

Corrosion behaviors of pure copper and Cu-Ni-Zn alloy in NaCl solution and artificial seawater

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Abstract. Corrosion behaviors of pure Cu and Cu-Ni-Zn alloy were investigated in 3.5% NaCl solution and artificial seawater by electrochemical impedance spectroscopy and potentiodynamic polarization technologies, and the corrosion morphologies were observed by field emission scanning electron microscopy. The results revealed that Cu-Ni-Zn alloy possessed better corrosion resistance than that of pure Cu in both 3.5% NaCl solution and artificial seawater. The corrosion morphology displayed the corrosion product films on Cu-Ni-Zn alloy were more compact and uniform than that on the pure Cu in both 3.5% NaCl and artificial seawater media.

1. Introduction

Copper alloys have been widely used in deep sea pipelines, bearings and electronics in marine engineering, due to their high strength, high thermal conductivity, good mechanical workability, and excellent corrosion resistance [1, 2]. Copper alloys are also used in marine environments to defend against biofouling by inhibiting microbial induced corrosion [3, 4]. In the ocean, microbial communities rapidly colonize and strongly adhere to metal surfaces, forming a layer of biofilm. The biofilms can damage expensive equipment, cause loss of production and increase maintenance costs [5, 6]. Therefore, it is necessary to study the corrosion behaviors of copper and copper alloys in marine environment.

In this work, the electrochemical corrosion behaviors of pure Cu and Cu-Ni-Zn alloy were investigated in both 3.5% NaCl solution and artificial seawater by measuring electrochemical impedance spectra (EIS) and potentiodynamic polarization curves. Field emission scanning electron microscopy (FESEM, S-4800) was used to examine the corrosion morphology of the samples after polarization measurement.

2. Materials and methods

The experimental material was Cu-Ni-Zn alloy plate, and its composition was listed in table 1. Before the electrochemical tests, the pure Cu and Cu-Ni-Zn alloy samples were machined into dimensions of 50 mm × 40 mm × 3 mm. The working surface was mechanically grinded with sandpaper from 400# to 1500# and then polished by using 2.5 μm diamond paste. The corrosion solutions were 3.5% NaCl solution and artificial seawater.



Table 1. Composition of Cu-Ni-Zn alloy (mass fraction, %).

| Element | Ni | Cu | Zn | Total impurities |
|-------------|-------|-------|-------|------------------|
| Composition | 16.03 | 56.81 | 26.35 | 0.82 |

The electrochemical experiments were performed on a PARSTAT2273 electrochemical workstation in both 3.5% NaCl solution and artificial seawater at room temperature. The area of working electrode was 1 cm². A conventional three-electrode system was used with pure Cu and Cu-Ni-Zn alloy as the working electrode, saturated calomel electrode as the reference electrode, and graphite rod as the auxiliary electrode. EIS was acquired over a frequency range of 100 kHz–10 mHz with an applied sinusoidal perturbation of 10 mV root-mean-square potential. Potentiodynamic polarization measurement was carried out at 0.332 mV/s. The corrosion morphology of the sample after polarization test was examined by an FESEM.

3. Results and discussion

3.1. Potentiodynamic polarization measurements

Figure 1 shows the representative potentiodynamic polarization curves of pure Cu and Cu-Ni-Zn alloy in 3.5% NaCl and artificial seawater. It is clearly seen from figure 1a and 1b that the curve shapes of pure Cu and Cu-Ni-Zn alloy in 3.5% NaCl solution are similar to those in artificial seawater. The pure Cu sample is quickly dissolved after the scanning potential over the corrosion potential in both 3.5% NaCl and artificial seawater media, showing no protective product film appears on the surface. On the contrary, the polarization curves of the Cu-Ni-Zn alloy have an obvious passive behavior, showing protective product films are formed on the Cu-Ni-Zn alloy in the two solutions.

The relative electrochemical parameters obtained from the polarization curves are listed in table 2. The corrosion potentials (E_{corr}) of pure Cu and Cu-Ni-Zn alloy are -0.242V and -0.226 V in 3.5% NaCl, and -0.230 V and -0.214 V in artificial seawater, respectively. A more positive E_{corr} means that the sample is nobler in the solution. As shown in table 2, the corrosion current density (I_{corr}) values of pure Cu and Cu-Ni-Zn alloy are 7.84×10^{-6} A/cm² and 1.73×10^{-6} A/cm² respectively in 3.5% NaCl, 4.79×10^{-6} A/cm² and 4.66×10^{-6} A/cm² respectively in artificial seawater. I_{corr} is an important parameter commonly used to assess the kinetics of corrosion reactions, and it is almost directly used to characterize the corrosion rate at E_{corr} . Compared with the pure Cu, the Cu-Ni-Zn alloy exhibits higher E_{corr} and lower I_{corr} in both 3.5% NaCl and artificial seawater, meaning it has higher corrosion resistance in the solutions. The results show that improved corrosion resistance in Cu-Ni-Zn alloy is brought about possibly by Zn and Ni additions [7]. Ni enhances the corrosion resistance of the alloy by its segregation into the defective lattice of Cu₂O, The addition of zinc to copper enhances both its mechanical characteristics and its corrosion resistivity to artificial seawater [8].

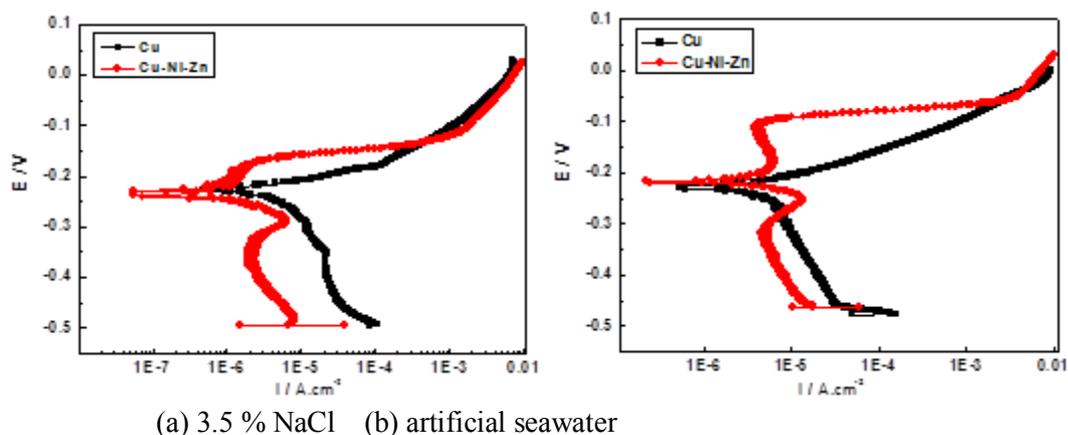


Figure 1. Polarization curves for pure Cu and Cu-Ni-Zn alloy in different solutions.

It also clearly shows that E_{pit} of the Cu-Ni-Zn alloy is much higher than that of pure Cu in both 3.5% NaCl and artificial seawater electrolytes, especially in the artificial seawater. Moreover, the E_{pit} values of the pure Cu and Cu-Ni-Zn alloy are a little lower in 3.5% NaCl solution than that in artificial seawater.

Table 2. Tafel fitting results of pure Cu and Cu-Ni-Zn alloy.

| Solution | Material | $I_{corr}/(A.cm^{-2})$ | E_{corr}/V | E_{pit}/V |
|---------------------|----------|------------------------|--------------|-------------|
| 3.5%NaCl | Cu | 7.84×10^{-6} | -0.242 | -0.163 |
| | Cu-Ni-Zn | 1.73×10^{-6} | -0.226 | -0.147 |
| artificial seawater | Cu | 4.79×10^{-6} | -0.230 | -0.139 |
| | Cu-Ni-Zn | 4.66×10^{-6} | -0.214 | -0.082 |

3.2. Electrochemical impedance spectroscopy (EIS) measurements

Figure 2 presents the EIS spectra of pure Cu and Cu-Ni-Zn alloy in 3.5% NaCl and artificial seawater. The EIS plots exhibit two capacitive loops, presented in the high frequency area and low frequency area, respectively. The EIS plots of the pure Cu sample also show the appearance of Warburg diffusion in the two solutions. Ma et al [9] also reported the EIS of 90 Cu-10 Ni alloy presented Warburg diffusion impedance in 3.5% NaCl solution. Whereas for the Cu-Ni-Zn alloy, there seems not to appear Warburg diffusion behavior, probably associated with the compact product film on the alloy. It is remarkable that the semicircle diameters of the Cu-Ni-Zn alloy are much bigger than those of pure Cu in both 3.5% NaCl and artificial seawater. Capacitive semicircle at high frequency is related to the formation of corrosion products whereas at low frequency is related to the double electric layer. It is obvious that Cu-Ni-Zn alloy displays much larger capacitive loops than pure Cu. Larger capacitive loop diameters mean higher impedance, indicating the effect of the corrosion product film on inhibiting corrosion. The result of EIS is good agreement with the polarization curves, they both display that the Cu-Ni-Zn alloy possesses better corrosion resistance in both 3.5% NaCl solution and artificial seawater compared with the pure Cu sample.

3.3. Corrosion morphologies

Figure 3 shows the corrosion morphologies of pure Cu and Cu-Ni-Zn alloy after polarization test in 3.5% NaCl solution and artificial seawater. It can be seen from the figure 3 that the surface of corroded Cu sample is covered with loose and non-uniform corrosion products; however, the corroded surface of Cu-Ni-Zn alloy is covered with dense and uniform products. Obviously, the dense and uniform corrosion product layer can effectively protect the Cu-Ni-Zn alloy from further corrosion in the two solutions.

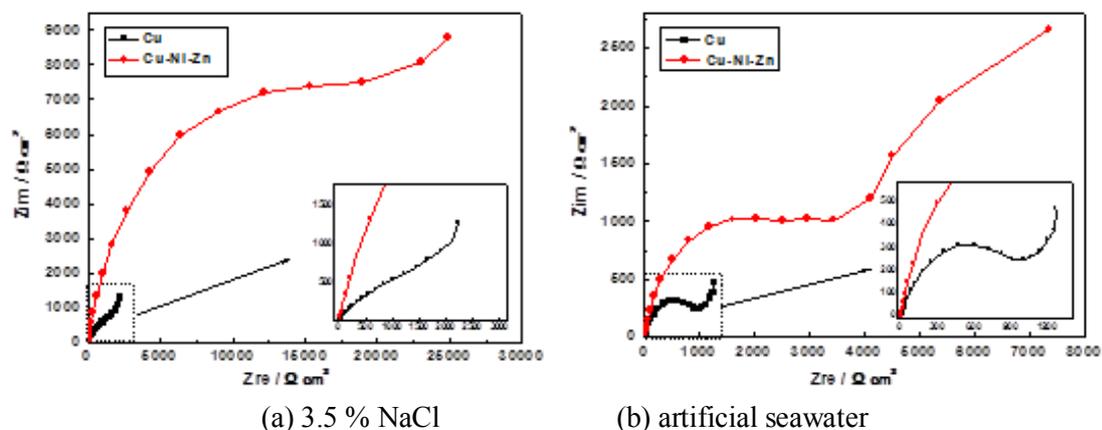


Figure 2. Nyquist plots of pure Cu and Cu-Ni-Zn alloy.

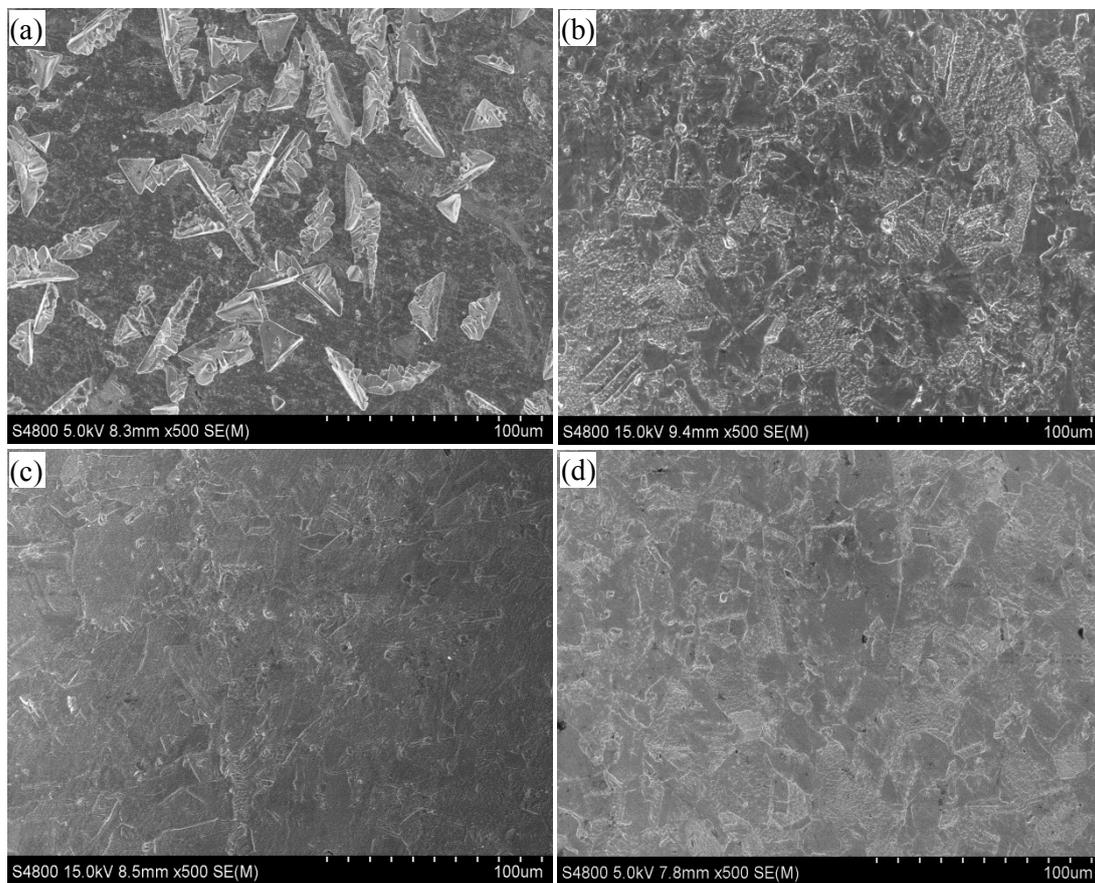


Figure 3. Corrosion morphologies of pure Cu (a, c) and Cu-Ni-Zn alloy (b, d) in 3.5% NaCl solution (a, b) and in artificial seawater (c, d).

4. Conclusions

The electrochemical corrosion behaviors of pure Cu and Cu-Ni-Zn alloy were studied in 3.5% NaCl solution and artificial seawater by electrochemical impedance spectroscopy and potentiodynamic polarization tests. The polarization curves of the Cu-Ni-Zn alloy presented an obvious passive behavior in the two solutions, showing protective product films were formed. Both polarization and EIS results revealed that Cu-Ni-Zn alloy possessed higher resistance than pure Cu in 3.5% NaCl solution and artificial seawater. The corrosion morphology displayed the corrosion product films on Cu-Ni-Zn alloy were more compact and uniform than that on the pure Cu in both 3.5% NaCl and artificial seawater media.

Acknowledgments

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