Determination of Activation Energy for Helium Diffusion in Nickel

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1. Introduction

Ni-based alloys are one of the candidate materials for in-core applications in molten salt reactor (MSR) because of their outstanding high-temperature strength and high corrosion-resistance. However, embrittlement due to helium atoms, which are primarily generated by neutron transmutation reaction of (n,α), is a potentially limiting factor for their application. The MSRE (Molten Salt Reactor Experiment) program showed that the most challenging issue for MSR structural materials was He embrittlement in Ni-based alloys, such as Hastelloy N [1,2]. Although the detrimental effect of He on the Ni-alloys is well-known, the atomistic behavior of He in Ni is little understood.

We are interested in fundamental understanding of He embrittlement in Ni-alloys. The first step is to evaluate the crucial parameter governing the behavior of He, which is the He diffusivity (D_{He}) in Ni. In this work, two types of He-diffusion mechanism are considered for evaluating the D_{He}; the interstitial migration and the dissociative mechanism. The activation energies for each mechanism were estimated by using a molecular dynamics (MD) code, LAMMPS 'Large-scale Atomic/ Molecular Massively Parallel Simulator' [3]. Then, the calculated activation energies for D_{He} will be employed for the subsequent study, which include the modeling for He embrittlement in Ni-alloys.

2. Methods

Diffusion is a random process, which follows an Arrhenius-type temperature dependence. This means that the diffusivity increases with temperature in an exponential manner such as:

$$D(T) = D_o exp\left(-\frac{E_m}{k_B T}\right) \quad (1)$$

where D_o is pre-exponential factor, E_m is the activation energy for diffusion, k_B is the Boltzmann constant and T is temperature. Because the energy E_m varies depending on the specific diffusion mechanism, its understanding is indispensable for determining E_m.

In estimating the activation energy for He diffusion in Ni, we used the LAMMPS code [3]. Two different methods for calculating the energy E_m were applied depending on the diffusion mechanisms. One is the interstitial diffusion and the other is the diffusion by dissociative mechanism (dissociative diffusion). We briefly describe each mechanism and its calculation method.

2.1 Interstitial Diffusion

Interstitial diffusion is a type of atomic diffusion in solids where small He atoms move through the interstices between Ni atoms, as shown in Fig. 1. It is generally faster than other diffusion mechanisms. The D_{He} in Ni has the following relation such as:

$$|\Delta r^2(t)| = 6\, D_{He} t \quad (2)$$

where $|\Delta r^2(t)|$ is the mean squared displacement (MSD) of He, which describes how far, on average, a particle of He migrates from the initial position after time t. Since the MSD is linearly proportional to the diffusivity and the time, we can readily estimate D from Eq. (2). In LAMMPS, the MSD of a group of atoms can be obtained from a proper command. By observing the MSD of He atoms as a function of temperature, E_m can be derived from the Arrhenius plot.

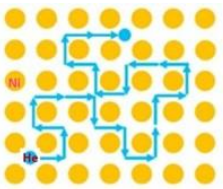

Fig.1. He diffusion path by interstitial mechanism (He: cyan, Ni-lattice atoms: yellow)

2.2 Dissociative Diffusion

At elevated temperature, He atoms in Ni might exist in substitutional sites, from which they diffuse by a dissociative mechanism. This mechanism refers to a mode of atomic motion in which He atom moves through Ni by breaking apart and then recombining with other vacancies as shown in Fig. 2. High concentration of vacancy is common under irradiation. In case of dissociative diffusion, the activation energy E_m can be calculated by applying the Nudged Elastic Band (NEB) Method [4]. The NEB is an optimization algorithm used in computational science to find the minimum energy

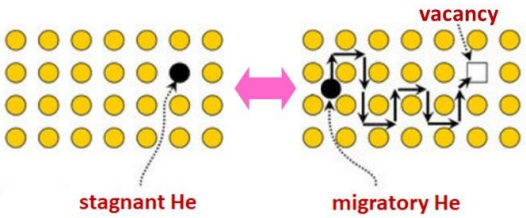

Fig. 2. He diffusion process in Ni by dissociative mechanism

pathways (MEPs) between two known states. Because this method is helpful in identifying reaction barriers, it is used in such areas as solid-state physics, catalysis and molecular simulations. In the LAMMPS code, the NEB method is implemented to find the MEPs. Hence, we applied this method to calculate the He activation energy, E_m by a dissociative diffusion and the results were described in the next section.

3. Results

3.1 Activation Energy from MSD Calculation

There is a built-in function of evaluating the MSD in LAMMPS, from which we determined the diffusivity and its activation energy. For a given temperature, the MSD was computed over large samples and its average was taken. Then, the linear regression model was applied for approximating the relation between D_{He} and MSD, as shown in Eq. (2). The slopes estimated from the linear regression model represent the diffusivity D_{He}, which are listed in Table I with the standard error. By plotting ln (D_{He}) vs. (1/T), we could determine the activation energy. The Arrhenius plot is displayed in Fig. 3, from which the activation energy for D_{He} in Ni was found to be 0.13 ± 0.02 eV.

Table I: Linear regression statistics of MSD

Temperature (K)	Slope	R-square
723	3.248±0.923	0.579
823	4.148±1.242	0.553
923	8.573±0.915	0.907
1023	11.938±1.550	0.868
1123	16.241±0.817	0.978

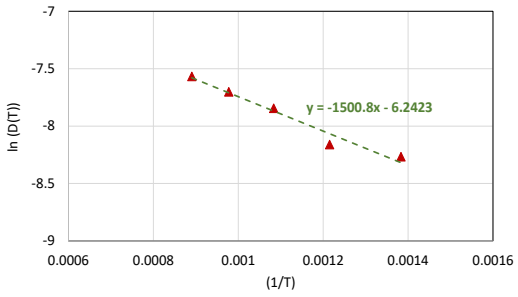

Fig. 3. Arrhenius plot of ln (D_{He}) vs. (1/T) for deriving the activation energy for He-interstitial diffusion

3.2 Activation Energy from NEB Methods

We used the NEB method in LAMMPS to calculate activation energies for D_{He} in Ni. In this method, the atomic configurations in the initial and final states need to be defined by the user. Fig. 4 shows two possible pathways of He migration in Ni. He atom, which was positioned initially in the lattice position, might move to the 2nd nearest interstitial positions, which are either tetrahedral or octahedral. The activation energy E_m for each migration path was evaluated by the LAMMPS code, which was displayed in Figs. 5. Depending on the choice of a spring constant k, there is somewhat difference in the activation energy. In these figures, the horizontal axis of reaction coordinate implies the diffusion path, where the number of zero represents the initial configuration and the number one is the final one.

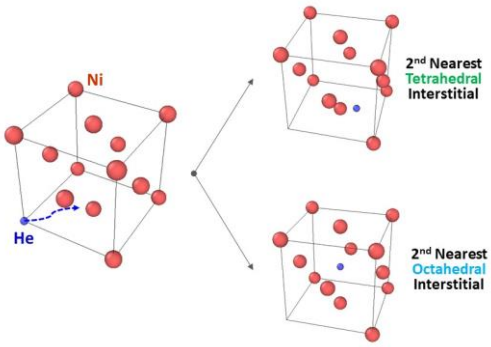

Fig. 4. Possible diffusion paths of He atom in Ni - Helium migration to the 2nd nearest tetrahedral (up) / octahedral interstitial position (down)

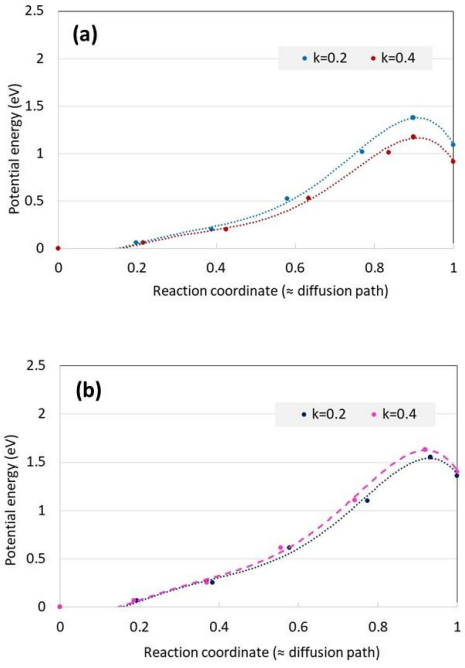

Fig. 5. Energy profile of He diffusion path for migrating to (a) tetrahedral and (b) octahedral interstitial site, as calculated by NEB method.

The activation energy for He migration to the tetrahedral position was 1.17 to 1.37 eV in Fig. 5(a), while that to the octahedral site ranged from 1.57 to 1.65 eV in Fig. 5(b). The differences in the activation barrier for dissociative mechanism were found depending on the diffusion path.

4. Discussion

The presence of He in Ni-alloys causes a negative effect on materials performance. A knowledge of the behaviors of He atoms in a metal lattice is the basis of fundamental understanding of He effects on materials. The critical parameters governing the He behavior in Ni are the energies of He atoms at specific sites in perfect and imperfect lattices. In this paper, we investigated the activation energies for D_{He} in Ni by employing the MD simulations.

The activation energies of D_{He} by the interstitial and dissociative mechanism were calculated by the LAMMPS code. The energy for He-interstitial diffusion, estimated from the MSD calculation, was 0.13 ± 0.02 eV, which is very close to the measured value of 0.14 ± 0.03 eV [5]. On the other hand, the activation energies by dissociative mechanism, evaluated by the NEB method, ranged from 1.17 to 1.65 eV, which varies with the diffusion paths. Reed et al. reported the activation energy of 1.3 eV from measurements and 1.29 eV from calculations [6]. The activation energy by dissociative diffusion was much higher since the dissociation process impedes the migration of He atoms by combining with vacancies. Under irradiation conditions, it is expected the dissociative diffusion would be prevalent due to the abundant presence of radiation-induced Frenkel defects. Finally, it should be pointed out that the parameters, related to D_{He} in Ni, would play an important role in predicting the bulk properties of Ni-alloys, which include embrittlement and swelling.

Acknowledgements

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