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Multiscale description of dislocation induced nano-hydrides

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Abstract—The interaction of hydrogen with the core and the strain field of edge dislocations is studied using a multiscale approach. We have therefore developed a combined thermodynamic and analytical model with full atomistic resolution that allows to quantify the local hydrogen concentration around the dislocation core as a function of temperature and hydrogen chemical potential. This model takes, as input, information from atomistic calculations, such as hydrogen–hydrogen interaction and the dislocation core structure, and faithfully reproduces results from a computationally much more expensive fully atomistic approach that combines the Embedded Atom Method with Monte Carlo simulations. The onset of nano-hydride formation and with it the activation of *hydrogen enhanced local plasticity* (HELP) is predicted through a parametric study of the hydride size as a function of temperature and bulk hydrogen concentration. The study reveals a sharp transition between hydride forming and non-hydride forming regimes. The transition between these two regimes corresponds to a critical hydrogen chemical potential μ_{H}^{c} related to the nano-hydride nucleus of the system.

Keywords: Hydrogen embrittlement; Hydrogen enhanced local plasticity, HELP; Dislocations; Hydrogen; Nickel

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1. Introduction

It is well-known that the exposure of metal systems to hydrogen gas, as present for example in humid air, often causes embrittlement (loss of toughness and ductility) and can lead to catastrophic material failure. This so-called hydrogen embrittlement is observed in a wide range of materials, such as Al [1,2], Ni [3–7], Ti [8], Fe and steels [9–12]. High mobility of hydrogen solutes in Fe makes the embrittlement phenomenon particularly severe in steels. Due to the relevance of high strength materials in achieving critical design targets for safety and weight reduction, interest in understanding hydrogen embrittlement has been steadily increasing over the years. Moreover, the importance of transitioning to a hydrogen-based economy has highlighted the need to address the embrittlement of high strength steels by hydrogen, since these materials are key structural materials for hydrogen storage. It is therefore critical to understand the underlying mechanisms responsible for hydrogen embrittlement.

Despite the fact that hydrogen embrittlement has been known for over a century [13], the precise mechanism by which hydrogen causes embrittlement is not well understood. This has lead to the proposal of several competing mechanisms behind hydrogen embrittlement. These mechanisms broadly fall into one of three categories: *hydride formation and cleavage, hydrogen enhanced decohesion* (HEDE), and *hydrogen enhanced local plasticity* (HELP).

For hydride forming metals, such as V, Nb and Ti, it is well accepted that the main mechanism for hydrogen embrittlement is through *hydride formation and cleavage*. Stress concentrations (for instance, ahead of a crack tip) in these metals promote the nucleation and growth of brittle hydride precipitates. As these precipitates grow and coalesce, the metal becomes more prone to brittle fracture through the cleavage of these hydrides. This phenomenon has been directly observed using transmission electron microscopy (TEM) [8] as well as scanning electron microscopy (SEM) of the fracture surface [14].

In the case of non-hydride forming metals, the origin of the embrittlement is less clear. One proposed mechanism for embrittlement in these metals is *hydrogen enhanced decohesion* (HEDE). In this model, hydrogen is envisioned to accumulate within the crystal lattice and along the grain boundaries. This accumulation results in the reduction of the cohesive strength of metal–metal bonds in the host matrix, which in turn promotes cleavage over other ductile processes. The HEDE mechanism is motivated by experiments relating the partial pressure of hydrogen to the onset of crack propagation [11,15] as well as by studies on the segregation of hydrogen to grain boundaries [3–5]. Theoretical models have also been developed to understand the HEDE mechanism [16,17].

However, despite the experimental and theoretical evidence supporting HEDE, there are some criticisms of the model. Although it is widely acknowledged that hydrogen

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can reduce the cohesive energy of metals, the magnitude of the effect is not well established. Direct measurement of this effect is difficult since the expected hydrogen concentrations that accumulate locally ahead of the crack tips are orders of magnitude higher than the maximum bulk H concentration. A qualitative decrease in cohesive bonding is not enough to validate the HEDE mechanism. In order for the HEDE mechanism to be viable, the reduction in separation energy must be sufficient that it is favored over other ductile mechanisms (i.e. emission of dislocations at the crack tip). Finally, models based on HEDE typically contain one or more adjustable parameters. A related mechanism has been discussed in a recent study by Song and Curtin on Ni and Fe systems [18,19]. Instead of directly causing brittle cleavage, the hydrogen accumulation at the crack tip shuts down emission of dislocations. This prevents the blunting of cracks and thus promotes brittle fracture.

An alternative mechanism for hydrogen embrittlement in non-hydride forming metals is *hydrogen enhanced local plasticity* (HELP), first proposed by Beachem [20]. In contrast to the HEDE mechanism, HELP proposes that hydrogen shields elastic interactions between dislocations and other obstacles. The origin of this shielding is due to the formation of a Cottrell cloud induced by the tensile field of the dislocation. Such elastic shielding leads to an increase in the density of dislocations at pile-ups, thus facilitating the nucleation of cracks leading to local fracture. This phenomenon is not contradictory to the experimentally observed embrittlement since the zone of ductile fracture is highly localized and the zone of plasticity remains small. From a macroscopic point of view, the result appears like brittle fracture. The HELP mechanism is supported by a wide array of experiments, ranging from the observation of shear localization on fracture surfaces to direct observation of dislocation activity using *in situ* environmental cell transmission electron microscopy (TEM) [1,2,6,9,10,21–23,26]. These experiments show increased dislocation velocities, as well as the formation of dense dislocation pile-ups. Several theoretical studies elucidated the details of the HELP mechanism [24,25,27] and in recent atomistic simulations of Ni–H systems, Pezold et al. [28] show that when the hydrogen–hydrogen attractive interaction is taken into account, nano-sized hydrides can form around edge dislocations even at very low bulk hydrogen concentrations for which bulk hydride formation is completely absent.

Despite the wealth of experimental and theoretical evidence supporting the model, HELP remains controversial primarily due to the lack of a direct, i.e. quantitative, connection between increased dislocation mobility and the actual embrittlement processes. To be able to make this connection, one must be able to bridge the length scales and time scales associated with the phenomenon. In this paper, we present a combined analytic-atomistic model that allows for the computation of the shape as well as the temperature–pressure dependent phase diagram of nano-hydride formation around dislocations. The model takes as input quantities that are readily computable by atomistic calculations and is thus able to take into account atomistic effects, such as hydrogen–hydrogen interaction and dislocation core relaxation, that are normally neglected in previous analytic models [29–32]. Once these atomistic inputs are calculated, the analytic nature of the model allows for the calculation of the equilibrium concentration profile of hydrogen, normally inaccessible to direct atomistic calculations due to time-scale constraints. We apply the model to an edge dislocation in the Ni–H system in order to enable a direct comparison with previous fully atomistic but computationally expensive results using embedded atom method coupled with Monte Carlo simulations [28].

2. Computational methods

Determining the equilibrium hydrogen concentration poses challenging problems due to the long range nature of a dislocation stress field, the time-scale associated with hydrogen diffusion required to reach the equilibrium configuration and the non-negligible influence of hydrogen–hydrogen interaction. A crucial ingredient of our model is therefore an explicit atomistic description of the dislocation core as well as of the hydrogen–hydrogen interaction.

For that purpose we used a semi-empirical embedded atom method (EAM) potential based on a potential developed by Angelo et al. [33]. The original potential exhibited a negative shear modulus C_{44} for the cubic NiH hydride, making it unsuitable to study systems wherein hydrogen localization and subsequently hydride formation occurs. Song et al. [18] and Pezold et al. [28] removed this instability by increasing the cut-off radius r_{cut} of Ni–H from 4.83 Å to 4.90 Å and 4.92 Å respectively without significantly affecting other relevant physical properties of the system. The former work applied the potential to study hydrogen localization at crack tips, while the latter applied it to hydrogen concentrations around Ni edge dislocations. Here, we will use the potential modified by Pezold et al. [28] since the focus of our work is likewise on hydride formation around dislocations and thus we will be able to validate our results directly. The materials properties that are obtained using this potential are summarized in Table 1.

To derive our analytic model, the elastic field around the dislocation is assumed to be isotropic. The small error induced by this approximation can be further reduced by analyzing the nature of the interactions occurring in the system. The elastic fields of dislocations in isotropic media are typically described in terms of the shear modulus G and the Poisson ratio ν [34]. In the system considered here, G would not be the appropriate elastic constant to use since the interaction between the dislocation and the hydrogen atoms is predominantly hydrostatic in nature. Additionally, the interaction between the Shockley partials is also predominantly hydrostatic. Therefore, we use the bulk modulus K and the Poisson ratio $\nu = (C_{11} + 2C_{12} - 2C_{44})/(2C_{11} + 4C_{12} + 2C_{44})$ in the coordinate system corresponding to the dislocation slip system ($[\bar{1}10] \times [111] \times [11\bar{2}]$) when calculating the elastic fields. Using these adapted elastic constants ensures a good agreement with hydrogen binding energies near the dislocation core as well as the correct partial–partial separation of 18.7 Å in the hydrogen-free case.

3. Dislocation-hydrogen interaction

3.1. Total interaction energy of the system

The total energy change due to the interaction between hydrogen atoms and an edge dislocation with line direction along $z = [11\bar{2}]$ and Burgers vector direction along $x = [\bar{1}10]$ can be expressed as