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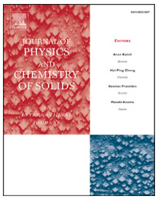

Diffusion coefficients of rare earth elements in fcc Fe: A first-principles study

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ABSTRACT

The diffusion data and corresponding detailed insights are particularly important for the understanding of the related kinetic processes in Fe based alloys, e.g. solute strengthening, phase transition, solution treatment etc. We present a density function theory study of the diffusivity of self and solutes (La, Ce, Y and Nb) in fcc Fe. The five-frequency model was employed to calculate the microscopic parameters in the correlation factors of the solute diffusion. The interactions of the solutes with the first nearest-neighbor vacancy (1nn) are all attractive, and can be well understood on the basis of the combination of the strain-relief effects and the electronic effects. It is found that among the investigated species, Ce is the fastest diffusing solute in fcc Fe matrix followed by Nb, and the diffusion coefficients of these two solutes are about an order of magnitude higher than that of Fe self-diffusion. And the results show that the diffusion coefficient of La is slightly higher than that of Y, and both species are comparable to that of Fe self-diffusion.

1. Introduction

In recent years, rare earth (RE) elements addition has received an increasing interest in steels [1–3]. Many studies have been performed to explore the effect of RE in steels [4–8], such as the purification, solidification, high-temperature oxidation resistance, corrosion resistance and phase transformation. In addition to their deoxidizing and desulfurizing effects, RE elements also form stable RE-rich oxide particles, and consequently refine the grains via the stimulation for nucleation of recrystallization [9,10]. RE elements improve the mechanical performance of steels, in particular the toughness by grain refinement and consequently suppress the grain boundary embrittlement [11], which involved with the segregation of RE in the austenite grain boundaries during thermal deformation process.

For the thorough understanding of the RE related kinetic processes in steels, reliable diffusion data and detailed investigation of the solute diffusivity in Fe are desperately needed, which are also beneficial for designing and preparing of RE alloyed steels [12]. Due to the very low solubility, and impurity contamination during the sample preparation, a precise determination of the RE diffusion coefficients in Fe-based alloys are challenging for the experimental investigation. Consequently, few systematic studies have been reported so far in the literature for the RE diffusivity in Fe [13].

The density functional theory (DFT) has been used to study the diffusivity of solute in several alloy systems. Choudhury et al. [14] systematically investigated the diffusion coefficients of Ni, Cr and Fe in ferritic Fe-Cr and Fe-Ni binary alloys. Taking into account the influence of magnetic moment, Ding and Huang et al. [15–17] investigated the diffusivity of W, Mo, Ta, Hf, Re, Os, Ir, Pt and Au in bcc Fe, and discussed the self-diffusivity of Fe and Co in their bcc lattice system. For the case of RE containing steel, Murali et al. [18] performed first-principles calculations to elucidate the diffusion mechanism of Y in bcc Fe. Our research group studied the diffusivity of La, Ce and Y in bcc Fe based on Le Claire's nine-frequency theory [19]. Apart from providing useful data for kinetic databases, computational investigations also present insights into the corresponding underlying mechanisms of the diffusivity.

In this work, to elucidate the diffusivity of RE in fcc Fe, we employ the density functional theory calculations in combination with the transition state theory (TST) and five-frequency theory to investigate the solute diffusion coefficients of RE (La, Ce and Y) and self-diffusion coefficient of Fe, and discuss the related mechanism via binding energy of solute-vacancy, migration energy of vacancy jumping, correlation factor and the activation energy. Additionally, in order to provide theoretical support for the study of niobium microalloyed steels, we also investigate the diffusivity of Nb in fcc Fe.

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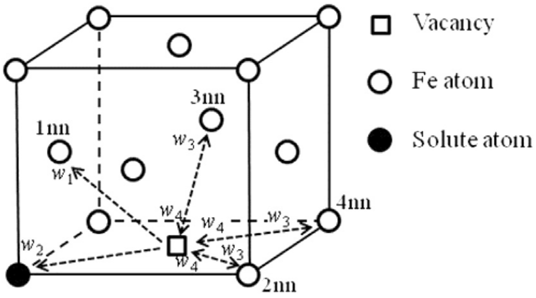

Fig. 1. Schematic drawing of the five-frequency theory for the fcc Fe lattice with a solute atom. w_0 denotes the Fe atom jump in the absence of solute, w_1 represents the Fe atom at the first nearest-neighbor site jump in which the vacancy does not move away from the solute atom, w_2 is the solute atom jump, w_3 is the host Fe atom jump away from the solute atom and vacancy, and w_4 denotes the reverse of jump w_3.

2. Methodology

Dominant mechanism in the process of diffusion for substitutional solutions and self-diffusion is based on vacancies, and comprises two steps: the formation of a vacancy near the solute atom and the migration of the vacancy to the position of the solute atom. We based our investigation on the assumption that the diffusion mechanism is mono-vacancy mediated [13]. For the fcc lattice, the coefficients of Fe self-diffusion and solute diffusion can be expressed as following [20]:

$$D_{self} = a^2 f_0 C_v w_0 \tag{1}$$

$$D_{solute} = a^2 f_2 C_v w_2 \exp(-\Delta G_b / k_B T) \tag{2}$$

where a is the fcc lattice parameter, $f_0 = 0.7815$ [21]is the correlation factor for self-diffusion, f_2 denotes the correlation factor for solute diffusion, C_v represents the vacancy concentration, w_0 and w_2 are the vacancy jump frequencies for Fe and impurity atoms to exchange with their 1nn vacancies, respectively. ΔG_b represents the binding free energy of solute-vacancy, k_B denotes the Boltzmann's constant and T is the absolute temperature. The vacancy concentration in thermal equilibrium is defined as:

$$C_v = \exp(-\Delta G_f / k_B T) = \exp\left(\Delta S_f^{vib} \big/ k_B\right) \exp(-\Delta H_f / k_B T) \tag{3}$$

where ΔG_f represents the free energy of vacancy formation, ΔH_f and S_f^{vib} are the enthalpy and vibrational entropy for vacancy formation, respectively. We calculated the vacancy formation enthalpy by the first-principles as $\Delta H_f = E_{vac}$-$[(N\text{-}1)/N]E_{bulk}$, where E_{vac} represents the total energy of the supercell which containing N-1 atoms and one vacancy, and E_{bulk} denotes the energy of the supercell within N atoms. And the vacancy formation entropy can be computed in a similar manner within the methodology of harmonic approximation [16]:

$$\Delta S_f^{vib} = k_B \left[\sum_{i=1}^{3(N-1)} \ln\left(k_B T / h\nu_i^{vac}\right) - \frac{N-1}{N} \sum_{i=1}^{3N} \ln\left(k_B T / h\nu_i^{bulk}\right) \right] \tag{4}$$

where h represents the Planck's constant, ν_i^{vac} is the vibrational frequencies in the supercell within N-1 Fe atoms and one vacancy, and ν_i^{bulk} represents the frequencies in the pure supercell containing N Fe atoms.

According to Eyring's reaction rate theory [22], the jump frequency of solute-vacancy exchange is described as following:

$$w = \nu^* \exp(-\Delta H_m / k_B T) \tag{5}$$

where ΔH_m denotes the vacancy migration energy, i.e. the energy difference of the investigated diffusing atom in its saddle-point position and the initial equilibrium lattice position. ν^* denotes the effective frequency in terms of Vineyard's harmonic TST (transition-state theory) [23]:

$$\nu^* = \prod_{i=1}^{3N-3} \nu_i^{vac} \Bigg/ \prod_{i=1}^{3N-4} \nu_i^{sad} \tag{6}$$

where ν_i^{vac} and ν_i^{sad} represent the vibrational frequencies for the atoms of investigated system in the initial state and transition state, respectively, and the product in the denominator neglects the imaginary frequency corresponding to the unstable mode of the transition state.

The binding free energy of solute-vacancy ΔG_b is calculated in terms of the binding enthalpy ΔH_b and entropy ΔS_b:

$$\Delta G_b = \Delta H_b - T\Delta S_b \tag{7}$$

where the binding enthalpy can be calculated as $\Delta H_b = E_{sol,vac} + E_{bulk}$-$E_{sol}$-$E_{vac}$, in which $E_{sol,vac}$ denotes the total energy of the supercell within one solute-vacancy pair, E_{sol} denotes the energy of the supercell with one solute atom, and a negative binding enthalpy means attractive interaction between the solute atom and its adjacent vacancy. And the binding entropy is written as following:

$$\Delta S_b = k_B \left[\sum_{i=1}^{3(N-1)} \ln\left(\nu_i^{vac} / \nu_i^{vac,sol}\right) + \sum_{i=1}^{3N} \ln\left(\nu_i^{sol} / \nu_i^{bulk}\right) \right] \tag{8}$$

where $\nu_i^{vac,sol}$ is the vibrational frequencies of a fcc Fe supercell with a solute-vacancy pair, and ν_i^{sol} denotes the frequencies of a fcc Fe supercell containing one solute atom.

The solute atom can jump back to its original site after it has exchanged position with its nearest-neighbor vacancy. One can measure the probability of the solute atom making a reverse jump via the correlation factor f_2, i.e. the correlation factor represents the extent to which the impurity diffusion deviates from the perfect walker. According to the five-frequency theory from Le Claire et al. [24], the correlation factor involves five jump frequencies as shown in Fig. 1, is expressed as following [25]:

$$f_2 = \frac{2w_1 + 7w_3 F}{2w_1 + 2w_2 + 7w_3 F} \tag{9}$$

where F is expressed in terms of the ratio of w_4 and w_0 [26]:

$$F = 1 - \frac{10\xi^4 + 180.5\xi^3 + 927\xi^2 + 1341\xi}{7\left(2\xi^4 + 40.2\xi^3 + 254\xi^2 + 597\xi + 436\right)} \tag{10}$$

where $\xi = w_4/w_0$.

For the case of five-frequency model, as shown in Fig. 1, there are three dissociative jumps w_3 from the 2nn 3nn and 4nn positions and three opposite jumps w_4 to these 3 positions, each of the jumps contains different distance and barrier. By taking account the distinct pathway for solute-vacancy dissociation and association, the effective rates of w_3 and w_4 are expressed as:

$$7w_{3(4)}^{eff} = 2w_{3(4)}^{2nn} + 4w_{3(4)}^{3nn} + w_{3(4)}^{4nn} \tag{11}$$

For convenience, the diffusion coefficients calculation Eqs. (1) and (2) can be convert into the Arrhenius form, and accordingly we can obtain the corresponding pre-factor D_0 and activation energy Q of diffusion:

$$D = D_0 \exp\left(-\frac{Q}{k_B T}\right) \tag{12}$$

We performed the first-principles calculations by using the projector augmented wave (PAW) method implemented in the Vienna Ab initio Simulation Package (VASP), and with the generalized gradient approximation of Perdew-Burke-Ernzerhof functional (GGA-PBE) [27]. The computations performed within a 3 × 3 × 3 fcc supercell containing 108 atoms. The solute-vacancy binding energies, vacancy formation energies