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Understanding of relationship between density of state and surface oxidation on Ni(111) using first principles method

Kwang Beom Ko, Jong Jin Kim and Ji Hyun Kim*
Ulsan National Institute of Science and Technology (UNIST)
100 Banyeon-ri, Eonyang-eup, Ulju-gun, Ulsan, Republic of Korea 689-798
**Corresponding author: kimjh@unist.ac.kr*

1. Introduction

Many metals and alloys are easily oxidized in high temperature water environment. In this environment, oxide layers are formed on the surface of structure materials.

Nickel based alloys are one of the most important structure materials in modern nuclear industry. Nickel based alloys have a good corrosion resistance and mechanical properties to tolerate harsh and extreme environments.

However, the interaction of nickel and nickel based alloys with water and oxygen atom causes dissolution of metallic atom and diffusion of elements [1]. After then, oxidation arises at the surface. Therefore, the formation of oxide layer is an unavoidable process in high temperature water environments. The oxidation process of nickel based alloys is at the origin of the initiation of stress corrosion cracking(SCC), Stress corrosion cracking is arisen from interaction of mechanical, metallurgical, and electrochemical factors. It can induce failure of structural materials. Hence, it is important to understand and solve stress corrosion cracking in nickel based alloys.

Therefore, this study's objective is to understand effect of surface oxidation of nickel through the simulation of the diffusion processes of oxygen in nickel surfaces.

2. Experimetal procedure

In this study, the ab-initio calculation was used as a computational chemistry method based on quantum chemistry. The calculations were performed using the generalized gradient approximation(GGA) by the CASTEP module of the Material Studio package and the exchange correlation energy was described using the Perdew and Wang 91 functional(PW91). The Ni(1 1 1) surfaces were modeled four layer because atomic oxygen interaction was expected by four layers [2] and performed 3x3x1 k-point mesh for surfaces. Figure 1, 2 illustrate Ni(1 1 1) surfaces after considered geometry optimization. In order to calculate of oxygen diffusion processes and oxygen effect, oxygen atoms were located fcc hollow site and hcp hollow site because fcc and hcp hollow site is most favorable site on Ni(1 1 1)surfaces[3].

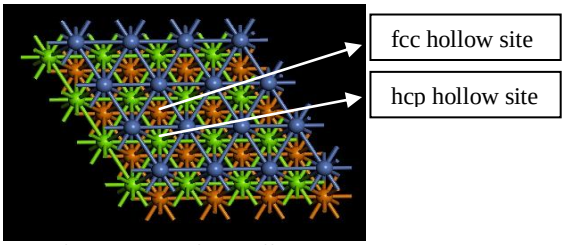

Fig 1. top view of Ni(1 1 1)surface(different colors indicate in layers: blue(1st layer), green(2nd layer), yellow(3rd layer))

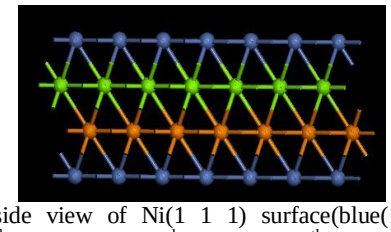

Fig 2. side view of Ni(1 1 1) surface(blue(1st layer), green(2nd layer), yellow(3rd layer), blue(4th layer))

3. Result and Discussion

3-1 One and Two oxygen atom on Ni(1 1 1) surface

The calculation result of barrier energy of oxygen diffusion on Ni(1 1 1) surface show the difference barrier energy by the number of oxygen atoms.

In case of one oxygen atom, one is oxygen atom on the fcc hollow site(reactant) and the other is oxygen atom on hcp hollow site(product) in Fig 3. And two oxygen atom cases, oxygen move from fcc-hcp site to another hcp-fcc site in Fig 4. In both cases performed geometry optimization prior to calculation of transition state search for calculation of oxygen diffusion processes and effect of oxygen on Ni surface.

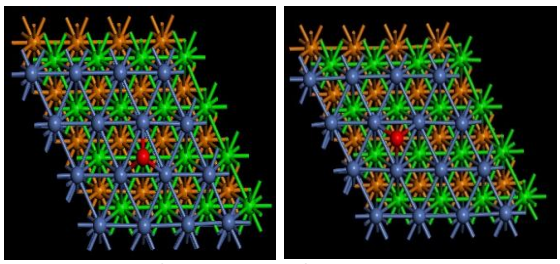

Fig 3. top view of Ni(1 1 1) surface and One oxygen atom located on hcp and fcc hollow site

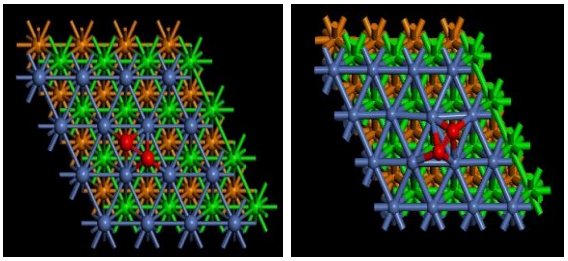

Fig 4. Top view of Ni(1 1 1) surface and two oxygen atom located on hcp and fcc hollow site

3-2 Transition state search

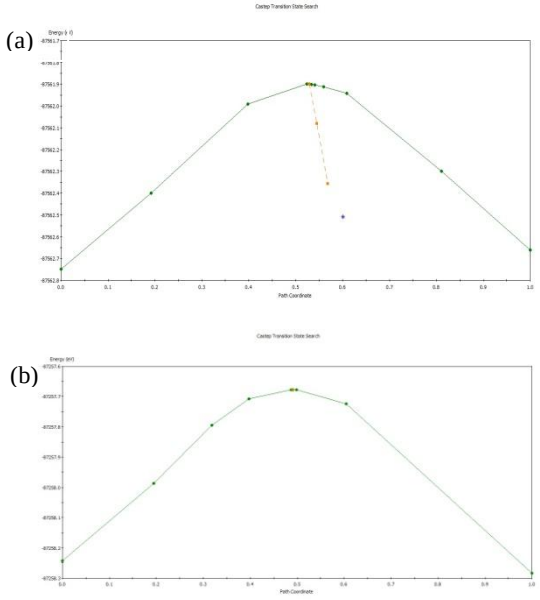

Fig 5. Transition state search result of Ni(1 1 1) surfaces (a)One oxygen, (b)Two oxygen

Table I: Barrier energy on Ni(1 1 1) surfaces

	Barrier For	(eV)		(eV)
1Oxygen atom	Reactant	0.5656	Barrier energy	0.5863
	Product	0.6070		
2Oxygen atom	Reactant	0.7651	Barrier energy	0.7313
	Product	0.6975		

The calculation result of barrier energy of oxygen diffusion on nickel surface. One oxygen case has lower barrier energy than two oxygen case in Table 1. and metallic atoms become positive charged(charge changed 0.02 to 0.11) after create Ni-O bonding in Table 2(ion 12, 52). The positive charged metallic atoms has repulsion force between them. Therefore, their bonds become loose(positive charged Ni-Ni bond length change 2.473 -> 2.588). This process arises the weakening of Ni-Ni bonds and expected to the dissolution of the metallic atoms from the surface.

Table II: Atomic populations in system

Species	Ion	Charge(e)	Spin(hbar)
Nickel	3	0.02	0.34
Nickel (Ni-O)	12	0.11	0.26
Nickel	18	0.04	0.35
Nickel (Ni-O)	52	0.11	0.26

3-3 Density of states

The density of states was performed for analyze the interaction mechanism between nickel surface and oxygen atom. The calculation result of density of states(DOS). The one oxygen adsorption on the Ni surface have a two peaks at -19.5 eV(The s orbital of oxygen combined with nickel atom) and -5.2eV(The p orbital of oxygen combined with nickel atom) in Fig 6. This peak indicates that hybridization between the oxygen p orbital and metal d orbital.

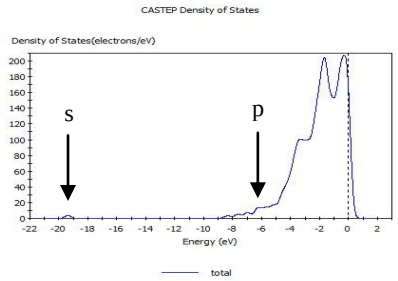

Fig 6.Density of states result of Ni(1 1 1) surfaces in one oxygen case

3. Conclusion

This work was focused on the prediction of oxygen diffusion in order to understand the fundamental oxidation behavior of nickel. According to the results, oxygen atoms have small energy barrier for diffusion on nickel surface and lead to dissolution of metallic atom.

4. Reference

[1] Nishith Kumar Das, Tetsuo shoji, Early stage oxidation of Ni-Cr binary alloy (1 1 1),(1 1 0) and (1 0 0) surfaces: Acombined density functional and quantum chemical molecular dynamics study, Corrosion Science, 73 (2013) 18-31.
[2] Nishith Kumar Das, Tetsuo shoji, A density functional study of atomic oxygen and water molecule adsorption on Ni(1 1 1) and chromium-substituted Ni(1 1 1) surfaces, Surface Science, 258 (2011) 442-447.
[3] S. Yamagishi, S.J. Jenkins, D.A. King, First principles studies of chemisorbed O on Ni{1 1 1}, Surface Science, 543 (2003) 12-18.