Available online at www.sciencedirect.com
ScienceDirect
Trans. Nonferrous Met. Soc. China 21(2011) s489−s493
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Effects of rotating electromagnetic on flow corrosion of copper in seawater

LI Ji-nan, ZHANG Peng, GUO Bin

School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, China

Received 10 May 2011; accepted 25 July 2011

Abstract: The flow corrosion of copper in seawater was investigated with the rotating electromagnetic corrosion experimental bench for 12 d. Scanning electron microscopy equipped with EDAX and X-ray diffraction (XRD) were used for the analysis of surface microstructure and phase composition of samples. The results indicate that the composition of Cu_2O and CuO is created in corrosion products film after drying in the air, and the flow corrosion process can be successively defined as uniform pitting corrosion, expansion, formation of corrosion film, solution of surface products and pitting corrosion. Corrosion inhibition of copper during flow corrosion can be significantly improved with rotating electromagnetic field in the seawater.

Key words: copper; corrosion inhibition; rotating electromagnetic; microstructure

1 Introduction

The effects of magnetic field on the corrosion behaviors of metals have been attracted more attention recently [1−2]. It was reported that magnetic field could decrease the corrosion rate of some metals, such as stainless steel, zinc, brass, and aluminum, while the corrosion inhibition is improved with the increase of the magnetic flux density [3−5]. There are also some controversial research conclusions. KELLY [6] found that the titanium corrosion rate increased in sulphate solution by a magnetic field. COSTA et al [7] indicated that magnetized Nd-Fe-B magnets exhibited larger mass loss than non-magnetized ones. The magnetic field plays an important role in the corrosion kinetics [8] and the mass transport [9−13], and the composition of corrosion products can be controlled by adjusting parameters of magnetic field [3].

In this work, the effects of rotating electromagnetic field on the corrosion micrographs and the corrosion products compositions of copper samples were investigated using scanning electron microscopy/energy dispersive analysis system of X-ray (SEM/EDAX), and X-ray diffraction (XRD). Meanwhile, corrosion behavior of copper under rotating electromagnetic field was also discussed.

2 Experimental

Figure 1 shows the cross-section structure diagram of rotating electromagnetic device which includes the rotating rotor and stator parts, air gap between the stator and rotor and the outer garment etc. The rotating rotor and stator parts are coaxial. The stator part is made up of duct, conducting bar, short-circuit rings of ducts and conducting bar welding circuit, which form cage type conductive circuits. The rotor part is a solid core, and several slots are prepared in the longitudinal direction, where permanent magnet is laid aside. When the rotor rotates are driven by external power, the rotating magnet magnetic field will be chained with stator components through the air gap, producing hysteresis, vortex in the cage type electric circuit, and inducing potential resistance loss of short-circuit current in the second generation. The heat energy transformed from loss is taken away by the sea water which is simultaneously in the rotating magnetic field and second field of short-circuit current, that will produce the synergy of magnetic and electric fields. The variation of rotating

Foundation item: Project (2008DFR60340) supported by the International Science and Technology Cooperation of China; Project (HIT.NSRIF.2009156) supported by Fundamental Research Funds for the Central Universities, China; Project (BS2011NJ002) supported by Promotive Research Fund for Excellent Young and Middle-aged Scientists of Shandong Province

Corresponding author: ZHANG Peng; E-mail: pzhang@yeah.net

magnetic field with time is shown in Fig. 2, and Fig. 3 presents the seawater temperature conditions.

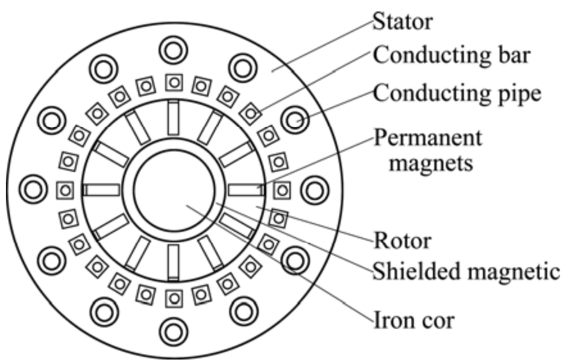

Fig. 1 Structure sketch of electromagnetic equipment

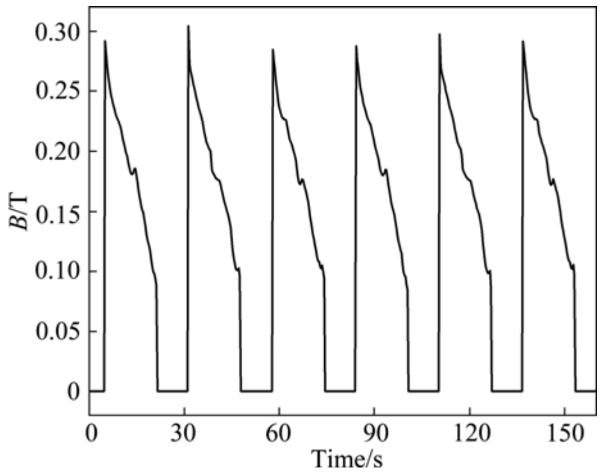

Fig. 2 Rotational magnetic field with time

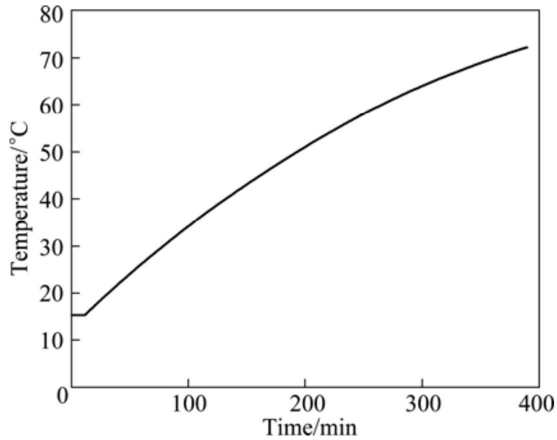

Fig. 3 Temperature variation of seawater

3 Results and discussion

3.1 Analysis of corrosion morphology

Figure 4 shows the the surface micrographs of copper sample during the flow corrosion process. It can be observed that the flow corrosion process in copper is pitting corrosion obviously. The copper sample corroded for 3 d is pitting corrosion initiation, and the corrosion products deposit on the surface. However, the corrosion resistance film is formed on the surface of copper samples, and the whole surface is coated with corrosion products after being corroded for 6 d, which restrained the development of the pitting corrosion. But the copper is dissolved and pitting depth increases during the corrosion process, which can be seen in Figs. 4(a) and

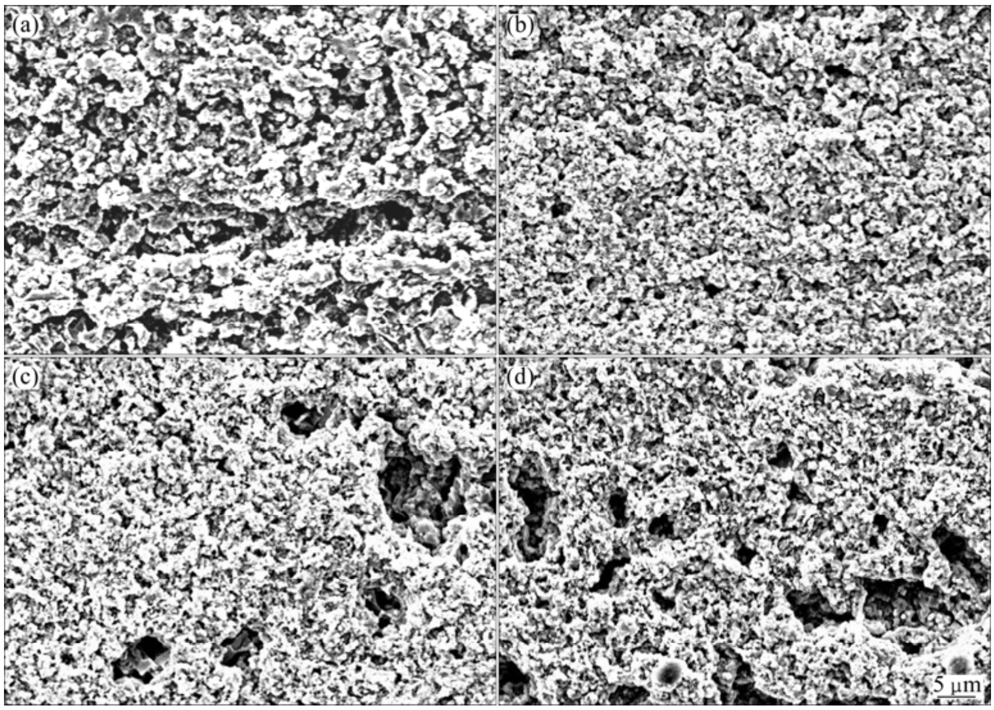

Fig. 4 SEM images of copper during corrosion process: (a) 3 d; (b) 6 d; (c) 9 d; (d) 12 d

(b). Fig. 5 shows the diameter augmentation and increasing depth of pitting wholes of copper samples during corrosion initiation. It can be seen that the average corrosion depth of copper increases rapidly, then decreases with prolonging the period of corrosion. As the corrosion products film generated, some of the regional pitting corrosion continued, leading to the depth of pitting corrosion increased rapidly in the middle stage.

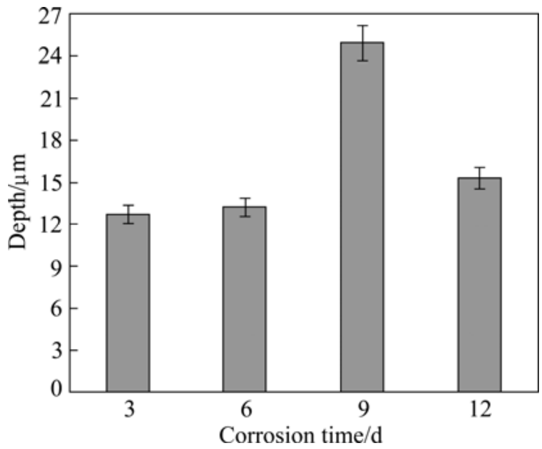

Fig. 5 Pitting depths of copper during corrosion process

3.2 Composition of corrosion products

Figure 6 shows energy spectrum of the corrosion products of copper sample. It can be found that the surface corrosion products mainly contain O element and Cu element. Along with the flow corrosion process, the contents of these two elements have not changed, which can be seen in Fig. 7. Figure 8 shows the XRD patterns of corrosion products of copper. It can be seen that the corrosion products of copper in seawater are mainly Cu_2O and CuO after drying in the air.

The flow corrosion mechanisms of copper in seawater can be described as follows [14−15]:

Anode reaction

$$2Cu+H_2O \rightarrow Cu_2O+2H^++2e^- \quad (1)$$

Cathode reaction

$$O_2+2H_2O \rightarrow 4OH^- \quad (2)$$

The Cu_2O layer initially formed on copper sample surface is partially oxidated into CuO, and the oxidation layer is mainly made up of Cu_2O and CuO after drying in the air. Although the seawater contains a lot of chloride ion, and the O^{2-} in the oxide lattice may be replaced by Cl^- [16], the final corrosion product is still copper oxide, because of rotating electromagnetic effect which changes the seawater properties, and promotes copper oxidation reaction.

3.3 Rotating electromagnetic effects corrosion performance evaluation

According to the XRD pattern, the surface corrosion products are formed by different oxidate film due to the

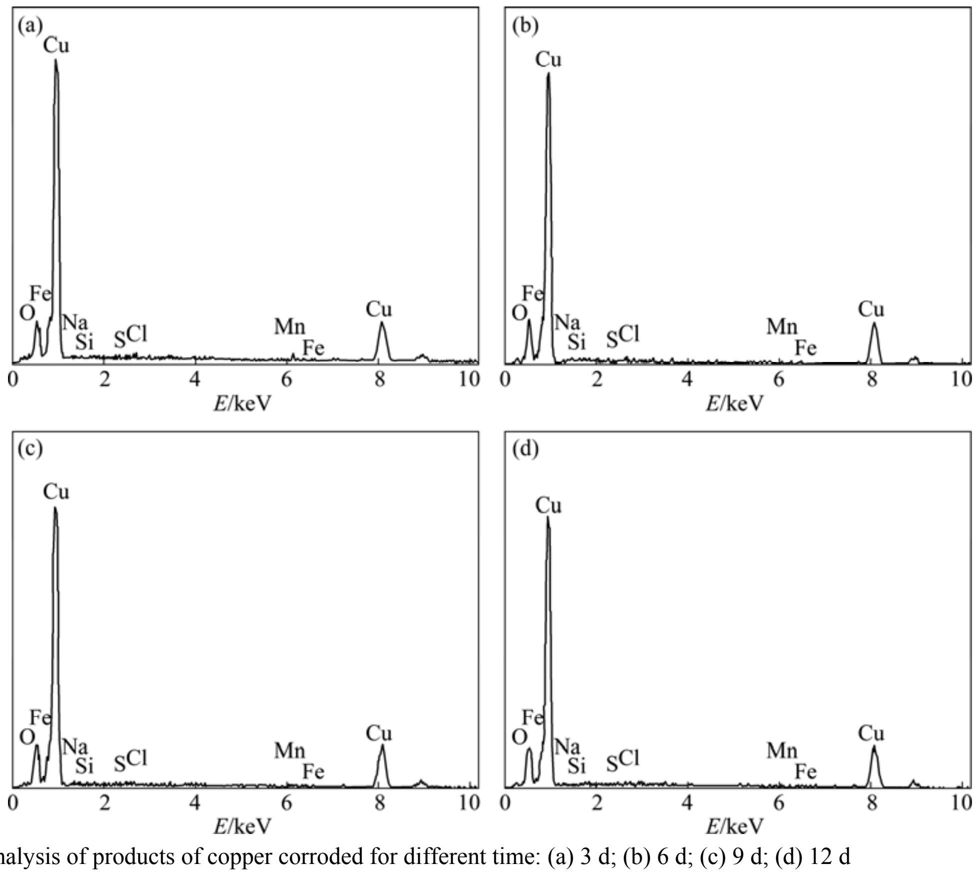

Fig. 6 EDAX analysis of products of copper corroded for different time: (a) 3 d; (b) 6 d; (c) 9 d; (d) 12 d

copper heat flow corrosion, and the reason can be attributed to the different thermodynamic stability, as seen in Fig. 9.

Whether the surface corrosion product is a protective film or not, the most important factor is decided to the integrity of the film. Usually, the volume of the metal oxide film V_{OX} is greater than that of the metal V_M, which can be called r.

$$r=\frac{V_{OX}}{V_M}=\frac{M\rho_M}{nA\rho_{OX}}=\frac{M\rho_M}{m\rho_{OX}} \quad (3)$$

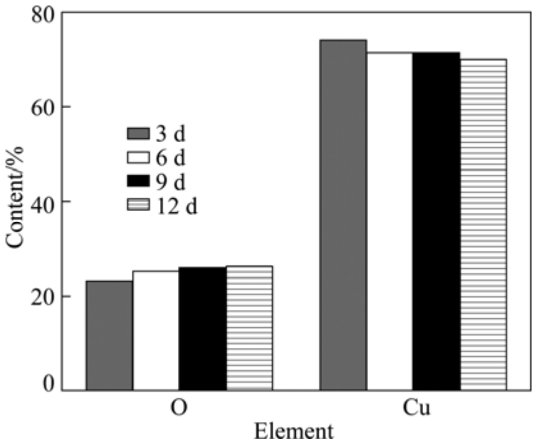

Fig. 7 Elements content of corrosion products of copper

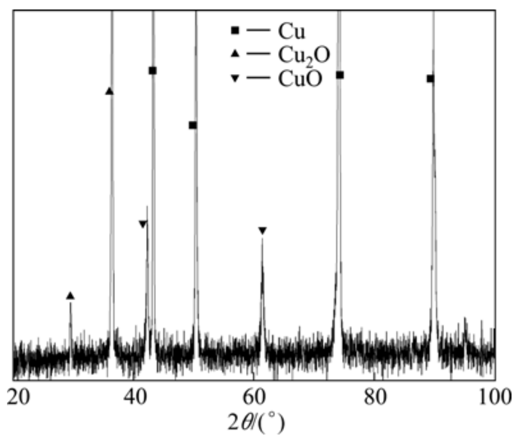

Fig. 8 XRD pattern of copper

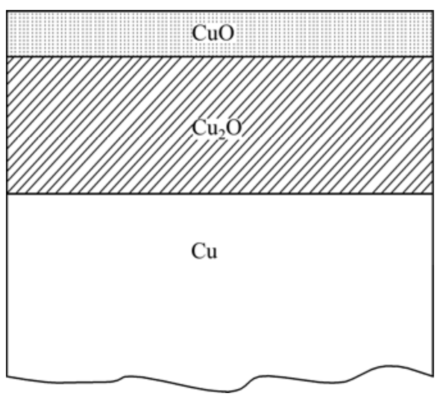

Fig. 9 Sketch of corrosion products

where M is metal oxide relative molecular mass; A is metal molecular atomic mass; n is the metal in the metal oxide valences; M is formation of metal oxide film quality consumed, $m = nA$; ρ_M and ρ_{OX} are metals and metal oxide density, respectively.

Generally, the oxidation film is considered to be complete when r>1. If r<1, the whole metal surface cannot be completely covered by the generated oxidation film, and the oxidation film will be porous, which cannot effectively segregate the metal and medium isolation, and makes the protectiveness of the oxidation film becoming weak. Cu_2O film is a protective oxide films due to its r=1.68.

4 Conclusions

1) Through the surface microstructure observation, the corrosion characteristics of copper under the action of rotating electromagnetic effect on sea water are pitting corrosion, the flow corrosion process contains uniform pitting corrosion, pitting corrosion expansion, corrosion products film, solution of surface products and pitting corrosive.

2) The compositions analysis shows that copper surface corrosion products contain mainly Cu and O, and the phases of corrosion products mainly include Cu_2O and CuO. Rotating electromagnetic field can improve corrosion resistance of copper in seawater corrode.

References

[1] ZHANG P, GUO B, JIN Y P, CHENG S K. Corrosion characteristics of copper in magnetized sea water [J]. Trans Nonferrous Met Soc China, 2007, 17: s189−s193.

[2] GUO B, ZHANG P, JIN Y P, CHENG S K. Effects of alternating magnetic field on the corrosion rate and corrosion products of copper [J]. Rare Metals, 2008, 27(3): 324−328.

[3] CHIBA A, KAWAZU K, NAKANO O, TAMURA T, YOSHIHARA S, SATO E. The effects of magnetic fields on the corrosion of aluminum foil in sodium chloride solutions [J]. Corrosion Sci, 1994, 36(3): 539−543.

[4] RUČINSKIENĖ A, BIKULČIUS G, GUDAVIČIŪTĖ L, JUZELIŪNAS E. Magnetic field effect on stainless steel corrosion in $FeCl_3$ solution [J]. Electrochemistry C, 2002, 4(1): 86−91.

[5] BIKULCIUS G. Change of mechanical properties of Fe-Cr-Ni steel after corrosion of steel in chlorine medium without and with magnetic field [J]. Compos Inte, 2002, 9(4): 355−364.

[6] KELLY E J. Magnetic field effects on electrochemical reactions occurring at metal/flowing-electrolyte interfaces [J]. J Elchem So, 1977, 124: 987−994.

[7] COSTA I, OLIVEIRA M C L, MELO H G DE, FARIA R N. The effect of the magnetic field on the corrosion behavior of Nd-Fe-B permanent magents [J]. J Magn Magn Mater, 2004, 278: 348−358.

[8] CHOPART P, DOUGLADE J, FRICOTEAUX P, OLIVIER A. Electrodeposition and electrodissolution of copper with a magnetic field: dynamic and stationary investigations [J]. Electr Act, 1991, 36: 459−463.

[9] LEE C C, CHOU T C. Effect of magnetic field on the research

kinetics of electroless nickel deposition [J]. Electr Act, 1995, 40: 965−970.
[10] SHINOHARA K, AOGAKI R. Magnetic field effect on copper corrosion in nitric acid [J]. Electroch, 1999, 67(2): 126−131.
[11] AABOUBI O, CHOPART J P, DOUGLADE J, OLIVIER A, GABRIELLI C, TRIBOLET B. Magnetic field effects on mass transport [J]. J Elchem So, 1990, 137(6): 1796−1803.
[12] LEE J, RAGSDALE S, GAO X, WHITE H S. Magnetic field control of the potential, distribution and current at microdisk electrodes [J]. J Electroanal Chem, 1997, 422(1−2): 169−177.
[13] MORI S, SATOH K, TANIMOTO A. The influence of static magnetic fields on mass transport [J]. Electr Act, 1994, 39: 2789−2794.
[14] TUTHILL H. Guidelines for the use of copper alloys in sea water [J]. Mater Performance, 1987, 26(9): 12−16.
[15] PINI G, WEBER J. Materials for pumping sea water and media with high chloride content [J]. Pumps, 1979, 158(11): 530−539.
[16] WANG Ju-lin, XU Chun-chun, LÜ Guo-cheng. Formation process of CuCl and regenerated Cu crystals on bronze surfaces in neutral and acidic media [J]. Applied Surface Science 2006, 252(18): 6294−6303 .

旋转磁场对海水中铜流动腐蚀的影响

李吉南，张 鹏，郭 斌

哈尔滨工业大学 材料科学与工程学院，哈尔滨 150001

摘 要：通过实验室中 12 d 的旋转电磁腐蚀实验，研究海水中铜的流动腐蚀。利用扫描电镜和 X 射线能量分散分析系统(SEM/EDAX)和 X 射线衍射仪(XRD)分析铜试样的表面微观结构和相组成，包括空干后腐蚀产物膜中的 Cu_2O 和 CuO 的组成。结果表明：流动腐蚀过程是坑蚀、扩展、腐蚀产物膜和表面产物溶液，最后是坑蚀。旋转电磁场抑制了铜在海水中的流动腐蚀。

关键词：铜；抑制腐蚀；旋转电磁；微结构

(Edited by ZHAO Jun)