Acta Materialia 145 (2018) 19–29

Contents lists available at ScienceDirect

Acta Materialia

journal homepage: www.elsevier.com/locate/actamat

Full length article

Sample-size-dependent surface dislocation nucleation in nanoscale crystals

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ARTICLE INFO

Article history:
Received 8 August 2017
Received in revised form
17 November 2017
Accepted 20 November 2017
Available online 1 December 2017

Keywords:
Nanoscale crystals
Surface dislocation nucleation
Surface stresses
Sample size effects

ABSTRACT

The finite-temperature mechanical strength of nanoscale pristine metals at laboratory strain rates may be controlled by surface dislocation nucleation, which was hypothesized to be only weakly dependent on the sample size. Previous studies on surface dislocation nucleation investigated factors such as surface steps, oxidation layers and surface diffusion, while the role of surface stresses and sample size remains unclear. Here we perform systematic atomistic calculations on the activation free energy barriers of surface dislocation nucleation in sub-50 nm nanowires. The results demonstrate that surface stresses significantly influence the activation processes of surface dislocation nucleation. This renders the strength strongly dependent on sample size; whether it is “smaller is stronger” or “smaller is weaker” depends on the combined effects of surface stress and applied axial stress, which can be universally explained in terms of the local maximum resolved shear stress. A linear relation between the activation entropy and activation enthalpy (Meyer-Neldel compensation rule) was found to work well across a range of stresses and sample sizes.

1. Introduction

Nanomanufacturing can create small-volume (with length scale of 10^1–10^2 nm) metals that contain little or no defects [1–7]. These *nanoscale pristine* metals represent an extreme state of crystals: they are free of pre-existing dislocations but have very high surface-to-volume ratio. (Indeed, one reason for the lack of dislocation storage is that image attractions to free surfaces tend to destabilize dislocation networks.) At low homologous temperatures, when nanoscale pristine metals are subjected to relatively high external stress, it is widely believed that plastic deformation initiates via thermally activated nucleation of dislocations on the surfaces [7–15]. This surface dislocation nucleation (SDN) process has been shown to be highly sensitive to surface conditions [16]. For example, the local configurations of surfaces such as surface steps [17–19], local morphology [13] and oxidation layers [20] can significantly influence the activation parameters of SDN. Mass-action processes such as surface diffusion of atoms may also couple strongly with SDN [7]. In addition to these extrinsic surface conditions and processes, large surface stresses are ubiquitous in nanoscale pristine metals as a result of the under-coordinated surface atoms [21–25]. These surface stresses are believed to impose intrinsic limits on the mechanical strength of nanoscale pristine metals [9,13,26–28], but their effects have not been investigated in detail.

SDN has been studied before from different perspectives. For example, within the framework of continuum mechanics, the activation energy of SDN has been usually modeled by analyzing individual contributions such as the elastic energy, stacking fault energy, surface ledge energy, etc [9,10,29,30]. These models generally suffer from the uncertainties on the dislocation core cutoff parameters employed. Alternatively, SDN has been treated based on the Peierls-Nabarro dislocation model [31], which incorporates atomistic information into the continuum approach. Computationally, activation parameters of SDN have been

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https://doi.org/10.1016/j.actamat.2017.11.048
1359-6454/

calculated using either reaction pathway sampling methods [8,9] or hyperdynamics simulations [32]. Generally, activation parameters obtained either analytically or computationally are stress dependent, which are then fed into finite-temperature transition-state theories whereby the nucleation stress can be obtained numerically for different strain rates. Such a modeling framework combining atomistic simulations/continuum mechanics and reaction rate theories has been shown to be useful in predicting the mechanical strength over a range of temperatures and strain rates that can be directly compared with laboratory experiments.

While the mechanical strength of nanoscale pristine metals has been successfully modeled with respect to external variables such as temperature and strain rate, the intrinsic sample size effects have only been treated briefly [8–10,30]. For example, surface effects were modeled by adding image forces to the nucleated dislocation loop, leading to an extra contribution to the activation free energy [10,30]. Also, surface stresses were taken into account by removing the surface-induced axial stress from the total axial stress during calculations [9]. In addition, it was shown that the number of SDN sites decreasing with sample size brings in a strengthening effect [8]. However, these studies focus mostly on the overall trend of material strength with respect to sample size. The exact role played by surface stresses in SDN remains unresolved.

Currently, there are several difficulties in understanding the intrinsic surface stress effects on SDN for both continuum modeling and atomistic calculations. First, the continuum mechanics framework requires numerical parameters from atomistic simulations. Second, how surface stresses contribute to the axial stress dependence and sample size dependence of the activation parameters is unclear. Third, the surface stresses effects may depend on many factors such as the geometry of the nanoscale sample, surface energy, crystallography and externally applied stress level, etc.; the most important factors need to be identified. Last but not least, current reaction pathway sampling methods such as free-end nudged elastic band (NEB) [8,33] or string method [9,34] are computationally too expensive to calculate the activation parameters for experimentally relevant samples (e.g., tens of nanometers in diameter, for a nanowire). Consequently, most previous studies only focused on very small sample sizes [8,9] (a few nanometers for the diameter of a nanowire) and the activation parameters obtained cannot be directly applied to larger samples.

In this work, we employ a modified activation-relaxation technique *nouveau* (ARTn) [35–37] to obtain the zero-*T* activation Gibbs free energy ($\Delta G_0(\sigma)$) or activation enthalpy ($\Delta H(\sigma)\equiv\Delta G_0(\sigma)$) for nanowires with diameters up to 50 nm, an experimentally relevant length scale that has been computationally prohibitive for typical transition path sampling techniques such as free-end nudged elastic band method [8,33] or free-end string method [34]. Based on the calculation results, the intrinsic surface stress effects on activation enthalpy have been evaluated. Furthermore, by using constrained molecular dynamics and thermodynamic integration method, we compute the *finite-temperature* activation Gibbs free energies $\Delta G(\sigma,T)$ that include thermal uncertainties (entropy) in the transition paths. By comparing the numerical $\Delta H(\sigma)$ and $\Delta G(\sigma,T)$, we discover the Meyer-Neldel (M-N) compensation rule [38] largely works in the parameter range relevant to laboratory time-scale (strain-rate) experiments. A single parameter T_{MN}, on the order of 900 K, can thus describe finite-temperature $\Delta G(\sigma,T)$, if the zero-temperature $\Delta H(\sigma)$ is known. Based on the calculated $\Delta H(\sigma)$ for SDN, we found obvious sample size dependence of strength for the sub-50 nm nanoscale pristine metals; the generally believed "smaller is stronger" trend is only valid when the external load counteracts the Laplace pressure [21] due to surface stresses, and it becomes "smaller is weaker" when the external load constructively superimposes on the Laplace pressure.

2. Simulation methods

We choose Cu nanowire with characteristic size from 2 nm to 50 nm as our model samples. Specifically, two widely studied types [8,9] of nanowires are considered in the current work, i.e., [100] oriented square nanowire under compressive loading and [110] oriented rhombic nanowire under tensile loading. Empirical potential for Cu [39] is used to describe the interatomic interactions. All nanowires have periodic boundary conditions in the axial direction and free surfaces in other directions. The aspect ratio for all nanowires is 2.5. First, different sized nanowires are elastically strained to the athermal stress limit using the athermal quasi-static loading method. During athermal quasi-static loading, energy minimization after each strain increment is performed via the conjugate gradient method. The strain increment is 0.05% while the force tolerance for energy minimization is 0.001 eV/Å. Then, the configurations of nanowires at different stress levels are extracted to first calculate the zero-*T* activation barrier.

In order to efficiently calculate the zero-*T* activation Gibbs free energies $\Delta G_0(\sigma)\equiv\Delta H(\sigma)$ for samples with sizes up to 50 nm, we employ ARTn [35–37] but with modifications based on the known information about the minimum energy path (MEP). The pathways searched by ARTn highly depend on the initial searching direction on the potential energy landscape (PEL), and choosing an appropriate initial direction could efficiently accelerate ARTn. The initial search direction can be specified in two ways. One way is to take advantage of athermal quasi-static loading, i.e., with increasing strain, the sample will finally reach a saddle point of the SDN event. Though saddle points differ from each other under different strains, they generally locate in a similar direction on the PEL with respect to the initial configurations. Thus, we can choose our initial searching direction as the displacement vector (plus a random noise vector) between the configuration at current strain and the configuration at the elastic limit during athermal quasi-static loading. For events that cannot be observed during athermal quasi-static loading but with known information on their MEP, a second way is to 'manually' manipulate atoms of interest to construct a tentative configuration near the saddle points of the potential MEP. Then the displacement vector (plus a random noise vector) between this tentative configuration and the initial configuration can be used as the search direction in ARTn. After choosing an appropriate initial search direction, the system is pushed step by step (at each step energy minimization is performed in the perpendicular hyperplane) along this direction and is considered to be out of the potential well when the smallest eigenvalue of the Hessian matrix falls below a negative threshold. Then, the search direction is switched to the eigenvector direction associated with the smallest eigenvalue of the Hessian matrix. The system is slightly activated along the eigenvector direction and energy minimization is performed in the perpendicular hyperplane after each activation. The eigenvector associated with the smallest eigenvalue of the Hessian matrix is updated before each activation, using the Lanczos algorithm. The system is considered to reach a first-order saddle point when the smallest eigenvalue of the Hessian matrix is negative and the magnitude of the hyper-space force vector is below 0.001 eV/Å. In this way, the modified ARTn algorithm can efficiently converge to the saddle point of SDN at different stresses.

Compared to the free-end NEB method, our modified ARTn can significantly reduce the computational cost in finding the saddle point. The factors contributing to this include a) only one configuration is used in ARTn while many replicas have to be used in NEB method to construct the 'elastic band' and b) NEB method updates individual replicas by also considering the inter-replica interactions whereas ARTn updates the single configuration solely based on