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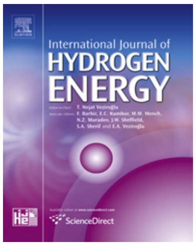

An atomic study of hydrogen effect on the early stage oxidation of transition metal surfaces

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ABSTRACT

Density functional theory (DFT) and tight-binding quantum chemical molecular dynamics (QCMD) have been applied to analyze the role of interstitial hydrogen in the process of oxygen adsorption to Ni (111) and Cr-doped Ni (111) surfaces and diffusion within these metal surfaces. The DFT calculations demonstrate that the fcc hollow and octahedral sites are the most favorable for hydrogen adsorption on the surface and subsurface, respectively. A clean metal surface has a slight inward relaxation in the topmost layer, whereas the metal atoms show outward relaxation (2%) due to interstitial hydrogen. The adsorption energies of oxygen and OH have decreased to 0.26 and 0.13 eV, respectively, and the metal atomic bond further extended in the range of 1–2% in order to hydrogen remained interstitial site. Hydrogen changes to a negatively charged in the interstitial site by receiving electron. The QCMD results reveal that the oxygen penetration depth increases when hydrogen occupy into interstitial octahedral site. The deeply diffused or interstitial hydrogen receives electrons from the metal. Additionally, interstitial hydrogen initiates the charge transfer and extends the metal atomic bond. The localized process weakens the metal–metal bonds and it makes the surface chemically active for further interaction. This process can help oxygen or other species to diffuse into the structure. As a result, the subsurface hydrogen accelerates the early stage of oxidation initiation.

1. Introduction

The interaction of water with solid surfaces is of great importance for many chemical, materials science, and biological phenomena, including in the fields of environmental chemistry, electrochemistry, and corrosion. More specifically, materials exposed to high temperature environment are of great concern for failure. Therefore, numerous researchers have focused on elucidating the mechanisms of that interaction [1,2].

Stainless steels and nickel-based alloys are generally degraded by the dissociative adsorption of water molecules, which produces oxygen, hydrogen and hydroxyl ions on the metal surface. These products subsequently interact and diffuse into the surface and the metal atoms dissolute from their initial position, resulting in oxidation. Surface oxidation is a process of that is a precursor to the early stages of cracking initiation. A recent study observed that the cracking initiation is related to the localization and acceleration of oxidation at the alloy and solution interfaces considering microstructure,

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surface condition, and local environments [3]. Furthermore, hydrogen is an element with a small atomic size, and it is an indispensable element that can immediately diffuse into and trapped within the interstitial sites of face-centered cubic (fcc) metals. Cailletet proposed the interrelationship between metal and interstitial hydrogen more than 150 years ago [4]. Subsequently, the effect of hydrogen on materials has been extensively studied using a variety of experimental and theoretical techniques [5–12]. The presence of trapped hydrogen may be associated with several types of problems in materials, such as hydrogen embrittlement, hydrogen-induced oxidation, hydrogen-enhanced crack growth, and hydrogen oxidation. These studies have accumulated a wealth of experimental and theoretical data, but further study is needed to clarify the role of hydrogen on oxidation initiation process.

Hydrogen induced decohesion causes embrittlement in metals and alloys, is a well known proposed mechanism [13–15]. The electrons from the hydrogen atoms in a solution with a transition metal will enter the d bands of the metallic core, which causes an overlap of the metallic *d* bands resulting in repulsion produce in metallic atoms. The electron concentration then increases in these bands, which results in an increase in the repulsive forces between the metallic cores or a decrease in the cohesive strength of the lattice [16]. The positively charged hydrogen atoms are mainly causing the embrittlement. In addition, several experimental studies have confirmed that the presence of hydrogen in metal increases the oxidation rate [17,18]. This increased oxidation rate due to the presence of hydrogen in metals has been explained by an increased transport rate of metal cations in the oxide, which occurs because the oxide film is more defective [19]. Recently, a transmission electron microscopy (TEM) study has reported that the hydrogen charged coupons of alloy 600 at 288 °C formed a thicker oxide film than uncharged coupons, and a hypothesis for the hydrogen enhanced transport of the cations was proposed [20]. However, the experimental observations concerning the potential role of hydrogen in the oxidation process have not been clearly stated, so it appears that further study is required for understanding the underlying mechanism. Computational chemistry can be a complementary tool for illustrating the promising role of trapped hydrogen in the initiation of the very early stage of oxidation from the atomistic level. Extensive studies have been performed to understand the fundamental mechanism of the interactions between the transitional metal and hydrogen, using the computational chemistry approaches [21–32]. Density functional theory (DFT) studies have focused on the bond strength, bonding nature and local electron transfer process. The hydrogen–transition metal bond is characterized by the charge transferred from the metal atoms to hydrogen. The principal bonding between hydrogen and the nickel surface is due to nickel 4*s*, 4*p* interactions, but there is also a significant contribution from the 3*d* electrons [29]. In addition, studies of hydrogen in ultrahigh vacuum (UHV) conditions have indicated that subsurface hydrogen is often more reactive than surface hydrogen [33]. Likewise, one study of an Nd–Dy–Fe–B alloy has shown that interstitial hydrogen enhances the oxidation [18]. It is clear from the cited literature that subsurface hydrogen plays an important role in the degradation process of materials. Shan et al. experimentally examined water interactions with hydrogen covered nickel surfaces [34]. The authors concluded that hydrogen significantly affects the interaction between the metal surface and water. Several experimental studies have shown that hydrogen influences the oxidation process or enhances oxygen diffusion in metals [17,35,36].

From the corrosion and passivation perspective, the oxygen diffusivity and the nature of oxygen bonding with the elements of the metal surface is important. The main motivation of the present work is to elucidate the role of subsurface hydrogen in oxygen bonding, oxygen diffusivity and the initial stage of oxidation of Ni (111) and Cr-doped Ni (111) surfaces, using DFT and quantum chemical molecular dynamics simulations.

2. Computational details

First-principles calculations and tight-binding quantum chemical molecular dynamics (QCMD) methods were used to separately analyze different phenomena. The first-principles method was applying for investigating the chemisorption energy, geometry and electronic structure of the Ni (111) and Cr-doped Ni (111) surfaces. First-principles calculations were carried out within the framework of the DFT as implemented in the Vienna ab-initio simulation packages VASP [37,38]. The spin-polarized calculations were performed within the projector augmented wave (PAW) method [39]. We adopted the generalized gradient approximation (GGA) with the Perdew and Wang (PW91) functional for the exchange–correlation interaction [40]. The wave functions are expanded in terms of plane waves with in energy cutoff of 400 eV. The Brillouin zone integration was calculated using a 5 × 5 × 1 k-point grid, which is generated automatically using the Monkhorst-Pack method [41]. The surface was described using a repeated slab approach. The Ni (111) and Cr-doped Ni (111) surfaces consisted of five layers with a 2 × 2 supercell, which corresponded to hydrogen, oxygen, OH and H_2O coverage of 0.25 ML. The surface consisted of twenty metal atoms. A chromium doped Ni system was modeled by replacing one of the Ni atoms on top of the surface with a Cr atom. The surface segregation energy is defined as the difference in the total energies of the system with the impurity in a surface layer and in the bulk [42]. The DFT calculated segregation energy is 0.175 eV, which is in agreement with the results of Ruban et al. [42,43]. One Cr atom doped into the second layer of Ni (111) showed a very small amount of negative value. It reveals the moderate segregation. A single Cr atom doping on top of Ni (111) surface is thermodynamically more stable than the subsurface. The vacuum spacing for both surfaces was approximately 12 Å to ensure that there were no significant interactions between the slabs. The convergence tests for the Ni (111) and chromium-doped Ni (111) surfaces indicated that this setup converged with respect to the slab thickness, vacuum spacing and k-point sampling. The calculated equilibrium lattice constant was 3.518 Å for the Ni and 3.51 Å for the Cr-doped Ni (6.25% of Cr) surfaces, which is in good agreement with the experimental values of 3.524 Å and 3.527 Å, respectively [44]. The energy relaxation iterated