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A reactive force field molecular dynamics simulation of nickel oxidation in supercritical water

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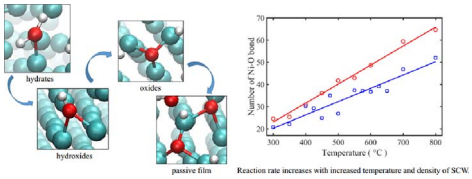
GRAPHICAL ABSTRACT



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ABSTRACT

The atomistic mechanism of nickel (Ni) oxidation in supercritical water (SCW) is investigated using molecular dynamics simulations with a reactive force field. The oxidation kinetics of Ni surfaces in SCW at 300 − 800 °C and 26 − 164 kg/m^3 are simulated. The adsorption, dissociation, and deprotonation processes of water, and the hydroxylation and oxidation processes of Ni are tracked. The oxidation potential of SCW is found to be higher than that of water at normal state. Charge analysis of deprotonation reveals that the dissociation of water is more likely to be a homolytic reaction instead of a heterolitic one under the supercritical state of relatively high temperatures and low densities. Oxidation in SCW prefers the free radical reaction pathway to the ionic pathway, which appears a gas/steam oxidation scope instead of aqueous oxidation. Reaction rate increases with increased temperature and density of SCW.

1. Introduction

Supercritical water (SCW) is receiving considerable attention in various applications, including the extraction of bioactive compounds in green plants [1], the oxidation of organic pollutants [2], and the gasification of low-rank coal [3]. In the field of energy, SCW is used as the working fluid in fossil power plants and nuclear reactors [4–6]. The designed operating parameters are increased significantly in recent years because thermodynamic efficiency is a strong function of steam temperature. Despite the economical benefits, the corrosion of structural materials becomes a bottleneck for the applications of SCW at extremely high temperature and pressure. The corrosion of structural materials in supercritical equipment results in a great amount of energy loss and safety issues and the applications of SCW are limited by the corrosion issues of structural materials.

Among several metallic alloys used for SCW equipment, nickel (Ni)-based alloys are considered to have good performance in the prevention of corrosion. Several experimental studies show the corrosion of Ni-based alloys in SCW [7,8]. However, the influence of temperature and density on Ni oxidation process in SCW still needs to be investigated.

Compared with high-cost and large-scale experiments, molecular dynamics (MD) simulation has become increasingly common to study the properties of SCW and the oxidation process. To describe the intermolecular forces, the potential energy is usually described as a function of the atomic degrees of freedom, which is known as a molecular model or force field. Involving a more realistic force field, MD

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simulations with the reactive force field have shown great efficiency in analyzing the resultant species of chemical reactions and understanding the reaction mechanism. ReaxFF, a reactive force field developed by van Duin and Gooddard III [9], provides a powerful potential model for the MD simulations of chemical reactions, which runs much faster than *ab-initio* methods. The parameters of specific element systems used in ReaxFF are usually trained from quantum-chemical calculation and density functional theory (DFT). Assowe *et* al. [10] developed a set of ReaxFF parameters for Ni-oxyhydroxide system, which agrees well with DFT methods. They simulated the reaction of Ni in aqueous solution at room temperature (300 K). In the absence of external electric field, water molecules are adsorbed to Ni surface, but no Ni composite is generated. Zou et al. [11] simulated the initial stage of oxidation in Ni, and the reaction is in an oxygen atmosphere. Verners and van Duin [12] simulated the Ni nanoplate stress corrosion in water. However, as far as we are concerned, no report on the ReaxFF simulations of Ni or any other metal oxidation in SCW exists. The corrosion behavior is expected to have great differences in SCW compared with those in normal ambient conditions. Zhang et al. [13] investigated the effect of SCW on coal pyrolysis and hydrogen production using ReaxFF MD, which demonstrates the feasibility of ReaxFF on describing the properties of SCW.

In the present paper, MD simulations with ReaxFF are employed to investigate the atomistic mechanism of Ni oxidation in SCW. The species and amounts of chemical products generated during the oxidation process are calculated and analyzed. Charge analysis is also performed to reveal the detailed oxidation mechanism. The effects of temperature, density, and interface orientation are investigated.

2. Computational details

The Ni-H_2O system is modeled using ReaxFF. The total energy is expressed in terms of bond orders, as shown in Eq. (1). Bond order depends on interatomic distances and describes the strength of the chemical bond between atoms. Bonded interatomic interactions are calculated through bond stretching, bending, and torsion within molecules.

$$E_{total} = E_{bond} + E_{val} + E_{tors} + E_{over} + E_{under} + E_{lp} + E_{H\text{-}bond} + E_{VdW} + E_{Coul} \quad (1)$$

Aside from the bond order energy (E_{bond}), other bond energy terms named as the valence angle energy (E_{val}), the torsion angle energy (E_{tors}), the overcoordination penalty energy (E_{over}), the undercoordination energy (E_{under}), the lone-pair energy (E_{lp}), and the hydrogen-bond energy ($E_{H\text{-}bond}$) also contribute to the total energy. The nonbonded energies of van der Waals (E_{VdW}) and Coulomb (E_{Coul}) are also considered in the total energy. The ReaxFF parameters used in this simulation are the same with those of Assowe et al. [10]. To evaluate the accuracy of the ReaxFF description of Ni/O/H, we compare the ReaxFF results with DFT calculation results. All periodic DFT calculations are performed with the CASTEP code [14], and the spinpolarized Perdew – Burke – Ernzerhof (PBE) flavor of DFT [15] and ultrasoft pseudopotentials (USP) [16] are utilized. The cutoff energy is chosen as 571 eV.

Fig. 1**(a)** shows the H–OH bond dissociation curves of isolated water molecule calculated using DFT and ReaxFF, respectively. The dissociation curves are constructed from the equilibrium geometries through single-point calculations while varying the H–OH bond length. ReaxFF provides an equilibrium bond length of 0.97 Å, which is in good agreement with the DFT result (0.98 Å). Fig. 1**(b)** shows the dissociation of water molecule on Ni surface. Structure of the reactant and product are optimized before calculating the energies. The transition state is found and its energy is calculated. The activation energy of dissociation of the adsorbed water molecule on Ni surface is 45.27 kcal/mol from DFT results or 55.66 kcal/mol from ReaxFF results. The reaction energy from reactant to product is −19.27 kcal/mol from DFT results or −26.24 kcal/mol from ReaxFF results. The ReaxFF parameters are good in describing the reaction of water molecule on Ni surface.

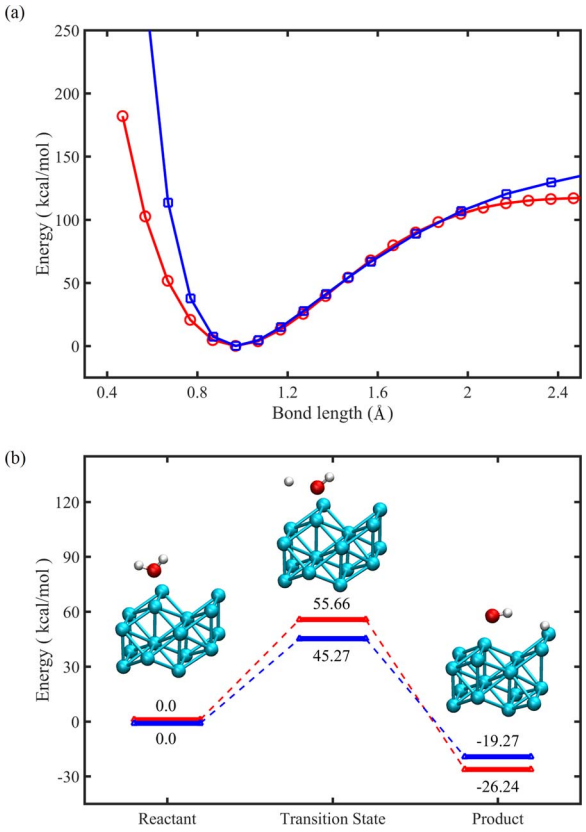

Fig. 1. ReaxFF and DFT data for H–OH bond dissociation. (a) Dissociation of isolated water molecule. Red open circle is the result from ReaxFF. Blue open circle is the result from DFT. (b) Dissociation of water molecule on Ni surface. Red bars stand for the energies calculated from ReaxFF. Blue bars stand for the results from DFT. The structures of reactant, product and transition state are plotted. Cyan balls stand for Ni atoms. Red balls stand for O atoms. White balls stand for H atoms. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

To provide additional validation of the parameters of ReaxFF, the adsorption energy of OH on the Ni(110) surface is calculated and compared with the data by DFT calculations. The binding energies are evaluated for various sites of Ni(110) (top, hollow, and bridge), as shown in Fig. 2. The most favorable binding site is found to be the bridge2 site with shorter Ni-Ni distance for both ReaxFF and DFT, which provide values of −73.38 kcal/mol and −71.69 kcal/mol, respectively. The binding energies on different sites also agree well.

The simulation model is shown in Fig. 3. The size of simulation domain is 28.896 Å × 28.896 Å × 51.896 Å. Ni is well known as a stable crystalline structure of face-centered cubic (fcc). In this work, the lattice constant is set to be 3.612 Å, which is determined through MD simulations with NPT ensembles. An 8 × 8 × 4 Ni super cell is placed at the bottom of the simulation domain. The oxidation process of Ni (110), Ni(100), and Ni(111) surfaces are studied, respectively. The size of super cells and the number of Ni atoms are shown in Table 1. The simulation is performed at 600 °C and 30 MPa, which are the typical parameters in the superheaters of SCW boilers [5].

A total of 150 water molecules are placed above the Ni layer. The density of water is decided according to FEQ Helmholtz equation by Waqner and Pruss [17], which is 87.4 kg/m^3 at 600 °C and 30 MPa. Simulations with NPT ensembles are performed to examine the ReaxFF parameters on describing the state of SCW. In these simulations, a total of 1000 SCW molecules located in a cubic simulation cell with periodic