INFLUENCE OF CRYSTAL ORIENTATION ON THE CORROSION BEHAVIOUR OF COPPER, ALUMINIUM AND NIOBIUM STUDIED USING FIRST-PRINCIPLES CALCULATION

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FACULTY OF SCIENCE AND NATURAL RESOURCES
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ABSTRACT

Corrosion has an important impact on the properties of metal materials. Copper (Cu), aluminum (Al) and niobium (Nb) are widely used in many important fields because of their excellent properties. However, all the three metals are prone to corrosion. In study, the corrosion behaviour of Cu and Al were systematically studied by experimental methods, and the corrosion mechanisms were analyzed by First-principles Calculation. Subsequently, the results of Cu and Al obtained were employed to predict the corrosion resistance of Nb films with different crystal orientations. Firstly, the electrochemical method was used to illustrate the corrosion resistance of Cu and Al with (100), (110) and (111) surfaces in 3.5wt% NaCl, 0.1M H_2SO_4 and 0.1M NaOH solution, respectively. Both the electrochemical impedance spectroscopy (EIS) and polarization curve results revealed that crystal orientation has significant effect to the corrosion resistance of Cu and Al. The order of corrosion resistance for copper was Cu(110) > Cu(100) > Cu(111), and for aluminium was Al(100) > Al(110) > Al(111). Moreover, the corrosion resistance sequence of Cu and Al was the same in 3.5wt% NaCl, 0.1M H_2SO_4, and 0.1M NaOH solution, suggesting that the solution type has no impact on the crystal orientation affecting the corrosion resistance of Cu and Al. Secondly, the surface energy, work function, Mulliken charge population analysis and vacancy formation energy were calculated through First-principles calculation to reveal the corrosion mechanism. The calculation results showed that the Mulliken charge distribution was closely related to the corrosion resistance. A higher value of Mulliken charge led to a greater number of electrons participating in the electrochemical reaction, which in turn resulted in a poorer corrosion resistance. The electron number on each atom on Cu(100), Cu(110), Cu(111) plane was 11.04 e, 10.94 e and 11.14 e, respectively. And the values of Al(100), Al(110), Al(111) was 2.96 e, 2.91 e and 2.99 e, respectively. The Mulliken value order was (111) > (100) > (110), indicating the corrosion resistance sequence was (110)> (100)> (111) for both Cu and Al. In addition, due to the vacancy effect of Al, the vacancy formation energy of Cu(100), Cu(110), Cu(111) were 6.76 eV, 6.71 eV and 7.38 eV, respectively. While the values of Al(100), Al(110), Al(111) were 5.11 eV, 4.63 eV and 5.32 eV, respectively. It indicated that the vacancy was easier to form on the surface of Al than Cu. In the early stage of corrosion process, the corrosion resistance was Al(110)> Al(100) >Al(111), which was controlled by surface effect. In the late period, the corrosion resistance order changed to Al(100)> Al(110) >Al(111), which controlled by surface effect and vacancy effect. To predict the corrosion resistance of Nb with (100), (112), (110) and (120) planes, the surface energy, work function, Mulliken charge population analysis and vacancy formation energy were also calculated through First-principles calculation. Based on the analysis results of Cu and Al, the Mulliken charge distribution was used to predict the corrosion resistance of Nb. Results showed the values of Mulliken charge on the surface atom for the four structures were 13.18 e, 13.13 e, 13.19 e and 13.21 e. Therefore, the order of corrosion resistance for niobium will be Nb(112) > Nb(100) > Nb(110) > Nb(120). This study implies that the First-principles calculation by Mulliken charge analysis and vacancy formation energy analysis can be used to explain the corrosion mechanism metals in different solutions. Moreover, metal-corrosion data can be used to explain the important development trend of metals through simulation approach.

ABSTRAK

PENGARUH ORIENTASI KRISTAL TERHADAP TINGKAH LAKU KAKISAN TEMBAGA, ALUMINIUM DAN NIOBIUM YANG DIKAJI MENGGUNAKAN PENGIRAAN PRINSIP PERTAMA

Korrosi mempunyai kesan penting pada ciri-ciri bahan logam. Copper (Cu), aluminum (Al) dan niobium (Nb) digunakan secara luas di banyak bidang penting kerana ciri-ciri mereka yang baik. Namun, semua tiga logam itu susah untuk kerosakan. Dalam kajian, perilaku kerosakan Cu dan Al telah secara sistematik dipelajari dengan kaedah eksperimen, dan mekanisme kerosakan telah dianalisis dengan Kalkulasi prinsip pertama. Kemudian, hasil Cu dan Al yang diterima digunakan untuk meramalkan perlawanan kerosakan filem Nb dengan orientasi kristal yang berbeza. Pertama, kaedah elektrokimia digunakan untuk memperlihatkan perlawanan korosi Cu dan Al dengan (100), (110) dan (111) permukaan dalam 3,5 wt% NaCl, 0,1M H2SO4 dan 0,1M NaOH penyelesaian, berdasarkan. Kedua-dua spektroskopi impedance elektrokimia (EIS) dan hasil kurva polarisasi menunjukkan bahawa orientasi kristal mempunyai kesan yang signifikan terhadap perlawanan korosion Cu dan Al. Jadual perlawanan korosion untuk tembaga adalah Cu(110) > Cu(100) > Cu(111), dan aluminium adalah Al(100) > Al(110) > Al(111). Selain itu, urutan perlawanan korosi Cu dan Al adalah sama dalam 3.5 wt% NaCl, 0.1M H2SO4, dan 0.1M NaOH penyelesaian, menyarankan bahawa jenis penyelesaian tidak mempunyai kesan pada orientasi kristal yang mempengaruhi perlawanan korosi Cu dan Al. Kedua, tenaga permukaan, fungsi kerja, Analisis populasi muatan Mulliken dan tenaga pembentukan tempat kosong dihitung melalui pengiraan prinsip pertama untuk mengungkap mekanisme kerosakan. Hasil pengiraan menunjukkan bahawa distribusi muatan Mulliken berkaitan dengan perlawanan korosion. Nilai yang lebih tinggi muatan Mulliken membawa kepada bilangan elektron yang lebih besar yang berpartisipasi dalam reaksi elektrokimia, yang menurutnya mengakibatkan resistensi korrosion yang lebih buruk. Nombor elektron pada setiap atom pada kapal Cu(100), Cu(110), Cu(111) adalah 11.04 e, 10.94 e dan 11.14 e, respectively. Dan nilai Al(100), Al(110), Al(111) adalah 2.96 e, 2.91 e dan 2.99 e, respectively. Turutan nilai Mulliken adalah (111) > (100) > (110) untuk Cu dan Al, yang menunjukkan bahawa urutan perlawanan korosion adalah (110)> (100)> (111). Kerana kesan tempat kosong Al, tenaga formasi tempat kosong Cu(100), Cu(110), Cu(111) adalah 6.76 eV, 6.71 eV dan 7.38 eV, respectively. Sementara nilai Al(100), Al(110), Al(111) adalah 5.11 eV, 4.63 eV dan 5.32 eV, respectively. Ia menunjukkan bahawa tempat kosong adalah lebih mudah untuk membentuk di permukaan Al daripada Cu. Pada tahap awal proses korosion, perlawanan korosion adalah Al(110)> Al(100) >Al(111), yang dikawal oleh kesan permukaan. Dalam masa lewat, perintah perlawanan kerosakan berubah kepada Al(100)> Al(110) >Al(111), yang dikawal oleh kesan permukaan dan kesan kosong. Untuk meramalkan perlawanan korosi Nb dengan (100), (112), (110) dan (120) pesawat, tenaga permukaan, fungsi kerja, analisis populasi muatan Mulliken dan tenaga formasi kosong juga dihitung melalui pengiraan prinsip pertama. Berdasarkan hasil analisis Cu dan Al, distribusi muatan Mulliken digunakan untuk meramalkan perlawanan korosion Nb. Hasil menunjukkan nilai muatan Mulliken pada atom permukaan bagi empat struktur adalah 13. 18 e, 13. 13 e, 13. 19 e dan 13. 21 e. Oleh itu, tertib penentangan korosion untuk niobium akan Nb(112) > Nb(100) > Nb(110) > Nb(120). kajian ini menunjukkan bahawa pengiraan prinsip-pertama oleh analisis muatan Mulliken dan analisis tenaga formasi kosong boleh digunakan untuk menjelaskan mekanisme kerosakan logam dalam penyelesaian yang berbeza. Selain itu, data kerosakan logam boleh digunakan untuk menjelaskan perkembangan penting logam melalui pendekatan simulasi.

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LIST OF ABBREVIATIONS

Cu	- Copper
Al	- Aluminium
Nb	- Niobium
OCP	- Open Circuit Potential
EIS	- Electrechemical Impedancy Spectroscopy
SCE	- Saturated Calomel Electrode
XRD	- X-ray Diffraction
FESEM	- Field Emission Scanning Electron Microscope
GGA	-Generalized Gradient Approximation
LDA	- Local Density Approximation
DFT	-Density Functional Theory
ORR	- Oxygen Reduction Reaction
HER	- Hydrogen Evolution Reaction
FCC	- Face Centered Cubic
BCC	- Body Centered Cubic
HCP	- Close-Packed Hexagonal
PBC	- Periodic Boundary Conditions

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CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Metallic materials have become an important basis for the development of human society (Johnson, 2009; Tao et al., 2007). Among all the metal materials, copper (Cu), aluminium (Al) and niobium (Nb) are widely used because of their excellent properties. Cu has the excellent thermal conductivity, electrical conductivity, and ductility (Xiao, 2021; Jmiai et al., 2018). Al possesses several fascinating properties, such as good electrical and thermal conductivity, low density and easy to process (Lucente, 2008; Cao et al., 2005). Nb has the characteristics of high melting point and high mechanical strength (Wang & Alfantazi, 2015; Gontad et al., 2016; De Freitas et al., 2016). All the three metals and their alloys are widely used in transportation, machinery, industries fields, etc.

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However, corrosion is likely to occur under high humidity or typical types of solutions, such as seawater, acidic or alkaline solutions (Kang, 2010). Corrosion refers to the phenomenon that the material transforms into a new phase, suffers damage, and loses its inherent properties due to harmful chemical, electrochemical or physical changes in the surrounding environment (Johnson, 2009). The free energy of the corrosion system decreases when the corrosion occurs. The serious corrosion metals are shown in Figure 1.1.

Corrosion is a serious problem in nearly every industry. Solving or delaying the corrosion rate of metal materials is a big challenge. Revealing the corrosion mechanism and improving the corrosion resistance are significant in material fields.

To investigate the corrosion mechanism, it is advisable to initiate the study by focusing on the factors that contribute to corrosion.

Figure 1.1 : Serious Corrosion of Metals

Many factors may cause the metal corrosion, like the environmental factors (such as the concentration, pH, temperature, pressure, etc.), the surface state of metal (about the dust, oil, water, oxide skin, rust and other surface defects). While the main factor attributes to the inner microstructure of the metal (Liu & Shang 2021b; Martinez-Lombardia et al., 2014; Hagihara et al., 2016; Yang et al., 2020). Many studies are focusing on the effect of crystal orientation on metal corrosion in recent years (Zbigniew et al., 2015; Song & Xu, 2012, Lopez-Sesenes et al., 2018; Zhu et al., 2022). They proposed that the corrosion behaviour was correlated with grains and orientation-dependent. Feng Wen investigated the effect of crystal orientations and precipitates on the corrosion behaviour of the Al-Cu alloy using single crystals, they viewed that the corrosion resistance of the alloy without precipitates was mainly determined by the atomic density of the crystal plane (Wen et al., 2022). Studying the corrosion mechanism of metal materials from crystal structure field is a good way to guide us designing more advanced corrosion-resistant materials.

As single crystal structure refers the atoms with regular arrangement and no grain boundaries to accelerate corrosion, many investigations choose the single crystal materials to investigate the correlation between the crystal orientation and corrosion behaviour (Zhu et al., 2022; Song et al., 2010; Seo et al., 2003). For Cu, Masatoshi Sugimasa, Fang, et al. try to reveal the corrosion mechanism through