

## Transition of creep mechanism in nanocrystalline metals

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(Received 6 September 2011; revised manuscript received 11 November 2011; published 12 December 2011)

Understanding creep mechanisms with atomistic details is of great importance to achieve the mechanical and thermodynamical stabilities of nanocrystalline (NC) metals over a wide temperature range. Here we report a molecular dynamics analysis of creep in NC copper dominated by competing deformation mechanisms. We found the dominating creep mechanism transits from grain boundary (GB) diffusion to GB sliding, and then dislocation nucleation with increasing stress. The derived stress exponent, small activation volume of  $0.1 - 10b^3$ , and grain size exponent all agree quantitatively with experimental values. We proposed a stress-temperature deformation map in NC metals accommodated by the competition among different stress-driven, thermally activated processes. The model is general to answer the question why deformation mechanism transits with stress in NC metals.

DOI: [10.1103/PhysRevB.84.224102](https://doi.org/10.1103/PhysRevB.84.224102)

PACS number(s): 62.20.Hg, 62.25.-g

### I. INTRODUCTION

Reducing the grain size of polycrystalline solids to nanolevel recently has opened a pathway to balance the trade-off between strength and ductility in materials.<sup>1,2</sup> However, creep which is expected to be enhanced in NC materials leads to a decrease in strength.<sup>3</sup> The creep properties of NC materials still remain unsolved for their applications. The dominating deformation mechanisms may vary a lot when the grain size decreases to nanometer (nm) regime.<sup>4-6</sup> For conventional coarse-grained metals and alloys, the steady-state creep rate  $\dot{\epsilon}$  is successfully described by the well-known Mukherjee-Bird-Dorn equation<sup>7</sup>

$$\dot{\epsilon} = A(1/d)^P \sigma^n \exp\left(-\frac{\Delta Q}{k_B T}\right), \quad (1)$$

where  $A$  is a temperature dependent constant,  $d$ ,  $\sigma$ , and  $T$  are the sample grain size, applied stress, and temperature, respectively.  $P$  and  $n$  are the grain size and stress exponents.  $\Delta Q$  is the activation energy for a specific thermally activated process, and  $k_B$  is the Boltzmann's constant. The  $(n, P, \Delta Q)$  combination is usually used to distinguish between different creep mechanisms. For example, Coble (GB diffusion),<sup>8</sup> Nabarro-Herring (lattice diffusion),<sup>9</sup> GB sliding,<sup>10</sup> and dislocation power-law<sup>11</sup> creeps are characterized by  $(1, 3, \Delta Q_{GB})$ ,  $(1, 2, \Delta Q_L)$ ,  $(2, 3, \Delta Q_{GB})$ , and  $(>4, 0, \Delta Q_L)$ , respectively.  $\Delta Q_{GB}$  and  $\Delta Q_L$  are the activation energy barriers for GB and lattice diffusion, respectively. However, the creep laws have not been fully understood in NC materials. In particular, the role of GB in nanocreep is still controversial. In conventional material, the collective intragrain dislocation activities carry the plasticity. But these dislocation behaviors are severely confined by the geometries of extremely small grains in lower nanoscale metals. Instead, source-controlled GB diffusion, GB sliding, and dislocation nucleation seem to be possible candidates dominating nanoplasticity.<sup>5,6</sup> Although molecular dynamics (MD)<sup>12-15</sup> and experiments<sup>16,17</sup> have identified several individual creep mechanisms in NC materials, there is still a lack of abundant evidence to constitute a complete creep-mechanism map in NC metals. Here we draw this map in NC copper by identifying  $(n, P, \Delta Q)$  at varying  $(\sigma, T, d)$  by MD. We understand the physical mechanisms underlying nanocreep by considering the competition among

different stress-driven, thermally activated processes. This model answers the question why transition of deformation happens with varying stress in NC metals.

### II. METHODOLOGY

The MD simulations are based on three-dimensional (3D) periodic NC copper cubes containing a body-centered cubic distribution of 16 identical Voronoi grains with random orientation [see Fig. 1(a)]. Four samples with varied grain size 8.0, 10.7, 13.4, and 16.0 nm are loaded over a wide range of stress and temperature. We have confirmed that the resulting creep rates in the following MD creep tests do not change significantly with model size and reasonable grain shape fluctuation (see Fig. S3 in the Supplementary Material<sup>18</sup>). We choose the embedded-atom method potential to describe the interatomic interaction.<sup>19</sup> The activation energy and volume are 66 kJ/mol and  $0.9b^3$  for vacancy diffusion in single crystal Cu based on the nudged-elastic band (NEB) calculation.<sup>4</sup> Here  $b$  is the magnitude of the Burgers vector for Cu. Whereas a typical energy barrier and activation volume for GB dislocation nucleation in NC copper are estimated to be on the order of magnitude of 100 kJ/mol and  $8b^3$  according to our minimum energy pathway search (see Fig. S2 in the Supplemental Material<sup>18</sup>). To observe creep, the samples are initially thermally equilibrated for 200 ps by a Nosé-Hoover thermostat after structural optimization.<sup>20</sup> Then we applied uniaxial tensile stress of different  $(T, \sigma)$  combined with an isothermal-isobaric ( $N\sigma T$ ) ensemble by the Parrinello-Rahman technique<sup>21</sup> to examine temporal evolution of strain.

### III. RESULTS AND DISCUSSION

#### A. Transition of creep mechanism with stress

Figures 1(b) and 1(c) show the creep curves for NC copper with grain size 10.7 nm at varying stress and temperature, respectively. The applied stress is controlled from 66 MPa to 3.5 GPa. (Some very low and high stress curves are not shown.) This wide stress range should include both diffusive and displacive deformation mechanisms. Temperature is controlled from 720 K to 1200 K at different stresses. The purpose of high

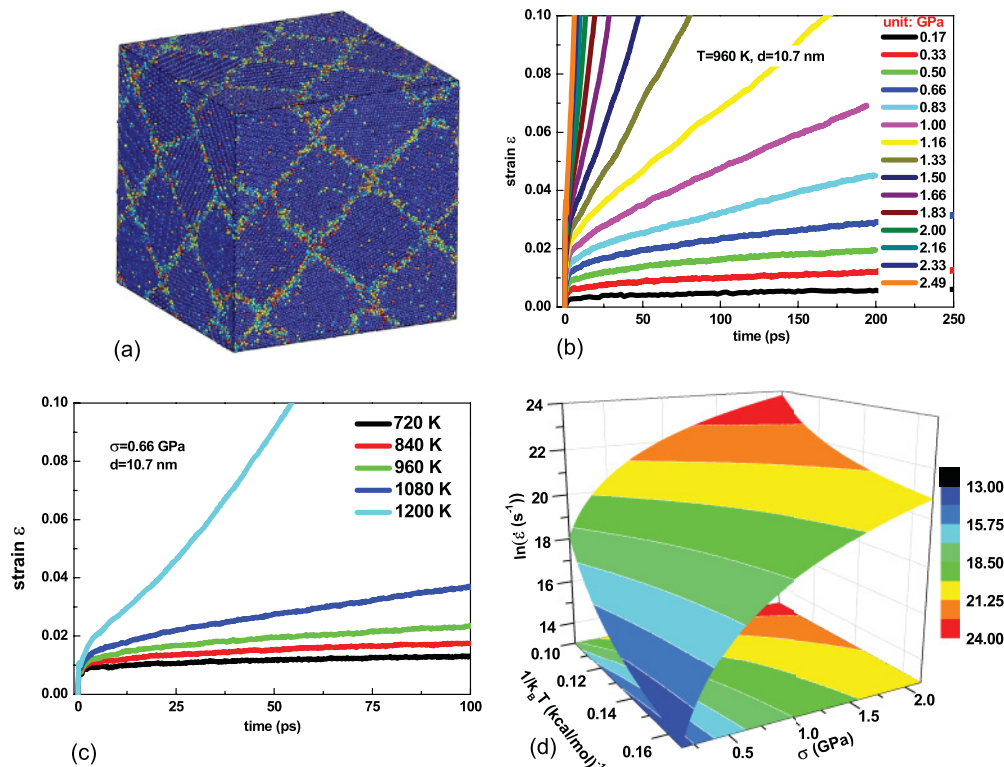


FIG. 1. (Color online) (a) Simulation model of the NC copper after thermal relaxation. Atoms are colored by centrosymmetry parameter,<sup>22</sup> which distinguishes the atoms in grain boundaries from those in a perfect face-centered cubic (fcc) lattice. The calculated creep curves at varying (b) stress and (c) temperature. The creep curves increase monotonically with increasing stress and temperature, respectively. (d) The natural logarithm plot of the determined steady-state creep rate  $\ln \dot{\epsilon}$  against stress and inverse temperature.

temperature here is to accelerate the deformation processes, so that we can reach steady-state creep within the limited MD time scale as some works did recently.<sup>12,13</sup> Then we can extrapolate the present results to lower temperature according to the rate-controlling equation. It is true that grain growth cannot be avoided at such a high temperature in experiment. However, what we are interested in is the mechanical properties of NC metals at constant grain size. Therefore we will avoid the global strain resulted by grain growth here. Fortunately, it can be neglected because considerable grain growth does not happen during the short MD time. At the very beginning, strain quickly reaches a finite value determined by the elastic relation  $\dot{\epsilon} \Delta t = \sigma/E$  within short time  $\Delta t$ , where  $E$  is the Young's modulus (calculated as 71 GPa at 960 K). Then the high creep rate evolves gradually to a constant value, which is termed as the steady-state creep. The creep rates under different  $(\sigma, T, d)$  conditions were determined by the slopes of these steady-state creep curves.  $\ln \dot{\epsilon}$  has been plotted as functions of both stress and inverse temperature based on our calculated  $\dot{\epsilon}(\sigma, T)$  data mesh [see Fig. 1(d)]. Reasonable trend shows that creep rate increases monotonically with increasing stress and temperature. By quantitatively correlating  $\dot{\epsilon}$  with  $(\sigma, T, d)$ , the creep mechanisms and their underlying physical senses can be understood.<sup>4</sup>

The stress exponent  $n$  (or inverse strain rate sensitivity  $m$ ) is an important parameter to understand the deformation mechanism in creep. It contains rich physical meaning because of its close relation to the apparent activation volume  $\Omega$

through  $n = \sigma \Omega / \sqrt{3} k_B T$  ( $\Omega$  is both stress and grain size dependent).<sup>4,23</sup> Besides, it can be directly compared with experimental data, providing a link between these two approaches. Assuming that creep rate holds a power-law relation with stress, namely  $\dot{\epsilon} \propto \sigma^n$ ,<sup>7</sup> the stress exponent can be obtained as  $n = \partial \log \dot{\epsilon} / \partial \log \sigma$ . The transition of the stress exponent is shown in Fig. 2(a). The plot is based on the results of sample with a 10.7 nm grain size at 960 K. The calculated creep rate ranges from the order of magnitude of  $10^6$  to  $10^{10} \text{ s}^{-1}$  as stress changes from 66 MPa to 3.5 GPa. At low stress of our simulation, namely 66–166 MPa, the stress exponent is determined as  $n = 1.17 \pm 0.12$ . This corresponds with Coble<sup>8</sup> or Nabarro-Herring<sup>9</sup> creep, where strain rate is proportional to stress. The basic consideration of diffusional creep is that the flux of defects or atoms causing macroscopic strain is proportional to  $\sigma \Omega$  when  $\frac{\sigma \Omega}{k_B T} \ll 1$ .<sup>24</sup> The finding of  $n \approx 1$  should be due to both GB and lattice diffusion at high temperature. However, considering a large volume fraction of GBs (about 15% in the model with grain size of 10.7 nm) in the nanoscale metals, Coble creep may dominate plasticity. With increasing stress, the stress exponent is found to be  $n = 2.01 \pm 0.10$  within 166–664 MPa. This is corresponding to the GB sliding creep.<sup>10</sup> The GB sliding itself is necessarily associated with diffusion. Diffusive mass transport can change the morphology of individual grains. They have to slide with each other to maintain the coherency at grain boundaries. The experimental data within this stress range are normalized by our simulation conditions,<sup>25</sup> shown in Fig. 2(a). The normalized strain rate for

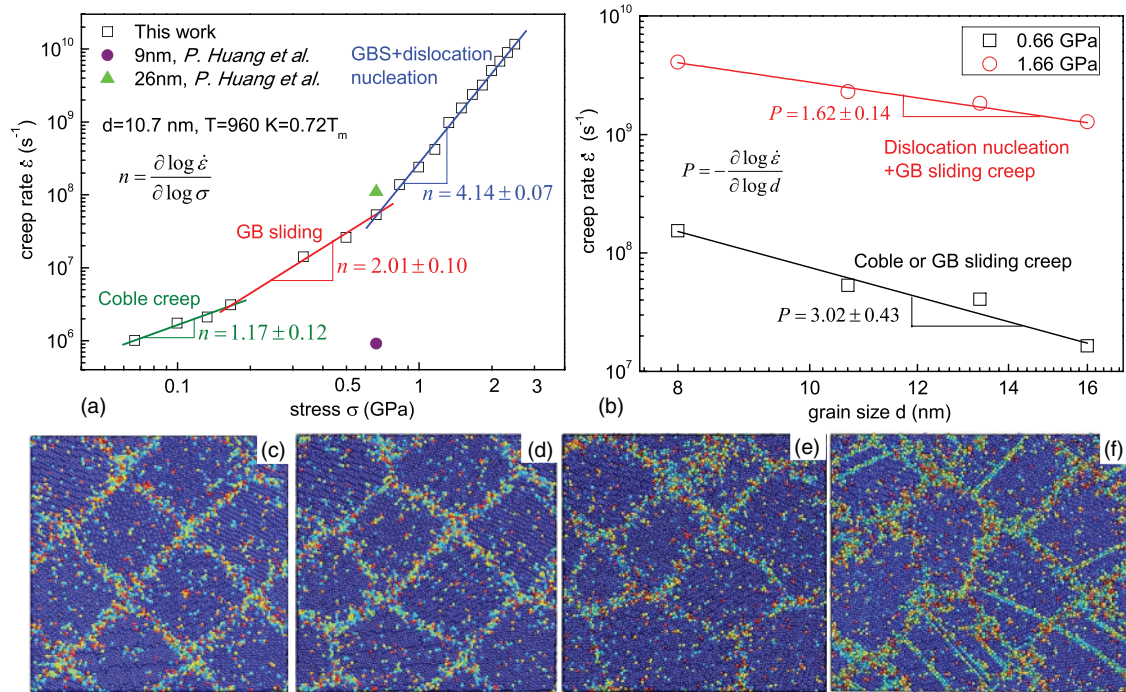


FIG. 2. (Color online) (a) Log-log plot of steady-state creep rate against stress. The experimental data from P. Huang *et al.* (Ref. 17) are normalized according to our simulation conditions (Ref. 25). (b) Log-log plot of creep rate against grain size at stress of 664 MPa and 1.66 GPa. The straight lines are linear fittings. The snapshots show (c) initial configuration before loadings, (d) 66 MPa, 300 ps,  $\epsilon = 0.23\%$ , (e) 166 MPa, 1000 ps,  $\epsilon = 0.95\%$ , and (f) 1.66 GPa, 30 ps,  $\epsilon = 3.28\%$ , respectively. (d) to (f) are within steady-state creep. Atoms are colored by centrosymmetry parameter,<sup>22</sup> which distinguishes those atoms in GBs and stacking faults. Detailed deformation mechanisms can be found in Movie 1(a)–1(c) in the Supplemental Material (Ref. 18).

NC Cu with grain size 26 nm agrees well with the calculated one. But the normalized data for 9 nm Cu is considerably lower. This discrepancy may be explained by grain growth during creep test for a really small grain sample in experiment. Our normalized conditions neglect the growth of grains.

While at higher stress greater than 664 MPa, our results lead to  $n = 4.14 \pm 0.07$ . It is in perfect agreement with a recent creep study on NC copper with a grain size of 26 nm, which concludes a strain rate sensitivity of  $m = 0.243$  (or  $n = 4.12$ ).<sup>16</sup> This is a typical value for power-law creep in copper,<sup>11</sup> which is governed by dislocation activities. As pointed out by previous studies, the dislocation nucleation from GB rather than collective dislocation dynamics inside grains may dominate the plastic deformation of confined volume.<sup>5,6,23,26</sup> The evidence of transition from diffusional to dislocation creep in NC copper could be found by MD snapshots at different stresses, as shown in Fig. 2(c)–2(f). Compared to the initial configuration, the shape of grains do not change substantially during creep at stress 66 MPa. However, one can observe obvious morphological variation at 166 MPa [see Fig. 2(e)]. On the other hand, the high stress level snapshot [Fig. 2(f)] shows that there are dislocations emitting from GB during steady-state creep. Combined with transition of stress exponent from  $n \approx 1$  to  $n \approx 2$ , and then to a value larger than 4, one may claim that deformation mechanism transits from diffusion to GB sliding, and then to dislocation nucleation.

In order to show more evidence about the proposed dislocation nucleation as a dominating deformation mechanism, we

pick out one grain among the simulation sample during steady-state creep at a bit lower temperature 480 K and high stress 1.66 GPa, and show it as Fig. 3. It is obvious to find a leading partial dislocation has just nucleated from one side of GB in the upper region, leaving a stack fault behind. Meanwhile, another leading partial has already terminated at the other side of GB in the lower region. As a result, a residual stacking fault transects the whole grain. Therefore, GBs in NC metals can be regarded as both sources and sinks of dislocations. Fig. 3 presents the atomistic details underlying Fig. 2(f) and Movie 1(c) (see the Supplementary Material<sup>18</sup>), which suggests dislocation nucleation as a creep mechanism at high stress. This is in contrast with the conventional coarse-grained metals, in which dislocation “forest” interaction accommodates power-law creep.

## B. Grain size dependence of nanocreeep

Besides stress exponent, grain size dependence is another factor to clarify creep mechanisms.<sup>24</sup> It is well accepted that the grain size exponent changes from  $P = 2$  for Nabarro-Herring creep to  $P = 3$  for Coble or GB sliding creep. In Nabarro-Herring creep, the vacancy flux is proportional to  $\exp(\pm\sigma\Omega/k_B T)/d$ . Consequently, the global strain rate can be determined as the flux divided by the grain size  $d$ . Thus, there is a  $1/d^2$  dependence of creep rate on grain size. However, in Coble or GB sliding creep, there is another factor  $\delta/d$  describing the ratio between the grain boundary cross section area and the grain itself, where  $\delta$  is the width of the grain boundary. Instead of having  $1/d^2$ , the grain size dependence

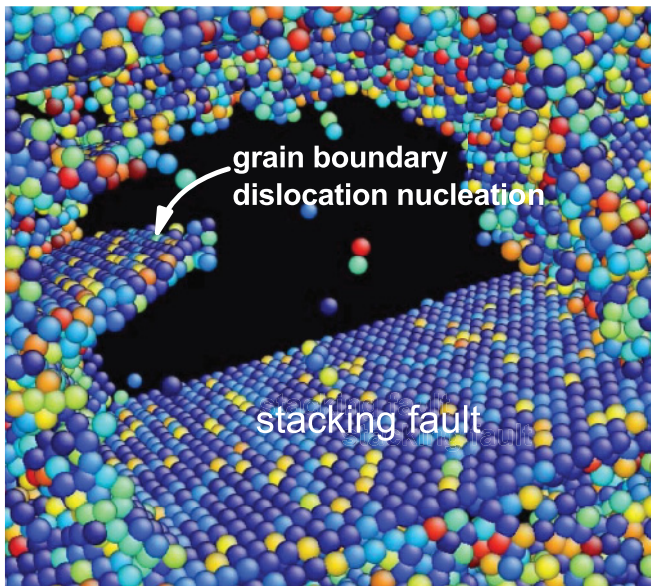


FIG. 3. (Color online) Dislocation nucleation from grain boundary and the left stacking fault during creep deformation at (1.66 GPa, 480 K), and 74 picoseconds. The grain size is 10.7 nm. Atoms are colored by centrosymmetry parameter,<sup>22</sup> while the perfect fcc atoms are not shown for clarity.

of Coble creep is  $1/d^3$ .<sup>8</sup> As a result,  $P$  equals 2 ~ 3 can be the indication of diffusional creep, or its accommodated GB sliding creep. The grain size exponents at two stress levels are shown in Fig. 2(b). At stress 0.66 GPa,  $P$  is near 3. This exactly corresponds to Coble or GB sliding creep.<sup>8,10</sup> On the other hand, we notice a stress exponent of  $P \approx 1.6$  at stress of 1.66 GPa. This is different from the conventional coarse-grained materials where the dislocation creep is size independent. This size effect on power-law creep is due to the distinct deformation mechanisms between nanoscale and conventional creep. The former is dominated by dislocation nucleation from GB, whereas the latter is governed by intragrain collective behaviors of pre-existing dislocations. The size effect of creep governed by dislocation nucleation in NC metals could be understood by a rate-controlling equation based on transition state theory, in which the transformation rate is a function of source number. In conclusion, our findings about diffusion, GB sliding, and dislocation nucleation competing creep in nanocrystalline copper are consistent with recent experimental studies.<sup>16,17</sup> The quantitative agreement between calculated parameters (stress and grain size exponents, and activated parameters which will be discussed later) and experimental results supports the proposed creep mechanisms.

### C. Activation volume

In NC metals, it is reasonable to describe creep as a stress-driven and rate-controlling process,<sup>4-6</sup> in which the creep rate is written as:

$$\dot{\epsilon} = A(1/d)^P \exp\left(-\frac{\Delta G}{k_B T}\right), \quad (2)$$

where  $A$  is a proportional factor. The grain size exponent  $P$  is either from the unit strain that each activated event

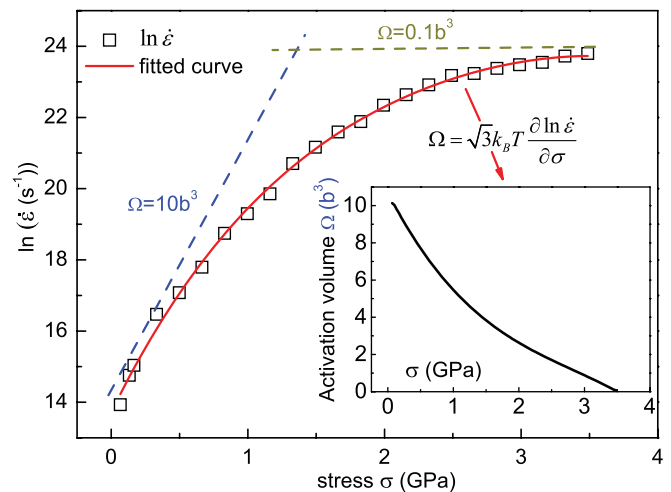


FIG. 4. (Color online) Natural logarithm plot of creep rate versus stress, and the red curve is the polynomial fit. The inset shows the activation volume as a function of stress.

contributes to global strain, or some factors related to the grain boundary volume fraction, which are both functions of grain size.  $\Delta G = \Delta Q - \tau\Omega - T\Delta S$  is the activation Gibbs free energy,  $\tau$  and  $\Omega$  are the effective local shear stress and its activation volume, and  $\Delta S$  is the activation entropy barrier. The term  $\tau\Omega$  could be served as the driving force to overcome different energy barriers during creep. In fact, the mentioned stress exponent transition is originated from the exponential dependence of creep rate on  $\tau\Omega/k_B T$ . Activation volume by definition is a partial derivative of the activation Gibbs free energy with respect to stress  $\Omega \equiv -\partial\Delta G/\partial\tau = \sqrt{3}k_B T \partial \ln \dot{\epsilon}/\partial\sigma$ , here  $\sigma$  is the applied uniaxial tensile stress, and  $\sqrt{3}$  arises from the Von Mises yield criterion.<sup>4</sup> The intuitive physical interpretation of  $\Omega$  is the volume of total activated atoms during the thermally activated process. It is a critical parameter to distinguish deformation mechanisms. For example, diffusion usually possesses a small activation volume less than one atomic volume, but dislocation nucleation and GB boundary sliding are collective motions of multiple atoms, so that  $\Omega$  could reach to several or dozens of  $b^3$  in true NC metals.  $\ln \dot{\epsilon}$  is plotted as a function of stress in Fig. 4. Activation volume spanning the whole stress range is shown in the inset. The two applied stress limits generate  $\Omega$  from  $10b^3$  to  $0.1b^3$  with increasing stress. The small activation volume quantitatively agrees with experimental finding of  $8b^3$  on NC copper with a grain size of 10 nm.<sup>27</sup> It also resembles the theoretical prediction of 3– $10b^3$  by R. J. Asaro *et al.*,<sup>23</sup> which is a mechanistic model describing dislocation nucleation from GB in NC metal. Activation volume decreases monotonically with increasing stress. Actually, the derived activation volume  $\Omega_{\text{eff}}$  is an effective value of a combination of several mechanisms, including diffusion  $\Omega_{\text{diff}}$ , GB sliding  $\Omega_{\text{gbs}}$ , and dislocation nucleation  $\Omega_{\text{disl}}$ , respectively. The activation volume of individual mechanisms all decrease with increasing stress. However,  $\Omega_{\text{diff}}$  has a weaker stress dependency compared to that of  $\Omega_{\text{disl}}$  and  $\Omega_{\text{gbs}}$ , so that the decrease in  $\Omega_{\text{eff}}$  is mainly attributed to that of GB sliding at low stress, and dislocation nucleation at high stress.  $\Omega_{\text{eff}}$  tends to have a very small value when the applied stress

approaches 3.5 GPa. The underlying physical mechanism is that dislocation nucleation has been totally awakened due to the work done by  $\tau\Omega$  at such high stress.

#### D. Deformation map and competition between rate-controlling processes

Now we can construct a stress-temperature creep map in NC metals based on the stress exponent  $n(\sigma, T/T_m)$  ( $T_m$  is melting temperature, a detailed mathematical derivation of  $n$  is shown in the Supplementary Material<sup>18</sup>), parallelly supported by grain size exponent and activation parameters. The result is shown in Fig. 5(a). Coble creep ( $n = 1$ ) exists in a limited stress range. Then it transits to GB sliding creep with increasing stress, characterized by a stress exponent around  $n = 2$ . The GB sliding itself could be accommodated by boundary diffusion. Thus the transition is continuous. Dislocation nucleation begins to dominate creep with stress greater than 1 GPa at medium  $T$ , replaced by 1.5 GPa at high  $T$ . The general trend is that dislocation nucleation tends to control nanocreeep at low temperature, with high stress ( $n > 4$ ). Whereas high temperature and low stress facilitates more diffusional mechanisms (GB diffusion and GB sliding). The proposed creep map shows a vivid story about the transition from diffusional to displacive deformation mechanism in NC metals. Although we do not have data for low temperature ( $T < 600$  K), one may predict the enhanced role of dislocation nucleation with decreasing temperature by a large stress exponent  $n$ . For example,  $n$  becomes larger than 7 at  $0.55T_m$  and 2.5 GPa.

The transition of plastic deformation mechanism could be understood by the competition among different stress-driven, thermally activated processes, as shown schematically in Fig. 5(b). The stress dependent creep rate contributions from individual GB diffusion  $\dot{\epsilon}_{\text{diff}}$ , GB sliding  $\dot{\epsilon}_{\text{gbs}}$ , and dislocation nucleation  $\dot{\epsilon}_{\text{disl}}$  are plotted by red (dash dot), blue (dash dot dot), and magenta (short dot) lines, respectively. Physically, these mechanisms themselves could be described well by the rate-controlling equations:<sup>24,28,29</sup>

$$\dot{\epsilon}_{\text{diff}} = \frac{\delta D_{\text{b0}}}{d^3} \exp\left(-\frac{Q_{\text{GB}}}{k_{\text{B}}T}\right) \sinh\left(\frac{\sigma\Omega_{\text{diff}}}{k_{\text{B}}T}\right) \quad (3)$$

$$\dot{\epsilon}_{\text{gbs}} = \varepsilon^T \frac{3\delta}{d} \nu_{\text{gbs}} \exp\left(-\frac{Q_{\text{GB}} - \sigma\Omega_{\text{gbs}}}{k_{\text{B}}T}\right) \quad (4)$$

$$\dot{\epsilon}_{\text{disl}} = \frac{b}{d} \nu_{\text{disl}} \exp\left(-\frac{Q_{\text{DN}} - \sigma\Omega_{\text{disl}}}{k_{\text{B}}T}\right). \quad (5)$$

Equations (3), (4), and (5) are corresponding to creep rate accommodated by GB diffusion,<sup>24,29</sup> sliding,<sup>28</sup> and dislocation nucleation,<sup>28</sup> respectively, where  $\delta$  is the width of the grain boundary. (Here we adopt  $\delta = 2b$ , and  $3\delta/d = 6b/d$  describes the grain boundary volume fraction per grain diameter  $d$ .)  $\varepsilon^T$  is the unit strain for each GB sliding event contributing to the global strain (on the order of  $\varepsilon^T = 0.015$ <sup>28</sup>).  $\delta D_{\text{b0}}$  is the pre-exponential factor of GB diffusion,  $\delta D_{\text{b0}}$  for copper is approximately  $5.0 \times 10^{-15}$  m<sup>3</sup>/s.<sup>30</sup> Because of the uncertainty in the width of grain boundaries, here we adopt it as a value five times larger, which makes good comparison with empirical equation for Coble creep, namely,  $\dot{\epsilon}_{\text{diff}} = \frac{148}{\pi} \frac{1}{d^3} \frac{\delta D_{\text{b0}} \Omega_{\text{diff}}}{k_{\text{B}}T} \exp(-Q_{\text{GB}}/k_{\text{B}}T) \sigma^8 \nu_{\text{gbs}}$  and  $\nu_{\text{disl}}$  are the physi-

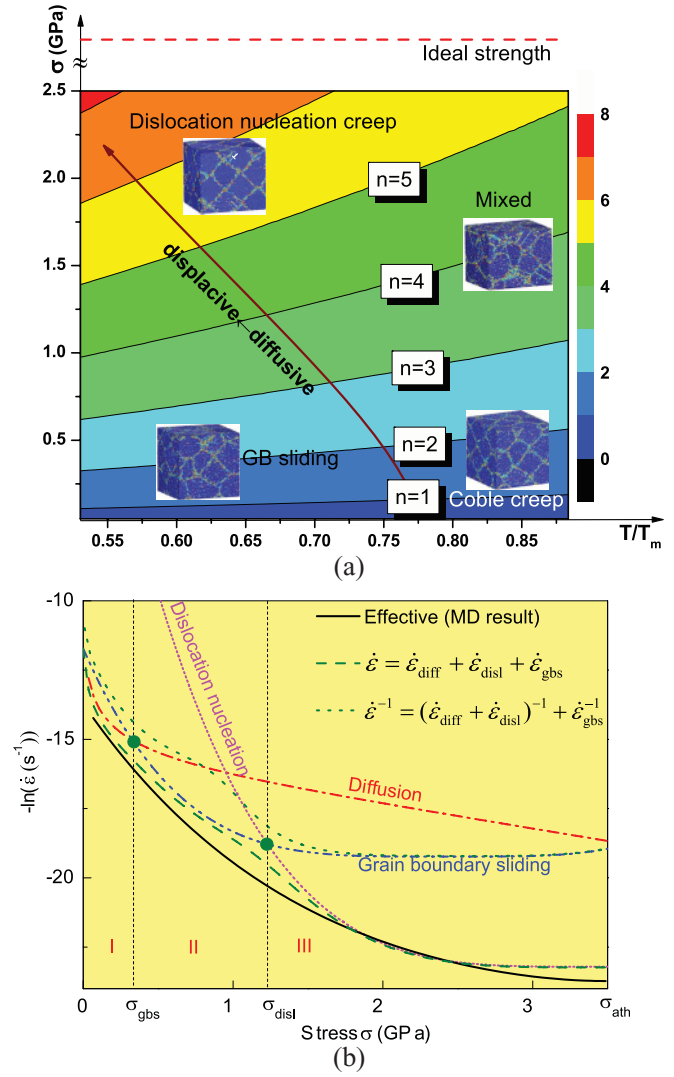


FIG. 5. (Color online) (a) The proposed deformation map in the temperature-stress space for nanocrystalline copper showing competition among diffusion, grain boundary sliding, and dislocation nucleation creep. (b)  $-\ln \dot{\epsilon}$  versus stress for creep governed by three individual mechanisms, the present MD results is plotted for comparison. The deformation mechanism transition is driven by the competition among these stress-driven, rate controlling processes. Region I, II, III define the stress range where GB diffusion, sliding, and dislocation nucleation dominate creep, respectively.

cal trial frequency for grain boundary sliding and dislocation nucleation from GBs, respectively. These prefactors should be lower than the atomic vibration frequency (about  $10^{13}$  /s) since both boundary sliding and dislocation emission usually involve the collective jumping frequency of multiple atoms in the activation volume  $\Omega$ . It is reasonable to assume  $\nu_{\text{disl}}$  to be on the range of  $5 \times 10^{11}$  /s according to the estimation of initial energy curvature along the minimum energy path of copper nanopillar surface dislocation nucleation.<sup>31</sup>  $\nu_{\text{gbs}}$  is adjusted to be  $10^{11}$  /s, which leads to a good comparison between the empirical equation for GB sliding creep:  $\dot{\epsilon}_{\text{gbs}} = 2 \times 10^{15} D_{\text{b0}} \exp(-Q_{\text{GB}}/k_{\text{B}}T) \frac{\mu b}{k_{\text{B}}T} (b/d)^3 (\sigma/\mu)^2$ ,<sup>10</sup> here  $\mu = 42.1$  GPa is the shear modulus of copper.  $Q_{\text{GB}}$  is the activation

energy for GB diffusion, including defect formation energy and migration energy in GBs. This value is dependent on the characteristics of GBs, and here we adopt a value of 60 kJ/mol based on a molecular dynamics modeling of self-diffusion along general high-angle GBs in copper based on the same interatomic potential.<sup>32</sup> The GB dislocation nucleation activation energy  $Q_{DN}$  also depends on the type of GBs. As shown in Fig. S2 in the Supplemental Material,<sup>18</sup> we have achieved a value of about 100 kJ/mol for it. We have also done NEB minimum pathway searches for dislocation nucleation from other type of GBs, which leads to activation energy reaching to several hundreds of kJ/mol. We adopt here 200 kJ/mol for  $Q_{DN}$ , which simplifies the analysis, while keeping the accuracy. The activation volume  $\Omega$  for each mechanism decreases with increasing stress. However, the decrease is nonlinear. Here we neglect the variation of  $\Omega_{diff}$  with stress, and take it as the atomic volume of copper ( $11.82 \text{ \AA}^3$ ). For dislocation nucleation and GB sliding, we use an empirical equation  $Q(\sigma) = Q(0)(1 - \sigma/\sigma_{ath})^\alpha$  to describe the stress-activation coupling, where  $Q(0)$  is the activation energy without stress. Here  $\sigma_{ath}$  is the athermal tensile strength for dislocation nucleation. It is set to be 3.5 GPa according to our MD calculations. We take this value as 2.4 GPa for GB sliding because the ideal shear resistance of the high angle grain boundary can be taken roughly to be half of the ideal pure shear strength in fcc Cu.<sup>28</sup>  $\alpha$  is taken as 4 to account for the variation of activation volume with increasing stress.<sup>26</sup> Finally, our simulation conditions for creep in NC copper are  $d = 10.7 \text{ nm}$  and  $T = 960 \text{ K}$ .

Because of the difference in magnitude of activation volumes, the activation free energy reduction due to stress is the fastest in dislocation nucleation, while the slowest in diffusion. Therefore  $-\ln \dot{\epsilon}$  decreases with increasing stress at a different rate for the three processes. The crossovers among them determine the critical stresses at which creep mechanism transits. Generally speaking, the effective creep rate  $\dot{\epsilon}$  could be determined by a different arrangement of these processes. In detail, if the coupling among them is weak, one may expect that they are in a parallel relation, leading to the effective rate  $\dot{\epsilon} = \dot{\epsilon}_{diff} + \dot{\epsilon}_{disl} + \dot{\epsilon}_{gbs}$ , which is shown as the dashed green line. On the other hand, diffusion and dislocation mechanisms may be independent with each other. However, GB sliding can be simultaneously accommodated by either diffusion or dislocation. Therefore, the effective rate could be expressed as  $\dot{\epsilon}^{-1} = (\dot{\epsilon}_{diff} + \dot{\epsilon}_{disl})^{-1} + \dot{\epsilon}_{gbs}^{-1}$ , where diffusion and dislocation are parallel (additive), simultaneously they are sequential (inverse additive) to GB sliding.<sup>24</sup> This arrangement is shown as the dotted green line. The former arrangement may be a reasonable guess according to the comparison between direct MD results, shown as the solid black curve. These processes which contribute the largest strain rate may dominate the creep mechanism at specific stress regime. The critical stresses  $\sigma_{gbs}$ ,  $\sigma_{disl}$  are determined by crossovers between  $\dot{\epsilon}_{diff}$  and  $\dot{\epsilon}_{gbs}$ ,  $\dot{\epsilon}_{disl}$

and  $\dot{\epsilon}_{disl}$ , respectively. They define three regions I, II, and III over the whole stress range. In detail, stress interval  $(0, \sigma_{gbs})$  defines Region I, where diffusion is the main creep mechanism. GB sliding contributes mostly to global rate within  $(\sigma_{gbs}, \sigma_{disl})$ , which is Region II. Above  $\sigma_{disl}$ , namely Region III, dislocation nucleation plays the most important role in deformation. This model intuitively explains the stress-induced creep mechanism transition in NC metals which is found in both our simulation and previous experiments.<sup>16,17</sup> This model is also used in general to explain the strain rate dependence of flow strength, and the failure of Hall-Petch relation in nanoscale materials, which are simultaneously governed by several competing deformation mechanisms.

#### IV. SUMMARY

In conclusion, we show a Coble, GB sliding, and dislocation nucleation competing creep mechanism in NC copper by molecular dynamics analysis. Our results confirm the creep mechanisms suggested by recent experimental studies. The calculated stress and grain size exponents of  $(n \approx 1, P \approx 3)$ ,  $(n \approx 2, P \approx 3)$ , and  $(n \geq 4, P \approx 1.6)$  agree quantitatively with experimental results for creep governed by GB diffusion, sliding, and dislocation nucleation, respectively. The finding of grain size dependence of dislocation creep is in contrast with conventional coarse-grained materials. A small activation volume of  $0.1-10b^3$  is consistent with experimental discoveries, validating the important role of GB diffusion in nanoplasticity. We have proposed a stress-temperature deformation map for NC metals based on the derived stress exponent. The physics behind the stress-induced transition of creep mechanism is explained by the competition among rate-controlling diffusion, GB sliding, and dislocation nucleation processes. We should note that while the creep mechanism transition model is constructed using NC copper, it should be also applicable to the other NC metals which exhibit qualitatively the same creep behavior, e.g., Ni,<sup>33</sup> Pd,<sup>34</sup> Au,<sup>35</sup> and Al.<sup>36</sup> The identified creep mechanisms provide a deeper understanding of the deformation of NC metals from a physics point of view. It is advisable to the experimentalists to propose strategies of improving the mechanical and thermodynamical stabilities of NC metals.

#### ACKNOWLEDGMENTS

The authors are indebted to Hajime Kimizuka and G. J. Jason Gao for helpful discussions. This work was partially supported by a Grant-In-Aid for JSPS Fellows (Grant No. P10370), and Scientific Research on Innovative Area, "Bulk Nanostructured Metals" (Grant No. 22102003), Scientific Research (A) (Grant No. 23246025), and Challenging Exploratory Research (Grant No. 22656030).

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