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Ab-initio Calculation of Diffusion of Atomic Oxygen in Nickel : Insertion and Substitution of Oxygen in Nickel

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1. Introduction

Nickel and nickel base alloys have been widely used as structural materials in nuclear systems because they have good mechanical properties at high temperature, high pressure and high corrosion resistance in oxidizing environment. Recently, however, these materials have shown to be suffered from the environment-assist cracking (EAC) such as primary water stress corrosion crack (PWSCC) in pressurized water reactor environments. SCC is a cracking phenomena because of a process involving conjoint corrosion and strain of a metal due to residual or applied stressed within the susceptible environment.

Many experimental studies have been performed to reveal the governing mechanism of PWSCC of nickel base alloys and have drawn several different arguments with some possible ways to reveal the process and prevent them, such as oxide rupture[1,2], accumulation of critical crack tip strain[3,4] or hydrogen induced cracking[5]. However, there is no general theory to explain the PWSCC of nickel base alloys, because the experiments of SCC usually take a lot of times, have difficulty to make specific environment of nuclear power plants water chemistry, and the corrosion (or oxidation) process takes place slowly in tiny localized area.

Meanwhile, according to the increase in the computer calculation speed, atomistic modeling and simulation method has been receiving much attention as a method to evaluate the mechanical properties, thermodynamics and kinetics characteristics of metals and alloys. Very recently, modeling and simulation studies have been performed to understand the fundamental mechanism of nickel and nickel base alloy corrosion (oxidation) process in high temperature water.

For pure nickel, Grruchet et al [6] evaluated diffusion of oxygen in nickel by the variable charge molecular dynamics, and Goerge A. Young et al[7] and Meg-chiche [8] evaluated the diffusion of oxygen in nickel using the ab-initio (first-principle) calculation. Also, Finnis et al [9] and Lozovoi et al[10] calculation explored some properties about oxidation of bimetal such as NiAl. All of them have compared the computational data with the experimental data and the results have shown good agreement.

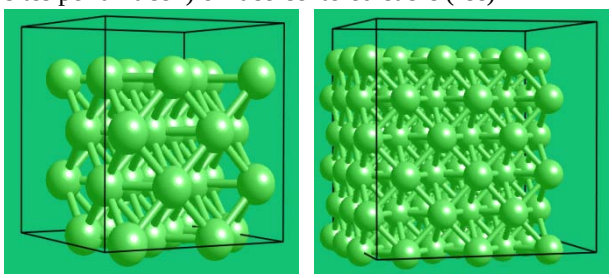
Still, however it is not enough to understand the corrosion behavior detail and to prove the accuracy of the computational results.

The purpose of this study is to understand the oxidation behavior of nickel base alloys through the simulation of diffusion processes of oxygen in nickel. Therefore the diffusivity and solubility of oxygen in nickel followed by previous study[8] was calculated. And, the vacancy formation energy of nickel was calculated and the calculation of insertion and substitution energy of oxygen in nickel was performed. Furthermore, this method will be applied to atomistic oxygen diffusion in nickel -chrome binary alloy.

2. Calculation method

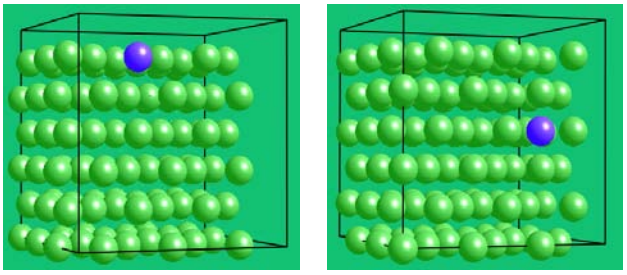
In this study, ab-initio calculation was used as computational method ab-initio calculation solves the Shrödinger equation with no experimental data. The calculations were performed by Vinena Ab-initio Simulation package (VASP) developed at the Institute für Materialphysik of the Universität Wien [11,12]. The calculation get the total energies, forces, and energy profiles using density function theory [13,14] with spin-polarization concerning, which calculation with the generalized gradient approximation(GGA) [15,16] and projected-augmented wave(PAW) method[17,18]. The GGA was used with the exchange-correlation functional of Perdew and Wang(PW91)[19]. The reason of using the GGA method is that it uses some recent theoretical studies which showed highest accuracy than other approximations such as the local density approximation to describe various properties of Ni bulk [20] or to calculate the formation and migration enthalpies of vacancies in nickel [21]

The plan-wave cut off energy set 400eV for all calculations and the kpoints used $4 \times 4 \times 4$ and $6 \times 6 \times 6$ Monkhost-Pack[24] meshes used to test the Brillouin zone in the reciprocal space, depending on the size of the studied unit cell. supercell were tested To determine the insertion and substitution energies of oxygen, 2x2x2 and 3x3x3 two sizes (32 and 108 lattice sites per unit cell) of face-centered cubic (fcc)



(a) 2x2x2(32atoms) (b) 3x3x3(108atoms)

Fig 1. Tested bulk Ni face-Centered Cubic(FCC) supercell



(a) Substitution (b) Insertion

Fig 2. Tested Supercell : (a) 107Ni + O, (b) 108Ni + O

Before the every test step, the lattice relaxation task was performed by using a conjugate-gradient algorithm for insertion energies and all ions were allowed to relax while the supercell volume was kept constant and shape could change. The charge transfer between oxygen and nickel was determined with the algorithm of Henkelman et al[25], which carried out a Bader decomposition[26] of the electronic charge density into atomic contribu-tions. In order to determine the diffusivity of oxygen in nickel, it was needed to calculate the activation energy E_0^{act} for the possible diffusion path way. For the saddle point corresponding to the migration of the atomic oxygen, the energy pathways was obtained by using the nudged elastic band(NEB) method of Henkelman and Jónsson [22] .

3. Results

The vacancy formation energy is defined as

$$E_{Ni}^{vac} = E_{nNi} + E_{Ni}^{coh} - E_{(n-1)Ni}$$

,where E_{Ni}^{coh} is the cohesive energy of nickel.

Table 1. Vacancy energy of Ni(eV)

2x2x2	3x3x3	Garruchet [27]
1.39	1.4	1.4 ~ 1.8

The vacancy formation energy of Ni was calculated to be 1.4eV in this work which is compatible with previous work[29 and references therein] The insertion Energy is defined as

$$E_0^{ins} = E^{nNi} + E_0 - E^{nNi+O}$$

,where E^{nNi+O} is the total energy of the supercell containing n Ni atoms and the O atom inserted in the octahedral or tetrahedral site, E^{nNi} is the total energy of the supercell, and E_0 is the energy of the oxygen atom.

Table 2. Insertion energy of O in Nickel(eV)

2x2x2	3x3x3	park [23]
4.39	3.38	3.12

The experimental values of E_0^{ins} 3.12eV, by the Park and Altstetter's work [23]

4. Summary

This work was focused on the prediction oxygen diffusion behavior in pure nickel in order to understand the fundamental oxidation behavior in nickel metals and nickel base alloys. The VASP calculation package was used for ab-initio calculation. The vacancy formation energy and Insertion energy of oxygen in nickel is 1.4eV and 3.38eV, respectively, and the results agree well with previous studies. The calculation of substitution energy of oxygen in nickel and activation energy of diffusion of oxygen with two possible path ways will be performed in the future. Furthermore, this calculations will be applied to atomistic oxygen diffu-sion in Ni-Cr binary alloy.

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