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Ab initio molecular dynamics simulation on interfacial reaction behavior of Fe-Cr-Ni stainless steel in high temperature water

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ABSTRACT

The interfacial reaction behavior of Fe-Cr-Ni stainless steel in 320 °C high temperature water is investigated using an ab initio Born-Oppenheimer molecular dynamics simulation. After the Fe-Cr-Ni stainless steel is immersed in water, the water molecule is dissociated into OH and H ions. The dissociated OH makes bond with the Cr and Fe atoms to form (Cr,Fe)-OH hydroxide, and the dissociated H adsorbs on the Fe atoms with a certain negative charge. The surface layers of Fe-Cr-Ni stainless steel are negatively charged before immersion, whereas after immersion there is a net positive charge in the surface layers. Most of the valence electrons lost from the surface layers transfer to the water solution through the interface, only a small amount of electrons comes into the inner layer atoms of Fe-Cr-Ni stainless steel. The dissociation characteristics of dissolved oxygen molecule and dissolved hydrogen molecule in high temperature water are also analyzed, and both of them can enhance the interfacial charge transfer.

1. Introduction

Austenitic stainless steels are materials commonly used for structural elements in the primary loop of nuclear power plants because of their superior mechanical properties and corrosion resistance. However, the corrosion resistance of austenitic stainless steels in high temperature water of primary loop is lower than that at room temperature [1,2]. Some corrosion problems, such as uniform corrosion [3–6], pitting corrosion [7,8], crevice corrosion [9–11] and stress corrosion cracking [12–16] et al. can still be observed in the primary loop. This will cause the potentially dangerous of safety and integrity of nuclear power plants.

The corrosion of austenitic stainless steels in high temperature water of primary loop is an electrochemical process in nature [17–19]. A detailed knowledge of the thermodynamics and kinetics of reactions at the metal/electrolyte interface plays an important role for the understanding and prediction of electrochemical processes on solvated metal surfaces. It is of interest to study interfacial reaction behavior with ab initio molecular dynamics simulation such as Born-Oppenheimer approach [20] that does not rely on any fitted parameters, in order to investigate directly some atomic scale phenomena not yet accessible to traditional experimental techniques. The Born-Oppenheimer molecular dynamics have higher computational accuracy and reliability than other methods [21,22] in the field of ab initio molecular dynamics. However, it is computationally very demanding and only in the past more than ten years the meaningful simulations have been possible with the development of computing power. Vassilev et al. [23] studied the interactions between the Pt (1 1 1) and Rh (1 1 1) surfaces and the water adlayer at room temperature using Born-Oppenheimer molecular dynamics. Jug et al. [24] investigated the processes of adsorption and dissociation of water molecules on the MgO (1 0 0) surface at room temperature by Born-Oppenheimer approach. For austenitic stainless steels, the major constituents are Fe, Cr, and Ni. However, to the best of our knowledge, there has not yet been any report on the interactions between Fe-Cr-Ni stainless steel and high temperature water by this approach. In this work, we will use ab initio Born-Oppenheimer molecular dynamics simulation within the framework of density functional theory to study the interfacial reaction behavior of Fe-Cr-Ni stainless steel in 320 °C high temperature water, and understand its microscopic mechanisms in depth at an atomic scale.

2. Computational methods

The employed model was the face-centered cubic Fe-Cr-Ni supercell, in which the atoms of the Fe substrate were randomly substituted by the Cr and Ni atoms based on the proportion of elemental compositions of 316L stainless steel. This supercell consisted of six layer slabs, including sixty-six Fe atoms, eighteen Cr atoms and twelve Ni atoms. The low-index face (1 1 1) was taken as the representative surface for the present study because it is known to exhibit one of the lowest energy for fcc

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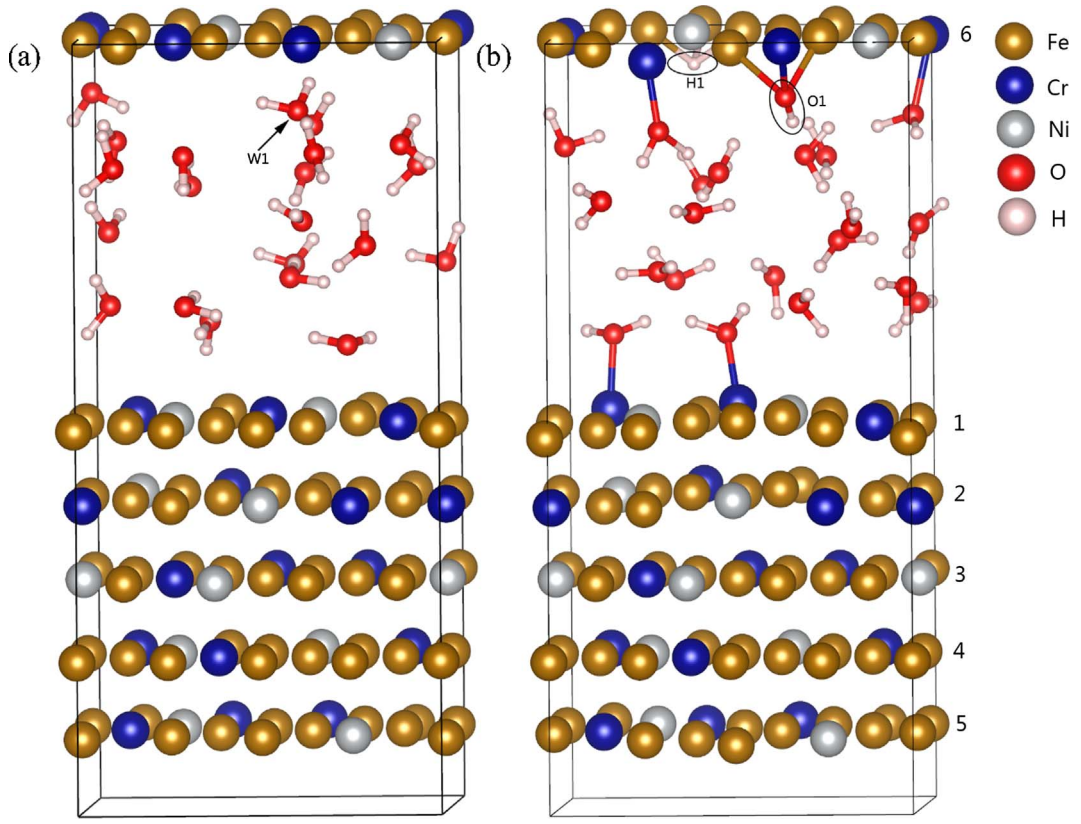

Fig. 1. The atomic morphologies of Fe-Cr-Ni(1 1 1) surface in high temperature pure water, (a) initial stage and (b) after 3 ps dynamics.

structure [25]. A vacuum layer of 10 Å along the z-direction perpendicular to the surface was employed to eliminate the interactions occurring between periodic images under application of the periodic boundary conditions. Before ab initio molecular dynamics simulation, a geometry optimization was performed to relax the Fe-Cr-Ni supercell using a DFT calculation. During the calculation, the middle two layers of the slab were frozen to the bulk positions while the rest of the layers were allowed to relax. The lattice parameters a = 8.63 Å, b = 9.87 Å, c = 20.95 Å, and $\alpha = 89.82^{\circ}$, $\beta = 89.73^{\circ}$, $\gamma = 90.12^{\circ}$ were obtained after geometry optimization. Subsequently, twenty-one water molecules were randomly filled in the vacuum layer of this supercell based on the density of the high temperature water $\rho = 0.76\ g/cm^3$ [17], and the interactions between hydrogen bonds as well as oxygen-oxygen bonds among H_2O molecules were optimized to minimize close contacts .

The Vienna Ab-initio Simulation Package (VASP) [26] was used to perform the Born-Oppenheimer molecular dynamics. The effect of core electrons in the valence density was taken into account by means of projector augmented wave (PAW) method [27] while the valence density was expanded in a plane-wave basis set with a cutoff energy of 400 eV. The Fe-$3d^6 4s^2$, Cr-$3d^5 4s^1$, Ni-$3d^8 4s^2$, O-$2s^2 2p^4$ and H-$1s^1$ electrons were treated as valence electrons. The generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) [28] was employed for the treatment of electron exchange and correlation. The integration over the Brillouin zone was performed with only gamma point for the large unit supercell using a Monkhorst-Pack k-point mesh. The first-order Methfessel-Paxton method was used for the Fermi surface smearing, with a width of 0.2 eV to obtain accurate forces. The convergence criteria of forces and energies were 0.05 eV/Å and 10^{-4} eV. All computations were conducted with spin polarization. The dynamics calculation was performed 3000 steps using a time step of 1 fs in the constant volume and constant temperature (NVT) canonical ensemble. Because it needs an extremely huge computing power for ab initio molecular dynamics simulation, the use of constant volume NVT ensemble can reduce the computation expense. Only the atomic position was relaxed in the NVT ensemble, and the lattice parameters of the supercell were not changed. A Verlet algorithm was used to integrate the equations of motion, and a target temperature of 320 °C based on the actual working condition in the primary loop of pressurized water reactor nuclear power plant was controlled by the velocity scaling method, in which the systemic temperature was always fixed at setting temperature at each time step.

3. Results and discussion

3.1. Reaction behavior in high temperature pure water

The atomic morphologies of Fe-Cr-Ni(1 1 1) surface in high