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A Molecular Dynamics Study on the Early Stage Oxidation and Corrosion Behavior of Nickel Surface

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1. Introduction

Stress corrosion cracking(SCC) of structural materials in nuclear power plants(NPPs) is one of the major issues for plant safety and life extension. In NPPs, a pressure vessel and steam generator(SG) consists of metal pipes and tubes mainly made of nickel-based alloy surfaces. In these applications, nickel-based alloys are normally exposed to high-temperature water, which may lead to cracking initiated by the oxide degradation process and numerous studies have been carried out to investigate the fundamental mechanism. Some studies have found that there is a correlation between early-stage oxidation and the cracking of Ni-based alloys, which is still in great debate. Thus there were many efforts to investigate the nature of oxidation and corrosion behavior of the nickel in atomistic or sub-atomistic scales because understanding of the nature of oxide film formed metal/gas or metal/water interfaces is one of the key parameters to understand the mechanism of SCC [1].

The early stage oxidation and corrosion behavior of metal/liquid interface have been studied using various techniques [2] to understand and quantify the corrosion resistance of nickel base alloys by oxide analysis [3]. However, these experimental studies did not fully to reveal the oxidation and crack initiation process on atomic scale. Therefore, computational simulation methods were performed overcome the experimental barrier such as scale, spatial limitations, etc. This study focused on the understanding of early stage oxidation and corrosion behavior of nickel/water interface by using molecular dynamics and reactive force field potential (ReaxFF) of nickel-water molecule system.

2. Computational Methods

2.1. Reactive force field potential

The molecular dynamics calculations were performed using ReaxFF potential. In the field of corrosion, the recent progresses in ReaxFF potentials, which were originally developed to study the hydrocarbon chemistry and the catalytic properties of organic compounds, have made it possible to investigate the reactivity of metals with water. Analysis of trajectories from molecular dynamics with ReaxFF(reactive force field) potential are able to show complex initiation chemistry for the nickel oxidation process.

The ReaxFF potentials have been specifically designed to describe the formation, transition and dissociation of chemical bonds during molecular dynamics with accuracy to quantum chemical method. [4-5].

The ReaxFF is a bond order based force field developed by Adri van Duin, William A. Goddard. ReaxFF method gives more accurate description of bond breking and formation by calculating the bond orders from interatomic distances which are obtained by every molecular dynamics simulation step.

2.2. Molecular dynamics

To investigate the early stage oxidation of Ni (100), (110), (111) in atomic scale, molecular dynamic calculation was conducted with Large-scale Atomic/ Molecular Massively Parallel Simulator (LAMMPS). LAMMPS is a classical molecular dynamics simulation code designed to be operated efficiently on parallel computers. In this study, ReaxFF potentials are used to investigate the early stage oxidation in the Ni/O system modeling. All calculations were modeled by the periodical array. The periodical array was cut in <0 0 1> direction to create the Ni (100), (110), (111) surface. To simulate detailed initial mechanism of the oxidation process of Ni/O system, 864 oxygen atoms and 6048 nickel atoms were positioned in a cubic periodic box with 59.73 × 42.24 × 59.73 Å. The vacuum slab was set over the nickel surface with lattice parameter is 3.52 Å. For the reactive simulations, the system was minimized first and constant volume–temperature (NVT) reactive simulations were performed at temperature of 550 K for a 20 nanoseconds. In each calculation, the lattice relaxation time was set as 10 ns. All oxygen atoms are randomly distributed over the nickel surface as shown in Fig. 1. The upper section of nickel substrate was divided into three sublayers in order to calculate radial distribution function (RDF) and lower substrate was fixed because nickel atoms that located in the substrate are not affected by oxygen atoms.

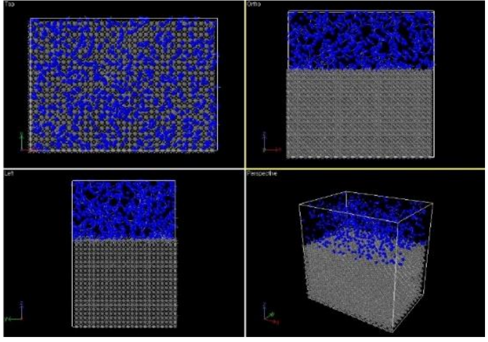

Figure 1. Perspective view of the Ni/Oxygen structure (Grey : Ni, Blue : Oxygen

3. Results and Discussion

3.1. Molecular dynamics simulation of Ni/O system

In this section, the molecular dynamics results that deducted by using ReaxFF potential are treated. Fig. 2. shows the final state of the Ni/O system. In this result, when the reaction of oxygen and nickel atoms at the surfaces are occurred, therefore it can be confirmed about Ni substrate was divided into several layer. When metal interacts with an atom or molecule, the d orbital of the metal combine with the atom or molecule. As illustrated in fig. 2, there are three different structure layers in the nickel substrate. The first layer is nickel oxide amorphous layer which is formed by the direct interaction with oxygen atoms. The interaction of oxygen atoms with nickel in high temperature environments leads to the dissolution of nickel atoms and the diffusion of elements It is due to the vigorous intermolecular interactions which is occurred between oxygen and nickel atoms at the surface. The second layer losses basic characteristic of nickel substrate by oxygen atom. It seems like amorphous and distorted trigonal system that has different lattice parameter than the existing nickel substrate. However, the sublayer3 is maintained as a Ni structure. Because, oxygen atom can not permeate into the sublayer3. The oxygen atom forms oxide layer into nickel sublayer 1 and 2 and the thickness of the oxide layer indicated in Table1. As shown Fig. 3, the RDF is calculated for each sublayer in order to investigate the structural change and the effects of oxygen permeation into nickel substrate. In this result, RDF of sublayer1(black line) indicates smooth curve. Sublayer1 can not be maintained basic characteristic of nickel substrate and forms amorphous nickel oxide layer. Also, sublayer2 is under the influence of oxygen atom, therefore, a difference in radial distribution is shown, which is the result of Ni.

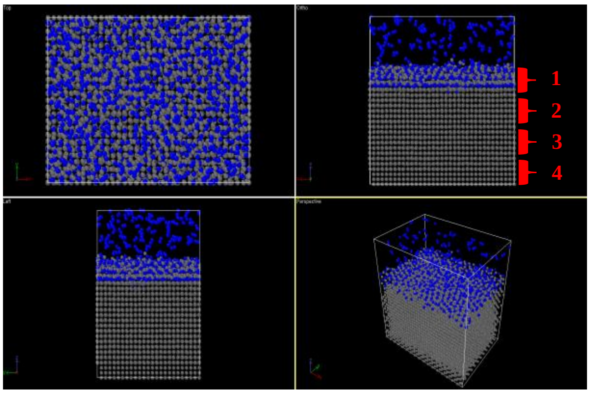

Figure 2. Final state of the Ni/Oxygen structure (Grey : Ni, Blue : Oxygen)

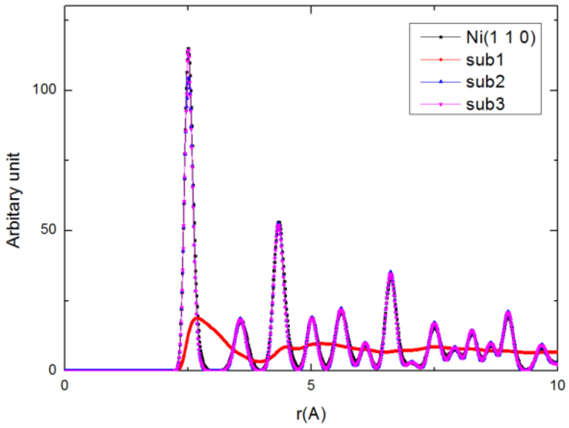

Figure. 3. The result of radial distribution function on Ni surface.

Table I: Thickness of nickel oxide layer

	Thickness (Å)
Ni (100)	5.2
Ni (110)	6.6
Ni (111)	3.4

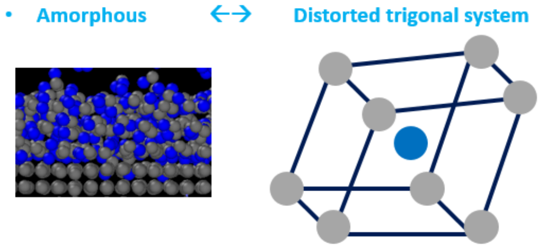

Figure 4. NiO structure from the LAMMPS simulation

4. Conclusion

This work was conducted to investigate the early stage oxidation in order to understand the fundamental oxidation behavior of nickel by using molecular dynamics. The LAMMPS was used for the molecular dynamics calculation. The ReaxFF potential was used to calculate the interatomic force between nickel, oxygen and hydrogen atoms. In the results, oxygen atoms were infiltrated into the nickel surface and interact with neighboring nickel atoms. the oxygen atoms and water molecule are absorbed on the nickel surface and they induce the dissociation of nickel atoms due to charge difference between nickel and oxygen atom. And, oxidation takes place at the surface, therefore, the nickel atom which is located in upper section of substrate is reacted with the oxygen atom and forms nickel oxide amorphous layer. This phase seems like trigonal system and it is a little distorted in Fig.4. The charge difference would be decreased during penetration due to reaction between oxygen and nickel atoms at sublayer2. And this is why the sublayer3 does not affected by oxygen atoms. The result of the RDF shows coincidence result with this phenomenon. Structural changes of nickel due to oxygen atoms were observed at the result of radial distribution function.

5. Acknowledgements

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