

## Discerning enhanced dislocation plasticity in hydrogen-charged $\alpha$ -iron nano-crystals

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(Received 1 February 2015; final form 14 May 2015 )

Supplementary Material Available Online

Novel atomistic simulations of  $\alpha$ -iron nano-crystals starting with pre-existing dislocation networks have been performed to identify the effect of high hydrogen concentrations on enhanced dislocation plasticity. Hydrogen is shown to decrease the dislocations free-surface nucleation stress, as well as increase the flow strength of crystals. The dislocation density is observed to increase in the presence of hydrogen due to dislocation pinning and enhanced dislocation self-multiplications. Hydrogen also changes the deformation morphology from discrete slip planes in hydrogen-free crystals to a homogeneous deformation in H-charged crystals due to the enhanced dislocations self-multiplication.

**Keywords:** hydrogen, dislocations, plasticity, nano-crystals, iron

Hydrogen (H) can be easily inserted, intentionally or not, in most materials,[1] which is well documented to lead to early failure of metals at low strains. This is a classical problem in the study of environmental effects on the mechanical degradation of metals and alloys. There has been a recent renewed interest in this problem, largely related to the increased use of H as an alternative energy source.

A number of hypotheses have been proposed over the years to explain the effects of H on metals. The two most prominent hypotheses are hydrogen-enhanced localized plasticity (HELP),[2,3] and hydrogen-enhanced decohesion (HEDE).[3] In HELP, an increase in the dislocation mobility in the presence of H is attributed to screening of dislocation–dislocation interactions and the decrease in the interaction energy between dislocations and interstitial H-atoms. HELP has been argued to occur in most metals, and direct *in situ* transmission electron microscopy (TEM) observations [4,5] seem to support this hypothesis at low/intermediate H concentrations. In HEDE, the increased solubility of H results in a decrease in the atom binding forces of the metal lattice. Thus, at sufficiently

high H concentrations the cohesive strength of the material decreases leading to a premature brittle intergranular fracture owing to the decrease in the binding forces.

For decades, it was presumed that the role of dislocation plasticity at high H concentrations is limited. However, recent experimental observations show a very dense and extensive dislocation microstructure forming in H-charged metals.[6–8] It was also shown that the degree of increase in dislocation density is a function of H concentration.[9] These studies promote the need to reevaluate the effect of H-atoms on dislocation plasticity in high-pressure H environments.

Most atomistic simulations addressing HE in the literature have focused on a few special cases in which the focus was only on dislocation nucleation in initially perfect crystals in the absence of pre-existing dislocations [10]; dislocation nucleation from crack-tips [11]; or H interactions with individual dislocations.[12,13] Atomistic simulations addressing H interaction with pre-existing dislocation networks received less attention. In fact, pre-existing dislocations are ubiquitous in all metals, and H-dislocation interactions will impact almost all

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stages of plastic deformation (yielding, flow, hardening, dynamic recovery by cross-slip, etc.). To address this, we perform novel molecular dynamics (MD) simulations to study the collective effect of H on microstructure evolution and plastic flow in body-centered cubic iron ( $\alpha$ Fe) nano-crystals, with pre-existing dislocation networks.

All MD simulations reported here were conducted using LAMMPS,[14] with the embedded atom method (EAM) potential for H- $\alpha$ Fe developed by Ramasubramaniam et al. [15] Cubic simulation cells, having relatively large dimensions, were modeled. The smaller simulation cell has an edge length of 50 nm, and the larger simulation cell has an edge length of 80 nm, corresponding to 10,997,000 and 45,091,000 atoms, respectively. Uniaxial tensile loading was imposed along the z-axis of the simulation cell, which coincides with the [100] crystal orientation. Non-periodic boundary conditions were employed along the three-directions, with the surfaces in the x and y directions being free surfaces. The uniaxial loading is imposed by fixing all atoms in the 14 bottom most atom-layers (in the negative z-axis direction), and applying a constant velocity in the positive z-axis direction to all atoms in the 14 top most atom-layers (in the positive z-axis direction). Thus, the simulations mimic tensile loading of  $\alpha$ Fe nano-crystals. All simulations were performed under two different conditions, H-free (0% H) and H-charged with 180 mass ppm (i.e. 1% atomic ct). In the H-charged simulations, H-atoms were randomly introduced into tetrahedral sites in the  $\alpha$ Fe lattice, which are the most energy favorable.[16] Energy minimization is subsequently imposed on the simulation cell. The system temperature is then increased to 300 K and then relaxed for a period of 50 ps. Equilibration is performed under a canonical NVT ensemble (constant number of atoms, volume and temperature) with a Nosé-Hoover thermostat. Uniaxial tensile loading is subsequently imposed at a constant engineering strain-rate of  $10^8 \text{ s}^{-1}$  along the [100] direction up to 10% engineering strain. A time step of 1 fs is applied, and the temperature is kept constant at 300 K under canonical NVT.

Visualization of the defect structure is obtained using the common neighbor analysis (CNA) method. [17–19] The open visualization tool OVITO,[20] and the dislocation extraction algorithm [21] were both used alternatively to analyze the simulations results. The evolving dislocation densities in the simulation cells were calculated by filtering dislocations from other defects (i.e. interstitial atoms and vacancies) using CNA, and dividing the dislocations total length by the initial cell volume.

Figure 1 shows the engineering stress and dislocation density curves as a function of engineering strain during the tensile loading of H-free and H-charged 80 nm perfect crystals (i.e. in the absence of pre-existing

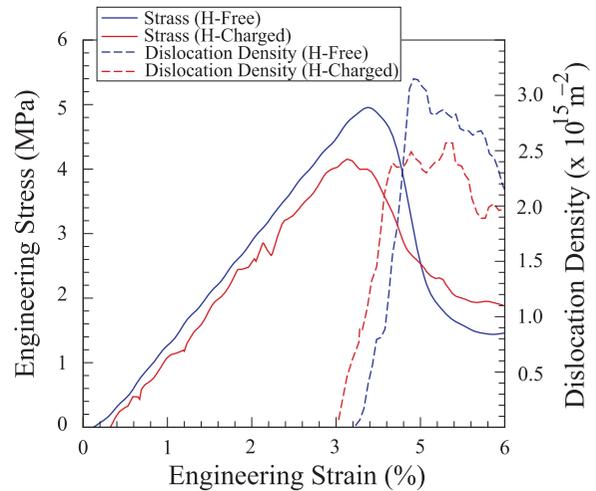


Figure 1. Engineering stress and dislocation density as a function of engineering strain during the tensile loading of H-free and H-charged 80 nm perfect  $\alpha$ Fe nano-crystals.

dislocations). In both cases the nanocrystal deforms elastically until the applied stress is high enough for dislocation nucleation from the corners of the simulation volume. As the dislocation density increases in the sample the stress drops considerably. By comparing the H-free and H-charged simulations, it is observed that the dislocation nucleation stress is 19% lower in the H-charged crystal. This reduction in the dislocation nucleation stress is in qualitative agreement with nanoindentation experiments showing a reduction in the pop-in load required for the formation of dislocations,[22] as well as nanoindentation MD simulations.[10] On the other hand, by comparing the dislocation density evolution curves, it is noted that the peak dislocation density in the H-free simulations is 28% higher than the H-charged case. This is attributed to the higher stress reached in the H-free case, which contributes to a faster dislocation multiplication.[23] This higher dislocation density subsequently results in reducing the stress in the H-free case further than that in the H-charged case, in agreement with the generalized size-dependent dislocation-based model.[24] The simulations are terminated after 6% strain at which the deformation is subsequently dominated by twinning due to the high imposed shear-stresses on the gliding dislocations.[25]

To avoid complications associated with twinning in  $\alpha$ Fe at high imposed stresses, and to investigate the effect of H on the evolution of pre-existing dislocations in  $\alpha$ Fe nano-crystals, which better mimics real defected crystals, an initial dislocation density is introduced in all subsequent simulations. The pre-existing initial dislocation network is generated in the simulation cells by randomly introducing dislocations lines by randomly choosing a {110}<111> slip-system, and a random line direction (edge or screw). The dislocation line is then

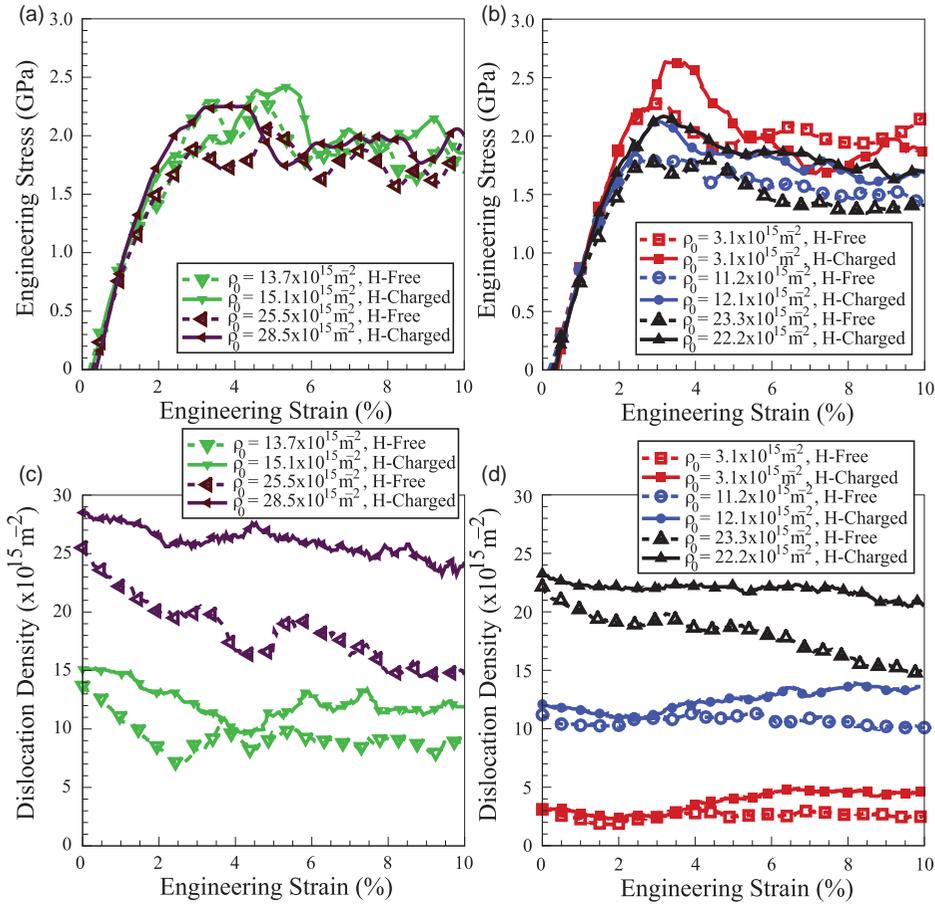


Figure 2. Engineering stress versus engineering strain for H-free (solid lines with open symbols) and H-charged (dashed lines with solid symbols) Fe nano-crystals, having sizes (a) 50 nm; and (b) 80 nm. The corresponding dislocation density evolution versus engineering strain for both crystal sizes are shown in (c) and (d), respectively.

extend from one surface to another, such that they do not end in the crystal. This process is repeated until the desired dislocation density in the crystal is reached. The appropriate atomic positions are then updated by computing the anisotropic displacement field resulting from all dislocations.[26] Three initial dislocation densities approximately equal to  $3 \times 10^{15}$ ,  $15 \times 10^{15}$ , and  $25 \times 10^{15} \text{ m}^{-2}$  were chosen. These densities qualitatively match those reported after dislocation nucleation in perfect crystals as shown in Figure 1, and are high enough to guarantee that at least a few dislocation sources will remain in the crystal throughout the plastic deformation. Thus, conditions of starvation are not reached.[24]

Figure 2(a) and 2(b) shows the engineering stress versus engineering strain curves of H-free and H-charged 50 nm, and 80 nm simulation cells, respectively. The corresponding dislocation densities evolutions are shown in Figure 2(c) and 2(d), respectively. Furthermore, a focused examination of occurring trends is shown in Figure 3. Unlike the perfect crystal simulations, the stress–strain curves with pre-existing dislocations show a considerably lower yield stress followed

by continuous flow. In addition, as shown in Figure 3, the strengths of H-free crystals are consistently lower than those of H-charged simulations for both crystal sizes. This indicates that H-atoms act as obstacles to dislocation glide (i.e. H-pinning effect [13]), and relatively higher applied stresses are required for yield and flow. These simulations are in qualitative agreement with recent H-free and H-charged vanadium micropillar compression experiments showing an increasing flow stress with increasing H concentration.[27]

In addition, Figure 2(c) shows that the evolution of the dislocation density in the 50 nm simulation cells with initial dislocation density  $15 \times 10^{15}$  can be divided into two stages. In the first stage, which is prominent before plastic flow, the dislocation density is observed to rapidly decreases. The rate of decay in H-free simulations is relatively larger than in H-charged simulations, which is a strong indication of the H-pinning effect on dislocation glide. In the second stage, at the onset of plastic flow, the dislocation density is observed to reach a steady-state dislocation density around  $\sim 9 \times 10^{15}$ , and  $\sim 12 \times 10^{15}$ , for H-free, and H-charged crystals, respectively. This steady-state stage indicates that the

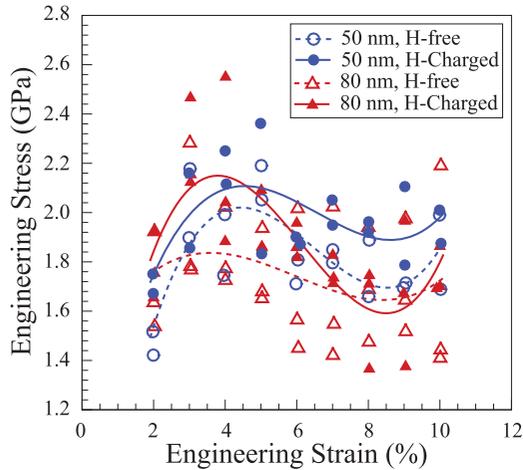


Figure 3. Composite plot of the H-effects on engineering stress as a function of engineering strain from all simulations.

dislocation multiplication-rate and the escape-rate are equal. The dislocation multiplication is accomplished through the continuous activation of single-ended dislocation sources (see supplementary movie #1) similar to observations from *in situ* TEM [28] and discrete dislocation dynamics simulations.[29]

For 50 nm simulation cells with initial dislocation density  $\rho_0 = 3 \times 10^{15}$  (not shown here), the dislocation density is observed to decrease rapidly until all pre-existing dislocations escape the crystals (i.e. mechanical annealing [30]). This is followed by an elastic rise in the applied stress until dislocations, and subsequently twins

nucleate in the nano-crystals. These simulation will then deform in a fashion similar to those reported in Figure 1.

On the other hand, 80 nm simulation cells with initial dislocation densities  $\rho_0 \leq 15 \times 10^{15}$ , the H-free simulations do not show any significant decay in the initial dislocation density. This indicates that the multiplication- and escape-rates are equal. However, the H-charged samples show a rise in the dislocation density during plastic flow, which indicates that H enhances dislocation plasticity even at high H concentrations similar to the ones considered in the current study. These results are in qualitative agreement with recent TEM observations that unlike in H-free crystals, very dense dislocation structures form in H-charged nickel,[6] palladium,[9] and  $\alpha$ Fe.[7,8] The dislocation microstructure, for the 80 nm simulation cells with initial dislocation density of  $\rho_0 = 12 \times 10^{15} \text{ m}^{-2}$ , at 0% and 10% strain are shown in Figure 4(a) and 4(b), respectively, for both the H-free and H-charged simulation cells.

By careful examination of the evolving dislocation network in these simulations (see supplementary movie #2), it is observed that H enhances dislocation self-multiplication through spiral motion around the pinning point of single-ended dislocation sources. These pinning points were formed by dislocation-forest interactions. This mechanism was first observed in uncharged molybdenum nano-crystals above a critical stress, which is higher than the maximum stresses reached in the crystals modeled here with pre-existing dislocations.[23] Since this self-multiplication mechanism is not observed in the current H-free simulations, this suggests that the critical

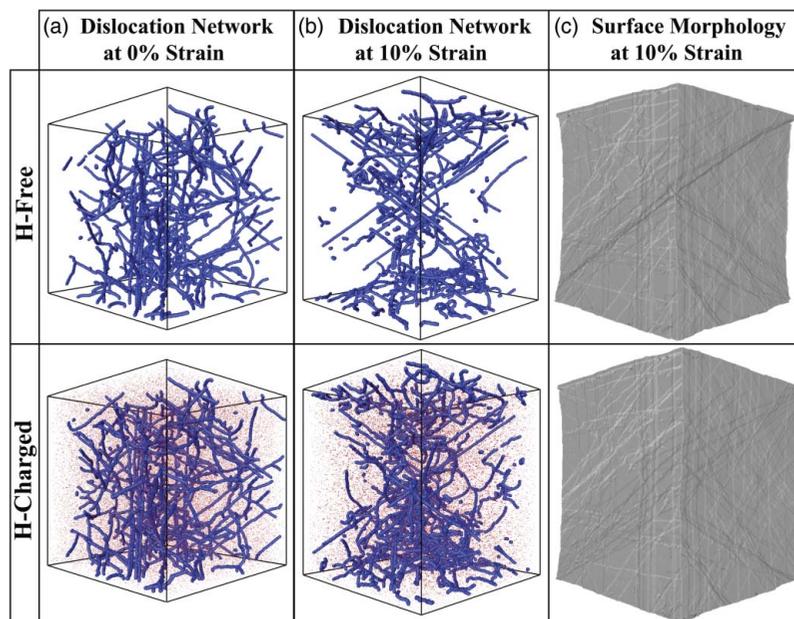


Figure 4. Dislocation microstructure and surface morphology for 80 nm simulation cells having an initial dislocation density of  $\rho_0 = 12 \times 10^{15} \text{ m}^{-2}$ , before and after deformation. (a) Initial dislocation microstructure; (b) dislocation microstructure at 10% strain; (c) surface morphology at 10% strain. In the H-charged cases the H-atoms are shown as red dots, and in all shown cases loading is along the vertical direction.

stress for this mechanism must decrease with increasing H concentration. This dependence is consistent with the defacing theory,[31,32] which suggests that H reduces the line-energy of a dislocation, and as a result dislocation formation is facilitated, leading to enhanced multiplication.

For H-free simulations of both sizes with initial dislocation densities  $\geq 20 \times 10^{15}$ , the dislocation density is observed to decrease with increasing strain in both crystal sizes. In these simulations, the rate of dislocations escape is much higher than the rate of dislocations multiplication, resulting in a continuous decrease in the dislocation density. On the other hand, in H-charged crystals, while the dislocation density is observed to decrease the rate of decrease is considerably smaller than that in H-free simulations. This can be attributed to two effects, H-pinning, and enhanced dislocation multiplication.

The surface morphologies of the 80 nm simulation cells with initial dislocation density of  $\rho_0 = 12 \times 10^{15} \text{ m}^{-2}$ , at 10% strain are shown in Figure 4(c). These surface morphologies are representative of the surface morphologies of both simulated crystal sizes and all modeled initial dislocation densities. For the H-free simulations, there is a pronounced localized plastic shear, in the form of a large slip steps on few discrete slip planes. This localized slip is associated with the continuous activation of the weakest single-ended source in the crystal, in a similar manner to that observed in microcrystal compression studies.[33] On the other hand, the surface morphology of H-charged simulations shows a more homogeneously distributed slip. This homogeneous deformation is attributed to self-multiplication of dislocations, leading to the activation of several slip-systems during the deformation process. These observations are consistent with experimental observations from vanadium microcompression tests.[27]

In summary, MD simulations were performed to investigate the effect of H on dislocation mediated plasticity in  $\alpha\text{Fe}$  nano-crystals under tension loading. It is observed that the dislocation nucleation stress in perfect nano-crystals decreases in the presence of H. In simulations starting with pre-existing dislocations H-charged simulations show an increase in the flow strength versus H-free simulations. This increase is a result of H-pinning of dislocations. The dislocation density is also observed to increase in the presence of H. This increase is due to the retention of dislocations in the crystal by H-pinning, as well as due to enhanced dislocation self-multiplications. The critical stress for dislocation self-multiplications is observed to decrease in the presence of H. Finally, H also changes the deformation morphology from discrete slip planes in H-free crystals to a homogeneous deformation in H-charged crystals due to the enhanced dislocations self-multiplication.

**Acknowledgments** J.A.E. acknowledges support by the National Science Foundation CAREER Award # CMMI-1454072.

**Disclosure statement** No potential conflict of interest was reported by the authors.

**Supplementary online material.** A more detailed information on experiments is available at <http://dx.doi.org/10.1080/21663831.2015.1052889>

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## References

- [1] Pundt A, Kirchheim R. Hydrogen in metals: microstructural aspects. *Ann Rev Mater Res.* 2006;36(1):555–608.
- [2] Steigerwald EA, Schaller FW, Troiano AR. The role of stress in hydrogen induced delayed failure. *Trans Met Soc AIME.* 1960;218:832–841.
- [3] Beachem CD. A new model for hydrogen-assisted cracking (hydrogen ‘embrittlement’). *Metall Mater Trans B.* 1972;3:441–455.
- [4] Tabata T, Birnbaum HK. Direct observations of hydrogen enhanced crack propagation in iron. *Scr Metall.* 1984;18(3):231–236.
- [5] Robertson IM. The effect of hydrogen on dislocation dynamics. *Eng Fract Mech.* 2001;68(6):671–692.
- [6] Martin ML, Somerday BP, Ritchie RO, Sofronis P, Robertson IM. Hydrogen-induced intergranular failure in nickel revisited. *Acta Mater.* 2012;60(6/7):2739–2745.
- [7] Martin ML, Sofronis P, Robertson IM, Awane T, Murakami Y. A microstructural based understanding of hydrogen-enhanced fatigue of stainless steels. *Int J Fatigue.* 2013;57:28–36.
- [8] Wang S, Martin ML, Sofronis P, Ohnuki S, Hashimoto N, Robertson IM. Hydrogen-induced intergranular failure of iron. *Acta Mater.* 2014;69:275–282.
- [9] Deutges M, Barth HP, Chen Y, Borchers C, Kirchheim R. Hydrogen diffusivities as a measure of relative dislocation densities in palladium and increase of the density by plastic deformation in the presence of dissolved hydrogen. *Acta Mater.* 2015;82:266–274.
- [10] Wen M, Zhang L, An B, Fukuyama S, Yokogawa K. Hydrogen-enhanced dislocation activity and vacancy formation during nanoindentation of nickel. *Phys Rev B.* 2009;80:094113-1–094113-5.
- [11] Song J, Curtin WA. A nanoscale mechanism of hydrogen embrittlement in metals. *Acta Mater.* 2011;59(4):1557–1569.
- [12] Taketomi S, Matsumoto R, Miyazaki N. Atomistic simulation of the effects of hydrogen on the mobility of edge dislocation in alpha iron. *J Mater Sci.* 2008;43(3):1166–1169.
- [13] Tang Y, El-Awady JA. Atomistic simulations of the interactions of hydrogen with dislocations in fcc metals. *Phys Rev B.* 2012;86:174102-1–174102-13.
- [14] Plimpton SJ. Fast parallel algorithms for short-range molecular dynamics. *J Comput Phys.* 1995;117:1–19.
- [15] Ramasubramaniam A, Itakura M, Carter EA. Interatomic potentials for hydrogen in  $\alpha$ -iron based on density functional theory. *Phys Rev B.* 2009;79:174101-1–174101-13.
- [16] Fukai Y. Site preference of interstitial hydrogen in metals.. *J Less Common Metals.* 1984;101:1–16.

- [17] Kelchner CL, Plimpton SJ, Hamilton JC. Dislocation nucleation and defect structure during surface indentation. *Phys Rev B*. 1998;58(17):11085–11088.
- [18] Zimmerman JA, Kelchner CL, Klein PA, Hamilton JC, Foiles SM. Surface step effects on nanoindentation. *Phys Rev Lett*. 2001;87:165507-1–165507-4.
- [19] Tsuzuki H, Branicio PS, Rino JP. Structural characterization of deformed crystals by analysis of common atomic neighborhood. *Comput Phys Commun*. 2007;177(6):518–523.
- [20] Stukowski A. Visualization and analysis of atomistic simulation data with ovito – the open visualization tool. *Model Simul Mater Sci Eng*. 2010;18:015012-1–015012-7.
- [21] Stukowski A, Ibe k. Extracting dislocations and non-dislocation crystal defects from atomistic simulation data. *Model Simul Mater Sci Eng*. 2010;18:085001-1–085001-13.
- [22] Barnoush A, Vehoff H. Recent developments in the study of hydrogen embrittlement ccc Hydrogen effect on dislocation nucleation. *Acta Mater*. 2010;58(16):5274–5285.
- [23] Weinberger CR, Cai W. Surface controlled dislocation multiplication in metal micro-pillars. *Proc Nat Acad Sci*. 2008;105:14304–14307.
- [24] El-Awady JA. Unraveling the physics of size dependent dislocation mediated plasticity. *Nat Comm*. 2015;6:5926-1–5926-9.
- [25] Marian J, Cai W, Bulatov VV. Dynamic transitions from smooth to rough to twinning in dislocation motion. *Nat Mater*. 2004;3(3):158–163.
- [26] Hirth JP, Lothe J. Theory of dislocations. New York: Wiley; 1982.
- [27] Deutges M, Knorr I, Borchers C, Volkert CA, Kirchheim R. Influence of hydrogen on the deformation morphology of vanadium (1 0 0) micropillars in the  $\alpha$ -phase of the vanadium-hydrogen system. *Scr Mater*. 2013;68(1):71–74.
- [28] Momprou F, Legros M, Sedlmayr A, Gianola DS, Cailard D, Kraft O. Source-based strengthening of sub-micrometer al fibers. *Acta Mater*. 2012;60(3):977–983.
- [29] Rao SI, Dimiduk DM, Parthasarathy TA, Uchic MD, Tang M, Woodward C. A thermal mechanisms of size-dependent crystal flow gleaned from three-dimensional discrete dislocation simulations. *Acta Mater*. 2008;56(13):3245–3259.
- [30] Shan ZW, Mishra RK, Asif SAS, Warren OL, Minor AM. Mechanical annealing and source-limited deformation in submicrometer-diameter Ni crystals. *Nat Mater*. 2008;7:115–119.
- [31] Kirchheim R. Reducing grain boundary, dislocation line and vacancy formation energies by solute segregation. I. Theoretical background. *Acta Mater*. 2007;55(15):5129–5138.
- [32] Kirchheim R. Reducing grain boundary, dislocation line and vacancy formation energies by solute segregation: Ii. Experimental evidence and consequences. *Acta Mater*. 2007;55(15):5139–5148.
- [33] Hussein AM, Rao SI, Uchic MD, Dimiduk DM, El-Awady JA. Microstructurally based cross-slip mechanisms and their effects on dislocation microstructure evolution in fcc crystals. *Acta Mater*. 2015;85:80–190.