Understanding of early stage oxidation on Ni surface using molecular dynamics simulation

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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 [1].

However, the interaction of nickel and nickel based alloys with water and oxygen atom causes dissolution of metallic atom and diffusion of elements [2]. 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. Almost all SCC on alloys in aqueous condition take place on their oxide films [3]. 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. Methods and Results

In this study, LAMMPS (Large scale Atomic/ Molecular Massively Parallel Simulator) was used. It is a classical molecular dynamics code that models an ensemble of particles in a liquid, solid, or gaseous state by Sandia National Laboratories.

2.1 Reactive force field potential

Analysis of trajectories from molecular dynamics with ReaxFF(reactive force field) potential is able to show complex initiation chemistry for the nickel oxidation process.

The ReaxFF is a bond order based force field developed by Adri van Duin, William A. Goddard. It provides accurate descriptions of bond breaking and bond formation. Because reactive force field method is determined by bond orders calculated from interatomic distances that are obtained every molecular dynamics step. In ReaxFF, the system energy expression is divided into contributions as shown in eq 1 and bond order term in eq 2. [4], [5].

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

$$BO_{ij} = BO_{ij}{}^{\sigma} + BO_{ij}{}^{\pi} + BO_{ij}{}^{\pi\pi}$$

$$= \exp\left[p_{bo1}\left[\frac{r_{ij}}{r_0{}^{\sigma}}\right]^{p_{bo2}}\right] + \exp\left[p_{bo3}\left[\frac{r_{ij}}{r_0{}^{\pi}}\right]^{p_{bo4}}\right]$$

$$+ \exp\left[p_{bo5}\left[\frac{r_{ij}}{r_0{}^{\pi\pi}}\right]^{p_{bo6}}\right] \quad (2)$$

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

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

$$\left. \exp\left[\frac{1}{2} \cdot a_{ij} \cdot (1 - \frac{f_{13}(r_{ij})}{r_{vdW}})\right] \right\} (4)$$

The parameters in eq 2 such as p_{bo1} - p_{bo6}, correspond to the bond orders of the sigma bond, first pi bond and second pi bond($\pi\pi$), respectively. The eq 3 and eq 4 indicate coulomb force and Van der Waals force, q_i and q_j is the charge on ion i and j, γ_{ij} is a parameter for shielding between atoms i and j.

2.2 The result of nickel-oxygen system

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 by charge difference between nickel and oxygen molecule. The reason why the nickel-oxygen system was calculated. Because the potential data between Ni-atom and water molecules are under-developing, this data is not obtained fully and it is assumed that the process forming nickel oxide layer effects on oxygen atom in water molecule.

To evaluate reaction process of oxygen consumption phenomenon and mechanism. The molecular dynamics simulations are performed with a constant volume and constant number of atoms at 550K for few nanosecond

were performed and this system has a 50 x 50 x 40 angstrom box and about 7000 atoms of nickel in the system.
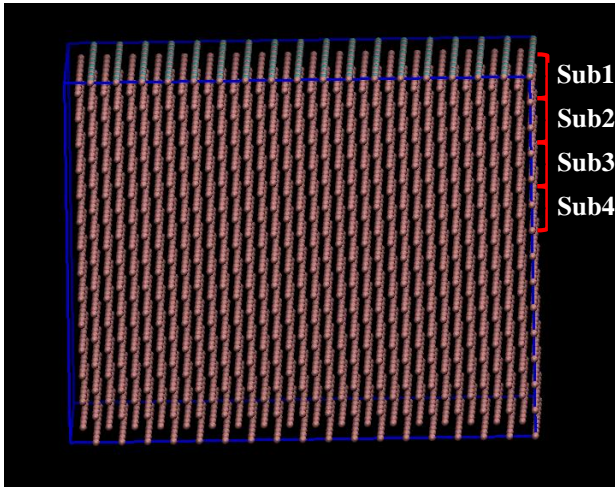

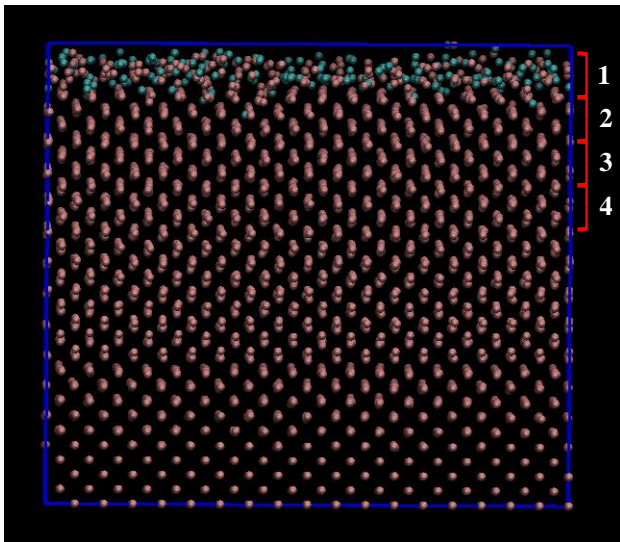Fig. 1. The initial state of nickel-oxygen system

Fig. 2. The final state of nickel-oxygen system

According to molecular dynamics result, When the reaction of oxygen and nickel at the surfaces, we can be confirmed about Ni substrate was divided into several layer in Fig. 2. The bottom layer (5-6 layer) maintained a Ni(110) structure. However, the top layer (4-7layer) change lattice structure due to the penetration of oxygen atom.

2.3 Radial distribution function

The radial distribution function (RDF) is a statistical mathematics function that is used to describe a cluster or aggregation of objects. RDF (g(r)) is a local measure of how close the observed distribution is to a uniform one. The mathematical definition of g(r) is,

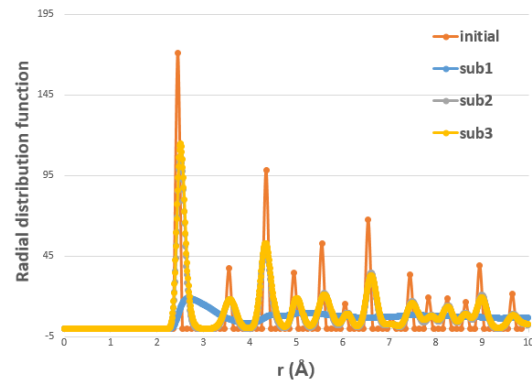$$g(r) = \frac{dN/N}{dV/V} = \frac{dN}{dV} \cdot \frac{V}{N} \quad (5)$$

Fig. 3. Radial distribution function result

As shown Fig. 3, the nickel substrate divided into four layer (sub1, sub2, sub3) in order to have the effects of oxygen permeation into nickel substrate. In this result, the oxygen atoms infiltrate into the Ni surface and change the structure of Ni substrate.

2.4 The method of nickel-water system

In order to more closely simulate the actual nuclear environment. The nickel-oxygen system was modified by using water molecule. The condition of system environment is similar to nickel-oxygen model.
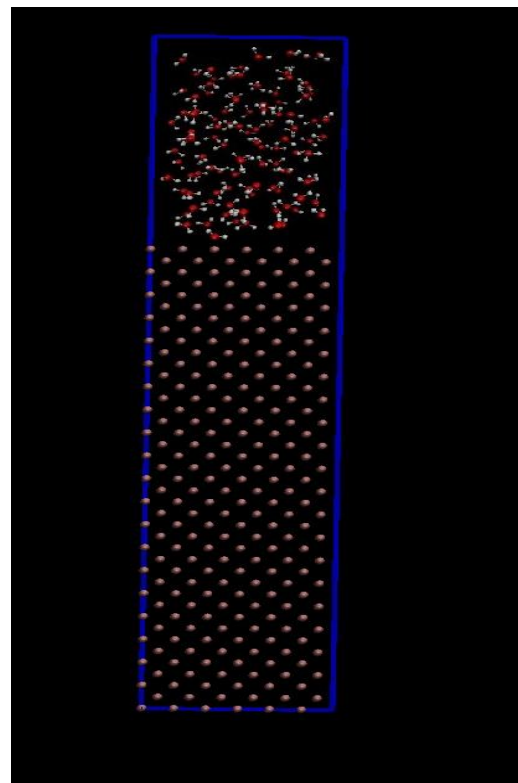

Fig. 4. The initial state of nickel-water system

3. Conclusions

This work was focused on the investigation of early stage oxidation in order to understand the fundamental oxidation behavior of nickel by using molecular dynamics. In this study, water and oxygen atom infiltrate into the nickel surface and interaction neighbor nickel atoms. The result of the radial distribution function indicate this phenomenon and water and oxygen atoms caused nickel structure change.

Acknowledgements

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