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A computational thermodynamic and kinetic study of chlorine binding to the Zr(0001) surface

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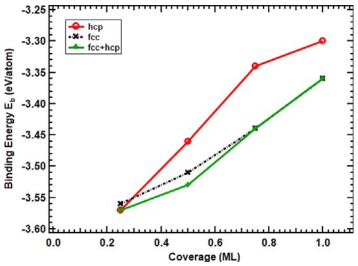
GRAPHICAL ABSTRACT



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ABSTRACT

The investigation of chlorine adsorption and binding to metallic surfaces is important for enhancing our understanding of corrosion and ultimately designing corrosion resistant materials. In this work, the stability and binding of atomic chlorine to various sites on the Zr(0001) surface has been studied by means of density functional theory (DFT) calculations for different surface coverages. The effect of the bound chlorine on the adsorption energy, workfunction, and charge redistribution was recorded and the induced dipole moments were calculated for the different cases. Next, the energy barriers for the chlorine hopping on the surface were investigated via a nudged elastic band calculation. This information was included in a kinetic Monte Carlo simulation which was used to explore the surface mobility. Finally, the surface diffusion coefficient was calculated for two cases; one which included next-nearest neighbor lateral interactions between the adsorbates and one that did not. The differences in the results were analyzed and discussed.

1. Introduction

The information currently available for the interaction of halogen molecules with transition metal surfaces is limited at the atomic scale, thus hindering a deep understanding of the role of these ubiquitous elements in affecting the corrosion resistance of structural and functional materials across nearly every industry. The utilization of zirconium and its alloys in various medical technologies [1–5] and marine environments exposes them to fluids which contain chloride ions at significantly higher concentrations than the atmosphere. Despite the good corrosion resistance of zirconium, it is known to have a relatively low breakdown potential in Cl^- solutions, and becomes more vulnerable to localized pitting corrosion than chromium and titanium in Cl^- solutions [6].

Chloride ions are known to be aggressive corrosion agents that may diffuse through the otherwise protective passive oxide film and deposit at the metal/metal oxide surface. This chloride adsorption to the metal is thought to facilitate metallic dissolution. This was certainly observed in the case of copper for instance where the chloride adsorption to the surface of the clean metal was shown to be a precursor to the

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dissolution of the metal via combination with another chloride ion to form $CuCl_2^-$ [7,8]. The dissolved complexes then react with oxygen to form an oxide. In addition, the adsorption process of chlorine on metallic surfaces and the subsequent dissolution lead to a situation of active oxidation where the ensuing formation of an oxide does not cause a passive layer to emerge but rather can trigger a situation of accelerated corrosion whereby the chloride ions are continuously diffusing through the oxide to the metallic surface and causing its dissolution [9,10]. There is little information in the literature on the thermodynamics or the kinetics involved in each of these crucial steps through which chlorine enhances corrosion. Hence, developing a better fundamental understanding of the thermodynamics and kinetics of the chlorine[1] adsorption and mobility on the metallic surface may be useful for corrosion purposes and the design of corrosion-resistant materials.

In addition to its significance from an applied perspective, chlorine adsorption to various metallic surfaces has also piqued scientists' interest due to the interesting behavior of these systems. In performing studies on chlorine adsorption on metallic surfaces, several intriguing scientific observations had been made on these system over the years. Doll et al. [11,12] proved through DFT calculations that the nature of this interaction for the case of Cl on the Ag(111) and Cu(111) surfaces was ionic. The change in surface charge of the metal was shown to be correlated to its workfunction which is the minimum energy required to remove an electron from a solid. The changes in the workfunction have been found to be material-dependent as well as coverage-dependent [13,14], and although increases in the workfunction are expected for electronegative species, decreases of the workfunction at certain coverages have been observed. Most of the given explanations for this phenomenon have been have focused on the surface polarization and charge transfer [14,15] and several observations and useful correlations were given for certain system relating the bond iconicity to the work function [16]. This issue is interesting for corrosion studies since the workfunction of a metal is known to be closely correlated to its corrosion properties and has been proposed as a useful sensitive parameter for investigating mechanisms responsible for corrosive wear [17,18]. Another interesting feature of this system is the nature of the observed adsorbate–adsorbate interactions in the adlayer. These interactions are expected to be repulsive and this was successfully shown to be the case for several systems [15]. However, attractive chlorine–chlorine adsorbate interactions have also been observed on transition metal surfaces leading to the formation of islands [19].

In this work, we will perform an ab initio investigation of the thermodynamic stability of different structures and configurations of atomic chlorine binding to different adsorption sites on the Zr(0001) surface and at different coverages which is a necessary step towards understanding the corrosive nature of chlorine. Furthermore, we will analyze the charge and workfunction changes induced by the binding process. Finally, the diffusion and mobility of the chlorine on the Zr (0001) will be studied by calculating the hopping barriers and via executing kinetic Monte Carlo simulations.

2. Computational details

2.1. Density functional theory (DFT) calculations

Spin polarized density functional theory calculations were carried out using the Vienna ab initio simulation package (VASP) [20,21] with the implementation of the Projector-Augmented-Wave (PAW) pseudopotentials [22,23]. A generalized gradient approximation (GGA) exchange correlation functional was used as parameterized by Perdew, Burke and Ernzerhof [24]. The valence electron eigenfunctions were expanded in a plane-wave basis set with an energy cutoff of 450 eV and a Methfessel-Paxton smearing of the first order of width 0.1 eV was used in the simulations [25]. The Zr(0001) surface was represented by a p(2 × 2) surface supercell and a seven-layer slab which was separated by a vacuum with a thickness of 20.78 Å to minimize interactions with slab images. The bottom four layers were fixed at bulk positions while the positions of atoms in the top three layers were allowed to relax. Reciprocal length integrations were performed using a (9 × 9 × 1) Monkhorst-Pack Γ-centered k-point grid [26]. The standard dipole correction was introduced along the z-direction in the DFT calculations for better accuracy.

Convergence with respect to the cutoff energy and the k-point mesh was checked. The convergence criterion for the electronic self-consistent calculation was set to 10^{-6} eV. Furthermore, the structure was allowed to relax until the forces acting on the atoms were less than 0.01 eV/Å.

3. Results and discussion

The clean Zr(0001) surface energy was calculated to be 0.92 eV/atom. The (0001) clean surface was observed to exhibit a slight inward relaxation of the top layer $\Delta d_{12} = -6.58\%$ accompanied by a slight expansion of the distance between the second and third atomic planes from the top $\Delta d_{23} = 2.59\%$. The workfunction of the clean slab was also determined to be 4.19 eV. These results are in agreement with previously calculated results for Zr(0001) zirconium surface [27–29] which report surface energy values of (0.81–1.05) eV, consistent results for the interlayer relaxation [28], and a workfunction in the range 4.15–4.23 eV [27,29].

Next, the binding energies for chlorine atoms on different sites of the Zr(0001) surface were determined. This was computed using equation (1) for a 0.25 ML coverage and the results are included in Table 1 below:

$$E_b = E(Zr, Cl) - E_{clean} - \frac{1}{2}E(Cl_2) \tag{1}$$

where $E(Zr, Cl)$ is the total energy of the zirconium slab with one adsorbed chlorine atom, and E_{clean} is the total energy of the clean slab. The total calculated energy for the chlorine molecule was −3.568 eV.

From Table 1 we observe that the adsorption process of chlorine on the Zr(0001) surface thermodynamically favors the fcc and hcp sites to the bridge sites. Hence, and for the rest of the study, we will only explore different configurations of chlorine on the Zr(0001) surface at these two sites and we will neglect the less favorable bridge sites. This finding suggests that a preference for either the fcc sites or the hcp sites could not be distinguished since this is a small difference that may be due to errors in the DFT calculations. These results are consistent with those of Zhu et al. [30] who studied chlorine adsorption on zirconium and also with experimental observation on the Ti(0001) [31] which behaves similarly to zirconium. In Zhu's work [30], the authors reported chlorine adsorption values of −5.01 eV and −5.00 eV for the fcc and hcp sites. The reason for the seeming disparity between these numbers and the ones reported in Table 1 is that the authors in that study reported the adsorption values relative to atomic chlorine rather than the chlorine molecule. When we performed this calculation with respect to atomic chlorine we obtained −5.08 eV and −5.07 eV for the fcc and hcp sites respectively which compares better with Zhu's work.

Table 1
Adsorption information for high symmetry sites for the Zr(0001) surface at a coverage of 0.25 ML.

Site	Fcc	Hcp	Bridge
E_b (eV)	−3.56	−3.57	−3.39
$R_\perp$ (Å)	1.84–1.89	1.88–2.22	1.89–2.06

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[1] In the surface adsorption case it is hard to say what is chloride vs chlorine as adsorbed atoms, such as hydrogen, oxygen and chlorine, tend to undergo a polarized covalent bond, thus creating a partial charge atom that is somewhere between a neutral atom and the anion.