

Adsorption and diffusion of fluorine on Cr-doped Ni(111) surface: Fluorine-induced initial corrosion of non-passivated Ni-based alloy



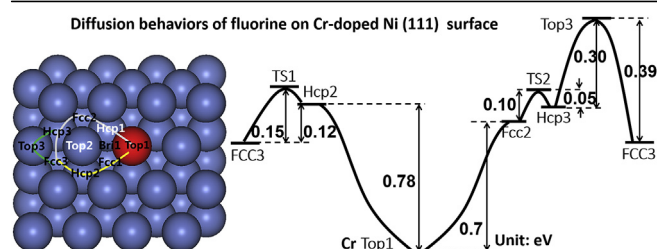
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GRAPHICAL ABSTRACT



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ABSTRACT

Adsorption and diffusion behaviors of fluorine on Cr-doped Ni(111) surface are investigated by using first-principles simulation. It shows that the Cr in the Cr-doped Ni(111) surface serve a trap site for fluorine with adsorption energy 3.52 eV, which is 1.04 eV higher than that on Ni(111) surface. Moreover, the Cr atom is pulled out the surface for 0.41 Å after the fluorine adsorption, much higher than that on Ni(111) surface. Further diffusion behaviors analysis confirms the conclusion because the fluorine diffusion from neighbored sites onto the Cr top site is an energy barrierless process. Detailed electronic structure analysis shows that a deeper hybrid state of F 2 *p*-Cr 3 *d* indicates a strong F–Cr interaction. The Ni–Cr bond is elongated and weakened due to the new formed F–Cr bonding. Our results help to understanding the basic fluorine-induced initial corrosion mechanism for Ni-based alloy in molten salt environment.

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1. Introduction

Molten-salt reactor (MSR) has been selected as one of most

promising next generation nuclear reactors, due to its desirable properties of online refueling and burning of minor actinides in spent fuels, along with the capability of hydrogen production [1–3]. The MSR is designed to run at high temperature (>700 °C) and uses molten fluoride salts mixtures as a coolant, and the fuel is dissolved in the coolant [4]. The high temperature molten fluoride salts intrinsically possess high corrosivity since the passive oxide films have been found to be chemically unstable under the molten salts environment [5]. The corrosion is driven by the difference in free

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energy of formation between the salt constituents and the most susceptible transition metal corrosion products [6,7].

Ni-based superalloy such as Hastelloy N alloy, due to its good high-temperature creep resistance, sufficient neutron radiation brittleness resistance, especially its excellent corrosion resistance to fluoride molten salts, are accepted as the main candidate materials for the structural materials of MSR [4,8]. Hastelloy N has good chemical compatibility with pure molten salts (low corrosion rate (<0.03 mm/y)) [4]. However, the corrosion with dissolution of Cr from the alloys would be aggravated when the salts contain oxidizing contaminants [5,9]. Devan and Briggs et al. [10,11] studied the corrosion behaviors for Ni-based alloy in pure fluoride salts and showed that the corrosion occurred predominantly by dealloying of Cr from the alloy. Olson et al. [12,13] investigated the corrosion behavior of several Ni-based alloys with different original Cr-contents in pure LiF-NaF-KF (FLiNaK) molten salt environments at 850 °C for 500 h, and showed that the higher original Cr-content of the alloys would accelerate the corrosion rate of tested alloys. It also showed that the corrosion mainly occur at the grain boundaries of these alloys. Ouyang et al. [14,15] investigated the corrosion behaviors of Hastelloy N in moisture-containing FLiNaK salt and showed that corrosion caused by aggregate dissolution Cr and Mo into salts. It also revealed that the Cr-, Mo-carbides are formed and precipitated during the corrosion, leading to intergranular corrosion and degradation in mechanical behavior of structural materials.

Actually, corrosion of alloys in fluoride molten salt are complex chemical processes at the alloy/salts' interface. Several steps are included for the corrosion processes, the alloy components susceptible to be corroded (e.g. Cr element) diffuse from the bulk to alloy surface while the corrosive species in molten salts diffuse to the interface. Then, the chemical reaction between the corrosive species and metal surface occurs due to their interactions. Lastly, the metal component diffuse into the molten salts. The surface adsorption and diffusion of the molten salts on alloy surface play an essential role in the chemical reaction processes. It is reported that the adsorption behaviors for H₂O, H₂, O₂ et al. on different metal surface should be the first task to explore their interaction mechanisms. Li et al. investigated the behaviors of H₂O on metal surface including Al [16], Pd [17,18], Ni [19] etc. and used spin-resolved projected density of states (PDOS) method to elaborating their bonding nature. Wippermann et al. [20] studied the H₂O behaviors on Ni surface with oxygen pre-adsorbed. These studies focused on the interaction behaviors between adsorbed molecules and clean metal surface. Until recently, Das and Shoji et al. studied on the early stage oxidation corrosion of binary alloys such as NiCr [21–23], FeCr [24,25] alloys under high temperature water environments by examining the H₂O adsorption and dissociation behaviors on Cr-doped metal surfaces. Except these common oxidizing species, the adsorption behaviors of halogens on metal surface such as Fe [26], Au [27], Cu [28], surfaces as well as Pd-/Pt-based alloy surfaces [29] were investigated to identify their binding behaviors. However, the atomic behaviors concerning about the adsorption and diffusion of the fluorine on alloy surface especially Ni-based alloy are rarely touched up until now.

In this work, to explore the early stage of the initial corrosion processes of non-passivated Ni-based alloy in fluoride salts environments, we systematically study the interaction behaviors of fluorine on the Ni(111) surface as well as Cr-doped Ni(111) surface. There are several hints that fluorine play an important role during the corrosion processes of Ni-based alloy in fluoride molten salts. Firstly, molten salts are in the form of ionic radicals at high temperature, and the fluorine anion radical can contact with the alloy directly [30]. Secondly, the oxidizing contaminants in the molten salts such as HF and F₂ could be catalytically dissociated to fluorine

on the Ni-based alloy surface. The interaction behaviors of fluorine with NiCr alloy and their bonding nature could provide important information for the initial stage corrosion of NiCr alloy in fluorine molten salts environment, which is not well understood yet.

2. Theoretical details

The firstprinciples calculations are performed by using the density-functional theory (DFT) implemented in the Vienna ab initio simulation package (VASP) [31]. The electron-ion interaction are described by using the projector-augmented wave (PAW) potentials and the exchange and correlation are treated with generalized gradient approximation (GGA) in Perdew-Burke-Ernzerhof (PBE) form [32–34]. The energy cutoff for the plane wave expansion is set to 400 eV to ensure good convergence. The geometry optimization is performed using conjugate gradient scheme with force convergence criterion 0.01 eV/Å. Various transition state calculations such as the reaction energy barriers and the diffusion energy barriers are estimated by using climbing-image nudged elastic band (cl-NEB) method [35–37].

To describe the adsorption and diffusion processes of fluorine on pure Ni(111) surface, a four-layer Ni(111) slab with atoms in the bottom layer fixed in their respective bulk positions is used to model the Ni(111) surface. The strategy of single-atom alloy (SAA) is used to model the Ni–Cr alloy. We use one Ni atom at the surface substituted by a Cr atom to model the Cr-doped Ni(111) surface, which has been proposed as an effective way to study the catalytic properties of binary alloys theoretically [38,39].

As shown in Fig. 1, the supercell of the slab is 9.96 × 8.62 Å and the repeated slabs are separated by about 15 Å in c direction to eliminate their interactions. The Brillouin zone is sampled with a Monkhorst-Pack 4 × 4 × 1 k-mesh [40].

The adsorption energy (E_{ads}) reported in present study is defined as the following equation:

$$E_{ads} = -[E_{F/slab} - 0.5 \times E_{F_2} - E_{slab}] \quad (1)$$

where E_{F_2} , E_{slab} , $E_{F/slab}$ are the energies of the F₂ molecule in vacuum, Ni(111) or metal substrate and fluorine adsorption on the metal substrate, respectively. With this definition, a more positive value of E_{ads} corresponds to stronger binding of fluorine on the surface. Herein, the spin-polarized energy are calculated for all of the models. The diffusion energy barrier (E_a) are calculated using the following formula:

$$E_a = E_{TS/slab} - E_{initial/slab} \quad (2)$$

where $E_{initial/slab}$, $E_{TS/slab}$, are the total energies for the initial state, transition state of fluorine on metal substrate, respectively.

Convergence test for the models were performed systemically. We calculated the bulk energy of Ni with 20 × 20 × 20 k-mesh to ensure the convergence. The lattice constant, binding energy and bulk modulus of bulk Ni are calculated to be 3.52 Å, 4.80 eV and 192.73 GPa, respectively, which are consistent with the experimental and other DFT results [41,42]. The convergence test shows that a 4 × 4 × 1 k-point mesh for the Ni(111) surfaces is sufficient (see Table S1). The total energy differences are about 20 meV with that of 7 × 7 × 1 and 8 × 8 × 1 k-point mesh. The energy cutoff is chosen to be 400 eV. The total energy differences are about 10 meV for the higher energy cutoff results (see Table S1). The structural relaxation of Ni(111) surface show that Ni(111) surface exhibit a first and second layer contraction about –1.1% and –0.2%, respectively, which agree well with several previous DFT results too [43,44].

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