First-principles Study of Chromium Effects on Oxygen Diffusion in Ni-Cr binary Alloy

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1. Introduction

Nickel base alloys have been widely used as structural materials in nuclear systems However, these materials have shown to suffer from environment-assisted cracking (EAC) such as primary water stress corrosion crack (PWSCC) in pressurized water reactor environments, which is generally considered as a cracking phenomenon caused by a combined process of corrosion/oxidation and strain on a metal due to residual or applied stressed within the susceptible environment. Many experimental studies have been performed to explain the governing mechanism of EAC of nickel base alloys and have drawn several different arguments with some possible ways to reveal the process and prevent it[1, 2]. However, there is no general theory to explain the EAC of nickel base alloys, because the EAC is a very complex phenomena affected by many parameters and the corrosion/ oxidation process takes place slowly in tiny localized areas. Meanwhile, according to the increase in the computer calculation capability, atomistic modeling and simulation methods have been receiving much attention as an alternative way to evaluate the mechanical properties and thermodynamic properties of metals and alloys.[3, 4]

Therefore, this study's aim is to understand the corrosion/oxidation behavior of nickel base alloys through the simulation of the diffusion processes of oxygen in pure Ni as well as Ni-Cr binary alloy.

2. Experimental Procedure

In this study, the first-principles calculation, which solves the Shro¨dinger equation with no experimental data, was used as a computational method. The calculations were performed by the Vinena First-principle Simulation package (VASP) [5] . The plan-wave cut off energy was set as 400 eV for all calculations and 3 × 3 × 3 and 5 × 5× 5 Monkhost-Pack meshes were used to test the Brillouin zone in the reciprocal space, depending on the size of the studied unit cell. To determine the insertion energies of oxygen and vacancy formation energy in Ni, three different sizes (2x 2x 2, 3x 3x 3 and 4x 4x 2) of FCC (face-centered cubic) supercell having 32, 108 and 128 lattice sites were used to calculate the Ni and NiO bulk energy. To calculate the chromium effects on oxygen diffusion, nickel replaced with chromium as the nearest-neighbor (NN) atoms of oxygen and calculation of the activation energy of oxygen diffusion were performed as the number of NN chromium atoms changes. Figure 1 illustrates the calculation model focusing on the oxygen and its NN chromium atoms for each supercell.

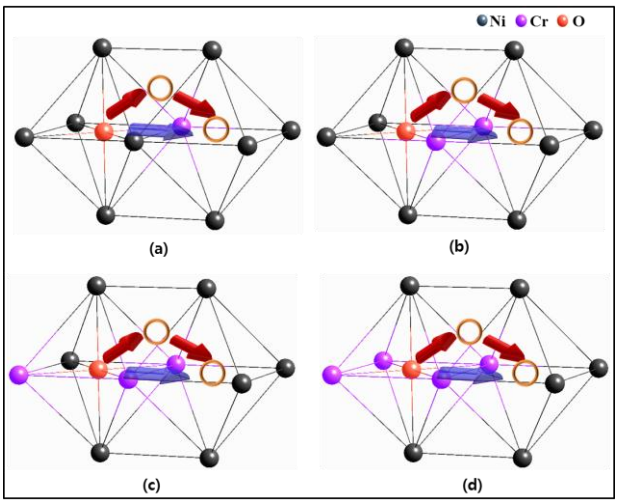

FIG. 1. Oxygen diffusion model with different number of nearest-neighbor(NN) chromium atoms
(a) 1 NN Cr, (b) 2 NN Cr, (c) 3 NN Cr, (d) 4 NN Cr

3. Results and Discussion

The calculation results of activation energy of oxygen diffusion in Ni-Cr binary alloy show the different aspect as the number of NN chromium atoms increase on oxygen. Figure 2 shows the energy of oxygen transport calculated by NEB method according to the number of NN chromium atoms in Ni-Cr binary alloy along the two difference pathway. In pure nickel, the activation energy of oxygen diffusion along the O-O pathway and O-T-O pathway are 144eV and 1.12eV, respectively.

In case of 1NN and 2NN Cr, the activation energy is lower than that in pure nickel. These chromium atoms exist on the middle of the diffusion pathway. The chromium has smaller atomic radius and number of electrons than those of nickel, which are 128pm and 24 electrons while nickel has 163pm van der vaals radius and 28 electrons. Therefore, the space for oxygen diffusion between nickel and chromium or chromium and chromium is larger than for nickel and nickel. And smaller number of electrons causes the lower repulsive force than for nickel when the oxygen comes closer, which account for the lower activation energy than that of pure nickel.

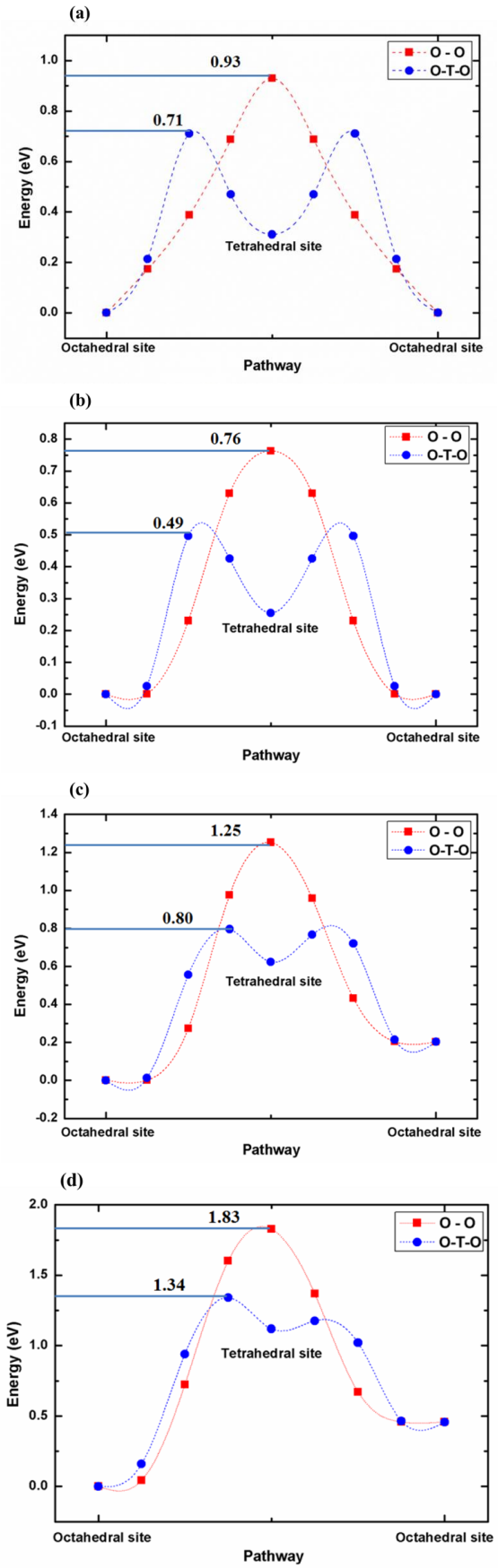

Fig 2. Energy of oxygen transport calculated by NEB method in Ni-Cr binary alloy
; (a) 1 NN Cr, (b) 2 NN Cr, (c) 3 NN Cr, (d) 4NN Cr

In case of 3 and 4 NN chromium, the activation energy of oxygen diffusion dramatically increases. That can be explained in terms of oxygen affinity. Since the 3rd and 4th chromium atoms added exist on the opposite direction of the oxygen diffusion, the oxygen should become far from 3rd and 4th chromium to diffuse. However, the chromium has very strong oxygen affinity thereby higher energy is required for the oxygen to diffuse. Finally, the activation energy of oxygen diffusion with 4 NN chromium atoms is higher than that of pure nickel.

It has been reported that, the Ni-Cr binary alloy forms FCC structure with <20wt% of chromium and the chromium gather each other and widely spread in nickel basement. Consequently, the oxygen diffusion in Ni-Cr binary alloy will be very similar to 4 NN chromium case in this study. According to the calculation results, it seems evident that the activation energy increases when chromium is included in this study, and the chromium plays a role of diffusion barrier.

CONCLUSION

This work was focused on the prediction of oxygen diffusion behavior in Ni-Cr binary alloy in order to understand the fundamental corrosion/oxidation behavior of nickel base structural alloys. The VASP calculation package was used for the first-principles calculation. According to the results, it can believe that the chromium take a role of diffusion barrier.

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