

Quantum Chemical Molecular Dynamics Study of Oxidation Process on Fe-Cr Alloy Surfaces in High Temperature Water

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ABSTRACT

Stress corrosion cracking has become the critical issue that dominates the lifetime of various metallic materials such as stainless steels used under harsh operating conditions. In the EAC process, chemical reaction of the metal surface at crack tip such as oxidation and/or anodic dissolution, and subsequent formation of an oxide film plays an important role for crack propagation. In this study, tight-binding quantum chemical molecular dynamics simulations were employed to understand the chemical reactions caused by water molecules on Fe-Cr alloy surfaces in nano-scale. The main targeted temperature was boiling water nuclear reactor (BWR) condition which is 561 K. Water molecules were dissociated on the Fe-Cr surfaces at 561 K. The chromium atoms at the top layer segregated from the surface to bond with the dissociated oxygen atoms. Oxygen concentration around the chromium atoms gradually increased to preferentially form Cr-O bonds during the simulation, which resulted in clustering of oxygen and chromium atoms on the surface. The clustering of oxygen and chromium is thought to bring about Cr-based oxide nucleation and therefore, the preferential formation of Cr-O bonds is considered to be the initial process of the formation of oxide films on the Fe-Cr surface.

Keywords: stress corrosion cracking, quantum chemical molecular dynamics, stainless steel, oxidation

1 INTRODUCTION

Stress corrosion cracking (SCC) of stainless steels used in nuclear pressure boundary components is a potentially critical issue concerning safety of plant operation and plant life extension. Since SCC behaviors are determined by material, mechanical and environmental factors that affect individually or have synergistic effects in crack growth enhancement, it is extremely difficult to examine the effects of all those factors by experiments. Hence, extensive efforts have been made to develop both the SCC models for various materials/environmental systems and quantitative prediction methodologies [1-4]. The film rupture/slip dissolution model explains that SCC includes the braking of oxide or protective film and creation of a new reactive clean metal surface. In this model, chemical reaction behavior of the metal surface at crack tip such as anodic

dissolution and subsequent formation of oxide or protective film is considered as essential process for crack propagation. The other SCC models also consider the transport of oxygen and/or alloying elements at near crack tip region [2, 3]. Therefore, it is desirable to get better description and deeper insight into the basic features of chemical reaction of water with metal surface. In order to analyze the chemical reaction processes, computational chemistry approach is very effective in obtaining detailed information on atomic scale for understanding the chemical and physical phenomena. Actually, numerous theoretical studies have been performed to analyze the electronic and structural properties of a wide range of metals including molecules, bulk solids, surface and interface. Density functional theory (DFT) is widely used to study the properties of different transition metal or alloy structures such as bulk, grain boundaries, surfaces, nano-particles, etc. With respect to the analysis of iron surface, initial stages of oxidation caused by water on the Fe [100] and [110] surfaces involving the process of water dissociation was studied [5]. The energies and electronic structure of passive film formed on iron [6] and H induced embrittlement process have also been studied by DFT calculation [7]. Although several theoretical studies employing various levels of approximations have been performed and succeeded in obtaining the useful information on atomic scale, there are few simulation studies that consider dynamics effects as well as the electronic interactions. In this study, in order to obtain better knowledge of the surface chemistry of iron based alloys in the presence of high temperature water, we applied a tight-binding quantum molecular dynamics calculation to study the initial oxidation stages of Fe and Fe-Cr alloy surfaces.

2 METHOD

Tight-binding quantum chemical molecular dynamics simulations were performed using the colors code [8-10]. The formalization of this program is based on the extended Hückel approximation. This method enables us much faster simulations than those based on the regular first principle calculation, and thus the complex systems requiring large simulation models can be solved in a relatively short time. All parameters used in the Hamiltonian of the extended Hückel approximation were determined to satisfy the diatomic (Fe-Fe, Fe-O, Fe-H, etc.) potential energy, and

structural properties of H₂, O₂, H₂O molecules and Fe, Cr, Fe₂O₃, Fe₃O₄, and Cr₂O₃ crystals such as the geometry, binding energies, atomic charges, and density of states obtained from DFT calculations or experiments. DFT calculations were performed by using Dmol³ code with the generalized gradient approximation (GGA) functional of the Perdew-Wang 1991 (PW91) [11]. All-electron double numerical plus polarization (DNP) basis sets with scalar relativistic corrections were used in the DFT calculations. For example, cohesive energies of Fe₂O₃ and Cr₂O₃ per formula unit obtained from the DFT, which were calculated as the energy difference between isolated atoms and the compound, were 26.17 eV and 28.72eV, respectively. The calculated cohesive energies of Fe₂O₃ and Cr₂O₃ using the defined parameters were 26.20 eV and 28.16 eV, respectively, which are in good agreement with the corresponding DFT values. In this study, the target material was an austenitic stainless steel and, as a first approximation, an iron [111] surface with a face-centered cubic structure was used as a periodic slab model. The surface models were represented by a slab which comprised of 3 layers with 16 atoms per layer, and thus the total number of metal atoms was 48 in the unit cell. For the Fe-Cr surface model, 6 iron atoms randomly replaced by chromium atoms from the pure Fe surface model (Cr/Fe atomic ratio = 0.14). Atomic positions of metallic atoms were relaxed at 300 K. To simulate chemical reactions of the Fe and Fe-Cr surfaces, 10 H₂O molecules were placed on the relaxed surfaces, which was monolayer adsorption of H₂O molecules on the surface. Simulation was carried out under the condition of constant volume and temperature. The main targeted temperature supposed was boiling water reactor (BWR) condition which is 561 K and pressure considers atmospheric. The verlet algorithm was used for atomic motions in the molecular dynamics simulations with a time step of 0.5×10^{-15} second. A total of 4,000 steps were performed in the simulation.

3 RESULTS AND DISCUSSION

3.1 Reaction dynamics of Fe/H₂O

The surface morphology changes of the clean Fe surface with respect to time are shown in Figure 1. At the beginning of the simulation, H₂O molecules were dissociated into OH and H atom. The number of OH groups increased with time, and some OH groups were dissociated further to oxygen and hydrogen atoms. It was found that some of H₂O molecules, OH groups, and dissociated hydrogen and oxygen atoms penetrated into the surface layer. After the penetration, the iron atoms at the top layer moved outward and the surface morphology became rough. The penetration of oxygen species seems to result from the weakening of Fe-Fe bonds due to the interaction of the iron atoms with oxygen and hydrogen atoms. These simulation results are qualitatively consistent with the experimental studies that have observed oxide formation in the reaction

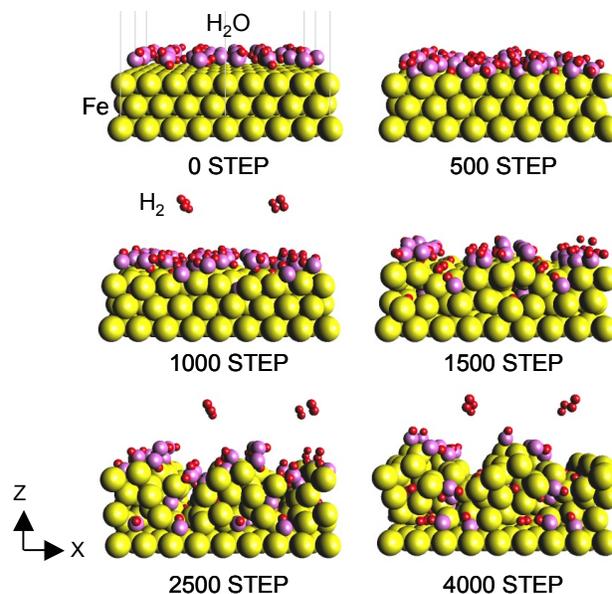


Figure 1: Change of morphologies of clean Fe surface with H₂O molecules at 561K.

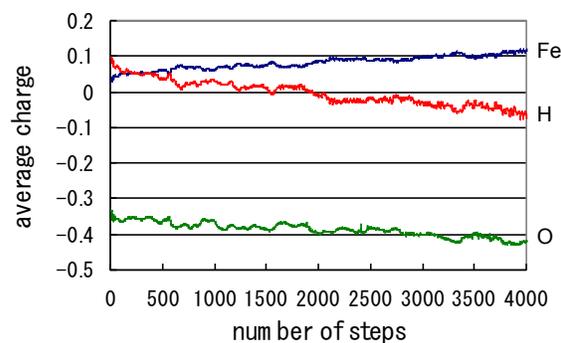


Figure 2: Time evolution of average charges of Fe, H and O.

of H₂O on iron single-crystal surfaces [12, 13]. The time evolutions of the average atomic charges obtained from Mulliken population analysis for each element are shown in Figure 2. This figure shows the gradual increase of the iron charge and decrease of both oxygen and hydrogen charges during the simulation, corresponding to iron losing valence electrons while both oxygen and hydrogen accepting those electrons. Donation of electrons from the iron atoms to the oxygen and hydrogen atoms leads to not only the formation of Fe-O and Fe-H bonds but also the weakening of Fe-Fe bonds due to the losing electrons which contribute to the bonding of Fe atoms. It is also interesting to note from this figure that hydrogen had a negative value of the charge after 2,000 step. We confirmed that hydrogen atoms of H₂O molecules had positive charge of about 0.1, whereas the interstitial hydrogen atoms in the iron surface had negative charge. Other theoretical studies have shown that the interstitial hydrogen in the iron structure remains negative charge [14, 15] and Zhong et al. have reported that main

mechanism of the hydrogen induced embrittlement of the iron structure is charge transfer with the hydrogen impurity acting as an electron acceptor [7]. Therefore, the interstitial hydrogen atoms acting as electron acceptor in the iron surface are considered to weaken Fe-Fe atomic bonds significantly. In addition to the weakening of Fe-Fe bonds due to the donation of electrons, since coulomb interaction between the iron atoms possessing positive charge acts repulsively, the system tried to lower the repulsion by segregation of iron atoms from the surface and penetration of oxygen species into the surface. As a result, iron atoms moved outward and the surface morphology became rough.

3.2 Reaction dynamics of Fe-Cr/H₂O

Figure 3 shows morphology changes of the Fe-Cr surface with respect to time. At the beginning of the simulation, H₂O molecules adsorbed on the surface, and some H₂O molecules dissociated to OH group and H atom. Further dissociation reaction OH → O + H was also observed. OH groups and dissociated oxygen and hydrogen atoms penetrated into the Fe-Cr surface, as similar to the simulation of the Fe surface. Figure 3 (b) shows the details of changes in the surface morphology of the Fe-Cr from 500 to 1,000 step. H₂O molecules moved close to chromium atoms at the top surface and subsequently, the chromium atoms moved outward to bond with the oxygen atoms. Segregation of iron atoms from the surface was also observed during the period, which looks like the penetrating oxygen atoms pushed out the iron atoms.

In order to gain more insight in the initial oxidation process of the Fe-Cr surface, we investigated the diffusion properties of iron and chromium atoms. The mean square displacement (MSD) values for iron and chromium atoms are plotted in Figure 4. In this figure, the MSD values of top layer and 2nd layer are average MSD values of iron or chromium atoms being in the top layer and second layer at the initial step, respectively. This figure clearly shows that the chromium atoms at the top layer had especially large values until 2500 step. This result indicates that chromium atoms segregated from the surface faster than the iron atoms to bond with oxygen atoms. After 2500 step, there is little change of the MSD value of the chromium atoms at the top layer. Formation of Cr-O bonds reduced chromium mobility because of the strong affinity between oxygen and chromium. On the other hand, the sharp increase of MSD value of chromium atoms in the second layer after 2,500 step was found. This is because the chromium atoms at the second layer moved towards the oxygen atoms on the surface and finally bonded with them. For the iron atoms, the MSD values of the top layer continue to increase during the simulation, indicating that the iron atoms at the top layer continued moving upward. We found that the iron atoms finally migrated far from the surface comparing with the chromium atoms. This iron diffusion behavior shows the selective dissolution of the iron atoms during the oxide film growth of the Fe-Cr surface in high temperature water.

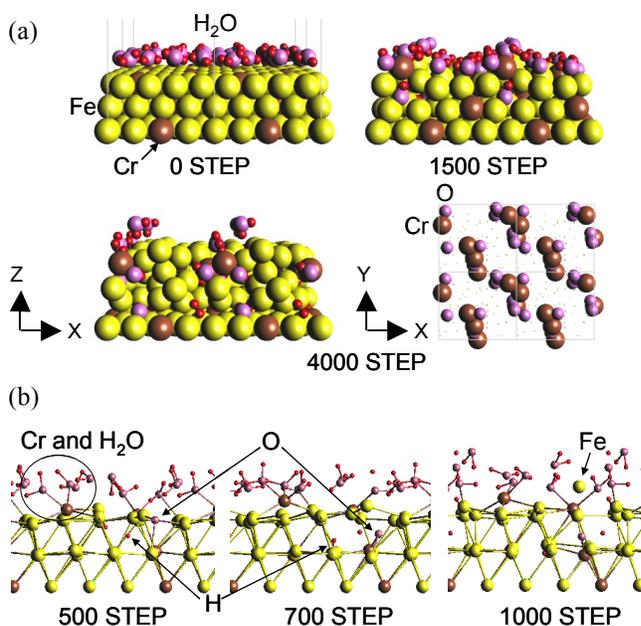


Figure 3: Change of surface morphologies of clean Fe-Cr with H₂O molecules at 561K; (a) snapshots at 0, 1,500 and 4,000 step, (b) inside bonding of the Fe-Cr surface.

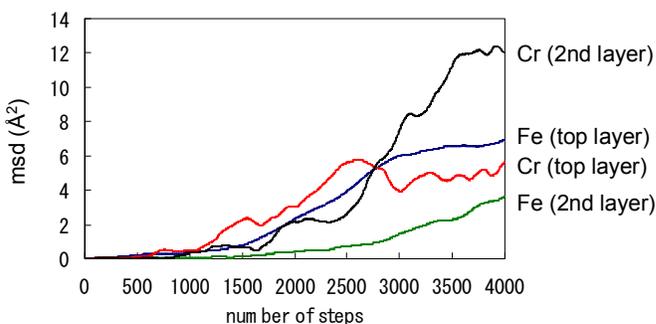


Figure 4: Mean square displacements of Fe and Cr.

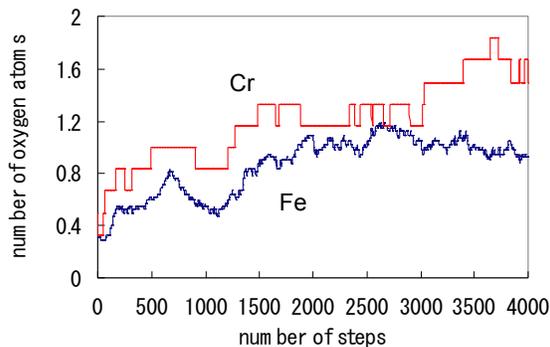


Figure 5: Average number of O atoms within 3.0 Å from metal atoms.

To describe the change in the structure with the oxidation process, we counted the number of oxygen atoms within 3.0 Å from metal atoms all over the calculated cell. Figure 5 shows the change of the average number of

oxygen atoms within 3.0 Å from metal atoms during the simulation. For chromium atoms, the number of oxygen atoms gradually increases with time, indicating that concentration of the oxygen atoms around chromium atoms gradually increased to form Cr-O bonds during the simulation. Compared with iron atoms, the number of oxygen atoms around chromium atoms was larger than that around iron atoms at all the steps. This result indicates that oxygen atoms preferentially bonded with chromium atoms on the Fe-Cr surface. We can confirm that the oxygen atoms were actually distributed around the chromium atoms and the clustering of oxygen and chromium atoms occurred from the snapshot viewed from XY plane at 4000 step in Figure 3(a). The clustering of oxygen and chromium atoms is believed to bring about Cr-based oxide nucleation. In general, the passive film of Fe-Cr alloys formed in an aqueous environment is enriched in chromium. Therefore, the preferential formation of Cr-O bonds is considered to be the initial process of the formation of oxide films on the Fe-Cr surface.

It is interesting to compare the oxidation process in Fe/H₂O with that in Fe-Cr/H₂O for understating the effects of chromium on the formation of surface oxide layers of the stainless steel. The attention paid here to the penetration of oxygen atoms into the surface layers. Figure 6 shows the trajectories of oxygen and spatial distribution of oxygen atoms at final step viewed from YZ plane in the Fe/H₂O and Fe-Cr/H₂O interfaces. When comparing with the trajectories plots, oxygen species penetrated into the Fe surface with greater ease than into the Fe-Cr surface. From the spatial distribution of oxygen, the number of oxygen atoms in the Fe-Cr surface was found to be less than that in the Fe surface. These results suggest that formation of Cr-O bonds prevented the penetration of oxygen deeply and further segregation of metal atoms from the surface in the Fe-Cr surface. We can confirm therefore, chromium atoms have a positive effect to the formation of oxide film on the Fe-based alloy surface in high temperature water.

4 CONCLUSIONS

We have performed quantum chemical molecular dynamics simulation of water in contact with Fe and Fe-Cr surfaces. H₂O molecules were dissociated on the surfaces at 561 K. The chromium atoms at the top layer segregated from the surface faster than iron atoms to bond with oxygen atoms. Some OH group and dissociated oxygen atoms penetrated into the surface layer and inner chromium atoms moved to the penetrating oxygen species to form Cr-O bonds. As a result, chromium concentration around the oxygen gradually increased during the simulation, which resulted in clustering of oxygen and chromium atoms. The clustering of oxygen and chromium is thought to bring about Cr-based oxide nucleation and therefore, the preferential formation of Cr-O bonds is considered to be the initial process of the formation of oxide films on the Fe-Cr alloy surface.

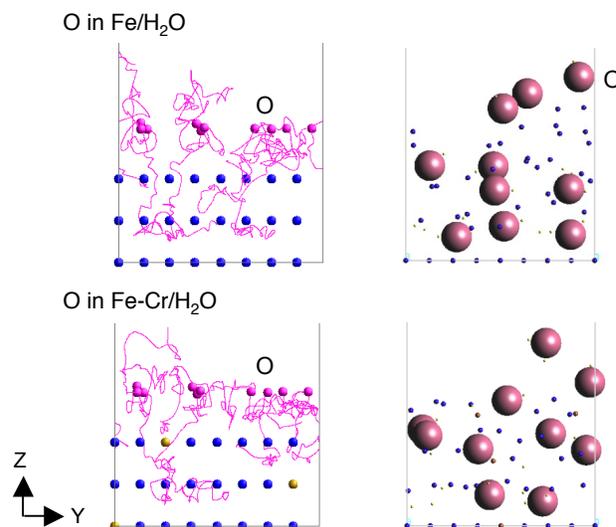


Figure 6: Trajectory plots of oxygen during the simulation and oxygen distribution at final step.

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