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Ab-initio Calculation of Diffusion of Atomic Oxygen in Ni and Ni-Cr

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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 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 and it growth along the grain boundary.

To reveal the major mechanism of SCC have done many experiments and have a lot of arguments with some possible ways to explain the corrosion process and many experts try to find the method to mitigate or prevent it.

There are many opinions such as Oxide rupture[1,2], accumulation of critical crack tip strain[3,4] or hydrogen induced cracking[5], but nothing can explain the mechanism clearly and the experiments of SCC usually take a lot of times , have difficulty to make specific environment like primary water in nuclear power plants and the corrosion takes place in tiny localized area, so it is hard to clearly defined.

. 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.

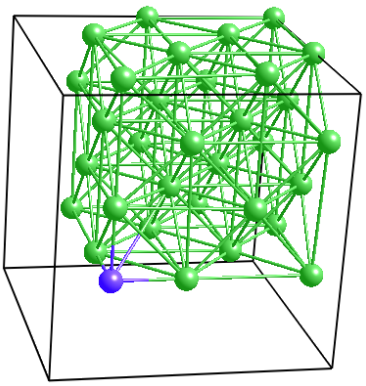
For pure nickel, S. Grruchet et al [6] evaluated diffusion of oxygen in nickel by the variable charge molecular dynamics, and Goerge A. Young et al [7] and E H Megchiche [8] evaluated the diffusion of oxygen in nickel using the ab-initio (first-principle) calculation.. But still it is not enough to understanding the corrosion behavior and to prove the accuracy of the computational results.

The purpose of this work is to understand the oxidation behavior of nickel base alloys through the simulation of diffusion processes of oxygen in nickel and nickel-chromium binary alloy

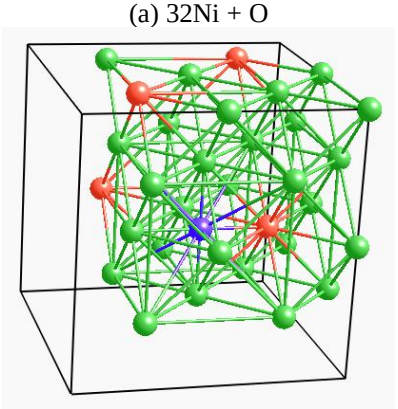
2. Calculation Method & Results

Ab-initio calculation solves the Shro¨dinger equation with no experimental data. The calculations are performed by Vinena Ab-initio Simulation package (VASP) developed at the Institute fu¨r Materialphysik of the Universtiat Wien [11]. The calculation get the total energies, forces, and energy profiles using Density Function Theory [12] with spin-polarization concerning, which calculation with the generalized gradient approximation(GGA)[13] and Projected augmented wave (PAW) method[14]. The GGA is used with the exchange-correlation functional of Perdew and Wang(PW91) for all calculation

Fig 1. Shows the supercells for calculation. The green balls represent nickel atoms, red balls represent chromium atoms and violet is oxygen.



(a) 32Ni + O



(b) 28Ni+4Cr+O

Fig 1. Calculcation supercells ((a) Pure Nickle, (b) Ni-Cr binary alloys)

The supercell contains 32 nickel atoms and 1 oxygen and to describe the Alloy 600 Ni-base alloy(Chemical composition : 72%Ni, 15%Cr wt%), 28Nickel + 4 Chromium supercell was used for Ni-Cr binary alloy

Fig. 2 Shows the possible diffusion pathway of oxygen in nickel. Oxygen diffuses from octahedral site to octahedral site directly(O-O, blue arrow), or step by tetrahedral site(O-T-O, red arrow).

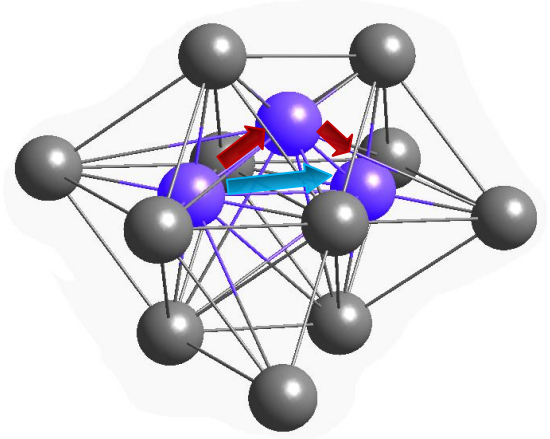
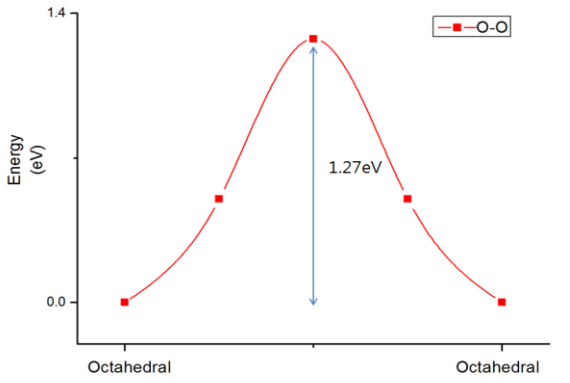
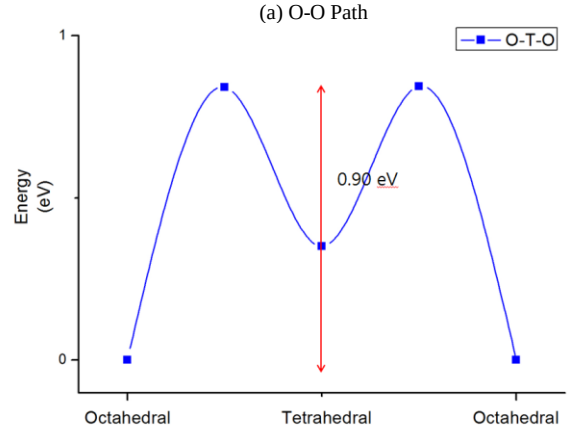


Fig 2. Calculcation supercell (O-O(blue arrow), O-T-O(red arrow))

Fig 3, and Table 1 Shows activation energy of O-O and O-T-O path way of oxygen diffusion in Ni



(a) O-O Path



(b) O-T-O Path

Fig. 3 activation energy of oxygen in Ni

	O – O	O – T – O
This work	**1.27 eV**	**0.9eV**
Megchiche [8]	**1.54 eV**	**1.25eV**

Table 1. activation energy of oxygen in Ni

The activation energy of oxygen in Ni through O – T – O path is lower than O-O path way , that means the octahedral – octahedral migration of oxygen arises through an intermediate tetrahedral site.And the results are compatible Megchiche[8] data.

3. Conclusions

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 results of activation energies for the oxygen diffusion in nickel is difference with diffusion path. O-T-O path way has lower activation energy than O-O path way. The results of activation energies for the oxygen diffusion in nickel and nickel chromium binary alloy and its difference between diffusion path will be mentioned.

In the future diffusivity of oxygen along $\sum 3$, $\sum 5$ grain boundary in nickel and it will be helpful to understand the oxygen behavior in nickel

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