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Modeling the role of hydrogen interstitial concentration on internal stress fields in iron matrix

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Abstract A numerical model was proposed to predict the hydrogen interstitial concentration in iron matrix both in the immediate surrounding of and far from an edge dislocation. The current formulation successfully incorporates the relaxation effect and, thus, correctly predicts the stress state around the dislocations.

Introduction

The influence of hydrogen (H) interstitials on the mechanical properties of metals has always been a pressing issue owing to the easy diffusion of H atoms into a solid during chemical reactions or manufacturing processes. Specifically, diffused H atoms increase the mobility of dislocations in metals by altering the internal stress fields, leading to localized plastic deformations. This phenomenon deserves even more attention these days as research on utilizing H as a fuel has gained momentum, making the storage of H, which has a low energy content by volume [1], a critical issue. This warrants research on development of the infrastructure for the storage of H and the behavior of metallic components in the corresponding high-pressure H environment [2].

The major effect of interstitials on the mechanical properties of the host field emerges as the relaxation of the internal stress fields [3]. In particular, a solute atmosphere around a stress source forms, such that the energy stemming from the interaction between the internal stress field of the solid and the solvent atoms is large enough to change the distribution of atoms around the dislocation and, thus, controls the dislocation mobility [4]. A basic assumption regarding the introduction of solute atoms to the matrix is that the internal stress field around a solute atom remains constant during the expansion of the lattice [4, 5], which, however, is only valid within the regions where the solution is dilute. Based on this approach, a Boltzmann approximation was forwarded to calculate the interstitial distribution around a dislocation [6], and the prediction of interstitial distribution at the immediate surrounding of dislocations, where singularity prevails, was further improved by introducing a Fermi–Dirac approximation [7]. Moreover, the influence of H on dislocation activities was investigated in various metal matrices, and the effect of H interstitials on increased slip planarity and dislocation mobility leading to hardness and H-enhanced localized plasticity was determined [8, 9].

An iterative model utilizing a Fermi–Dirac approximation took the additive stress relaxation effect of the interstitials into account, and successfully predicted the H concentration at the vicinity of an edge dislocation; yet, the predictions were far from accurate remote from the dislocation [10]. This article approaches the problem from a phenomenological perspective and presents a model featuring a formulation for the interstitial concentration both in the immediate surrounding of and far from a dislocation. This study also aims to predict the correct distortion of the lattice due to the relaxed stress field of a single edge dislocation in the presence of H atoms. The model considers ideal conditions, where the lattice is considered as an elastic continuum containing a single edge dislocation, featuring unconstrained boundary conditions without any other external forces acting on it.

The proposed model was applied to simple iron (Fe)–H media to predict the stress relaxation and interstitial

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concentration. Only the interstitial volumetric effect was considered while predicting the relaxed stress field since the effect of additional host metal modulus change with the introduction of interstitial on relaxation is negligible [8, 10].

Modeling the stress state around a single edge dislocation

The planar interaction energy due to the volumetric expansion in the lattice between the interstitial atom and the existing internal stress field is given by [4, 10, 11]

$$W_{\mathrm{int}} = -\frac{\sigma_{xx} + \sigma_{yy}}{2} \frac{V_{\mathrm{I}}}{N_{\mathrm{A}}} \tag{1}$$

where V_{I} is the partial molar volume of the interstitial atom at the host matrix, and N_{A} is the Avogadro's number. The pointwise hydrostatic stress field around a singular dislocation can be defined as [10, 12]

$$\frac{\sigma_{xx} + \sigma_{yy}}{2} = -\frac{G}{2\pi(1-\nu)}\left(b\frac{\sin\theta}{r}\right) \tag{2}$$

where r and θ define the coordinates of the point in consideration originated from the dislocation, and G, υ, and b are the Shear modulus, Poisson's ratio, and Burgers vector, respectively (Table 1).

The interaction energy between the interstitial and the internal stress field is used to predict the interstitial concentration in a pointwise fashion around a dislocation based on a Fermi–Dirac formulation [7, 10]:

$$C = \frac{C_0}{\frac{C_0}{\beta N_{\mathrm{L}}} + \left[1 - \frac{C_0}{\beta N_{\mathrm{L}}}\right] \exp\left[\frac{W_{\mathrm{int}}}{kT}\right]} \tag{3}$$

where C stands for the number of interstitial atoms per unit host lattice volume, C_0 is the initial stress-free interstitial concentration, β defines the number of interstitial sites per solvent atom, N_{L} is the number of host atoms per unit lattice volume given by the ratio of molar volume to N_{A}, k is the Boltzmann's constant, and T is the ambient temperature taken as 298 K in this study (Table 1). The relation between the numbers of interstitial atoms per unit lattice volume and per solvent atom is specified as [10].

$$C = cN_{\mathrm{L}} \tag{4}$$

where a local concentration $c_0 = 0.1$ is accepted as an initial guess for iteration. Considering the volumetric expansion due to the introduction of H atom into the host matrix is given by [10, 12]:

$$\Delta v = \frac{V_{\mathrm{I}}}{N_{\mathrm{A}}} \tag{5}$$

The corresponding volumetric strain is defined as a polynomial function of local interstitial concentration, such that

$$e^{\mathrm{H}} = \frac{(c^3 - c^4)\Delta v}{\Psi} \tag{6}$$

where

$$\Psi = \frac{V_{\mathrm{M}}}{N_{\mathrm{A}}} \tag{7}$$

and V_{M} represents the molar volume of the host metal matrix. Considering the dislocation stress field and the relaxation stress due to interstitials, it is important to note that the rate of decrease of the relaxation stress with respect to the distance from the dislocation must be higher than the rate of decrease of the dislocation stress in the regions close to the dislocation, where the stress gradients are large, in order to still have a positive stress field upon relaxation. Even though the magnitude of the positive pointwise dislocation stress is higher than the magnitude of the negative pointwise relaxation stress at the regions close to dislocation, if the decrease rate of the dislocation stress is higher than the rate of relaxation stress, then there is a certain distance from the dislocation at which the magnitude of the negative stress field exceeds that of the positive one and the total stress field turns into compressive state, leading to an incorrect prediction of the interstitial distribution.

While calculating the transformation strain within the lattice due to the introduction of H atoms, the fourth-order polynomial proposed in Eq. 6 ensures a faster decrease of the relaxation stress than that of the dislocation stress, which ideally makes the model valid not only within regions close to the dislocation but also remote from the dislocation. Accordingly, considering that the pointwise strain component is given by [10]

$$\varepsilon_{ij}^{\mathrm{H}} = \frac{e^{\mathrm{H}}\delta_{ij}}{3} \tag{8}$$

the relaxation stress of the H atoms introduced to the host Fe matrix is calculated by

$$\sigma_{ij}^{\mathrm{H}} = -C_{ijkl}\varepsilon_{ij}^{\mathrm{H}} \tag{9}$$

Table 1 The parameters and constants utilized in the model

V_I [13]	G [7]	υ [7]	b [7]
2.66×10^{-6} m^3 mol^{-1}	86 Gpa	0.29	0.248 nm
V_M [14]	β [15]	N_L	k [16]
7.11×10^{-6} m^3 mol^{-1}	6	0.846×10^{29}	1.3806×10^{-23} J K^{-1}

Assuming that the lattice is initially a perfect crystal, a uniform volumetric dilatation is expected upon the introduction of H atoms into the matrix. Thus, in order to determine the relaxation stress of H atoms around a dislocation in Eq. 9, the difference between the local H-induced strain in Eq. 8 and the uniform strain in the case of perfect crystal should be taken, which would give the net strain. However, the elastic modulus Fe is very high, such that the uniform strain in the case of perfect lattice is negligible as compared to H-induced local strain. Therefore, it is not taken into account in Eq. 9.

An iterative model was adopted to calculate the relaxed stress field and the corresponding H distribution around the dislocation. Assuming a local H concentration of $c_0 = 0.1$ at the undistorted regions far from the dislocation, the H distribution around the dislocation was computed without taking the additive relaxation effects into account, which serves as an initial guess for the iteration. Afterwards, the computed initial H distribution was substituted for in Eqs. 6 and 9 to obtain the pointwise transformation strain and relaxation stress. The relaxed stress field was computed by the superposition of the dislocation stress field and the relaxation stress field, and was employed in Eqs. 1 and 3 to compute the new H distribution. The iteration continues until the interstitial distribution error converges to 10^{-5}.

In Fig. 1, the magnitude of the hydrostatic stresses due to the dislocation, and the modified and initial relaxation stresses are shown with respect to the distance from the edge dislocation. Note that the relaxation stresses are indeed negative; however the absolute values are presented in Fig. 1, in order to better visualize the modification. Accordingly, the proposed relaxation stress distribution has a large gradient at the regions close to the dislocation, and as the distance from the dislocation increases, both the magnitude of the relaxation stress and its gradient become smaller (Fig. 1). The low relaxation stress gradient of the initial model predicts the magnitude of the negative relaxation stress larger than the positive dislocation stress field, which yields a compressive field at a distance of 25 Burgers vectors from the dislocation.

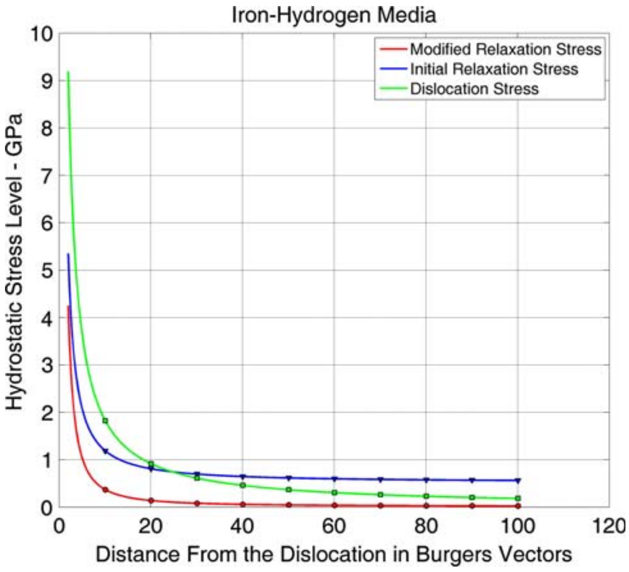

Fig. 1 Evolution of hydrostatic stress with distance from an edge dislocation in Fe–H system

Results and discussion

The current model was proposed with the motivation that a compressive stress field cannot exist around an edge dislocation upon relaxation induced by interstitials, since the interstitial concentration cannot relax the entire tensile stress field around the dislocation, where an ideal case with unconstrained boundary conditions was considered. Specifically, the upper limit of the relaxation is set by the condition that the dilatation caused by the interstitial can be equal to the initial distortion around the dislocation field in magnitude [6]. This means that the deformation upper limit is the expansion of the lattice below the dislocation to the state without distortion, but any further expansion causing compressive stresses is not possible. The interaction energy due to the introduction of interstitials decreases with the expansion of the lattice, such that saturation will take place gradually, where the increase of interaction energy will diminish and no further expansion will take place.

Application of the proposed model to niobium (Nb)–H media yielded results which match those of a previously forwarded model that predicted the H concentration within the vicinity of an edge dislocation [10]. Furthermore, correct prediction of the relaxation stress gradient with the modified model and the corresponding saturation allowed for the computation of the interstitial concentration remote from the dislocation, which was not within the capability of the earlier model [10]. Figure 2 demonstrates the role of additive relaxation on the H distribution in Nb matrix. It is shown that the additive relaxation effect decreased the normalized concentration to almost 50% in the vicinity of the dislocation. The effect of relaxation decreases with distance from the dislocation since the solution becomes more dilute and the normalized concentration approaches unity.

Figure 3 compares the H distributions around an edge dislocation in Fe matrix with and without the additive relaxation effect. Comparing the two sets of results, one can note a remarkable shift in the H concentration at the regions close to the dislocation owing to the additive relaxation. The change in the H concentration with the incorporation of additive relaxation becomes less as the distance from the dislocation increases, since the solution

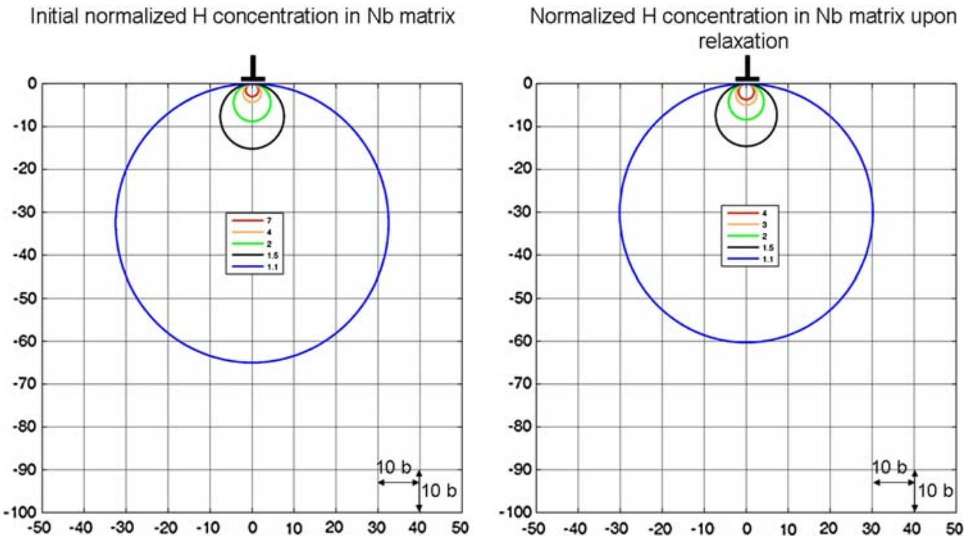

Fig. 2 Initial and post-relaxation H concentration around an edge dislocation in Nb matrix

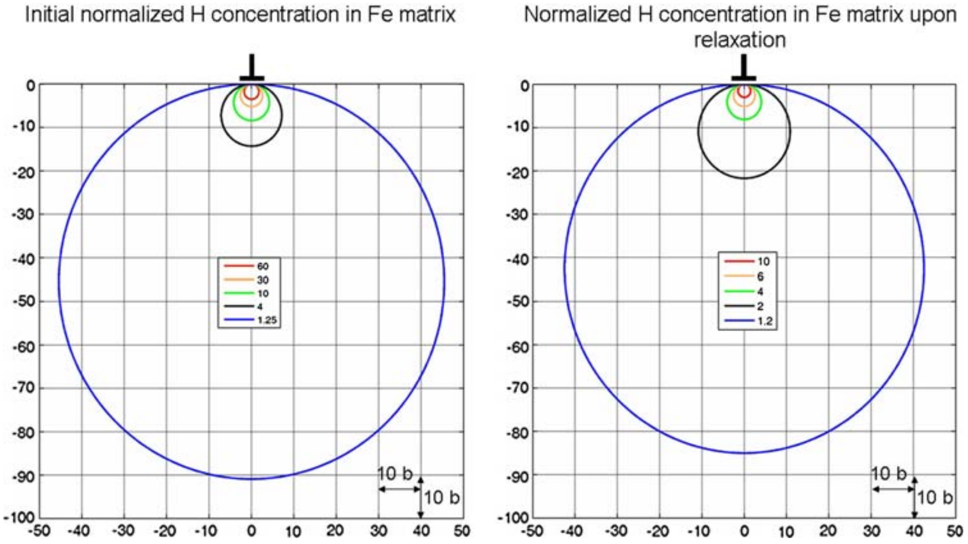

Fig. 3 Initial and post-relaxation H concentration around an edge dislocation in Fe matrix

becomes dilute and additive relaxation effect decays concomitant with the distance from the core of the edge dislocation.

Compared with that of the Nb matrix, the higher interaction energy stemming from the introduction of H into the Fe matrix results in higher H concentration. Specifically, the additive relaxation shifts the concentration around the dislocation significantly in the Fe matrix (Fig. 3), further emphasizing the importance of proper incorporation of the relaxation effects (especially) in the metal matrices with high elastic moduli, where the corresponding interaction energy between internal stress field and interstitials is large and the relaxed and nonrelaxed concentrations differ significantly.

Due to the relaxation of the internal stress field which acts as barriers against slip, the correct prediction of the interstitial distribution around a dislocation is crucial for predicting its mobility [10, 17]. Especially the interstitial concentration remote from the dislocation is of utmost importance for the metal matrices with high moduli, where the concentration is still high at remote from the dislocation as compared with the undistorted regions within the matrix since the relaxation effects on the lattice is effective on larger areas compared with low-modulus materials. Moreover, correct prediction of the final stress state both close to and remote from a dislocation would yield a better estimation of the resulting structure of the lattice upon plastic deformation. The current results show that the proposed model successfully incorporates the mechanical effect of relaxation in the lattice in ideal conditions around a single edge dislocation. Thus, the correct estimation of the lattice structure and its stress state both close to and remote from dislocations opens a new venue for carrying out coupled or dynamic analyses, where more than one mechanical deformation mechanisms, such as planar and cross slip, dynamic strain aging, and dislocation-impurity interactions, are taken into account and wider regions of lattice come into consideration. Predicting the lattice structure in the presence of all such mechanisms may link the effects of interstitial relaxation on the microscopic scale to the macroscopic deformation behavior.

Conclusions

A numerical model was proposed in order to obtain a solution for the problem of mechanical effects of stress relaxation induced by interstitial atoms around a single edge dislocation. The model correctly estimated the relaxed hydrostatic stress distribution around a single edge dislocation due to the introduction of interstitials and the resultant interstitial concentration around the matrix. Specifically, the model takes into account the additive relaxation effect induced by the interstitials, which is even more important in the metallic systems with high elastic moduli where the resultant interaction energy is also high. Moreover, the correct prediction of the relaxation stress field ensures a more realistic estimation of the lattice distortion at the regions relatively far from the dislocation. Consequently, proper incorporation of mechanical effects of interstitials on metal matrices both close to and far from the dislocations constitutes an initial step for developing further models for coupled and dynamic analyses, where both correct estimation of interstitial concentration and lattice distortion are necessary.

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