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Full Length Article

The influence of crystal faces on corrosion behavior of copper surface: First-principle and experiment study

Zhengwei Zhang*, Qiang Wang, Xu Wang, Lin Gao

The key Laboratory of Plant Resources and Chemistry of Arid Zones, the Xinjiang Technical Institute of Physics & Chemistry, Chinese Academy of Sciences, 830011 Urumchi, China

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ABSTRACT

When the MBT^-:Cl^- ratio is 50–10:1 in a solution containing of NaCl and Na-MBT (sodium salt of 2-mercaptobenzothiazole), the copper sample-1 (S1) was passivated; when the ration is 10–5:1, it was corroded. The copper sample-2 (S2) had no anti-corrosive ability in all solutions with MBT^-:Cl^- = 50–5:1. First-principle calculation revealed that the Cu atoms of (220) face, the main face of S1, have more unsaturated and energetic electrons than that of (200) and (111) faces, the main faces of S2. The highest chemical activation of the (220) face leads the S1 surface to show a better anti-corrosive ability.

1. Introduction

2-Mercaptobenzothiazole (MBT) molecule (Fig. 1) contains sulfur element, which is allocated into the category of "soft base", and has ability to form strong bond with many metallic cations, the "soft acid". This characteristic makes MBT to be an effective corrosion inhibitor for some metals.

Copper is extensively used, especially in circuit components, circuit board, power transmission line and suchlike fields. Researchers have focused on the corrosion inhibition of copper worked in various corrosive environments, by using of MBT or other molecules with similar structures as inhibitors. Marconato and coworkers [1] studied the inhibition of the electrode process on copper by MBT in ethanol solution. The copper as working electrode was studied in water-ethanol solution containing MBT and $HClO_4$. The MBT formed film to inhibit the anodic copper dissolution and cathodic hydrogen evolution reaction. Kazansky and coworkers [2] studied the MBT adsorption on copper from phosphate solution. The working electrode of copper was tested in phosphate buffer solution (pH 7.4) with MBT. When the concentrate of MBT is above of a critical value 0.7 mmol/l, the copper surface is completely protected. Finšgar and coworkers [3] studied the MBT as corrosion inhibitor of copper long-term immersed in 3 wt% NaCl solution. The exocyclic S atom of the MBT was involved in the molecule adsorption on copper surface. Finšgar [4] studied the 2-Mercaptobenzimidazole (MBIH) as corrosion inhibitor of copper by using of X-ray photoelectron spectroscopy. It was found that MBIH molecules are directed toward the Cu surface through S atom. He and coworkers [5] studied the inhibition behavior of mercaptobenzothiazole on copper by using of real-time bulk acoustic wave. Authors believed that I^- could effectively offer help in the synergistic formation of film with MBT. Ramji [6] and coworkers studied the synergistic inhibition effect of MBT and Tween-80 on the corrosion of brass in NaCl solution.

The MBT was also used to protect Fe surface. Zhang and coworkers [7] studied the adsorption behavior of MBT derivatives on Fe surface immersed in CO_2 saturated solution. The derivative could effectively protect Fe surface and mainly used the two MBT rings to attach the surface.

Moreover, the MBT was employed to modify some noble metal surface. Yang and coworkers [8] studied the MBT monolayer for anticorrosion on zinc surfaces. On Zn surface, the MBT molecules formed monolayer via the two S atoms in the molecule and the other moieties of the molecule were away from the surface. Shervedani and coworkers [9] studied MBT self-assembled monolayer on polycrystalline gold electrode as a nanosensor for determination of Ag^+. The MBT molecule adsorbs on gold surface by the two sulfur atoms. The modified gold electrode could be used to determine Ag^+. Cui and coworkers [10] confirmed that MBT adsorbed on Au(111) surface in a tilted configuration and interacted with the substrate with terminal thiol and sulfur in the heterocycle, through the method of in situ STM. They also obtained photos which showed the MBT molecules orderly assembled at lower potential of 0.15 V, but they are disordered at a higher potential of 0.55 V.

* Corresponding author.
E-mail address: zzw_dxj@sohu.com (Z. Zhang).

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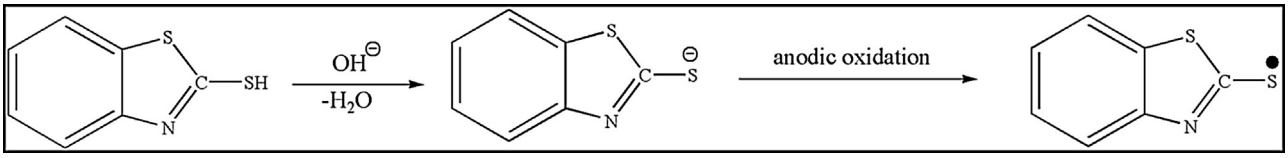

Fig 1. 2-Mercaptobenzothiazole is neutralized by NaOH and its anion is oxidized into radical on anode.

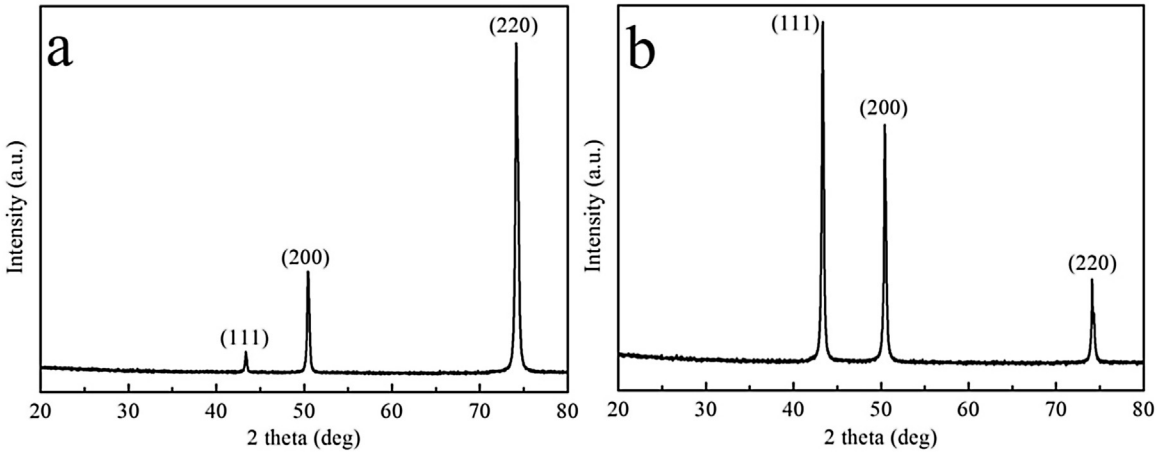

Fig. 2. The crystal faces of S1 surface (a) and S2 surface (b).

The references [1–10] have revealed the anti-corrosion effect mainly from the point of adsorbates in passivation layer. Researchers freshly care the influence of nature of metal surface on its anti-corrosion ability. In the present paper, we are going to investigate the roles of crystal faces in corrosion and anti-corrosion behavior of copper surface.

2. Experiment

Two kinds of copper foil (sample-1 and −2, Sinopharm Chemical Reagent Co., Ltd) surfaces have different crystal faces. The copper foils were cut into small squares with a tail as outgoing line. The side length of square is 10 mm. The squares were polished with emery paper and washed subsequently with acetone and ethanol. Crystal faces of the copper foils were analyzed by X-ray diffraction (XRD) on a PAN-analytical-X'Pert PRO X diffractometer equipped with Cu Kα radiation (λ = 0.15406 nm).The FTIR tests were performed with surface reflection method by using of Nicolet 6700. Electrochemical tests were performed in solution containing Na-MBT (sodium salt of MBT) and NaCl, by employing of Versatile Multichannel Potentiostat 2/Z (VMP2, Princeton Applied Research). The potential was obtained by using of calomel reference electrode in the electrochemical tests. The potential sweeping speed is 10 mV s^{-1} in this work.

3. Computation

According to the XRD analysis, three models of slabs (111), (200) and (220) (p 4 × 4) were prepared with 5 layers of atoms and vacuum range of 20 Å. A single of Cl atom was arbitrarily placed on slabs. The Cl^- anion could freely move on lattice and finally stay at a stable site. The stable adsorption of MBT^- anion on metal surface is adsorbing by using of two sulfur atoms [9,10], so it was placed on slabs in a tilted way. The two kinds of anions adsorb on copper surface after an anodic process. The stable adsorbed surface is electric neutrality. We calculated the thermodynamic and electronic properties of MBT-(220), MBT-(200), MBT-(111), Cl-(220), Cl-(200) and Cl-(111) in their electric neutrality states.

Computations were performed by using of CASTEP code, which adopts fully self-consistent DFT calculations to solve Kohn-Sham equations. The generalized gradient approximation (GGA), with the functional PBE for metallic surfaces, was employed. The electronic wave functions were expanded as a linear combination of plane waves, with a kinetic energy cutoff of 450 eV. The ultrasoft pseudopotentials for Cu, MBT and Cl were used in all calculations. The energy convergence tolerance was 2×10^{-5} eV per atom.

4. Results and discussion

4.1. XRD and FTIR of samples surface

The XRD peaks of Fig. 2 shows the crystal faces of sample-1 (S1) and sample-2 (S2) surfaces. Most of S1 surface is occupied by the (220) face; the (111) and (200) are the main faces of S2 surface. Fig. 3 shows the FTIR spectra of S1 and S2 polarized in Na-MBT (5.0×10^{-2} mol L^{-1}) solution. There are no IR peaks of MBT on S1 surface after potential sweeping from −0.5 to 0 V. In the same potential sweep range, it has IR peaks of MBT on S2 surface. When the potential sweep range was broadened, from −0.5 to 1.0 V and from −0.5 to 2.0 V, the MBT shows characteristic peaks on both of the surfaces of S1 and S2.

The MBT^- anion can actually adsorb on copper surface, and is not easy to adsorb on S1 surface in low potential, but S2 surface is easy to abstract MBT^- anion in lower potential.

4.2. Electrochemical polarization

The pictures of Fig. 4 -(a) and (b) are respectively the electrochemical polarization curves of S1 and S2. Fig. 4-(a1-1) and (b1-1) are orderly the cyclic voltammetry (CV) curves of S1 and S2, which were tested in NaCl (1.0×10^{-2} mol L^{-1}) solution. The path line of positive and negative sweep in both of the two pictures are overlapped. There is no passivation factor, and the two copper samples were absolutely corroded in the NaCl solution. The Cl^- anion begin attack the S1 surface at −0.21 V, see Fig. 4-(a1-2), and attack S2 sur-

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