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Ab-initio Calculation of Diffusion of Atomic 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 and high pressure and 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 due to 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 explain the governing mechanism of PWSCC of nickel base alloys and have a lot of 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 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, S. Grruchet et al [6] evaluated diffusion of oxygen in nickel by the variable charge molecular dynamics, and Goerge A. Young et al [7] and E H Meg-chiche [8] evaluated the diffusion of oxygen in nickel using the ab-initio (first-principle) calculation. Also, M.W. Finnis et al [9] and Alexander Y. 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.

But still it is not enough to understanding the corrosion behavior 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 and calculation of the diffusivity and solubility of oxygen in nickel followed by previous study [8]. Temperature variation is considered and accuracy is improved in the calculation.

2. Method of Calculation

2.1 Vienna Ab-initio Simulation Package

Ab-initio calculation solves the Shrödinger equation with no experimental data.

The Shrödinger equation is

$$\mathrm{H}\Psi = \mathrm{i}\frac{\partial\Psi}{\partial \mathrm{t}} \tag{1}$$

,where H is Hamiltonian operator, given as sum of kinetics and potential energy

$$\mathrm{H}_{\mathrm{Schrödinger}} = \mathrm{T} + \mathrm{V} \tag{2}$$

$$\mathrm{T} = \frac{\mathrm{P}^2}{2\mathrm{m}} = -\frac{1}{2\mathrm{m}}\nabla^2 \tag{3}$$

The calculations are performed by Vinena Ab-initio Simulation package(VASP) developed at the Institute für Materialphysik of the Universität Wien [11,12]. The calculation of using the VASP get the total energies, forces, and energy profiles using Density Function Theory [13,14], which calculation with the generalized gradient approximation(GGA) [15,16] and the pseudo-potential method [17]. The reason of using the GGA method is that it used some recent theoretical studies showed more good accuracy than other approximations such as the local density approximation to describe various properties of Ni bulk [20,21] or to calculate the formation and migration enthalpies of vacancies in nickel [22]

To solve the Kohn-Sham equations of DFT use the plane wave basis set[18] and projector augmented-wave (PAW) method [19] to decrease the computational time.

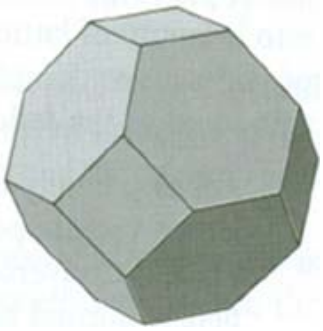

Fig 1. First Brillouin zone for Ni(fcc)

Concerning the computational parameters, $4 \times 4 \times 4$ and $6 \times 6 \times 6$ Monkhost-Pack[26] meshes are 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, two sizes (32 and 108 lattice sites per unit cell) of face-centered cubic (fcc) primitive cell were tested. Before the every test step, the lattice relaxation task performed by using a conjugate-gradient algorithm for insertion energies and all ions are allowed to relax whiled the supercell volume is kept constant. The charge transfer between oxygen and nickel is determined with the algorithm of Henkelman et al[27], which carries out a Bader decomposition[28] of the electronic charge density into atomic contributions.

2.2 Diffusivity and solubility of oxygen in nickel

In order to determine the diffusivity of oxygen in nickel, it is need to calculate the activation energy E_O^{act} for the possible diffusion path way. For the saddle point corresponding to the migration of the atomic oxygen, the energy pathways are obtained by using the nudged elastic band (NEB) method of Henkelman and Jónsson [23,24] as same as E H Megchiche [8] work
The diffusivity is defined as

$$D = D_0 \exp\left(-\frac{E_O^{act}}{RT}\right) \quad (4)$$

And the solubility is defined as

$$C^s = C_0^s \exp\left(-\frac{E_O^{sol}}{RT}\right) \quad (5)$$

,where the E^{sol} is the solution energy, given by

$$E_O^{sol} = E_O^{ins} - \frac{1}{2}E_{O_2} \quad (6)$$

The E_{O_2} is the dissociation energy of the O_2 molecule in the gas phase. And the insertion Energy is defined as

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

,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_O is the energy of the oxygen atom.

The experimental values of E_O^{ins} and E_O^{act} are 3.12eV and 1.71eV, respectively, by the Park and Altstetter's work [25].

There are two possible ways for oxygen to diffuse in nickel. The first one is the movement of the oxygen from the octahedral site to the other octahedral site directly, and the second is moving the oxygen from octahedral site and stop by the tetrahedral site and then reach the other octahedral site. To find the proper oxygen path way in nickel, the activation energy at each case is calculated and compared.

3. Summary

This work is 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 is used for Ab-initio calculation, and the diffusivity and solubility of atomic oxygen in nickel are calculated and compared with experimental data. Furthermore, this work is performed with temperature change to know the temperature effect on the diffusivity and solubility. Finally, from the comparison with the each activation energies of two possible diffusion ways of oxygen, it is possible to show the oxygen paths in nickel as a function of temperature.

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