Chapter 2

Free-energy-based Atomistic Study of Nucleation Kinetics and Thermodynamics of Defects in Metals; Plastic Strain Carrier “Plaston”

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2.1 Introduction

Unlike elastic deformation, which tends to occur with a broader and more uniform strain distribution, plastic deformation proceeds in a more localized manner. It is realized through the nucleation and migration of local atomistic defects, including dislocations, disconnections, disclinations, vacancies/impurities/interstitials in crystals, and shear transformation zones in glasses. These defects are collectively called “plastons” in this book, as described in the previous section. The defects function as “carriers” of plastic strain, releasing the elastic tension/compression (reducing internal elastic strain energy) by their motion in plastically deformable materials, such as metals. These defect activities eventually induce changes in the material structure and texture (e.g., phase transformation, twinning, stacking fault formation, crack propagation and blunting, surface morphology change, grain growth and rotation, and glass relaxation). In plasticity and its dynamics, temperature- and stress-dependent deformation kinetics (e.g., the strain rate and its temperature and stress dependencies) are crucial factors. These factors often shift the dominant deformation process in a material by changing the kinetics of the available defect activities. For example, the dominant deformation process in creep transits from diffusive (atomic diffusion and grain boundary (GB) migration and sliding) to more displacive (dislocation glide) with increasing stress and/or decreasing temperature (Wang et al. 2011). Therefore, studying all the available defect activities and the corresponding kinetics under different temperatures and stress conditions is vital for understanding, and thus controlling, plasticity dynamics.

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The question arises as to what can be done for understanding and controlling plasticity dynamics. Uncovering the free-energy landscape with an appropriate corrective variable (CV) for the available defect activities is a potential answer. The free-energy landscape directly provides kinetic-related information about defects via the activation energy, which is characterized as the difference in free energy between the local equilibrium and saddle states of the considered defect activity. Additionally, the temperature and stress dependencies of kinetics are naturally described from those of free energy via parameters such as the activation parameters of activation volume and activation entropy. Furthermore, thermodynamics are fully described according to the free-energy difference between local equilibrium states. Hence, once the free-energy landscape covering the possible (accessible) defect activities is understood, the plasticity dynamics of the materials can be completely defined and predicted for any temperature and stress conditions. Atomistic modeling methods based on a reliable energy description, such as density functional theory and sophisticated interatomic interaction, are promising tools for elucidating the free-energy landscape of the defect activities, because these activities are usually in atomic scale. Fortunately, substantial advances in atomistic modeling methods have recently reported to elucidate the free-energy landscape.

Notably, the free-energy landscape exhibits a multiscale nature in many cases, as mentioned in classical nucleation theory. For example, studying a dislocation nucleation process from a nucleation site in a material according to the free-energy concept can reveal a saddle point configuration at a loop size during the dislocation loop expansion process. However, a careful examination of a segment of the dislocation line and its motion at the atomic scale can reveal “local” saddle points attributable to the individual segment motion successively overcoming the Peierls potential barrier. All these saddle points contribute to the kinetics of the dislocation loop nucleation; however, the former saddle point defines the activation free-energy barrier of the entire loop nucleation process.

In this section, atomistic modeling studies on dislocation kinetics and thermodynamics, such as the nucleation of deformation twins and the heterogeneous and homogeneous nucleation of dislocations, are introduced from the free-energy standpoint.

2.2 Shuffling Dominant $\{10\bar{1}2\}\{10\bar{1}\bar{1}\}$ Deformation Twinning in Hexagonal Close-Packed Magnesium (Ishii et al. 2016)

In deformation twinning (DT) (Christian Mahajan 1995), a crystal is transformed into a mirrored configuration with transformation strain $\varepsilon_{\text{final}}$, which is as important deformation mode as dislocation. Although many atomistic DT simulation and experiments have been performed, the DT nucleation pathway and kinetics are still unclear. These issues remain controversial issues in the study of plasticity. The nucleation pathway and kinetics must be dominated by twin boundary nucleation and migra-

Fig. 2.1 Atomic arrangements of perfect and twinned hexagonal close-packed (HCP) configurations viewed from $[1\bar{2}10]$ (Ishii et al. 2016). The four-atom supercell shape is depicted by the red dotted line

tion, which can be driven by local atomic-scale shear deformation. In many cases, interatomic-layer sliding can realize atomic-scale local shear deformation. However, in some cases, for instance, the following hexagonal close-packed (HCP) case, more complicated atomic motion, such as nonaffine atomic “shuffling”, is occurs because of its lower activation Gibbs free energy.

Figure 2.1 presents perfect ($\lambda = 0$) and twinned ($\lambda = 1$) HCP atomic structures corresponding to $\langle 1\bar{2}10 \rangle$, at $\sigma = 0$. The four-atom supercell ($M = 4$) includes atoms A, B, C, and D is the minimum lattice correspondence pattern unit required to render the atomic arrangements during $\{10\bar{1}2\}\langle 10\bar{1}\bar{1} \rangle$ twinning shear deformation (Li and Ma 2009; Wang et al. 2013). The deformation unit has internal degrees of freedom geometrically independent of lattice strain. Importantly, external stress cannot independently control the internal degrees of freedom, referred to as the so called nonaffine atomic “shuffling,” from the lattice strain because the internal degrees of freedom are only “slaves” of the affine lattice strain. However, actual deformation transpires at finite temperatures. Thermal fluctuations are induced by thermal energy. Thermal energy can independently disturb the internal degrees of freedom from the lattice strain (i.e., free the degrees of freedom from slavery) and excite them. Therefore, it can enable to attain instability point (saddle point) on the Gibbs free-energy landscape to not be taken only by the application of stress, where the soft mode is mostly along the direction of the nonaffine atomic shuffling. Thus, the method for applying stress at zero temperature may not discover these instability points. A Gibbs free-energy landscape in a space spanned by lattice strain and shuffling degrees of freedom can resolve this issue, thereby allowing the estimation of minimum energy

pathway (MEP) and corresponding activation Gibbs free energy considering the nonaffine atomic shuffling in addition to affine lattice strain.

A scalar for representing the shuffling degree of freedom (Ishii et al. 2016) is defined as

$$I \equiv (\mathbf{s} - \mathbf{s}^{\text{ini}})^T \mathbf{H}_0^T \mathbf{H}_0 (\mathbf{s}^{\text{fin}} - \mathbf{s}^{\text{ini}}) / M \quad (2.1)$$

where $\mathbf{s}^{\text{ini}}$ and $\mathbf{s}^{\text{fin}}$ indicate the internal coordinates of the labeled atoms before and after deformation ($\lambda = 0$ and 1), respectively, for a given $\boldsymbol{\sigma}$. Note that, the $\mathbf{s}$ differences in (2.1) corresponds to the changes in internal coordinates with no periodic boundary condition (PBC) wraparound. The unit of I is $\text{\AA}^2$. When the deformation is complete, I takes the meaning of mean square nonaffine displacements (MSDs). The crystal is transformed from a reference configuration to another configuration with strain $\boldsymbol{\varepsilon}_{\text{final}}$. The supercell that describes the deformation can be taken as an irreducible lattice correspondence pattern, which can be greater than the host lattice primitive cell. The deformation can be atomistically express as

$$\mathbf{x}_m(\lambda) = \mathbf{H}(\lambda) \mathbf{s}_m(\lambda), \quad \mathbf{H}(\lambda) = \mathbf{R}(\lambda) (\mathbf{I} + 2\boldsymbol{\varepsilon}(\lambda))^{1/2} \mathbf{H}_0, \quad (2.2)$$

where $\mathbf{x}_m$ denotes the Cartesian position, λ denotes the reaction progress variable (scalar), and $\mathbf{s}_m = [s_{m1}; s_{m2}; s_{m3}] \in [0, 1)$ refers to the reduced coordinate vector of atom m under PBC. Further, $\mathbf{H} = [\mathbf{h}_1 \mathbf{h}_2 \mathbf{h}_3]$ is a 3×3 matrix, where $\mathbf{h}_1$, $\mathbf{h}_2$, and $\mathbf{h}_3$ corresponding to the three edge vectors of the supercell and $m = 1, \dots, M$ is the atom index in the supercell. $(\mathbf{I} + 2\boldsymbol{\varepsilon}(\lambda))^{1/2}$ and $\mathbf{R}(\lambda)$ are the equation components corresponding to the irrotational and rotational parts of the deformation gradient, respectively, where $\boldsymbol{\varepsilon}(\lambda)$ denotes the Lagrangian strain with respect to the initial configuration.

The MEP with the least M can then be computed based on ab initio first-principles computation at constant external stress $\boldsymbol{\sigma}$, yielding the activation Gibbs energy $G(\lambda, \boldsymbol{\sigma})$ versus reaction coordinate λ , that is parametrized by $\boldsymbol{\sigma}$. An algorithm, such as the nudged elastic band (NEB) method (Jonsson et al. 1998), can be employed to obtain the MEP and fix the saddle point on the MEP:

$$Q(\boldsymbol{\sigma}) \equiv G(\lambda^*, \boldsymbol{\sigma}) - G(0, \boldsymbol{\sigma}) \quad (2.3)$$

on the joint $\boldsymbol{\varepsilon} \otimes \mathbf{s}$ space (Sheppard et al. 2012), where $\lambda = 0$ and 1 denote the state before and after deformation, respectively, and λ^* denotes a saddle point, at constant external stress $\boldsymbol{\sigma}$. The Gibbs free-energy landscape can be numerically estimated using ab initio first-principles computation by changing $\boldsymbol{\varepsilon}$ and $\mathbf{s}$.

$$G(\boldsymbol{\varepsilon}, \mathbf{s}, \boldsymbol{\sigma}) \equiv U(\boldsymbol{\varepsilon}, \mathbf{s}) - W(\boldsymbol{\varepsilon}, \boldsymbol{\sigma}), \quad (2.4)$$

where $W(\boldsymbol{\varepsilon}, \boldsymbol{\sigma})$ is the work performed by constant external Cauchy stress $\boldsymbol{\sigma}$ (Wang et al. 1995):

$$W(\boldsymbol{\varepsilon}, \boldsymbol{\sigma}) \equiv \int_0^1 dl \det |\mathbf{J}(\boldsymbol{\eta} = l\boldsymbol{\varepsilon})\mathbf{H}_0| \times \text{Tr} [\mathbf{J}^{-1}(\boldsymbol{\eta} = l\boldsymbol{\varepsilon})\boldsymbol{\sigma}\mathbf{J}^{-T}(\boldsymbol{\eta} = l\boldsymbol{\varepsilon})\boldsymbol{\varepsilon}], \quad (2.5)$$

where $\boldsymbol{\eta} = l\boldsymbol{\varepsilon} = 1/2(\mathbf{J}^T\mathbf{J} - \mathbf{I})$ denotes the Lagrangian strain tensor, and $\mathbf{J}$ denotes the corresponding deformation gradient tensor,

$$\mathbf{J} = \mathbf{R}(\mathbf{I} + 2\boldsymbol{\eta})^{1/2} \quad (2.6)$$

where $\mathbf{R}$ is an additional rotation matrix $\mathbf{R}^T\mathbf{R} = \mathbf{I}$ that is completely defined when the transformation coordinate frame convention is selected. Although $G(\boldsymbol{\varepsilon}, \mathbf{s}, \boldsymbol{\sigma})$ is now defined using (2.4), its direct visualization is difficult because the $\boldsymbol{\varepsilon} \otimes \mathbf{s}$ space is $3M + 6$ -dimensional. Therefore, (2.1) can be used to aid visualization. We can uniquely compute $G(\gamma, I, \boldsymbol{\sigma})$ by implementing energy minimization to all degrees of freedom of the supercell system other than γ and I :

$$G(\gamma, I, \boldsymbol{\sigma}) \equiv \min_{\boldsymbol{\varepsilon} \in \gamma, \mathbf{s} \in I} G(\boldsymbol{\varepsilon}, \mathbf{s}, \boldsymbol{\sigma}) \quad (2.7)$$

Figure 2.2 presents the Gibbs free-energy landscapes $\Delta G(\gamma, I)$ obtained at different external Cauchy shear stresses ($\sigma_{yz} = \sigma_{zy} = 0.0, 1.0$, and 2.0 GPa in the twinning direction). The red curves on the Gibbs free-energy landscapes indicate the MEPs from the original to the twinned configuration under these external shear stresses, which were determined using the NEB method. The change in the external shear stress shifts the equilibrium state before and after the twinning as well as the saddle point. Notably, the saddle point is located at a point of finite I and the MEP parallels the I -axis more closely than it parallels the γ axis, suggesting that I dominates the DT process. In this case, merely achieving the shear strain γ is insufficient to overcome the activation Gibbs free-energy barrier. Figure 2.4a shows the Gibbs free-energy profile along the MEP at different external shear stresses. The change in the Gibbs free-energy barrier with respect to the external shear stress are presented in Fig. 2.4b. To confirm the above discussion, two NEB calculations were independently performed: (1) with respect to internal atomic configuration I , where the supercell shape is relaxed under the predefined external stress (I -control NEB) and (2) with respect to γ , where the internal atomic configuration $\mathbf{s}$ is relaxed for each supercell frame shape (γ -control NEB). In Fig. 2.4b, the Gibbs free-energy barriers of the two calculations are compared; results indicates that the Gibbs free-energy barrier obtained using I -control NEB matches that obtained using the two-dimensional Gibbs free-energy landscape. Alternatively, the Gibbs free-energy barrier using γ -control NEB is substantially greater than that obtained using I -control NEB. These results clearly indicate that DT corresponding to an I -dominant (nonaffine-displacement dominant) deformation and not γ -dominant. Hence, the twinned structure can be generated first without producing local shear strain because the phonons can toggle the “internal cog” at finite temperatures. After flipping the internal cog, the local γ can later spontaneously relax along the twinning configuration. Because these processes actually occur almost simultaneously in the DT process, it is impossible to use DT atomic motion observations to determine whether I - or γ -dominant. The

Fig. 2.2 Gibbs free-energy landscapes $\Delta G(\gamma, I)$ at $\sigma_{yz} = \sigma_{zy}$ = values of **a** 0.0, **b** 1.0, and **c** 2.0 GPa. The red-dashed curves denote the minimum energy paths (MEPs) of the deformation twinning processes (Ishii et al. 2016)

Gibbs free-energy landscape analysis is required to obtain insights into the fundamental mechanism. Figure 2.3 shows the atomic position and supercell shape change along the MEP under the stress-free conditions. A uniform supercell shape change (shear strain) with a staggered rotation of A–B and C–D bonds is clearly observed. Intuitively, the latter bond rotation behavior is hard to archive only using an external shear stress along the DT direction. Figure 2.4b demonstrates that a very high critical external shear stress of ~ 3.0 GPa is necessary to realize the DT by γ -control at

Fig. 2.3 Atomic position and supercell shape change along the MEP (Ishii et al. 2016). The green and black atoms are located in different atomic layers

Fig. 2.4 **a** Gibbs free-energy profile along the MEP and **b** change in the energy barrier along the MEP with respect to change in applied external shear stress. Figure (b) indicates the DT process is *I*-dominant, because the Gibbs energy barrier of the *I*-controlled NEB reproduces the Gibbs free-energy barriers obtained using the two-dimensional Gibbs free-energy landscape (2D-land) (Ishii et al. 2016)

athermal condition, while considerably less lower external shear stress is required at finite temperatures because the thermal energy activates the system toward the *I* direction.

Hence, the free-energy landscape with appropriate CVs, such as *I* and γ , successfully describes the hidden saddle point of the shuffling-dominant deformation twinning of HCP. Notably, deformation using shuffling should not be specific to HCP DT, it should be omnipresent and thus should be found in shear deformations in FCC and BCC metals, glasses, and ceramics with complicated crystal structures.

2.3 Dislocation Nucleation from GBs (Du et al. 2016)

The dislocation nucleation from interfacial defects dominates the plastic deformation of materials with limited small volumes, which may have a limited number and/or activities of plastic deformation carriers. For instance, the plastic deformation of nanocrystalline metals exhibiting high strength, is led by dislocation nucleation from GBs (Wang et al. 2011) at low temperatures and high strain rates; this dislocation nucleation is activated at a stress higher than that necessary for the usual dislocation motion. Molecular dynamics (MD) is among the best tools for examining the dislocation nucleation from GBs because the nucleation event is atomistic, thus enabling a close examination of the details. However, in MD simulations, the typical strain rate $\sim 10^6 \text{ s}^{-1}$ substantially differs from that in the experiments ($\sim 10^{-3} \text{ s}^{-1}$) because of the MD simulations' limited timescale. Therefore, to study the temperature and strain rate sensitivities, accelerated MD methods, such as adaptive-boost MD (ABMD) (Ishii et al. 2012, 2013), can be used, which is also free-energy-based atomistic modeling. The benefit of using ABMD is that it enables the direct computation of not only stress-dependent but also temperature-dependent activation free energy.

The ABMD method was employed to study the dislocation nucleation event from a GB, $\Sigma = 9(110)\{221\}$ symmetric tilt grain boundary in FCC Cu, under conditions of lower external stress and temperatures, where regular MD is not applicable because of the longer incubation time for dislocation nucleation. The ABMD directly estimate the nucleation frequency (incubation time). Based on the nucleation frequency, the free-energy barrier and activation enthalpy and entropy, can be computed using the transition-state theory. A bias potential (boost potential) is added by the ABMD method to the original potential, and the bias potential leads to a boost force on "boosted atoms" to accelerate the events. The boost potential is automatically constructed as a function of predefined CV via MD canonical ensemble sampling. The CV is a function of the positions of boosted atoms. To apply the ABMD method to the dislocation nucleation, a relative displacement of adjacent atomic plane along the slip direction can be considered as the CV.

In a conventional MD simulation at 300 K and 2.8 GPa, the $\Sigma 9$ GB emits partial dislocations using the collective multiple-dislocation nucleation mechanism on a timescale of picoseconds (Fig. 2.5a, b). However, at lower uniaxial tensile stress (similar to that at 300 K and 2.5 GPa, wherein only accelerated MD (i.e., ABMD) can be employed) a shuffling-assisted single-dislocation nucleation first occurs on a timescale of seconds (Fig. 2.5c, d). This finding suggests that the free-energy barrier exhibited by the shuffling-assisted single-dislocation nucleation mechanism is lower than that exhibited by the collective multiple-dislocation nucleation mechanism at lower stresses. To calculate the activation free energy $Q(\sigma, T)$ at finite temperatures, the nucleation frequency $\nu(\sigma, T)$ provided by ABMD or conventional MD is associated with $Q(\sigma, T)$ as

$$\nu(\sigma, T) = N\nu_0 \exp\left(-\frac{Q(\sigma, T)}{k_b T}\right) \quad (2.8)$$

Fig. 2.5 **a** Atomistic displacement vector field of the collective multiple-dislocation nucleation mechanism and **b** the corresponding partial dislocation colored as per centrosymmetry (Kelchner et al. 1998). **c** Atomistic displacement vector field of the shuffling-assisted single-dislocation nucleation mechanism and **d** the corresponding partial dislocation colored as per centrosymmetry. Du et al. (2016) Reprinted figure with permission from [Du JP, Wang YJ, Lo YC, Wan L, Ogata S, Physical Review B, 94, 104110 (2016).] Copyright (2016) by the American Physical Society

where $nu_0 \sim 10^{11} \text{ s}^{-1}$ denotes the attempt frequency, which is calculated using the curvature of the MEP (Zhu et al. 2008) N indicates the number of equivalent nucleation sites, and k_B denotes the Boltzmann constant. Figure 2.6a shows the activation free energies. There is a clear crossover (shoulder of each plot) of two mechanisms, such as the shuffling-assisted single-dislocation nucleation and collective multiple-dislocation nucleation, at all temperatures. Additionally, $Q(\sigma, T)$ dramatically decreases with an increase in T at specific σ , indicating a strong temperature dependence in the partial dislocation nucleation rate and large positive activation entropy. In experiments, deformation tests are performed at a constant strain rate in many cases, and the strain rate dependence of the dislocation nucleation stress is estimated. In nanocrystalline metals, the dislocation nucleation stress is directly related to the yield stress, because the dislocation activities in the grain are fairly restricted. At specific tensile strain rates, the critical dislocation nucleation stress can be obtained by solving the following equation (Zhu et al. 2008; Weinberger et al. 2012):

$$\frac{Q(\sigma, T)}{k_B T} = \ln \left[\frac{k_B T N \nu_0}{E \dot{\epsilon} \Omega(\sigma, T)} \right] \quad (2.9)$$

where E denotes the apparent Young's modulus, $\dot{\epsilon}$ represents the strain rate, ν_0 denotes the attempt frequency, and N represents the number of equivalent nucleation

Fig. 2.6 **a** Activation free energies for shuffling-assisted single-dislocation nucleation (solid symbols) and collective multiple-dislocation nucleation (open symbols) mechanism. The free-end nudged elastic band method was used for the 0 K energy profile. ABMD (solid symbols) and conventional MD (open symbols) were used to construct the finite-temperature energy profiles. **b** Magnified view of **(a)** (Du et al. 2016). Reprinted figure with permission from [Du JP, Wang YJ, Lo YC, Wan L, Ogata S, Physical Review B, 94, 104110 (2016).] Copyright (2016) by the American Physical Society

sites. For simplification, activation energy $Q(\sigma, T)$ in Fig. 2.6 was fitted using analytical functions for the two mechanisms. The activation volume, i.e., the activation free-energy derivative with respect to stress can be calculated using the fitted analytical function. The mechanism with lower critical nucleation stress can be viewed as the dominant mechanism at a specific strain rate. Figure 2.7 presents the strain rate dependence of the critical nucleation stress. Here, the shuffling-assisted single-dislocation nucleation and collective multiple-dislocation mechanisms transpire at low strain rates (e.g., at 10^{-3} s^{-1} in the evaluated temperature range) and high strain rates (e.g., at 10^9 s^{-1} in the examined temperature range), respectively, which has been observed in the conventional high-strain rate MD simulation. The dislocation nucleation mechanism transition can be found as a kink of each plot, which cannot be detected in the conventional MD simulation. The mechanism transition can be observed even in actual experiments at experimentally feasible strain rates and temperatures, including at $\sim 10^1 \text{ s}^{-1} \sim 10^3 \text{ s}^{-1}$ and 300 K.

Hence, state-of-the-art atomistic modeling and free-energy-based analysis shed light on the possible mechanism transition of dislocation nucleation from GBs with respect to temperature and strain rates and its influences on mechanical properties.

2.4 Homogeneous Dislocation Nucleation in Nanoindentation (Sato et al. 2019)

In nanoindentation experiments, displacement bursts, known as “pop-in,” are noticeable under load-controlled conditions. In particular, the first pop-in has been well studied because the indentation load at the first pop-in can be related to the ideal strength of the target material and thus the critical stress of homogeneous dislocation

Fig. 2.7 Strain rate dependence of the critical nucleation stress for the shuffling-assisted single-dislocation nucleation and collective multiple-dislocation nucleation mechanisms (solid and dashed lines), respectively. A clear mechanism transition can be seen as a “kink” in each plot; this kink cannot be detected using the conventional MD simulation. Du et al. (2016) Reprinted figure with permission from [Du JP, Wang YJ, Lo YC, Wan L, Ogata S, Physical Review B, 94, 104110 (2016).] Copyright (2016) by the American Physical Society

nucleation (Shim et al. 2008; Morris et al. 2011; Li et al. 2012; Wu et al. 2015; Phani et al. 2013). Because the homogeneous dislocation nucleation is a thermally activated event, the first pop-in load exhibits strong temperature and loading rate dependencies, actually following the thermal activation theory (Mann and Pethica 1996, 1999; Biener et al. 2007; Rajulapati et al. 2010; Franke et al. 2015; Schuh and Lund 2004; Schuh et al. 2005; Mason et al. 2006). Recently, an atomistically informed prediction for the temperature and loading rate dependencies of the first pop-in load was achieved by formulating a homogeneous nucleation rate based on the free-energy analysis.

Sato et al. (2019) proposed an atomistic modeling-based multiscale (two-scale) method that avoids the timescale issue and consists of three steps. This method was verified for BCC Fe and Ta using the embedded atom method interatomic potentials (Mendelev et al. 2003; Ravelo et al. 2013). They first performed a simple MD simulation under various indentation loads below the first pop-in load and determined the stress state beneath the indenter (Step 1). Thereafter, they conducted NEB analysis (Henkelman and Jönsson 2000) of homogeneous dislocation nucleation using a perfect crystal atomic model by superimposing the stress state at each indentation load obtained in Step 1 to determine the indentation load-dependent activation energy for the homogeneous dislocation nucleation (Step 2). Next, using the indentation load-dependent activation energy obtained in Step 2, they analytically estimated the probability distribution and critical load of the pop-in event, as well as the corresponding

Fig. 2.8 Atomic model for Step 1 nanoindentation simulation of **a** Fe and **b** Ta (Sato et al. 2019)

temperature and loading rate dependencies (Step 3). Further details regarding each step are described as follows.

(Step1) By the direct MD nanoindentation simulation to an atomistic model (Fig. 2.8), the local stress tensor was determined via the atomic stress tensor analysis (Thompson et al. 2009) with the Voronoi atomic volume (Du et al. 1999; Rycroft 2009). At the first instability points for Fe and Ta, the stress tensor components along the slip plane (in the coordinate system shown in Fig. 2.8) are

$$\sigma_{\max}^{\text{Fe}} = \begin{bmatrix} -37.8 & -23.3 & 10.2 \\ -23.3 & -42.1 & 10.5 \\ 10.2 & 10.5 & -20.4 \end{bmatrix} \text{ GPa}, \quad (2.10)$$

$$\sigma_{\max}^{\text{Ta}} = \begin{bmatrix} -21.1 & 13.5 & 4.7 \\ 13.5 & -25.4 & -5.0 \\ 4.7 & -5.0 & -10.6 \end{bmatrix} \text{ GPa}. \quad (2.11)$$

These stress states are very complicated, and are far from the pure shear condition. The non-shear components are known to change the critical stress of lattice instability owing to the elastic anisotropy and the non-linear elasticity of the materials. Interestingly, although they shear the same BCC structure, Fe and Ta exhibit different stress states. This difference is attributed to their different elastic anisotropies. Consequently, the first instability point (dislocation nucleation point) also differs between Fe and Ta (Fig. 2.9).

Fig. 2.9 Images indicating before and after the first pop-in of **a** Fe and **b** Ta (Sato et al. 2019); colors denote to the central symmetry parameter (Kelchner et al. 1998)

Fig. 2.10 Superimposition of the stress state beneath the indenter onto the NEB model (Sato et al. 2019)

(Step 2) The activation energy–indentation load relation of homogeneous dislocation nucleation, was determined using the NEB method. To mimic the dislocation nucleation event beneath the indenter under the actual indentation load using a perfect crystal model, the actual stress at the position exhibits the maximum resolved shear stress, as obtained in Step 1. This stress was superimposed onto a supercell that contains a perfect crystal (Fig. 2.10) by deforming the supercell shape. During NEB computation, the strained supercell shape was fixed. A perfect crystal without and with a dislocation loop on the $(1\bar{1}0)$ plane can be reasonably selected as the initial and final NEB images, respectively. Figure 2.11 presents the typical energy change along the minimum energy path and corresponding dislocation loop state (Fe and Ta at $P = 1.73 \times 10^{-2} \mu\text{N}$ and $P = 4.01 \times 10^{-2} \mu\text{N}$ and $z_{\text{ind}} = 0.080 \text{ nm}$ and $z_{\text{ind}} = 0.102 \text{ nm}$, respectively). The indentation load-dependent activation

(a) Fe

(b) Ta

Fig. 2.11 Dislocation loop nucleation and potential energy change along the minimum energy path at the position showing the maximum resolved shear stress (Sato et al. 2019)

energy, $E(P)$, corresponds to the potential energy difference between the initial (perfect crystal) and saddle point (with an embryonic dislocation loop) configurations. Figure 2.12 presents $E(P)$, which is normalized by the square of the indenter radius R . $E(P)$ monotonically decreased with increasing indentation load (Barnoush et al. 2010) in both Fe and Ta. Ta exhibited a higher activation energy than Fe. $E(P)$, which can be reasonably fitted using the form proposed by Kocks et al. (1975), $E(P) = E_0 \{1 - (P/P_c)^\alpha\}^\beta$, where E_0 denotes the activation energy under the stress-free condition, P_c represents the indentation load at the instability point, and α and β are parameters.

Such a two-scale modeling, including an MD indentation simulation to obtain the stress distribution (scale 1) and NEB analysis to determine the activation energy

Fig. 2.12 Indentation load-dependent activation energy $E(P)$ for dislocation loop nucleation. The solid lines are the fitted curves (Sato et al. 2019)

(scale 2), implicitly assumes the scale invariance of the stress distribution beneath the indenter. The assumption is reasonable when the indenter radius is sufficiently larger than the dislocation loop size at the saddle point. In other words, the stress must be approximately constant within the dislocation loop area.

(Step3) Finally, to estimate the temperature and loading rate dependencies of the first pop-in load, the probability distribution of dislocation nucleation with respect to the indentation load must be determined. As per transition-state theory, probability distribution $p(P)$ and cumulative probability $Q(P)$ of the pop-in event can be expressed as

$$p(P) = \frac{k(P) \exp \left[-\dot{P}^{-1} \int_0^P k(P') dP' \right]}{\int_0^{P_c} k(P) \exp \left[-\dot{P}^{-1} \int_0^P k(P') dP' \right] dP}, \quad (2.12)$$

$$Q(P) = \int_0^P p(P) dP, \quad (2.13)$$

where

$$k(P) = \sum_i^N k_0(\mathbf{R}_i) \exp \left(-\frac{G(P, \mathbf{R}_i)}{k_B T} \right), \quad (2.14)$$

$$G(P, \mathbf{R}_i) = E(P, \mathbf{R}_i) \left(1 - \frac{T}{T_m} \right). \quad (2.15)$$

$k(P)$ denotes the load P -dependent dislocation nucleation rate and $G(P, \mathbf{R}_i)$ is the activation-free energy with temperature-dependent factor $(1 - T/T_m)$ (Zhu et al. 2008), where T indicates the absolute temperature, T_m can be approximately set to the melting temperature, k_B denotes the Boltzmann constant, k_0 denotes the attempt frequency at nucleation site i , $\mathbf{R}_i$ indicates the position of the possible nucleation site i , and N indicates the number of possible nucleation sites. $E(P, \mathbf{R}_i)$ refers

Fig. 2.13 Predicted temperature dependence of the pop-in cumulative probability for **a** Fe and **b** Ta. The load is normalized by the square of R_{sim} (Sato et al. 2019)

to the activation energy at 0 K at nucleation site i . Here, nucleation at the maximum resolved shear stress site is assumed to dominate the nucleation rate $k(P)$ because the high-stress spot should be well localized. Moreover, the dislocation nucleation rate exponentially decreases with shear stress; thus,

$$k(P) \approx N_{\text{eq}} k_0(\mathbf{R}_{\text{MRSS}}(P)) \exp\left(-\frac{G(P, \mathbf{R}_{\text{MRSS}}(P))}{k_B T}\right), \quad (2.16)$$

where, $N_{\text{eq}} = 8$ for BCC, which equals the number of equivalent slip systems, and $\mathbf{R}_{\text{MRSS}}(P)$ denotes the position exhibiting the maximum resolved shear stress at indentation load P . Figures 2.13 and 2.14 present the calculated temperature and loading rate dependencies of cumulative probability $Q(P)$. The first pop-in load decreases with increasing temperature and decreasing loading rate, as observed in other experimental studies (Biener et al. 2007; Rajulapati et al. 2010; Franke et al. 2015) and expected based on theory (Schuh and Lund 2004). The pop-in load of Fe is more sensitive to both temperature and loading rate than that of Ta.

Hence, atomistically informed two-scale modeling and free-energy landscape analysis allow us to predict the pop-in load and its temperature and loading rate dependencies, which cannot be evaluated using the conventional MD simulation methods because of spatial and temporal scale limitations.

Fig. 2.14 Predicted nanoindentation loading rate dependence of pop-in cumulative probability at $T = 300$ K for **a** Fe and **b** Ta. The load is normalized by the square of R_{sim} (Sato et al. 2019)

2.5 Summary

The three free-energy-based atomistic studies on defect nucleation were briefly introduced. The state-of-the-art atomistic modeling methods enable us to accurately elucidate the free-energy landscape of defect nucleation, as well as migration and propagation under different temperatures and stresses, resulting in a full description of the kinetics and thermodynamics of the defects. The next step is to determine how to control the kinetics and thermodynamics, i.e., how to design the free-energy landscape and tune materials' plasticity to manage their mechanical properties. Mechanical properties are well known to be tuned through the control of the loading conditions, such as temperature and strain rate, and possibly through the control of the chemical environment and the management of the texture and its evolution in materials and alloying. However, deducing the best conditions remains challenging because it is a highly nonlinear inverse problem. Combining atomistic free-energy analysis and machine learning technique can be a promising approach for overcoming this challenge.

Acknowledgements This work was supported by the Elements Strategy Initiative for Structural Materials (ESISM) of MEXT (Grant number JPMXP0112101000).

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