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Trapping/detrapping kinetic rates of hydrogen around a vacancy in nickel and some consequences on the hydrogen-vacancy clusters thermodynamic equilibrium

Arnaud Metsue*, Abdelali Oudriss, Xavier Feaugas

Laboratoire des Sciences de l'Ingénieur pour l'Environnement, UMR CNRS 7356, Université de La Rochelle, Avenue Michel Crépeau, 17000 La Rochelle, France

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ABSTRACT

The jump rates of H in the interstitial sites of a perfect crystal and in the vicinity of a vacancy in nickel have been determined accurately from *ab initio* calculations up to 1200 K. The migration free energy of H implemented in the Wert and Zener theory for interstitial diffusion is expressed as a sum of static energy, thermal expansion, vibration and electronic contributions. We show that the thermal expansion and the vibrations of the lattice are the major corrections to the migration energy at finite temperature. The computation of the jump rates indicates that the ratio between the trapping and the detrapping frequencies decrease from $\sim 10^4$ at 300 K to ~ 100 at 1200 K. The effects of the elastic displacement field induced by the vacancy on the jump kinetic rates are minor and the solute diffuses similarly to the perfect crystal out of the vacancy core. Finally, we implement a macroscopic rate equation model to evaluate the concentration of mobile and trapped hydrogen atoms as function of time in a one-dimension sample of 1 μm. The comparison of the H-vacancy cluster concentrations formed during H diffusion with the concentrations given by the quasi-equilibrium condition indicates that the system can develop internal stresses at low temperature due to an oversaturation of H-poor defects. These internal stress fields may be associated with the formation of superabundant vacancies and voids implied on the H embrittlement processes.

1. Introduction

The incorporation of hydrogen may lead to irreversible alteration of the mechanical properties and damages in metallic structures at different scales (See Refs. [1–4] for a partial review on the topic). Therefore, the control of the diffusion of this solute in metal is a key factor to prevent hydrogen embrittlement phenomenon. In the case of nickel, previous measurements of the diffusion coefficient D(T) have been conducted with several techniques including permeation tests on single and poly- crystals [5–10]. The values of D(T) are about $10^{-13}\,m^2{\cdot}s^{-1}$ at ambient temperature and increase up to $10^{-8}\,m^2{\cdot}s^{-1}$ for temperatures close to the melting point [7–9]. However, the diffusion coefficient measured experimentally is an apparent diffusion coefficient since it can be influenced by the presence of intrinsic and extrinsic crystal defects: vacancies, dislocations or grain boundaries, as example. Hence, the contribution of each type of crystalline defect on the diffusion coefficient has to be clarified in order to understand and to discuss the values of D(T) obtained experimentally. In addition, it has been demonstrated that hydrogen favors the formation of superabundant vacancies in metals (see Ref. [11], as example), which can also affect the diffusion of the solute. Therefore, the dynamics of the formation of such additional defects and the H diffusion cannot be treated separately.

The crystalline defects interact with H and may act as a diffusion barrier through a so-called trapping phenomenon or may accelerate the diffusion in relation with the notion of excess volume [12]. An energetic profile putting in forward the trapping and the detrapping of a solute is illustrated in Fig. 1. It has been suggested that the vacancy cores are irreversible traps with trapping energies between 0.4 eV and 0.7 eV in fcc crystals [1,12,13]. Previous models have been used to discuss the influence of defects on the H diffusion at meso- and macroscopic scales from analytical derivation of the Fick's equations [14–19] or from Monte Carlo simulations [20,21]. These kinetic models give information on the H apparent diffusion coefficient in presence of defects but have not been used to follow the H-vacancy cluster concentrations with time. From an atomistic point of view, the presence of crystalline defects and their displacement fields changes the value of the diffusion activation energy barrier, i.e. the migration energy [18]. Experimentally, the migration energy for the diffusion as well as the trapping and the detrapping energies of H for each crystalline defect

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* Corresponding author.
E-mail address: arnaud.metsue@univ-lr.fr (A. Metsue).

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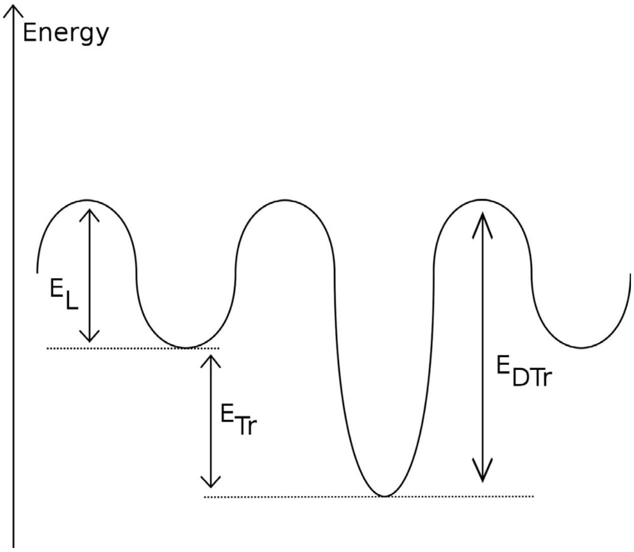

Fig. 1. Illustration of the H potential energy in a crystal containing traps. The migration energy in the lattice E_L, the trapping E_{Tr} and detrapping E_{DTr} energies are defined in the figure.

type can be measured with the thermal desorption spectroscopy (TDS) apparatus and from electrochemical permeation tests [22]. However, some discrepancies exist between the energy values determined from both techniques [23]. Moreover, several uncertainties on the migration energy arise from the evaluation of the temperature in the TDS apparatus or from the formation of a native oxide layer during the permeation test [24], which make difficult a discussion on the contribution of each crystalline defect on the macroscopic diffusion of hydrogen in metals. In addition, the results extracted from the TDS apparatus can be affected by the sample thickness and the heating rate used to measure the hydrogen concentration [25].

An alternative way to determine the migration energy in the perfect crystal or in the vicinity of a crystalline defect is the implementation of atomic scale calculations combined with the Wert and Zener theory [26]. In this theory, the diffusion of the solute is viewed as jumps between the interstitial sites by passing a transition state of high energy. The jump frequency Γ is determined from the migration free energy $\Delta G_{mig}(P,T)$, which is the free energy difference between the transition state along the diffusion path and the free energy at the starting point of the diffusion:

$$\Gamma(T) = \frac{k_B T}{h} e^{\frac{-\Delta G_{mig}(P,T)}{k_B T}} \tag{1}$$

The H diffusion coefficient in Ni perfect crystal has been calculated previously with this technique and the results are in good agreement with experiments up to the melting temperature [27]. The success of the study of Wimmer et al. on the calculation of D(T) comes from the account of the lattice vibration and the thermal expansion contributions to the migration free energy. More recently, *ab initio* calculations have been conducted to determine the trapping and the detrapping energies of H in the vacancy core in nickel [21,28]. However, these previous studies have been limited at static conditions including the zero-point motion energy from the H vibration modes only. This approximation leads to large errors on the jump frequencies compared to the case where all the vibration modes of H and the host matrix are taken into account in the calculation of the migration free energy [27].

In this paper, we calculate accurately the jump frequencies of hydrogen to move in the elastic displacement field induced by a vacancy but also in the defect core in nickel up to 1200 K. We compare these results with the H jump frequency in a perfect crystal. Our method is based on the Wert and Zener theory combined with *ab initio* calculations of the migration free energy, which is expressed as a sum of static energy, thermal expansion, vibration and electronic excitations contributions. Finally, we implement all the calculated H jump frequencies in a one-dimension macroscopic rate equation model proposed by Hodille et al. [29,30], which has been used to model the thermal desorption curves of H in tungsten. We apply this model to follow the kinetics of the H-vacancy cluster formation during diffusion through a membrane. The concentrations of such H-vacancy clusters are compared with the values given by the quasi-equilibrium condition in order to identify possible oversaturation defect concentrations formed during H diffusion.

2. Methods

2.1. Calculation of the H trapping/detrapping jump frequencies at finite temperature

We calculate the hydrogen jump frequencies between the interstitial sites in the displacement field induced by a vacancy but also between the sites inside the defect core. As a reference, we conduct an additional calculation of the jump frequency between two octahedral sites by passing the metastable tetrahedral site in a perfect crystal, since it is the minimum energy diffusion path in fcc Ni [27]. The investigated paths for the H diffusion in the vicinity of the vacancy core are presented in Fig. 2. We investigate also the migration path tangent to the vacancy core in the elastic displacement field induced by the defect following the O2-T2-O2 sequence according to the definition given in Fig. 2.

The jump rate of H is calculated following Eq. (1), which is based on the Wert and Zener theory for the interstitial diffusion [26]. In this equation, the main quantity is the migration free energy $\Delta G_{mig}(P,T)$, which is the free energy difference between the transition state of highest energy along the diffusion path and the starting point of the jump. The transition state for all investigated paths has been determined using the climb nudged elastic band method [31]. We express the migration free energy at finite temperature as a sum of three contributions:

$$\Delta G_{mig}(P,T) = \Delta H_{mig}^{lattice}(P,T) + \Delta G_{mig}^{vib}(P,T) + \Delta G_{mig}^{elec}(P,T) \tag{2}$$

In the previous equation, $\Delta H_{mig}^{lattice}(P,T)$ is static migration energy for the pressure P at the temperature T, $\Delta G_{mig}^{vib}(P,T)$ and $\Delta G_{mig}^{elec}(P,T)$ are the lattice vibration and the electronic excitations contributions to the migration free energy. We limit our study in the case where no hydrostatic pressure acts on the material (i.e. P = 0 bar) and we neglect the effect of the internal pressure at the transition state. $\Delta H_{mig}^{lattice}(P,T)$ is calculated following the thermal equation of states of Ni, which has been determined in a previous study [32], for the volumes corresponding to the temperatures of 0 K and from 300 K to 1200 K with a step of 100 K. The vibration and electronic contributions are calculated at constant volume condition and are converted at constant pressure condition with the same expressions used previously to calculate the solubility of H in Ni [33,34] where the vibration modes are calculated with a direct method implemented in the PHON code [35] and the electronic states from an accurate computation of the electronic density of states. Here, the effects of temperature are evaluated in the quasi-harmonic approximation (QHA), which gives accurate results for the thermodynamic properties of Ni up to 1200 K [32,36]. In addition, we do not consider a possible effect of the ferromagnetic to paramagnetic transition on the H diffusion properties since the temperature dependence of the diffusion coefficient does not exhibit clear discontinuity at the Curie temperature [9].

All of the calculations have been conducted using the framework of the density functional theory (DFT) [37,38], in its spin-polarized implementation in the PWSCF code of the Quantum ESPRESSO package [39]. We use pseudopotentials for H and Ni built with the projected augmented wave method [40], in the formulation of Kresse and Joubert