Acta Materialia 107 (2016) 144–151

Contents lists available at ScienceDirect

Acta Materialia

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

Full length article

Multiscale modeling of hydrogen enhanced homogeneous dislocation nucleation

G.P.M. Leyson*, Blazej Grabowski, Jörg Neugebauer

Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf 40237, Germany

ARTICLE INFO

Article history:
Received 22 September 2015
Received in revised form
14 January 2016
Accepted 17 January 2016
Available online xxx

Keywords:
Homogenous dislocation nucleation
Nanoindentation
Hydrogenhydrogen interaction
Dislocations

ABSTRACT

A multiscale approach is proposed to predict how the presence of hydrogen influences the onset of homogeneous dislocation nucleation (HDN) and thus of plasticity. The model takes inputs that can be solely obtained from atomistic calculations, such as dislocation core structure, stacking fault energy and hydrogen–hydrogen interaction. The equilibrium hydrogen concentration around the dislocation loop is calculated using a recently developed self-consistent iterative method [1]. The complex nature of the dislocation field, as well as the equilibrium hydrogen concentration around the loops, is taken into account. The onset of HDN as a function of bulk hydrogen concentration and temperature is quantitatively predicted and is consistent with nano-indentation experiments on hydrogen loaded samples. Applying the approach to Ni, we find that even low hydrogen concentrations of about 1 at-% result in largely reduced HDN energy barriers and thus largely reduce the critical shear stress.

1. Introduction

Hydrogen embrittlement is a century-old problem [2] that is known to occur in a wide range of materials [3–14]. This phenomenon is particularly severe in ferritic high strength steels due to the high mobility of hydrogen solutes in bcc iron. However, despite the growing interest in the topic, the underlying mechanisms that cause hydrogen embrittlement are not well-understood. The difficulty is rooted in the different time- and length-scales associated with the phenomenon. Hydrogen diffusion at relevant temperatures is fast relative to experimental time-scales, but not fast enough to be easily simulated using current computational technology. On the other hand, both atomic and mesoscopic length-scales are relevant due to nontrivial solute–solute interactions and defects such as dislocations and cracks with long-range elastic fields.

Several conceptual frameworks have been proposed to explain hydrogen embrittlement, including hydride formation and cleavage [10,15], hydrogen enhanced decohesion (HEDE) [5–7,13,16–18], and hydrogen enhanced local plasticity (HELP) [3,4,8,11,12,19–24]. In particular, the HELP mechanism is based on the localization of hydrogen around dislocations. Once this happens, it is thought that the hydrogen modifies the interaction of dislocations with other defects (such as other dislocations) and results in local plasticity that is macroscopically similar in fracture appearance to brittle fracture. While various aspects of this mechanism have been extensively studied, a quantitative connection between the hydrogen localization around dislocations and the actual brittle-like macroscopic behavior has yet to be made. In order to make this connection, the interaction between the hydrogen solutes and dislocations must be accurately quantified and understood.

A powerful experimental methodology to study this interaction is through *in situ* electrochemical nanoindentation experiments charged with hydrogen [25]. In these experiments, homogeneous dislocation nucleation (HDN) in hydrogen-charged metal samples is initiated by a nanoindenter. These experiments have the advantage of having a well-defined system that facilitates the comparison between experiments and theory. Due to the small sampling volume, grain boundaries and other hard-to-characterize and describe defects (i.e. forest dislocations) do not affect the results, and one can reasonably assume that the region at which the nucleation occurs locally resembles a perfect crystal. The system also circumvents the common problem when describing the energy of systems containing dislocations. A straight dislocation has a long-range stress field which scales like $1/r$. This means that, in principle, the interaction with solutes very far away from the dislocation cannot be ignored. Dislocation loops, however, do not have a long-range field and only solutes close to the dislocation are relevant in

* Corresponding author. Max-Planck-Straße 1, 40237 Düsseldorf Germany.
E-mail address: g.leyson@mpie.de (G.P.M. Leyson).

http://dx.doi.org/10.1016/j.actamat.2016.01.036
1359-6454/

the analysis. Finally, analytic solutions to the stress field underneath the indenter prior to dislocation nucleation are well-defined [2].

The effect of hydrogen on nanoindentation experiments has been attributed to changes in the shear modulus, dislocation core structure and/or stacking fault energy due to hydrogen [25,26]. These changes were treated as fitting parameters for the experimental data and the localization of hydrogen around the dislocation was not explicitly taken into account. More recently, Kirchheim [27] proposed a thermodynamic framework wherein hydrogen acts to lower the dislocation line energy through favorable interaction with the dislocation. To quantitatively evaluate this effect, one has to know how much hydrogen is localized around the dislocation loops as well as determine the strength of the interactions. Apart from the solute-dislocation interaction, hydrogen–hydrogen interaction also plays a crucial role and may even lead to the formation and stabilization of hydrides around dislocations [1,28].

In this paper, we derive and employ a multiscale approach that allows us to describe the full complexity of forming and stabilizing a dislocation loop both in the absence and presence of hydrogen. Specifically, we develop an analytic model that is informed by atomistic inputs, such as hydrogen–hydrogen interaction and the geometry of the dislocation core, and takes into account the discrete nature of the system. The model calculates the equilibrium hydrogen concentration around a dislocation at finite temperature and quantitatively predicts the onset of HDN as function of applied shear stress.

2. Computational methods

A schematic representation of our simulation box is shown in Fig. 1. An orthagonal supercell is created with principal directions corresponding to the $[\bar{1}10](111)$ slip system. The size of the simulation box is 63.5 Å × 72.1 Å × 63.9 Å, containing 28080 Ni atoms. The size of the simulation box was chosen such that the elastic energy of the largest dislocation loop considered is converged with respect to system size to within 0.1%. Faulted hexagonal loops with partial Burgers vector $\boldsymbol{b}^p = a_{\mathrm{Ni}}/6[\bar{1}2\bar{1}]$ are considered, where a_{Ni} is the lattice parameter of Ni. This is because, at small loop radii that are relevant to nucleation, faulted hexagonal loops are energetically more favorable than full dislocation loops in *fcc* metals [29]. Hydrogen atoms are assumed to occupy only the octahedral sites in the system.

The energetics of the system is described using an analytic model that takes key inputs from atomistic calculations, such as local hydrogen–hydrogen interaction and dislocation core structure. In the analytic model, the system is assumed to be an isotropic linear elastic material. The hydrogen solutes are approximated as point dilatational sources. Since the most important interaction in the system is that of the hydrogen solutes and the stress fields, the elastic constants chosen are the bulk modulus K and the Poisson ratio ν in the coordinate system above.

The atomistic calculations were performed using a modified semi-empirical embedded atom method (EAM) potential based on a potential developed by Angelo et al. [30]. The modification of the original potential was done in Ref. [28] by increasing the cut-off radius r_{cut} of the Ni–H interaction from 4.83 Å to 4.92 Å in order to remove elastic instabilities arising from a negative C_{44} of the rocksalt Ni–H structure without affecting other relevant properties of the system. The materials properties that are obtained using this potential are summarized in Table 1.

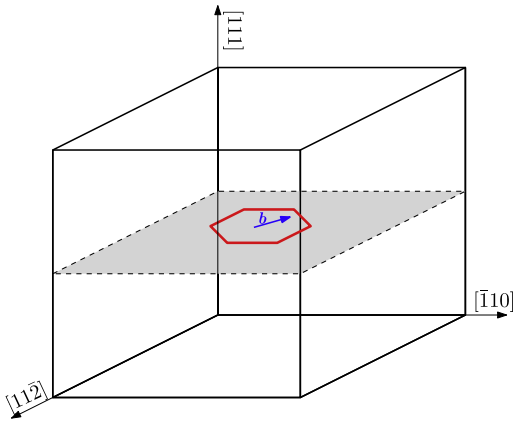

Fig. 1. A schematic representation of the simulation cell used to model Homogeneous Dislocation Nucleation (HDN). A faulted hexagonal dislocation loop (solid red line) with Burgers vector $\boldsymbol{b}^p = a_{\mathrm{Ni}}/6[\bar{1}2\bar{1}]$ is introduced to the system. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3. Energetics

To determine when the homogeneous dislocation nucleation can spontaneously occur, the free energy of the system at finite temperature must be considered. Consider a system coupled to a hydrogen reservoir with chemical potential μ_{H}. The temperature T along with μ_{H} determines the equilibrium bulk hydrogen concentration $c_{\mathrm{H}}^{\mathrm{bulk}}$. We define the bulk hydrogen concentration as the ratio between the actual number of hydrogen atoms in the defect free, unstressed bulk and the maximum number of available bulk interstitial sites they can be incorporated. The latter number is identical to the number of Ni atoms. When the bulk hydrogen concentration $c_{\mathrm{H}}^{\mathrm{bulk}} \ll 1$, the free energy f° per host atom is,

$$f^{\circ} = e_{\mathrm{Ni}} + c_{\mathrm{H}}^{\mathrm{bulk}}\left[(e_{\mathrm{H}} - \mu_{\mathrm{H}}) + kT \ln c_{\mathrm{H}}^{\mathrm{bulk}}\right], \tag{1}$$

where e_{Ni} is the energy of pure fcc Ni per atom, e_{H} is the energy of inserting one H atom in the Ni matrix in the dilute limit. Hydrogen–hydrogen interaction is assumed to be negligible in Eq. (1), since $c_{\mathrm{H}}^{\mathrm{bulk}}$ is small in typical experimental conditions. It should be emphasized that $c_{\mathrm{H}}^{\mathrm{bulk}}$ refers specifically to the concentration of hydrogen in the unstressed bulk. The local concentration of hydrogen can be significantly higher in regions with large tensile stresses. The term e_{H} is determined by molecular static calculations using 5 × 5 × 5 conventional supercells,

$$e_{\mathrm{H}} = E_{\mathrm{tot}}^{1H} - E_{\mathrm{tot}}^{\mathrm{bulk}}, \tag{2}$$

where $E_{\mathrm{tot}}^{1\mathrm{H}}$ is the energy of the supercell containing one H atom and $E_{\mathrm{tot}}^{\mathrm{bulk}}$ is the total energy of the supercell without any H atoms. The equilibrium bulk hydrogen concentration can be determined by minimizing Eq. (1) with respect to $c_{\mathrm{H}}^{\mathrm{bulk}}$,

$$c_{\mathrm{H}}^{\mathrm{bulk}} = \exp\left(-\frac{e_{\mathrm{H}} - \mu_{\mathrm{H}}}{kT}\right). \tag{3}$$

When a dislocation loop is introduced in the system, the stress gradient induced by the loop changes the local hydrogen concentration around the loop. The change in free energy with respect to the perfect bulk is,

$$\Delta F^{\mathrm{loop}} = \sum_{i}^{N_{\mathrm{oct}}}\left(\Delta f_i^{\mathrm{f}} + \Delta f_i^{\mathrm{lb}} + \Delta f_i^{\mathrm{S}}\right) + \Delta F^{\mathrm{disl}}, \tag{4}$$

where