256. Christian J. Crystallographic theories, interface structures, and transformation mechanisms. *Metallurgical and Materials Transactions A* **25**, 1821-1839 (1994).

- 257. Bakker H, Zhou G, Yang H. Mechanically driven disorder and phase transformations in alloys. *Prog Mater Sci* **39**, 159-241 (1995).
- 258. Buehler WJ, Gilfrich J, Wiley R. Effect of low temperature phase changes on the mechanical properties of alloys near composition TiNi. *Journal of applied physics* **34**, 1475-1477 (1963).
- 259. Grässel O, Krüger L, Frommeyer G, Meyer LJIJop. High strength Fe-Mn-(Al, Si) TRIP/TWIP steels development—properties—application. **16**, 1391-1409 (2000).
- 260. Lebedev A, Kosarchuk V. Influence of phase transformations on the mechanical properties of austenitic stainless steels. *International Journal of Plasticity* **16**, 749-767 (2000).
- 261. Park HS. Stress-induced martensitic phase transformation in intermetallic nickel aluminum nanowires. *Nano letters* **6**, 958-962 (2006).
- 262. Li Z, Pradeep KG, Deng Y, Raabe D, Tasan CC. Metastable high-entropy dual-phase alloys overcome the strength–ductility trade-off. *Nature* **534**, 227 (2016).
- 263. Wang L, *et al.* In situ atomic-scale observation of continuous and reversible lattice deformation beyond the elastic limit. *Nature communications* **4**, 2413 (2013).
- 264. Tadaki T, Otsuka K, Shimizu K. Shape memory alloys. *Annual Review of Materials Science* **18**, 25-45 (1988).
- 265. Park HS, Gall K, Zimmerman JA. Shape memory and pseudoelasticity in metal nanowires. *Physical Review Letters* **95**, 255504 (2005).
- 266. Cheng Q, Wu H, Wang Y, Wang X. Pseudoelasticity of Cu–Zr nanowires via stressinduced martensitic phase transformations. *Applied physics letters* **95**, 021911 (2009).
- 267. Chen S, *et al.* Real-time observations of TRIP-induced ultrahigh strain hardening in a dualphase CrMnFeCoNi high-entropy alloy. *Nature Communications* **11**, 1-8 (2020).
- 268. Luhman T, Curzon A. An electron diffraction study of a Ti-22 at.% Nb alloy containing unequal populations of the four variants of the ω-phase. *Journal of Materials Science* 7, 710-712 (1972).
- 269. Sikka S, Vohra Y, Chidambaram R. Omega phase in materials. *Progress in Materials Science* 27, 245-310 (1982).
- 270. Kutsar A. T-p diagram of hafnium and phase transitions in shock waves. *Fizika Metallov i Metallovedenie* **40**, 787-793 (1975).

- 271. Hickman B. The formation of omega phase in titanium and zirconium alloys: a review. *Journal of Materials Science* **4**, 554-563 (1969).
- 272. Kuan T, Ahrens R, Sass S. The stress-induced omega phase transformation in Ti-V alloys. *Metallurgical Transactions A* **6**, 1767 (1975).
- 273. Vohra Y, Menon E, Sikka S, Krishnan R. High pressure studies on a prototype omega forming alloy system. *Acta Metallurgica* **29**, 457-470 (1981).
- 274. Hsiung L, Lassila D. Shock-induced omega phase in tantalum. *Scripta materialia* **38**, 1371-1376 (1998).
- 275. Landman U, Luedtke W, Ringer EM. Atomistic mechanisms of adhesive contact formation and interfacial processes. *Wear* **153**, 3-30 (1992).
- 276. He Y, *et al.* Atomistic observation on diffusion-mediated friction between single-asperity contacts. *Nature Materials*, (2021).
- 277. Zheng S, Shinzato S, Ogata S, Mao S. Experimental molecular dynamics for individual atomic-scale plastic events in nanoscale crystals. *Journal of the Mechanics and Physics of Solids*, 104687 (2021).
- 278. Cieplak M, Smith ED, Robbins MO. Molecular origins of friction: the force on adsorbed layers. *Science* **265**, 1209-1212 (1994).
- 279. Persson B, Tosatti E, Fuhrmann D, Witte G, Wöll C. Low-frequency adsorbate vibrational relaxation and sliding friction. *Physical Review B* **59**, 11777 (1999).
- 280. Berman D, Deshmukh SA, Sankaranarayanan SK, Erdemir A, Sumant AV. Extraordinary macroscale wear resistance of one atom thick graphene layer. *Advanced Functional Materials* **24**, 6640-6646 (2014).
- 281. Ouyang W, de Wijn AS, Urbakh M. Atomic-scale sliding friction on a contaminated surface. *Nanoscale* **10**, 6375-6381 (2018).
- 282. Martin JM, Erdemir A. Superlubricity: Friction's vanishing act. *Physics Today* 71, (2018).
- 283. Donnet C, Fontaine J, Grill A, Le Mogne T. The role of hydrogen on the friction mechanism of diamond-like carbon films. *Tribology Letters* **9**, 137-142 (2001).
- 284. Takeda S, Yoshida H. Atomic-resolution environmental TEM for quantitative in-situ microscopy in materials science. *Microscopy* **62**, 193-203 (2013).
- 285. Ryu S, Kang K, Cai W. Predicting the dislocation nucleation rate as a function of temperature and stress. *Journal of Materials Research* **26**, 2335-2354 (2011).

286. Mason JK, Lund AC, Schuh CA. Determining the activation energy and volume for the onset of plasticity during nanoindentation. *PHYSICAL REVIEW B* **73**, (2006).