



Corrosion behavior of T2 copper in 3.5% sodium chloride solution treated by rotating electromagnetic field

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Abstract: Copper is susceptible to producing corrosion problems in corrosive environments, which leads to serious safety problems. Thus, investigating the corrosion behavior of copper is of great significance. The effects of rotating electromagnetic field on corrosion behavior of T2 copper in 3.5% sodium chloride solution with electrochemical measurements were investigated. The results showed that rotating electromagnetic field changed properties of 3.5% sodium chloride solution by increasing the values of temperature and pH and decreasing the values of conductivity and dissolved oxygen. The rotating electromagnetic field improved the corrosion resistance of T2 copper. The corrosion products of T2 copper in treated 3.5% sodium chloride solution were composed of Cu_2O and CuCl . The low corrosion rate of T2 copper was resulted from the decrease of dissolved oxygen in 3.5% sodium chloride solution treated by rotating electromagnetic field.

Key words: corrosion behavior; rotating electromagnetic field; electrochemical measurement; copper

1 Introduction

Copper and its alloys are used widely in marine environments due to their excellent electrical and thermal conductivity, good machinability, corrosion resistance, and low cost etc [1–4]. Although copper and its alloys are resistant towards the influence of atmosphere and many chemicals, they are susceptible to corrosion problems such as pitting corrosion in aggressive media. Copper and its alloys are corroded easily in chloride containing aqueous solution, which may cause enormous economic loss and serious safety hazards [5]. Thus, investigating the anticorrosion behavior of copper and its alloys in seawater is necessary. The main method to slow down the corrosion rate in seawater is adding inhibitors, which include imidazole, thiazole and sulfoxide derivative. OTMACIC et al [6] found that methylimidazole promoted the formation of protective film on copper surface in simulated seawater. Adding amino phenyl triazole (ATA) into simulated seawater reduced

current of cathodic reaction process and the inhibition efficiency reached 98% [7]. DAFALI et al [8] discovered that sulfhydryl-methylimidazole had excellent inhibition effect on copper in simulated seawater. KHIATI et al [9] indicated that developed benzotriazole inhibitor had good inhibition effect on copper in seawater. However, there is a potential impact on the seawater environment by adding inhibitors. Thus, many scholars begin to research new inhibitors and methods which are non-toxic, biodegradable and environmentally friendly to slow down corrosion rate.

Many scholars have studied the influence of electromagnetic field on the corrosion behavior of metals. HU et al [10] discovered that the open circuit potentials (φ_{op}) of beryllium copper in sodium chloride solution were shifted by a horizontal magnetic field. The limiting current density was changed by a horizontal magnetic field with different concentrations. SUEPTITZ et al [11] proposed that superimposed magnetic field decreased the current density of copper in 0.05 mol/L H_2SO_4 solution in the transition and pre-passive region. CHOUCANE

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et al [12] indicated that the corrosion resistance of alloys with low alloy nickel content was improved significantly by magnetic field. HUANG et al [13] used electric field to slow down the corrosion rate of copper. KELLY [14] found that magnetic field increased the corrosion rate of some metallic materials such as titanium in sulphate solutions. The electromagnetic field has effect on the corrosion behavior of copper in seawater [15,16]. Although some conclusions about the influence of electromagnetic field on the corrosion have been obtained, significant inhibition effect has not yet been reached. GUO et al [17] found that rotating electromagnetic field had remarkable effect on the electrochemical corrosion of copper and the inhibition efficiency reached 89.14%. LU [18] proposed that magneto-electrochemistry could serve a novel approach for investigating reaction mechanisms and kinetics for complex electrode systems. CHEN et al [19] found that the presence of a static magnetic field can suppress effectively the corrosion of copper alloy. YUAN et al [20] proposed that the magnetic field affects the anodic dissolution of copper in chloride media. Researches indicated that electromagnetic field reduces the corrosion rate of some metals, but the influence of electromagnetic field on the corrosion behavior of metals has not been studied in detail.

In this work, the 3.5% sodium chloride solution was treated by rotating electromagnetic field. The properties such as pH, dissolved oxygen, temperature and conductivity of 3.5% sodium chloride solution after treatment of rotating electromagnetic field were investigated experimentally. Electrochemical measurement was used to investigate corrosion behavior of copper in magnetic treated solution. The mechanism of corrosion behavior of copper in treating solution was also revealed.

2 Experimental

Experimental T2 copper was selected to conduct corrosion experiments. The sample sizes were 20 mm × 20 mm × 2 mm. The chemical composition of T2 copper is shown in Table 1. The specimen surfaces were polished by 1500 grit waterproof abrasive papers, smoothed by polishing cloth at last, cleaned by acetone and alcohol, and dried successively.

A rotating electromagnetic device was proposed to

Table 1 Chemical composition of T2 copper (mass fraction, %)

Cu	Fe	Pb	S	O	Sn
99.9	0.005	0.005	0.005	0.06	0.002
As	Sb	Ni	Bi	Zn	
0.002	0.002	0.002	0.002	0.005	

obtain rotating electromagnetic field. The structure sketch of electromagnetic pyrogenic device referred to the work of LI et al [16]. The intensity of magnetic field with fixed direction changed with time in this work. The amplitude of magnetic field intensity was in the range of 0 to 0.25 T as shown in Fig. 1.

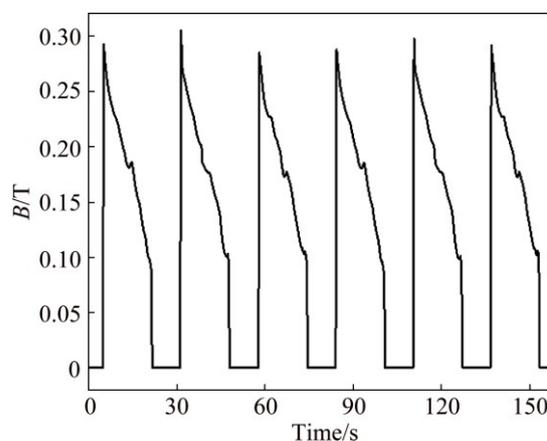


Fig. 1 Rotational magnetic field intensity with time

The medium of electrochemical corrosion experiment was two kinds of 3.5% sodium chloride solution. One is 3.5% sodium chloride solution without treatment. The other is 3.5% sodium chloride solution treated by rotating electromagnetic field with different frequencies. Experiments of testing water quality and electrochemical corrosion behavior of T2 copper were simultaneously carried out in the untreated and treated 3.5% sodium chloride solution. The treated 3.5% sodium chloride solution maintained the treated temperature when the corrosion test was carried out. The water quality of solution was measured by DDSJ-308A conductivity meters, JPSJ-605 dissolved oxygen meters and PHS-3C pH meter; the polarization curves and electrochemical impedance spectroscopy were measured by CHI660D electrochemical workstation. The frequencies parameters of rotating electromagnetic field were 50, 100, 150 and 200 Hz and treatment time was 3, 6, 9 and 12 h.

3 Results and discussion

3.1 Properties of 3.5% sodium chloride solution treated by rotating electromagnetic field

Figure 2 shows the variation of temperature of 3.5% sodium chloride solution treated by rotating electromagnetic field. The temperature of solution firstly increases with the increase of treatment time, and then reaches a relatively stable value at a constant frequency. The higher the frequency is, the faster the temperature increases. The result shows that the 3.5% sodium chloride solution is heated by the rotating

electromagnetic field. Figure 3 shows the variation of pH of 3.5% sodium chloride solution treated by rotating electromagnetic field. With the increase of treatment time, the pH of solution firstly increases quickly, and then the pH reaches a stable state after 3 h. This indicated that the effect of electromagnetic frequency on pH is not

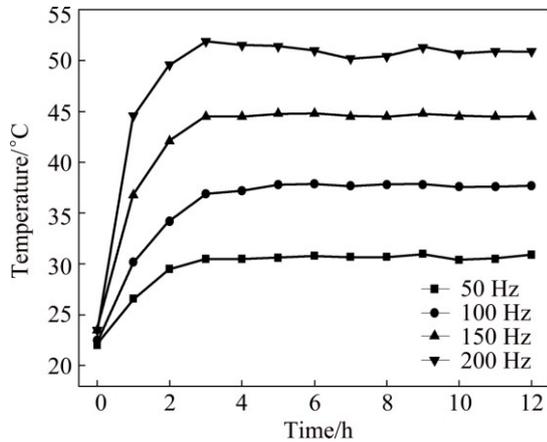


Fig. 2 Variation of temperature of 3.5% sodium chloride solution treated by rotating electromagnetic field

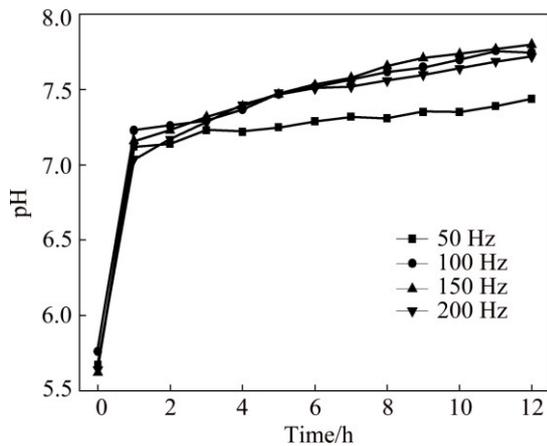


Fig. 3 Variation of pH of 3.5% sodium chloride solution treated by rotating electromagnetic field

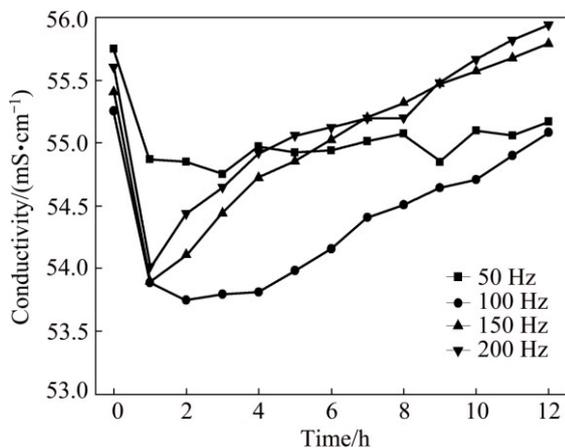


Fig. 4 Variation of conductivity of 3.5% sodium chloride solution treated by rotating electromagnetic field

obvious. Figure 4 shows the variation of conductivity of 3.5% sodium chloride solution treated by rotating electromagnetic field. The conductivity of solution firstly reduces, then increases with the increase of treatment time. The conductivities of solution treated at 50 Hz and 100 Hz are always lower than that in untreated solution. The conductivities of solution treated at 150 Hz and 200 Hz for 9 h are higher than that in untreated solution. Figure 5 shows the variation of dissolved oxygen of 3.5% sodium chloride solution treated by rotating electromagnetic field. With the increase of treatment time, the dissolved oxygen in solution treated at 50 Hz and 100 Hz reduces, and then reaches a relatively stable value. The dissolved oxygen of solution treated at 150 Hz and 200 Hz firstly reduces, and then increases to a stable value. The effect of rotating electromagnetic field on water quality contains magnetized and thermal effects. The magnetized effect has influence on association state of solvent water molecules and hydration state of ion. The thermal effect has influence on solubility of CO₂ and O₂. Thus, the water quality parameters of 3.5% sodium chloride change as above. The properties of 3.5% sodium chloride solution are changed by the rotating electromagnetic field, such as the temperature, the pH, the conductivity and the dissolved oxygen. The changes of these parameters affect the corrosion behavior of T2 copper in 3.5% sodium chloride solution.

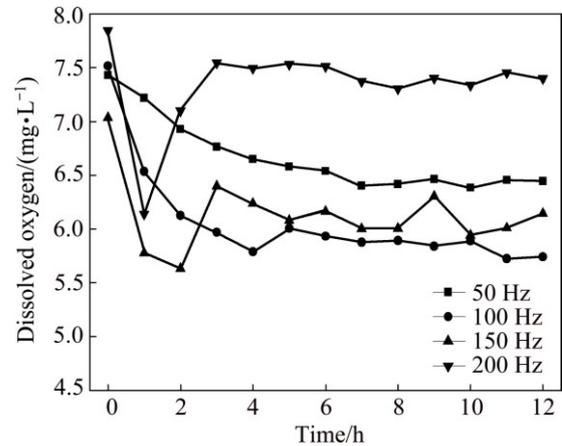


Fig. 5 Variation of dissolved oxygen of 3.5% sodium chloride solution treated by rotating electromagnetic field

3.2 Analysis of polarization curve

Figure 6 shows the polarization curves of copper in 3.5% sodium chloride solution treated with frequency of 50, 100, 150 and 200 Hz.

The corrosion rate v_{corr} is expressed as follows [17]:

$$v_{\text{corr}} = \frac{\Delta m}{St} = \frac{A}{nF} J_{\text{corr}} \quad (1)$$

where A , n and F are atomic mass, number of electrons and Coulomb coefficient respectively, and J_{corr} is the

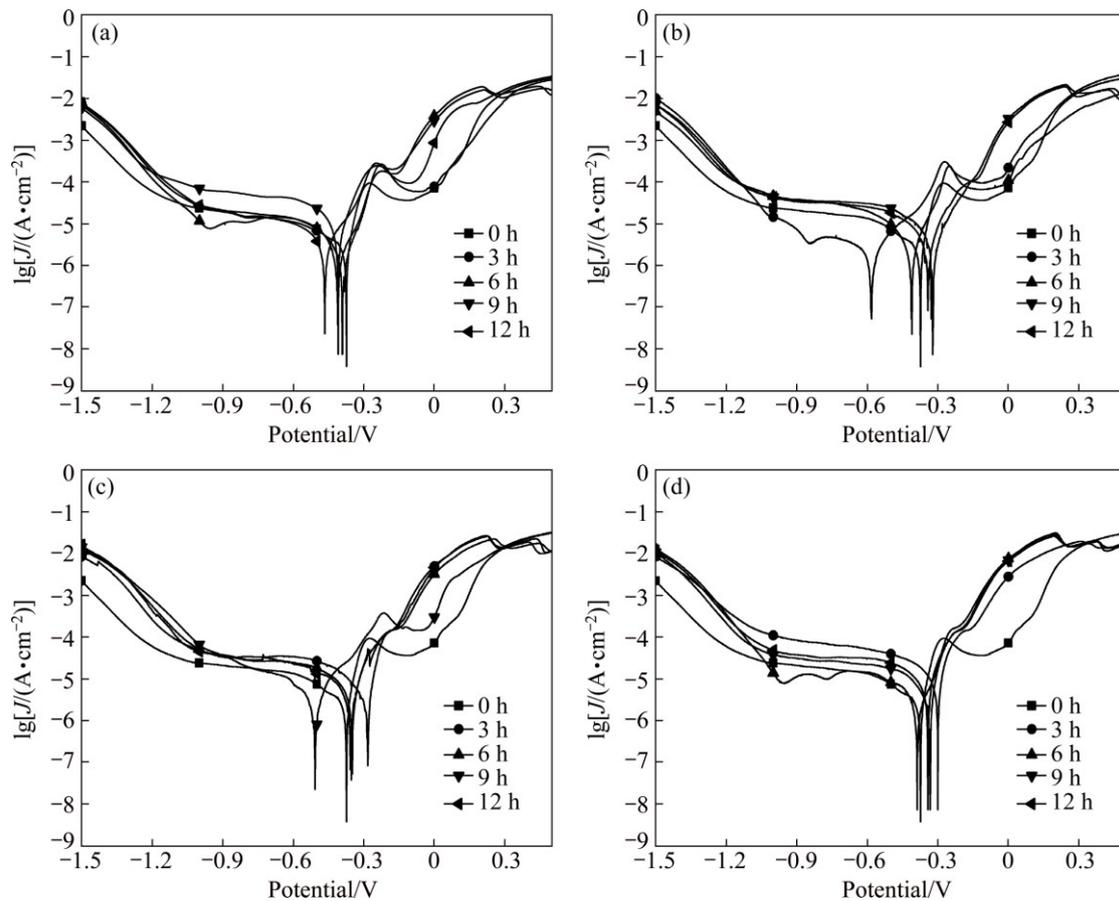


Fig. 6 Polarization curves of T2 copper in 3.5% sodium chloride solution treated with different frequencies: (a) 50 Hz; (b) 100 Hz; (c) 150 Hz; (d) 200 Hz

corrosion current density. It shows that the corrosion rate v_{corr} is proportional to the corrosion current density. Therefore, the corrosion current density is used to represent the corrosion rate.

The corrosion current densities of different polarization curves were obtained by Tafel extrapolation method as shown in Fig. 7. It can be found that the corrosion current density of T2 copper in 3.5% sodium chloride solution treated by rotating electromagnetic field changes significantly. The corrosion current density of T2 copper in treated 3.5% sodium chloride solution is smaller than that in untreated solution except the results at 200 Hz for 3 h. The lower the electromagnetic frequency is, the smaller the corrosion current density is when the solution is treated for 3 h. When the treatment time is 6 h and 9 h, the corrosion current density increases sharply at 50 Hz. The corrosion current density in solution treated at 200 Hz is the minimum for 9 h. When the treatment time is 12 h, the minimum corrosion current density is 0.075 A/m^2 in solution treated at 100 Hz. Based on all the experimental data, the optimal processing parameter is 50 Hz treated for 3 h.

Typically, inhibition efficiency in electrochemical corrosion is expressed as follows [17]:

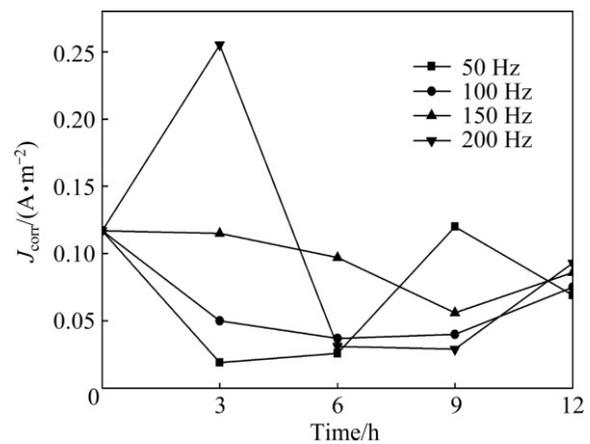


Fig. 7 Corrosion current densities of T2 copper in 3.5% sodium chloride solution treated by rotating electromagnetic field with different frequencies

$$\eta = \frac{J_{\text{corr}} - J'_{\text{corr}}}{J_{\text{corr}}} \quad (2)$$

where J_{corr} and J'_{corr} are the corrosion current densities in untreated solution and treated solution, respectively. The inhibition efficiency is obtained according to Eq. (2), and those results are shown in Table 2. Table 2 also shows other properties of 3.5% sodium chloride.

Table 2 Properties of 3.5% sodium chloride solution with different treatment conditions

Treatment condition	Inhibition corrosion efficiency/%	Temperature/ $^{\circ}\text{C}$	pH	Dissolved oxygen/ $(\text{mg}\cdot\text{L}^{-1})$	Conductivity/ $(\text{mS}\cdot\text{cm}^{-1})$
50 Hz, 3 h	83.60	30.5	7.23	6.76	54.35
100 Hz, 6 h	68.84	37.9	7.52	5.93	54.16
150 Hz, 9 h	51.95	7.71	6.3	55.47	
200 Hz, 9 h	74.79	51.3	7.6	7.4	55.48

3.3 Analysis of electrochemical impedance spectroscopy (EIS)

Figure 8 shows the Nyquist plots of T2 copper in 3.5% sodium chloride treated by rotating electromagnetic field. Nyquist plots of T2 copper are composed by two approximately semicircles. There is a big difference between maximum imaginary part and the span of real part of the impedance from these results. The maximum imaginary part and the real part span of the impedance of the first semicircular is more than the second when the solution is treated at 100 Hz for 6 h and 200 Hz for 3 h. The difference is smaller than that in the untreated solution.

Figure 9 shows the equivalent circuit of Fig. 8. The equivalent circuit is composed by three units in series; the three units are resistance R_s , constant phase angle element Q_{dl} and resistor R_{po} in parallel, constant phase angle element Q_{ox} and resistor R_{po} in parallel respectively. Constant phase angle element Q_{dl} is dominated by electric double layer capacitor and constant phase angle element Q_{ox} is dominated by oxide capacitance.

The values of solution resistance R_s under the different treatment conditions are shown in Table 3. The values of solution resistance R_s increase at 50 and 100 Hz from 3 to 12 h. The values of solution resistance R_s decrease firstly and then increase at 150 and 200 Hz from 3 to 12 h.

3.4 Analysis of surface morphology

Figure 10 shows surface morphologies of electrochemical corrosion specimens in both corrosion media. The surface morphologies of specimen corroded in treated 3.5% sodium chloride are uniform compared with those in untreated solution. Surface morphologies of specimen corroded are different in solutions under different electromagnetic frequencies. Figure 10(b) shows the least pitting defects treated by 50 Hz, and those minimum defects improve corrosion resistance of that T2 copper specimen.

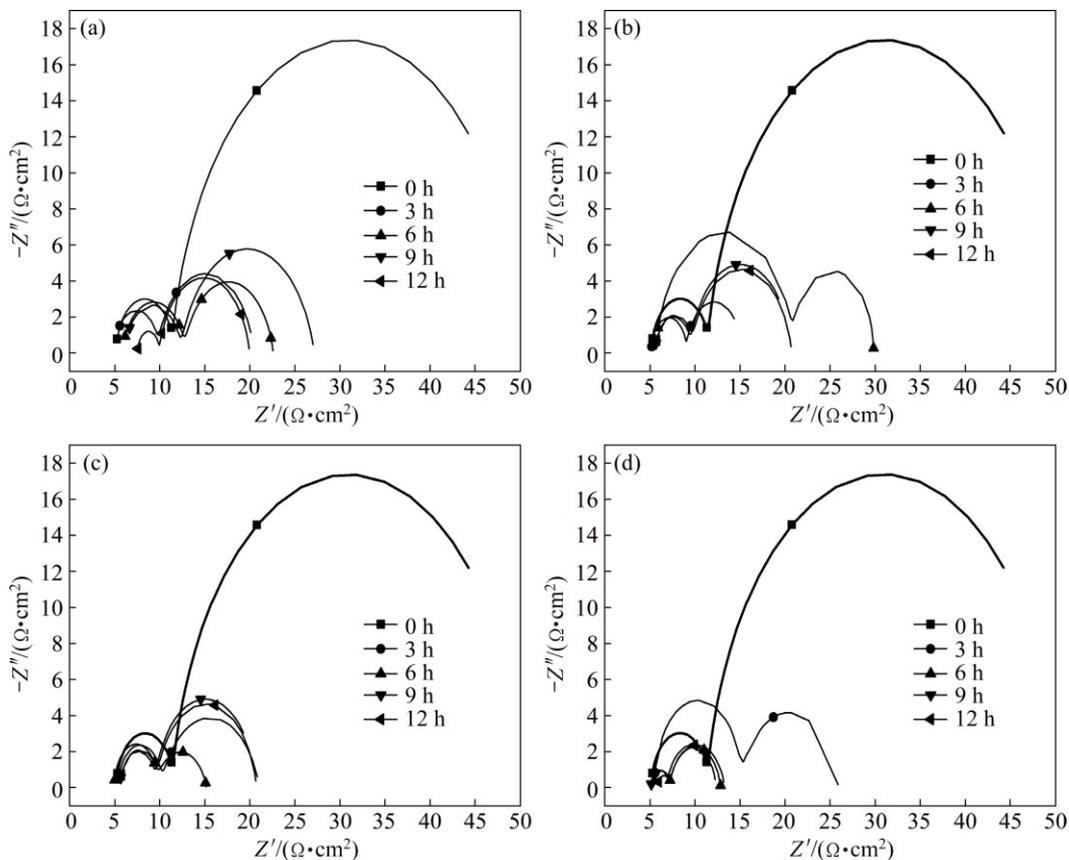


Fig. 8 Nyquist plots of T2 copper in 3.5% sodium chloride solution treated by rotating electromagnetic field with different frequencies: (a) 50 Hz; (b) 100 Hz; (c) 150 Hz; (d) 200 Hz

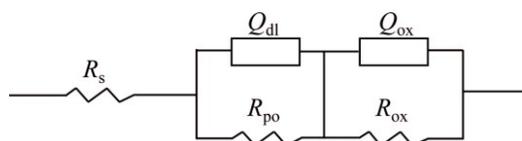


Fig. 9 Equivalent circuit of electrochemical impedance spectroscopy

3.5 Analysis of phase components

Figure 11 shows phase components of corrosion products of T2 copper in 3.5% sodium chloride solution treated by rotating electromagnetic field. The corrosion

Table 3 Solution resistance R_s under different treatment conditions

Frequency/Hz	R_s/Ω				
	0 h	3 h	6 h	9 h	12 h
50	5.106	4.955	5.822	6.024	7.546
100	5.106	5.128	5.551	5.556	5.641
150	5.106	5.326	4.927	4.597	5.16
200	5.106	5.501	5.398	5.142	5.899

product of T2 copper in untreated 3.5% sodium chloride solution is Cu_2O . The corrosion products of T2 copper in treated 3.5% sodium chloride solution are Cu_2O and CuCl . There is new phase component of CuCl among

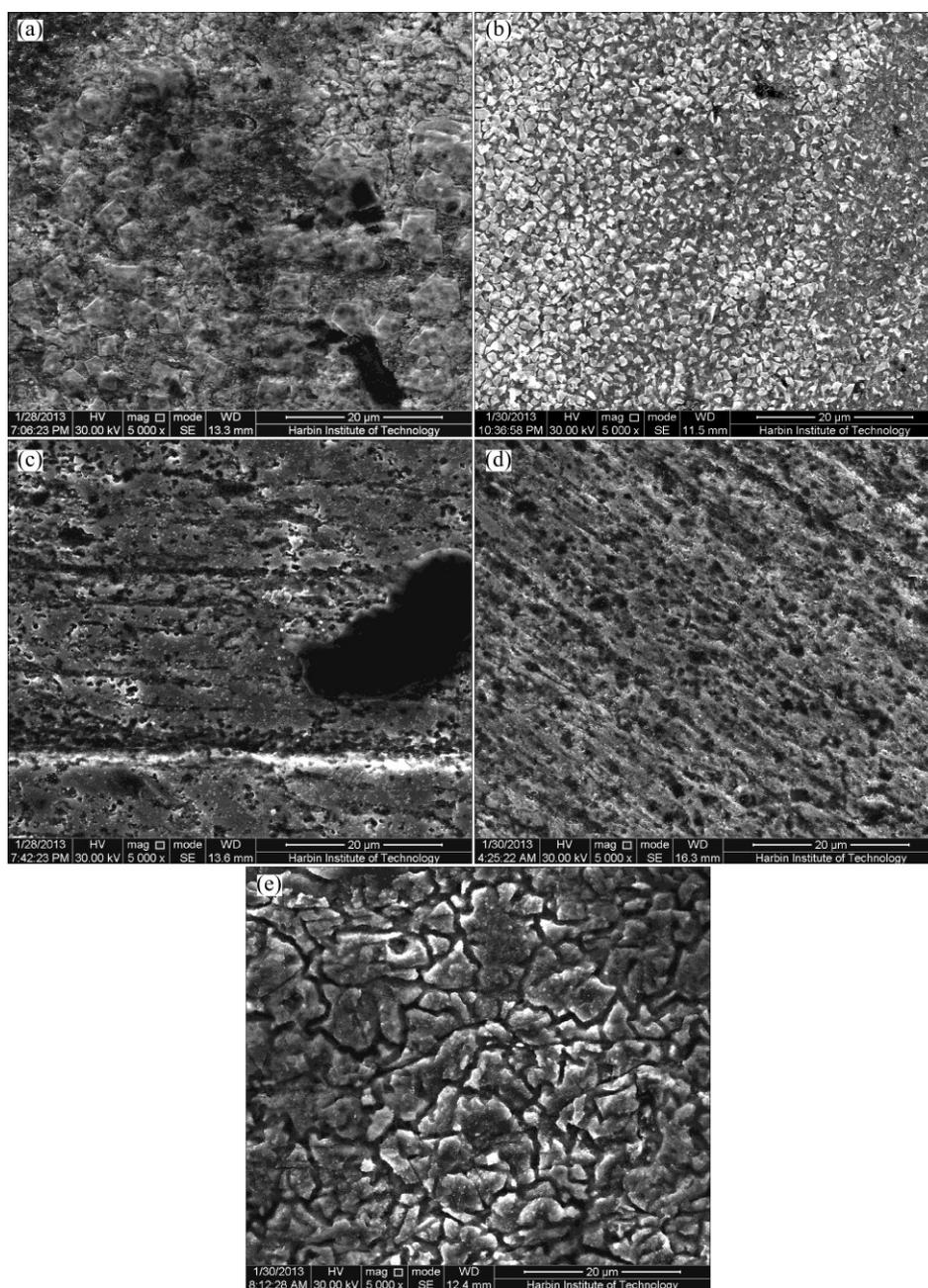


Fig. 10 Surface morphologies of T2 copper corroded in 3.5% sodium chloride solution treated under different conditions: (a) Untreated; (b) Treated at 50 Hz for 3 h; (c) Treated at 100 Hz for 6 h; (d) Treated at 150 Hz for 9 h; (e) Treated at 200 Hz for 9 h

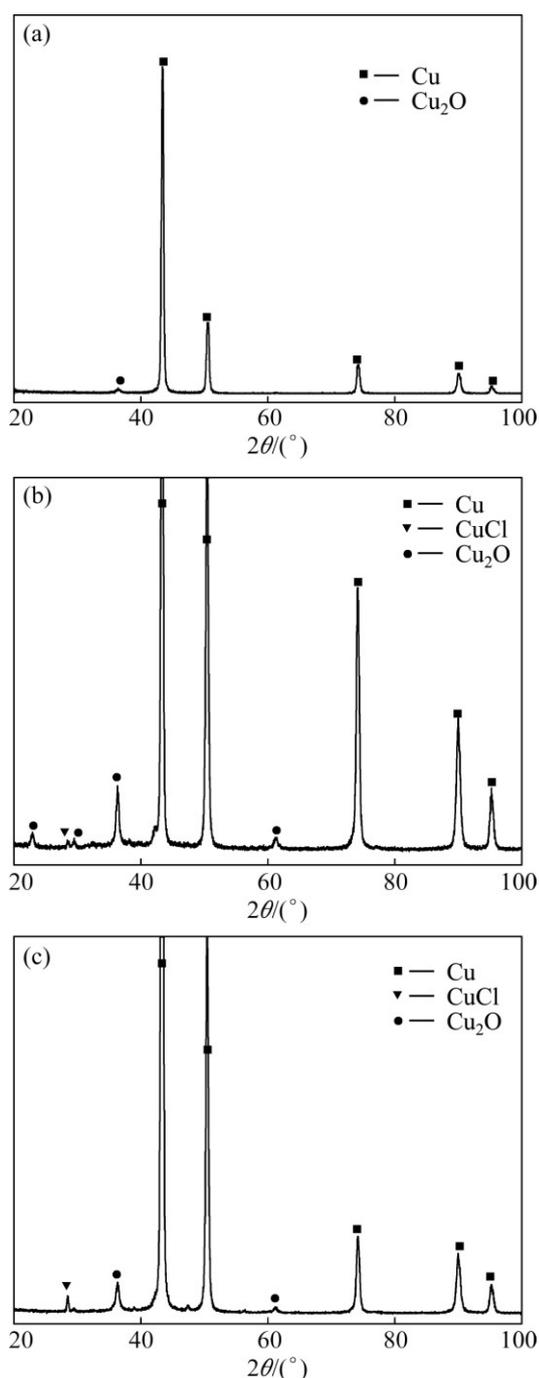


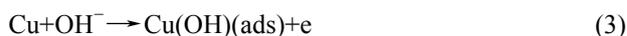
Fig. 11 Phase components of corrosion products of T2 copper in 3.5% sodium chloride solution treated by rotating electromagnetic field for 0 h (a), 3 h (b) and 12 h (c)

corrosion products in treated solution. The influence of treatment time on the formation of Cu_2O and CuCl is slight.

3.6 Analysis of corrosion products

According to the corrosion morphology, XRD and electrochemical corrosion results, the electrochemical corrosion mechanisms of T2 copper in treated 3.5% sodium chloride solution can be described as follows [17].

Firstly, processes controlled by cathode reaction of oxygen depolarized are expressed as follows:



Secondly, process controlled by oxidation reaction of dissolved oxygen is expressed as follows:



Thirdly, processes controlled by complex reaction of chloride are expressed as follows:



The reactions of T2 copper in 3.5% sodium chloride solution contain the above three processes. The processes are hindered in treated 3.5% sodium chloride solution, which are controlled by cathode reaction of oxygen depolarized and oxidation reaction of dissolved oxygen. It is because that the reduction of dissolved oxygen in treated 3.5% sodium chloride solution results in cathodic reaction slowing down. Further, it causes the anodic reaction slowing down. It is one of the reasons for the low corrosion rate of T2 copper in treated 3.5% sodium chloride solution.

4 Conclusions

1) Temperature and pH of treated 3.5% sodium chloride solution are higher than those of untreated solution. The maximum values of temperature and pH are 52°C and 7.8, respectively.

2) Conductivity and dissolved oxygen of treated solution are lower than those of untreated solution. The minimum values of conductivity and dissolved oxygen are 53.75 mS/cm and 5.74 mg/L , respectively. The decrease of dissolved oxygen slows down corrosion rate of T2 copper in 3.5% sodium chloride solution.

3) Surface morphologies of specimen corroded in treated solution are uniform compared with that in untreated solution. The corrosion products of T2 copper are Cu_2O and CuCl in treated 3.5% sodium chloride solution.

4) The maximum inhibition efficiency of 83.60% is obtained under the condition of 50 Hz treated for 3 h.

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T2 紫铜在旋转电磁场处理的 3.5%氯化钠溶液中的腐蚀行为

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摘 要: 铜在腐蚀环境中容易产生腐蚀问题, 这会带来非常严重的安全问题。因此, 铜的腐蚀行为的研究具有重大的意义。通过电化学测量方法研究了旋转电磁场对 T2 紫铜在 3.5%氯化钠溶液中腐蚀行为的影响。结果表明: 旋转电磁场改变了 3.5%氯化钠溶液的性质, 提高了溶液的温度和 pH 值, 降低了溶液的电导率和溶氧量。旋转电磁场改善了 T2 紫铜的耐腐蚀性能。T2 紫铜在旋转电磁场处理的 3.5%氯化钠溶液中腐蚀产物由 Cu₂O 和 CuCl 组成。T2 紫铜在旋转电磁场处理过的 3.5%氯化钠溶液的低腐蚀速率是由于旋转电磁场导致溶液中溶氧量减少造成的。

关键词: 腐蚀行为; 旋转电磁场; 电化学测量; 紫铜

(Edited by Yun-bin HE)