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Experiment and Research on Corrosion Resistance of Surface Film of Modified Multi-element Copper Alloy

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In this paper, a novel copper-nickel-aluminum multi-element alloy was prepared and the corrosion products, average corrosion rate, and polarization characteristics of the alloy at different corrosion duration and pH values were studied. The results have shown that as the corrosion duration increases, the corrosion products on the surface of multi-element copper alloys change. After etching for 72h, it was Cu_2O; for 168h, it was a mixture of Cu_2O and CuO; for 336h, it was mainly CuO. The longer the corrosion duration and the greater the pH value, the lower the average corrosion rate of the copper alloy. And copper alloys showed significantly lower corrosion rate in alkaline environments than that in acidic conditions. The corrosion process of the multi-element copper alloy can be divided into three stages, namely, the stage of generating the corrosion product film, the stage of forming a dense corrosion film on the surface of the copper alloy, and the stage of generating a stable passivation film on the surface of the copper alloy. In the alkaline condition, there was no oxide of Cu^{2+}, and the final product was $Cu_2(OH)_3Cl$ that would not destroy the formed Cu_2O dense passivation film. The corrosion products on the alloy surface protect the internal alloy.

1. Introduction

The modified copper alloy is a combination of various metallic alloy elements mainly composed of nickel element added to a copper-based alloy, also called the copper-nickel alloy, featuring high elastic modulus, high strength, corrosion resistance, anti-pollution and easy processing, etc., for which it has been now widely used in the surface coating of various types of machinery (ships, pipelines, electronic components, etc.) (Klassert and Tikana, 2007). In recent years, the nickel-alloy surface coating on marine large vessels still failures in the corrosion resistance. Therefore, the corrosion resistance of copper-nickel alloys under severe conditions still needs further research (Lenard, 2002; Shen et al., 2014; Yuan and Pehkonen, 2007; Zhu and Lei, 2002).

At present, researches have been made more on the corrosion resistance of copper-nickel alloys such as B10 and B30 with relatively simple compositions, such as the modified characteristics of copper-nickel alloys corroded by chloride ions (Badawy et al., 2005; Badawy et al., 2010; Badawy et al., 2006; Alfantazi et al., 2009; Chervyakov et al., 2004), the improvement of different metallic elements added for copper-nickel alloys (Seo et al., 2002; Fang et al., 2009; Li et al., 2010), and the influence of the surface state of materials on corrosion resistance (Drolenga et al., 2015; Al-Thubaiti et al., 2005). However, most of the above researches were carried out in laboratory conditions with single influencing factors. In contrast, copper-nickel alloys are affected by various factors such as the pH value, corrosion duration, and chloride ion concentration in practice (Rajasekaran and Mohan, 2013; Martinez and Metikoš-Huković, 2006).

In this paper, a new type of copper-nickel-aluminum multi-element alloy was prepared to eliminate some limitations in previous researches, and the corrosion resistance of the alloy under different corrosion duration and pH values was studied, whose results can provide new research paths for the engineering application of new copper-nickel alloys.

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2. Experimental materials and rationale

The content of various metal elements in the modified copper-nickel alloy prepared in this paper is shown in Table 1.

Table 1: Content of Metal Elements in Modified Copper-Nickel Alloy (%)

Ni	Al	Fe	Cr	Si/Ti/Mn/Zr	Cu
18.0	4.0	2.5	2.0	4.0	69.5

The modified alloy was fabricated to have the dimension of Φ800mm×Φ650mm×100mm, and the chloride ion corrosion specimen was 50mm×25mm×5mm in size. After successful preparation, the specimen underwent grinding, ultrasonic cleaning, drying, and polishing.

Chloride ion corrosion test: The concentration of NaCl was 5%, and the NaCl solution was added with different concentrations of HCl in the order of pH=2-12. After etching for a period of duration, the lost weight of the specimen was measured. And then the corrosion rate of the modified copper-nickel alloy, R, was calculated by the weight loss as follows:

$$R = \frac{8.76\times\left(m_0 - m_1\right)}{ST\rho} \tag{1}$$

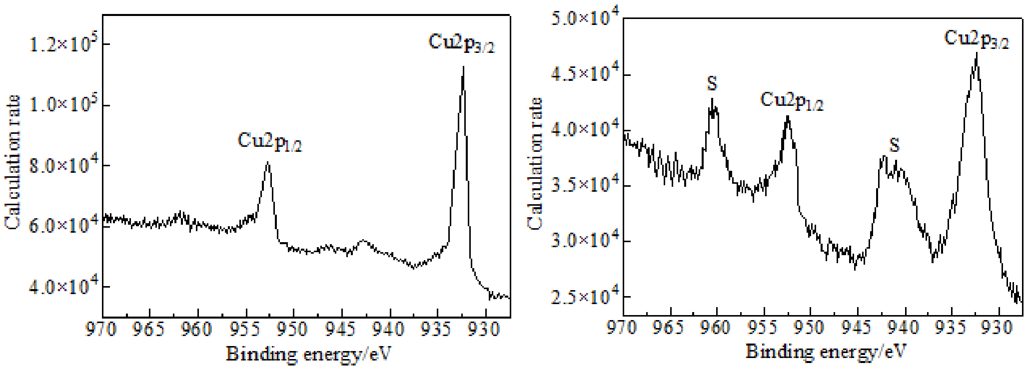
Corrosion product analysis: Multi-functional spectrometer; polarization curve measurement: IM6ex Electrochemical Workstation

3. Experimental methods and analysis

3.1 The influence of corrosion duration on corrosion of modified multi-element copper alloy

First, the influence of corrosion duration on the corrosion of the modified multi-element copper alloy was studied. Figure 1 shows the results of Cu2p narrow-spectrum analysis of specimens at different etching duration. The main corrosion product of the specimen was $Cu_2(OH)_3Cl$. As can be seen from the figure, after the sample was immersed for 72 hours, two split spectral lines $Cu2p_{1/2}$ and $Cu2p_{3/2}$ appeared mainly in the spectrum; when the etching duration increased to 336h, two shape-up peaks S were added between the two split lines.

The binding energy of Cu2p was almost the same under different etching duration. Combined with the energy spectrum analysis, it can be seen that with the increase of corrosion duration, the surface corrosion product of multi-element copper alloy was only Cu_2O for 72h, a mixture of Cu_2O and CuO for 168h, and mainly CuO for 336h.



(a)72h Cu2p Narrow spectrum (b)336h Cu2p Narrow spectrum

Figure 1: Cu2p narrow-spectrum analysis results of specimens at different etching duration

Figure 2 shows the overall corrosion rate of the prepared multi-element copper alloy at different etching duration. It can be seen from the figure that the longer the etching duration was, the lower the corrosion rate of the alloy was. When the etching duration was 72h, the corrosion rate was 0.021mm/a; when the etching duration increased to 336h, the average corrosion rate dropped to 0.001mm/a. According to the corrosion resistance standard of metal alloys, the multi-element copper alloy prepared in this paper had sound corrosion resistance.

Figure 3 shows the polarization curves of multi-element copper alloys at different etching duration. After being eroded by chloride ions, the multi-element copper alloy formed a passive film on the surface. When the potential increased gradually, the current increased. When the current density was 1E5—1E4A/cm^2, the polarization curve showed a clear passivation film. The longer the etching duration, the greater the passivation platform formed. The corrosion product on the alloy surface well protected the internal alloy.

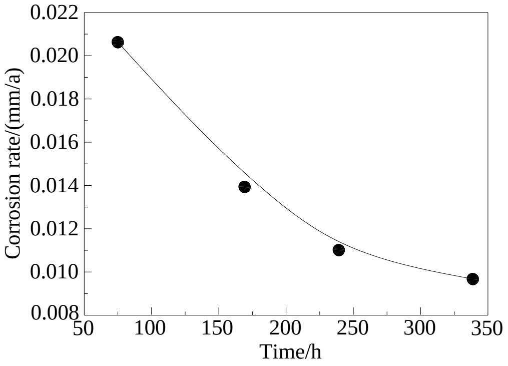


Figure 2: Average corrosion rate of multi-element copper alloys at different etching duration

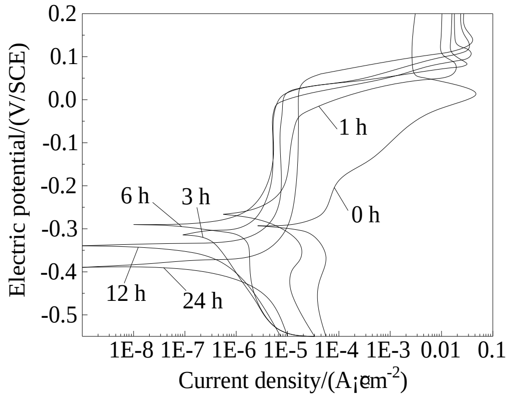


Figure 3: Polarization curves of multi-element copper alloys at different etching duration

According to the above analysis, the corrosion process of the multi-element copper alloy could be divided into three stages:

(1) The corrosion product film started to be generated, with the anode reaction in the solution as:

$$\begin{cases} Cu + 2Cl^- \rightarrow CuCl_2 + e \\ 2CuCl_2 + H_2O \rightarrow Cu_2O + 4Cl^- + 2H^+ \end{cases} \tag{2}$$

The main component of the corrosion pattern in the initial stage was Cu_2O in light yellow.

(2) A dense corrosion film formed on the surface of the copper alloy, with the anode reaction as:

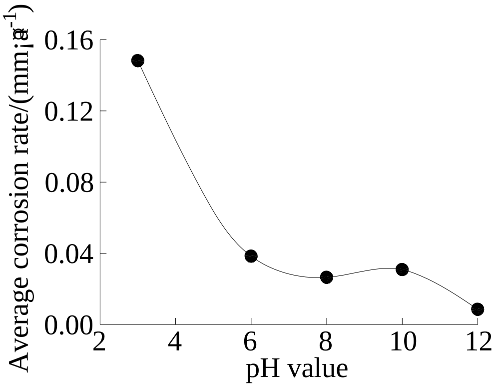
$$2Cu + H_2O \rightarrow Cu_2O + 2H^+ + 2e \tag{3}$$

At this duration, the Cu element on the surface of the copper alloy was directly etched to generate Cu_2O in purple red.

(3) A stable passive film formed on the surface of copper alloy:

$$Cu_2O + 1/2O_2 + Cl^- + H_2O \rightarrow Cu_2\left(OH\right)_3Cl + OH^- \tag{4}$$

At this point, the final product on the surface of the passivation film was $Cu_2(OH)_3Cl$, and the film was in blue-green. It has been found that Cu2(OH)3Cl does not destroy the formed dense Cu_2O passivation film.



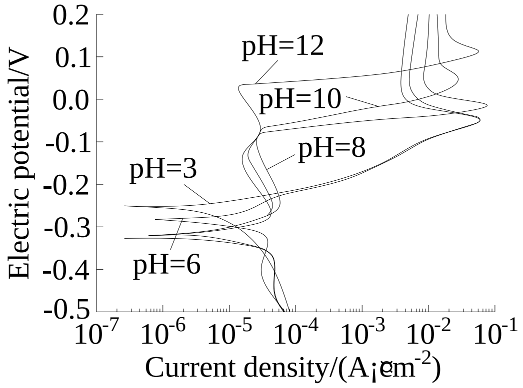


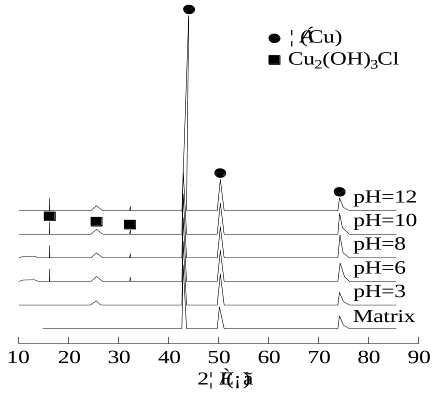
Figure 4: Average corrosion rate of multi-element copper alloys at different pH values

Figure 5: Polarization curves of multi-element copper alloys at different pH values

3.2 The Influence of pH values on corrosion of modified multi-element copper alloy

The influence of the pH values of corrosion solution on the corrosion of multi-element copper alloys was further explored. Figure 4 examines the average corrosion rate of multi-element copper alloys at different pH values. From the figure, the higher the pH value, the lower the corrosion rate of the copper alloy. And the average corrosion rates of copper alloys at pH=6 and pH=12 were only 1/5 and 1/30 of that at pH=3, respectively.

Figure 5 shows the polarization curves of multi-element copper alloys at different pH values. As can be seen from the figure, the polarization characteristics of multi-element copper alloys differed greatly at different pH values. When the pH value was higher than 7, the copper alloy was more likely to undergo passivation reaction, resulting in a clear "passivation platform". While the passivation platform was smaller when Ph <7 and the solution was alkaline, the corrosion current density of the copper alloy was positively proportional to the polarization potential, with the width of the passivation platform generally between 150 mV and 250 mV. The larger the width of the passivation platform, the more stable the oxide film on the surface of the copper alloy was, and the better the internal protection of the copper alloy was. Therefore, the corrosion rate of copper alloys in an alkaline environment was significantly lower than that in an acidic condition.



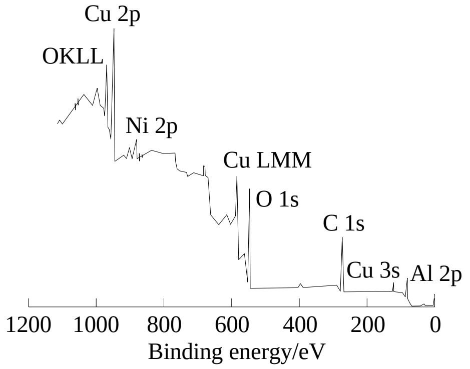


Figure 6: XRD spectra of corrosion products of multi-element copper alloy at different pH values

Figure 7: XPS spectra of corrosion products of multi-element copper alloys at pH=12

Figure 6 shows the XRD spectra of corrosion products of multi-element copper alloys at different pH values. As can be seen from the figure, when the pH value was higher than 7, $Cu_2(OH)_3Cl$ particulate corrosion products were generated on the surface of the alloy.

Fig. 7 and Fig. 8 show the XPS spectra and Cu2p narrow-spectrum analysis results of the corrosion products of the multi-element copper alloy at pH=12. From Figure 6 - Figure 8, it can be observed that in the alkaline environment, Ni2p and Al2p bands also existed in the copper alloy surface spectrum besides Cu2p. The peaks of $Cu2p_{1/2}$ and $Cu2p_{3/2}$ split spectral lines were located at 952.8 and 932.6 eV, respectively, and there was no vibration peak S beyond $Cu2p_{1/2}$ and $Cu2p_{3/2}$. Then it can be concluded that there was no Cu^{2+} oxides in alkaline conditions.

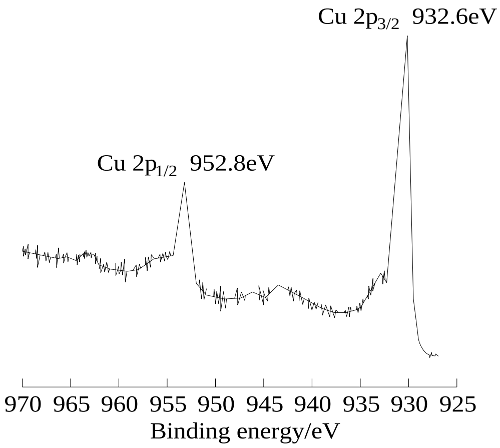


Figure 8: Cu2p narrow-spectrum analysis results of the multi-element copper alloy at pH=12

4. Conclusion

In this paper, a novel copper-nickel-aluminum multicomponent alloy was prepared, and the corrosion products, average corrosion rate, and polarization characteristics of the alloy at different corrosion duration and pH values were studied. The conclusions are as follows:

(1) As the corrosion duration increases, the corrosion products on the surface of the multi-element copper alloy also change. After etching for 72h, it was Cu_2O; for 168h, it was a mixture of Cu_2O and CuO; for 336h, it was mainly CuO. The longer the etching duration, the lower the average corrosion rate of the copper alloy and the greater the passivation platform formed. The corrosion product on the alloy surface can protect the internal alloy.

(2) The greater the pH, the lower the corrosion rate of the copper alloy. When pH>7, the copper alloy was more prone to passivation reaction, resulting in a clear "passivation platform". And the greater width of the passivation platform indicates more stable oxide film on the surface of the copper alloy and better protection of the copper alloy inside. Therefore, the corrosion rate of copper alloys in an alkaline environment is significantly lower than that in acidic environments.

(3) The corrosion process of the multi-element copper alloy is divided into three stages, namely, the stage of generating the corrosion product film, the stage of generating the dense corrosion film on the surface of the copper alloy, and the stage of generating a stable passivation film on the surface of the copper alloy. In the alkaline condition, there is no oxide of Cu^{2+}, and the final product is $Cu_2(OH)_3Cl$ that will not destroy the Cu_2O dense passivation film generated.

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