Effect of Ti content on corrosion behavior of Cu−Ti alloys in 3.5% NaCl solution

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Abstract: The corrosion behavior of the Cu−Ti alloys with different Ti contents in 3.5% (mass fraction) NaCl solution was investigated using electrochemical measurements, immersion tests, mass loss measurements and SEM observation. The results show that Ti dissolved in the Cu matrix changes the corrosion process of the alloys. Pure Cu sample exhibits a typical active–passive− transpassive corrosion behavior. The anodic polarization current densities of the Cu−Ti alloys steadily increase with increasing applied potential, indicating that active dissolution of copper proceeds due to the potential difference in the galvanic coupling of Cu and Ti. The increase of Ti content decreases the corrosion resistance of the Cu−Ti alloys.

Key words: Cu−Ti alloy; potentiodynamic polarization; mass loss; immersion test

1 Introduction

Copper and its alloys have been extensively used as materials for the preparation of ship apparatus exposed to seawater and marine environments because of their low susceptibility to corrosion [1]. Among the materials used, pure copper is mainly used for conductive parts such as electric circuit boards and wires, Cu−Ni alloys are used for condenser tubing in marine applications, and Cu−Al and Cu−Mn alloys are often used for pump valves, shaft sleeves and pipe fittings. The corrosion behavior of copper and copper alloys has been widely reported [2−7]. Various inhibitors [2−4] and surface films [5] have been used to improve the corrosion resistance of these materials because copper and most copper alloys are poorly passivated in seawater or artificial seawater [6,7]. Even though there are many copper alloys used on ships, there is a need for more variety and the rational application of these materials, which is the ultimate goal in future development.

Dilute Cu−Ti alloys (containing approximately 1%−5% (mass fraction) Ti) are widely known as a substitute for expensive and toxic Cu−Be alloys [8]. They have been used as conductive springs and interconnections with high strength and good electrical conductivity. Most of the research has focused on their mechanical properties and electrical conductivity [9,10]. Their investigation was focused on the aging process in dilute Cu−Ti alloys, which illustrates the relationship between the hardness, tensile strength, electrical conductivity, and evolution of the microstructure. Because dilute Cu−Ti alloys have attractive mechanical properties and favorable electrical conductivity, it is necessary to gain a better understanding of the underlying corrosion mechanism to be able to expand their application. However, only a few researchers are investigating the corrosion behavior of dilute Cu−Ti alloys [11]. We have explored the correlation of aging precipitates with the corrosion of Cu−4%Ti (mass fraction) alloys in 3.5% (mass fraction) NaCl solution [11]. The effect of Ti dissolved in the Cu matrix on the corrosion behavior of the Cu−Ti alloys is still not clear. A fine scale precipitation Cu_4Ti phase forms in Cu−Ti alloys prepared by solution treatment if the Ti content exceeds 4.0% (mass fraction) [12]. Therefore, Cu−2%Ti and Cu−4%Ti (mass fraction) alloys were used to carry out the study and to eliminate the effect of precipitate on the corrosion behavior of dilute Cu−Ti alloys.

In the present work, we investigated the corrosion behavior of dilute Cu−Ti alloys in 3.5% (mass fraction)

NaCl solution to clarify the mechanism of the corrosion process. The effect of Ti content on the corrosion behavior of the alloys was analyzed using electro-chemical techniques and immersion tests.

2 Experimental

2.1 Preparation of materials

Alloy ingots with a nominal composition of Cu−2%Ti and Cu−4%Ti (mass fraction) (Jiangxi Ke Thai New Materials Co., Ltd., Jiangxi, China) were prepared by melting pure copper (99.99%) and titanium (99.99%) in an argon atmosphere. Cu−2%Ti and Cu−4%Ti alloys were named Cu−2Ti and Cu−4Ti alloys, respectively. To clarify the effect of Ti dissolved in the Cu matrix on the corrosion behavior of the Cu−Ti alloys, pure copper was also tested for comparison. Electrochemical measurements and immersion tests were performed using 10 mm × 10 mm × 6 mm plates that were cut from ingots. The Cu−Ti plates were solution-treated at 1203 K for 2 h and quenched in water at ambient temperature. The pure copper plates were annealed at 973 K for 2 h.

A copper wire was encircled and mounted in epoxy resin. A surface area of 100 mm^2 was exposed for use in the electrochemical tests. Specimens for the electrochemical measurements and immersion tests were ground to 2000 grit, polished, and cleaned with acetone (Chuandong Chemical Co., Ltd., Chongqing, China) and deionized water before tests. All corrosion measurements were carried out at ambient temperature and conducted in naturally aerated solution. The electrolyte was 3.5% (mass fraction) NaCl solution (3.5 g of NaCl per 96.5 mL deionized water, Chuandong Chemical Co., Ltd., China).

2.2 Electrochemical measurements

Electrochemical measurements were conducted using an electrochemical workstation CS350. A conventional three-electrode apparatus was used, which consists of a working electrode, a counter electrode made of platinum foil, and a saturated calomel electrode (SCE) as the reference electrode. Before electrochemical tests, all specimens were immersed in 3.5% NaCl solution for 90 min to stabilize the open circuit potential (φ_{ocp}). Following this, impedance measurements were performed at φ_{ocp} over a frequency range from 1×10^5 Hz to 1×10^{-2} Hz with a signal amplitude perturbation of 5 mV. The electrochemical impedance spectroscopy (EIS) data points were fitted using ZSimpWin software. The potential for potentiodynamic polarization test was scanned from −1500 to 1000 mV (vs SCE) at a scan rate of 1 mV/s. All cyclic voltammetry measurements were carried out using a scan rate of 10 mV/s. Each electrochemical experiment was carried out at least three times, and the results were duplicated.

2.3 Immersion tests

After they were ground, polished, cleaned and dried, the specimens were weighed with an electronic balance (QUINTIX213−1CN, Sartorius AG, Germany) to an accuracy of 0.1 mg to find the initial mass (m_0). Then, the specimens were immersed in 100 mL of 3.5% NaCl solution for 4 and 8 d at room temperature. The corroded specimens were cleaned with deionized water and dried. The corrosion products were analyzed by TD−3500 X-ray diffraction (XRD). After that, the specimens were immersed in a solution of 0.6 mol/L hydrochloric acid (Chuandong Chemical Co., Ltd., China) for 3 min to remove the corrosion products, washed quickly with deionized water, dried and then weighed to obtain their final weights (m_1). The surface morphologies of the corroded specimens without corrosion products were observed by TESCAN VEGA3 scanning electron microscope (SEM).

3 Results

3.1 Electrochemical measurements

The impedance measurement results of the Cu, Cu−2Ti and Cu−4Ti alloys are shown in Fig. 1. The Nyquist plots obtained from all of the specimens exhibit a depressed semicircle in the high frequency region followed by a straight line in the low frequency region. The low frequency impedance is known as the Warburg's impedance, which means that the corrosion of both Cu and Cu−Ti alloys is originated from mass transport to some extent. Moreover, the radius of the semicircles observed for the Cu−Ti alloys decreases with increasing Ti content (Fig. 1(a)), demonstrating a decrease in the corrosion resistance. The corresponding Bode plots, shown in Figs. 1(b) and (c), further indicate the variation in the corrosion resistance for all specimens. Both the resistance value and the phase angle decrease with increasing Ti content. The impedance measurement results show that the corrosion resistance degrades as a result of the addition of Ti to copper.

To specifically investigate the electrochemical processes in the interface between metal and electrolyte, impedance parameters were obtained using the software ZSimpwin by fitting Nyquist plots. The equivalent circuit model [11] used for fitting is given in Fig. 2, which is suitable for all samples under study, with the chi-squared values of 1.694×10^{-4}, 6.771×10^{-4} and 1.654×10^{-4}, corresponding to Cu, Cu−2Ti and Cu−4Ti, respectively. In this work, R_1 represents the solution resistance, R_2 is the resistance of the film formed on the specimen surface, and R_3 is the charge transfer resistance. Q_1 and Q_2 represent the constant phase elements (CPEs).