

A Molecular Dynamics Study on the Early Stage Oxidation of Nickel-Water interface

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1. Introduction

In recent years, nickel based alloys are one of the most important structure materials in modern industries because they have excellent performance at high temperature aqueous environments [1]. In spite of these advantages, recently, the failure of nickel based alloys have been reported such as stress corrosion cracking (SCC) as they are exposed to harsh environments with long exposure time and residual stresses. Almost all SCC on alloys in aqueous condition take place on their oxide films. It can induce failure of structural materials.

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 water/solid interfaces is one of the key parameters to understand the mechanism of SCC [2]. The early stage oxidation of the metals and alloys have been studied using various techniques [3-4], and many researches have been performed to understand and quantify the corrosion resistance of nickel base alloys by oxide analysis [5-7]. However, these experimental studies did not fully to reveal the oxidation and crack initiation process on atomic scale. Computational simulation methods are gathering numerous interest from assorted science and engineering fields because it can overcome the experimental barrier such as scale, spatial limitations, etc and obtain detailed instructions such as a bond length between oxygen and metal atoms, a diffusivity, and electron density absorption energy and so on. Several computational studies have been conducted to characterize the atomistic structure and oxidation process of Ni and Ni-base alloys [8]. This study, observes the structural change and the early stage oxidation behavior on the nickel surface and focused on the understanding of interaction of a nickel substrate and oxygen or water molecules by molecular dynamics using reactive force field potential (ReaxFF) of nickel-water molecule system.

2. Methods and Results

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. And also it considers the non-bonded interactions between atoms by using coulomb force and van der Waals term. In ReaxFF, the system energy expression is divided into several terms as shown in Equation (1).

$$E_{\text{total}} = E_{\text{bond}} + E_{\text{tor}} + E_{\text{coulomb}} + E_{\text{VdW}} + E_{\text{h-bond}} \quad (1)$$

To investigate the early stage oxidation of Ni 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. Many researchers have begun to focus on atomistic modeling to evaluate the interfacial phenomena between materials and water by using LAMMPS. In this study, ReaxFF potentials are used to investigate the early stage oxidation in the Ni/H₂O system modeling.

All calculations were modeled by the periodical array. The periodical array was cut in <0 0 1> direction to create the Ni surface. To simulate detailed initial mechanism of the oxidation process of Ni/H₂O system, 864 water molecules 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 10 nanoseconds. In each calculation, the lattice relaxation time was set as 5 ns. All water molecules are randomly distributed over the nickel surface (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.

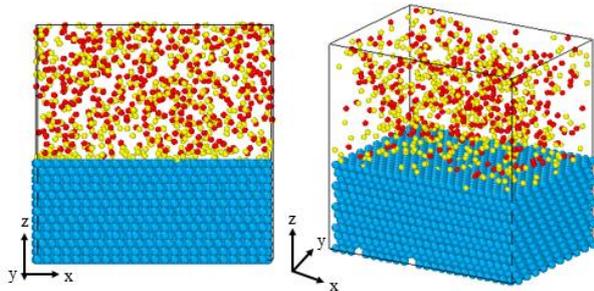


Fig. 1 Perspective view of the Ni/H₂O structure (Red: Oxygen, Yellow: Hydrogen, Blue: Nickel)

2.1 Molecular dynamics simulation of Ni/H₂O system

In this section, the molecular dynamics results that deduced by using ReaxFF potential are treated.

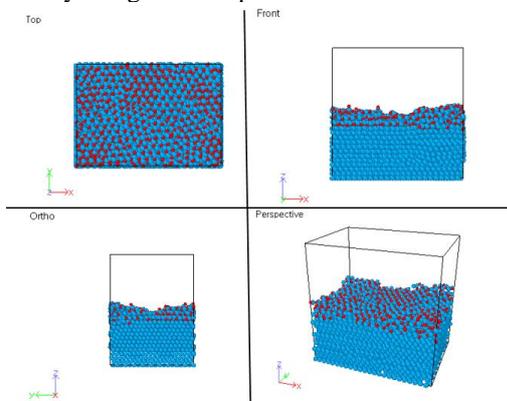


Fig. 2 Final state of Ni/H₂O structure system (Red: Oxygen, Blue: Nickel)

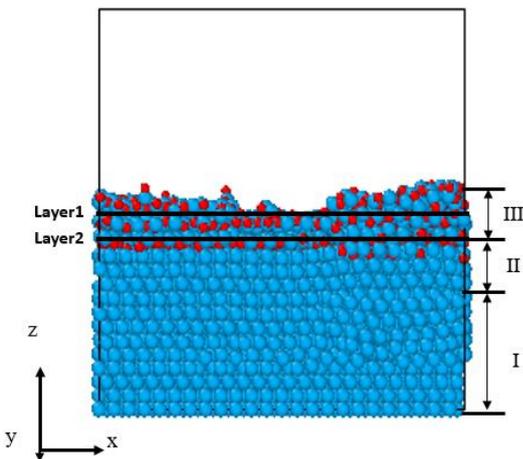
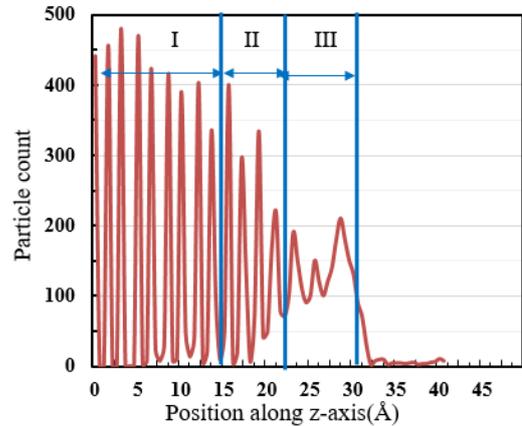


Fig. 3 Final state of Ni/H₂O structure system (Red: Oxygen, Blue: Nickel)

The final state of the Ni/H₂O system (Fig. 2) performed an energy minimization after completing the reaction of nickel and water. 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.



I : Ni layer (lattice parameter : 3.52)

II : Ni layer + Oxygen atom (lattice parameter : 3.9±0.21)

III : NiO layer

Fig. 4 The result of particle count

As illustrated in fig. 3&4 there are three different structure layers in the nickel substrate. The layer III 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. Also, the layer II is reacted oxygen atoms layer which permeated through the nickel surface. This layer loses basic characteristic of nickel substrate by oxygen atom and forms another nickel oxide layer that has different lattice parameter than the existing nickel substrate. However, the layer I is maintained as a Ni structure. Because, oxygen atom can't permeate into the layer I.

The oxygen atom forms oxide layer into nickel layer II and III and the thickness of the oxide layer is about 6.0 ~ 6.6 Å for each case. As shown Fig. 4, the particle count was calculated for each layer in order to investigate the structural change and the effects of oxygen permeation into nickel substrate.

2.2 Analysis of early stage oxidation behavior on nickel surface

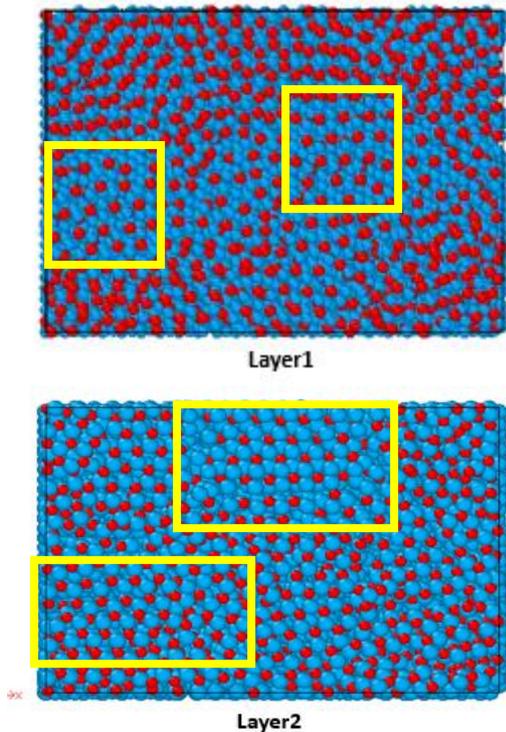


Fig. 5 Top side view of the Layer1 and Layer2

When the nickel atoms interact with oxygen or water molecules, nickel atom has a plus charge(0.45e) and oxygen atom has a minus charge (-0.56e). Therefore, 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 (Yellow box) and it is a little distorted in Fig.5.

In the results of molecular dynamics, when we compare the layer1 and layer2 shows that the internal oxide layer turns into trigonal system. However, Layer1 can be seen a lot of amorphous layers due to the continuous reaction with oxygen and surface defects(vacancy, interstitial defect etc.).

3. Conclusions

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. In additional to, this nickel oxide layer is formed distorted trigonal system by interaction between oxygen and nickel atom. 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.

ACKNOWLEDGMENTS

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