

Understanding of early stage oxidation on Ni using first principles calculation and molecular dynamics simulation

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 processes of early stage oxidation through the first principles method and molecular dynamics simulation.

2. Experimental procedure

In this study, the molecular dynamics and ab-initio calculation were used as a computational chemistry method based on quantum chemistry. First, ab-initio calculation was 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 interaction of oxygen and nickel substrate were expected from first to fourth layer [2] and performed 3x3x1 k-point mesh for surfaces. Also convergence tolerance and self consistent field tolerance values are 1.0e-6 and 2.0e-6. Figure 1, 2 illustrate Ni(1 1 1) surfaces after considered geometry optimization.

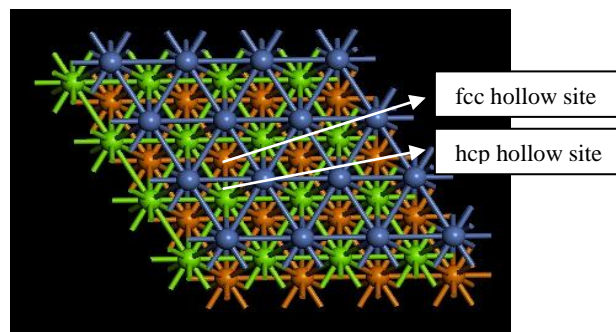


Fig 1. top view of Ni(1 1 1)surface(different colors indicate in layers: blue(1st layer), green(2nd layer), yellow(3rd layer))

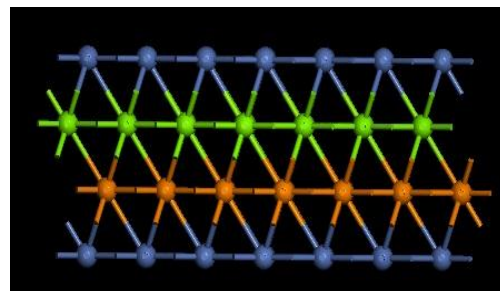


Fig 2. side view of Ni(1 1 1) surface(blue(1st layer), green(2nd layer), yellow(3rd layer), blue(4th layer))

And then, to investigation of early stage oxidation on Ni(111) in large scale by using result data of CASTEP in order to expand into molecular dynamics(LAMMPS). LAMMPS stands for Large-scale Atomic/ Molecular Massively Parallel Simulator and it is a classical molecular dynamics simulation code designed to run efficiently on parallel computers. In this study, the reactive force field potentials are used for Ni/O system modeling.

The Reactive force field potentials have been specifically designed to describe the formation, transition and dissociation of chemical bonds during molecular dynamics with accuracy close to quantum chemical method.

To simulate detailed initial mechanism of the oxidation process of nickel and oxygen molecule model, we placed 40-50 O₂ molecules in a cubic periodic box with 50Å sides. The parameters used in the present study were Ni/O reactive force field parameters. For the reactive simulations, the system was minimized first and constant volume-temperature (NVT) reactive simulations were performed at temperatures 500K for few hundred ps.

3. Result and Discussion

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

In case of one oxygen atom, one 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 oxidation processes on Ni(1 1 1) surface by using molecular dynamics.

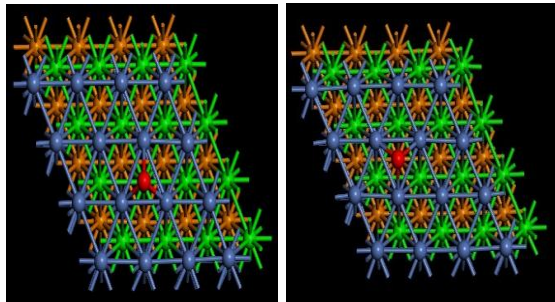


Fig 3. top view of Ni(1 1 1) surface and One oxygen atom located on hcp and fcc hollow site

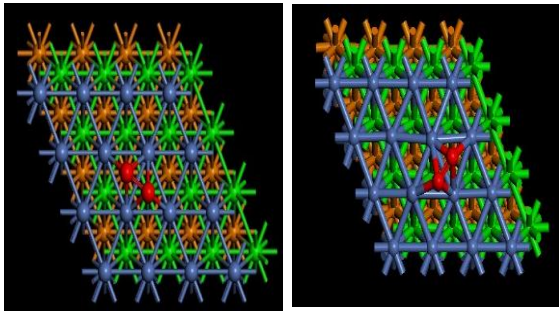


Fig 4. Top view of Ni(1 1 1) surface and two oxygen atom located on hcp and fcc hollow site

3-2 Transition state search

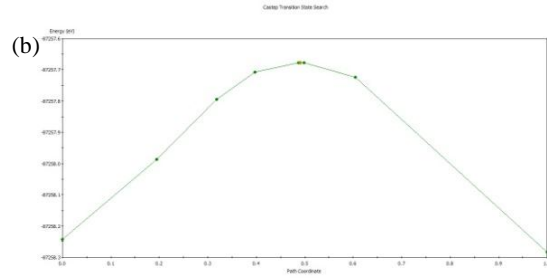
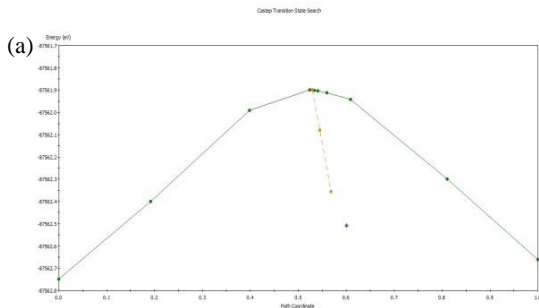


Fig 5. Transition state search result of Ni(1 1 1) surfaces (a)One oxygen, (b)Two oxygen

Atomic Populations (Mulliken)							
Species	Ion	s	p	d	f	Total	Charge (e)
O	1	1.90	4.62	0.00	0.00	6.52	-0.52
Ni	1	0.69	0.64	8.71	0.00	10.03	-0.03
Ni	2	0.52	0.75	8.68	0.00	9.95	0.05
Ni	3	0.53	0.79	8.68	0.00	10.00	0.00
Ni	4	0.68	0.66	8.71	0.00	10.05	-0.05
Ni	5	0.69	0.65	8.71	0.00	10.04	-0.04
Ni	6	0.53	0.75	8.68	0.00	9.95	0.05
Ni	7	0.52	0.75	8.68	0.00	9.95	0.05
Ni	8	0.66	0.64	8.72	0.00	10.02	-0.02
Ni	9	0.68	0.66	8.71	0.00	10.05	-0.05
Ni	10	0.52	0.75	8.68	0.00	9.95	0.05
Ni	11	0.52	0.75	8.68	0.00	9.95	0.05
Ni	12	0.58	0.65	8.65	0.00	9.88	0.12

Transition State Found!
Energy of reactant: -87691.24383 eV
Energy of product: -87692.57758 eV
Energy of transition state: -87691.09053 eV
Location of transition state: 0.22521
Barrier from reactant: 0.15330 eV
Barrier from product: 1.48705 eV
Energy of reaction: -1.33375 eV

Fig 6. The calculation result of first principles method

The partial data of the calculation result of first principles method on nickel surface in Fig 6. In this result, when oxygen atom is absorbed on the nickel surface, metallic atoms become positive charged (charge changed -0.05-0.05 to 0.11-0.14) after create Ni-O bonding in Table 1. The positive charged metallic atoms have 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 I: Compare atomic charge

Species	Charge(e)	Spin(hbar)
Nickel	-0.05-0.05	0.34
Nickel (Ni-O)	0.11-0.14	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 oxygen adsorption on the Ni surface have a two peaks at -19.5 eV(The s orbital of oxygen combined with nickel atom) and -5.7eV(The p orbital of oxygen combined with nickel atom) in Fig 7 and 8. This peak indicates that hybridization between the oxygen p orbital and metal d orbital.

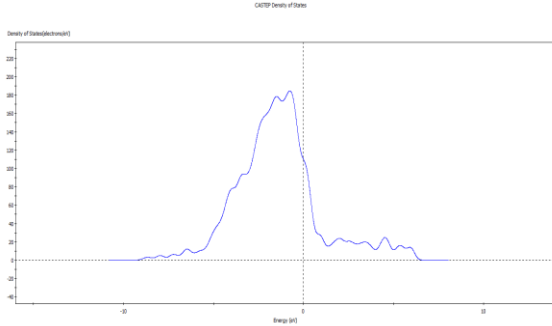


Fig 7. Density of states result of Ni(1 1 1) surfaces

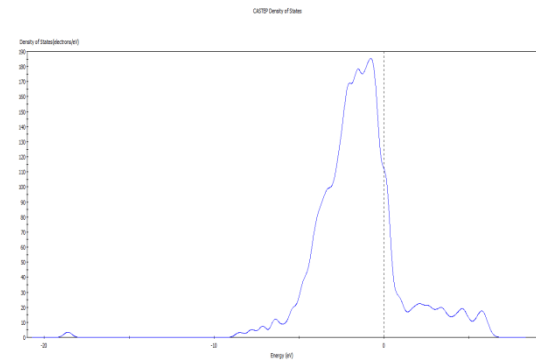


Fig 8. Density of states result of Ni(1 1 1) surfaces + oxygen case

3-4 Molecular dynamics

In general, when a nickel is brought into contact with oxygen molecule, the first portent indicating the occurrence of nickel oxidation is the consumption of oxygen molecule. To evaluate the reaction process and mechanism, a series of constant temperature molecular simulations 550K for few hundred ps were performed. Analysis of trajectories from molecular dynamics with ReaxFF reactive force field potential is able to show complex initiation chemistry for the nickel oxidation process.

In ReaxFF, the system energy expression is divided into contributions as shown in eq 1 [3], [4].

$$E_{total} = E_{bond} + E_{tors} + E_{Coulomb} + E_{vdW} + E_{H-bond} \quad (1)$$

$$E_{coulomb} = C \cdot \frac{q_i \cdot q_j}{[r_{ij}^3 + (1/r_{ij})^3]^{1/3}} \quad (2)$$

$$E_{vdWalls} = D_{ij} \cdot \left\{ \exp\left[a_{ij} \cdot \left(1 - \frac{f_{13}(r_{ij})}{r_{vdW}} \right) \right] - 2 \cdot \exp\left[\frac{1}{2} \cdot a_{ij} \cdot \left(1 - \frac{f_{13}(r_{ij})}{r_{vdW}} \right) \right] \right\} \quad (3)$$

The partial contributions in eq 1 include bond energies, torsion angle energies, valence angle energies, van der Waals interactions, and non-bonded Coulomb. The Coulomb(Eq 2.) and van der Walls interaction part(Eq 3.) of ReaxFF force field potential is modified by using result data of first principles method in Fig 9. As shown in Fig 10, Ni/O system was designed in order to calculate interaction of oxygen molecule and nickel substrate.

H	0.8930	1.0000	1.0080	1.3550	0.0930	0.8203	-0.1000	1.0000
	8.2230	33.2894	1.0000	0.0000	121.1250	3.7248	9.6093	1.0000
	-0.1000	0.0000	61.6606	3.0408	2.4197	0.0003	1.0698	0.0000
	-19.4571	4.2733	1.0338	1.0000	2.8793	0.0000	0.0000	0.0000
O	1.2450	2.0000	15.9990	2.3890	0.1000	1.0698	1.0548	6.0000
	9.7300	13.8449	4.0000	37.5000	116.0768	8.5000	8.3122	2.0000
	0.9049	0.4056	59.0626	3.5027	0.7640	0.0021	0.9745	0.0000
	-3.5500	2.9000	1.0493	4.0000	2.9225	0.0000	0.0000	0.0000
Ni	1.8862	2.0000	65.3900	1.9200	0.2998	0.4828	-1.6836	2.0000
	11.5134	18.3776	2.0000	0.0078	0.0000	2.0219	5.7915	0.0000
	-1.2000	0.0000	266.4838	5.3430	10.1260	0.7590	0.0000	0.0000
	-3.0614	2.1158	1.0338	6.2998	2.5791	0.0000	0.0000	0.0000

Fig 9. LAMMPS ReaxFF potential data

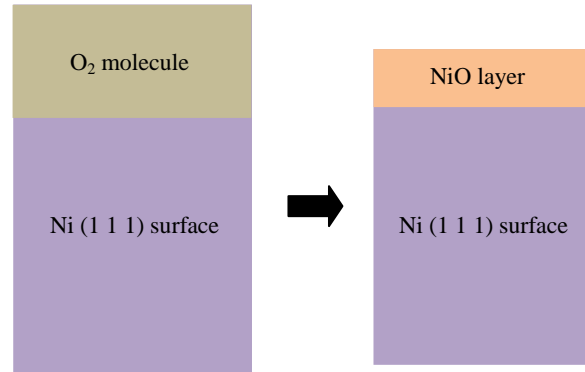


Fig 10. Schematic design of nickel/oxygen system

As shown in 3-2 and 3-3, the charge analysis and calculation of density of states were performed in order to verify the accuracy of the calculation.

In this result, metallic atoms become positive charged after create Ni-O bonding. It is contribute to weakening of nickel-nickel bonding.

According to result of density of states, density of states of pure nickel and nickel + oxygen case has two different peaks in -19.5eV and -5.8eV. It can be found bonding orbital between oxygen and nickel substrate.

3. Conclusion

This work was focused on the investigation of early stage oxidation in order to understand the fundamental oxidation behavior of nickel by using first principle method and molecular dynamics. Also,

ReaxFF reactive force field was modified potentials for Ni/O systems.

Acknowledgements

This work was financially supported by the International Collaborative Energy Technology R&D Program(No.20138530030010, No.20128540010010) of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) granted financial resource from the Ministry of Trade Industry and Energy.

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] Jonathan E. Muellker, Adri C.T. van Duin, William A. Goddard, Development and Validation of ReaxFF Reactive force field for Hydrocarbon Chemistry Catalyzed by Nickel, J. Phys. Chem., 114 (2010) 4939-4949.
- [4]Adri C.T. van Duin, Siddharth Dasgupta, Francois Lorant and a William A. Godard, ReaxFF: A Reactive force field for hydrocarbons, J. Phys. Chem, 105 (2001) 9396-9409.