

SEAWATER CORROSION OF A Cu-Ni ALLOY IN INTERMITTENT IMMERSION^①

Zhu Xiaolong, Lin Leyun, Li Zhongjian

General Research Institute of Non-Ferrous Metals, Beijing 100088

Lei Tingquan

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

ABSTRACT The characteristics and concentration depth profile of the corrosion product film of 70Cu-30Ni alloy exposed to seawater in intermittent immersion were investigated. The results showed that the corrosion product film of incompletely recrystallized 70Cu-30Ni alloy is uniform, rich in Ni and Fe and high in seawater species such as O, Ca, Al, etc. This probably is related with the sufficient oxygen provided under such condition. Because of potential difference between deformed and recrystallized grains of incompletely recrystallized Cu-Ni alloy, corrosion develops in preference along the grain boundaries of the two kinds of grains and intergranular corrosion occurs.

Key words Cu-Ni alloy seawater corrosion intermittent immersion

1 INTRODUCTION

Cu-Ni alloys are important marine engineering materials for their good corrosion and bio-fouling resistances. They are widely used as condenser tubes and other pipes in ships, heat exchangers of seashore power plants and seawater desalination systems. The corrosion resistance of Cu-Ni alloys mainly depends on the protective characters of the corrosion product film^[1, 2].

The formation of the corrosion product film is closely related to the alloy nature and the seawater environment. For the alloys, the main influence factors are iron content, microstructure and initial surface^[3, 4]. Factors of marine environment include flowing velocity, temperature, oxygen dissolved, sulfides polluted and marine organisms, etc^[5, 6]. To improve the corrosion resistance of the alloys, researchers applied some surface pretreatments, such as the addition of FeSO₄ in exposure media and the pre-exposure of alloys in clean seawater^[7, 8], to the alloys so as to form protective corrosion product films.

To explore new way of forming protective corrosion product films of Cu-Ni alloys, the present paper studied the influence of intermittent immersion on the behavior of corrosion of commercial 70Cu-30Ni alloy in seawater by investigating the characteristics of its corrosion product film formed in natural seawater.

2 EXPERIMENTAL AND RESULTS

The microstructure of 70Cu-30Ni alloy was observed on optical microscope Neophot 2.

Electrochemical tests were carried out by corrosion measurement system M351. The pH value of corrosion media (3.5% NaCl) was regulated between 8.2~8.4 by adding HCl or NaOH solution. Polarization resistance R_p was measured by weak polarization near the corrosion potential E_c , i. e. $E_c \pm 20$ mV (scanning velocity 0.1 mV/s). Strong polarization was carried out by scanning from cathodic part to anodic part (scanning velocity 0.166 mV/s).

Natural seawater corrosion tests were per-

① Supported by the National Natural Science Foundation of China and State Key Laboratory for Corrosion and Protection

formed in Qingdao seawater corrosion station ($36^{\circ}03' N$, $120^{\circ}25' E$), the main environmental factors of which are shown in Table 1.

Table 1 Main environmental factors of Qingdao seawater corrosion station

Salinity /mg· L ⁻¹	Oxygen /mL· L ⁻¹	pH	Temperature/ °C			Velocity /m·s ⁻¹	Average tide level/m
			High	Low	Average		
32.23	5.57	8.16	27	1.1	13.6	0.1	2.7

Tubes of 70Cu-30Ni alloy were cut into $d25 \text{ mm} \times 200 \text{ mm} \times 1 \text{ mm}$ specimens, which were then degreased and cleaned by acetone, formaldehyde or other organic solvents. After dried, specimens were put in drying containers for 24 h, and then exposed to seawater.

The specimens were fixed on the test platform with plastical tubes situated 0 ~ 0.3 m above average middle tide level. The exposure time is separately 3, 6, 24 and 48 months. The corrosion product film was analysed by SEM (JSM-800) and EPMA (TN5500). The depth profile of the elements of corrosion product films was obtained by AES ($\Phi595$) with Ar ion sputtering (accelerating voltage 4.5 kV). The relative content of elements was ascertained by measuring the peak-to-peak height of prominent auger lines and semiquantitatively computed with sensitive factors for each element.

Microstructure observation showed the specimens consisting of deformed and recrystallized grains. After intermittently immersed for 3 and 6 months, the specimens formed corrosion product films rich in Ni, Fe and O and containing a lot of seawater species (Fig. 1). The 6 months intermittent immersion film was thick with cracks and high in Ni, Fe and S, on which there were white crystallized seawater species (Fig. 2).

After 24 months intermittent immersion, specimen was moved into 3.5% NaCl solution, in which its polarization resistance was determined as $50 \text{ k}\Omega$, while that of the specimen immersed only in 3.5% NaCl solution for 35 d was determined to be $17 \text{ k}\Omega$. The polarization curves of the two specimens are shown in Fig. 3. There is a wide passive zone in the intermittently im-

mersed specimen, and the width of the current platform stands for the polarization overpotential. The film can endure before it breaks down. But the polarization curve of the specimen immersed only in NaCl solution has no such current platform, it shows that the alloy is in the active state when immersed in NaCl solution or seawater. Therefore, incompletely recrystallized alloy can form the passive corrosion product film in the intermittent immersion.

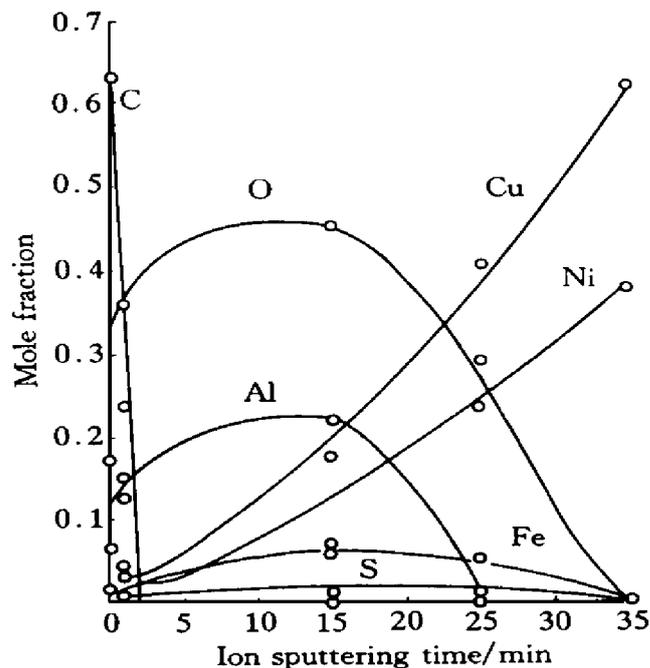


Fig. 1 Depth profile of the concentration of corrosion product film of 70Cu-30Ni alloy after 6 months intermittent immersion

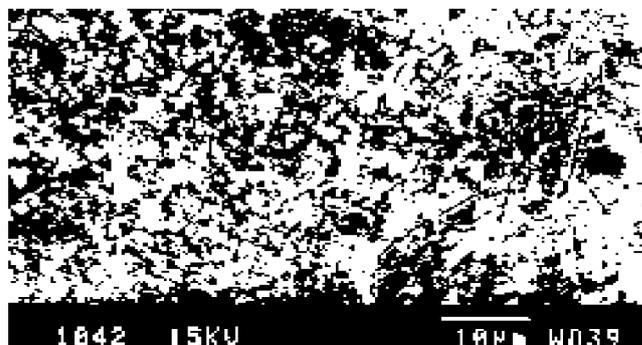


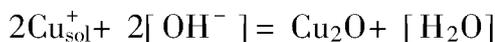
Fig. 2 Corrosion product film of 70Cu-30Ni alloy after 6 months intermittent immersion

After intermittently immersed in seawater for 48 months, the specimen formed corrosion

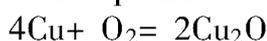
product film rich in Ni (Fig. 4(a)) and intergranular corrosion appeared where the film scaled off (Fig. 4(b)), which indicates that although the incompletely recrystallized alloy can form uniform and protective corrosion product film under intermittent immersion conditions, intergranular corrosion of the matrix after long time exposure still occurs beneath the film.

3 DISCUSSION

In intermittent immersion, specimens were taken out of seawater half a day and immersed in it half a day repeatedly. Oxygen provided for the specimens is dissolved in seawater when they are immersed, and the content of oxygen is equivalent to that in marine atmosphere. From the Evans' pH-potential figure^[9], Cu-Ni alloys can form a layer of protective corrosion product film,



or the following reaction takes place on the surface of the specimen:

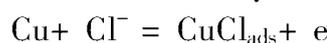


The oxide film adheres solidly to the matrix. With the increase of exposure time, the corrosion product film thickens, Ni and Fe diffusing to the film increases the resistance of anodic process but the resistance of cathodic process has no obvious change. When the IR drop of the corrosion product film is big enough and the corrosion potential reaches $E_{\text{Cu}_2\text{O}/\text{Cu}_2(\text{OH})_3\text{Cl}}$, the outer layer of the film comes to form, *i. e.*

$$2[\text{Cu}_{\text{sol}}^{2+}] + 3[\text{OH}^-] + \text{Cl}^- = \text{Cu}_2(\text{OH})_3\text{Cl}.$$

When the specimen is taken out of seawater, dissolved alloying elements and dehydrated seawater species precipitate on its surface and oxygen in the air diffuses to the surface film, so that the film contains a great amount of O, Al, Si, Ca and S. Sulfides are of advantage for adsorption of carbides on the surface, and carbon in the film will increase electronic conductivity and so improve the cathodic process^[1].

The microstructure of the incompletely recrystallized Cu-Ni alloy consists of deformed and recrystallized grains. The alloy exists in the active state in seawater. Chloride can adsorb on the surface of the alloy:



and form dissolvable copper complexes:

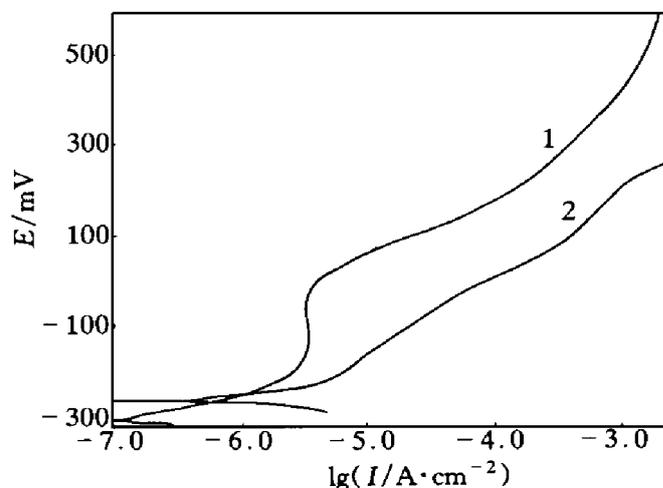


Fig. 3 Polarization curves of 70Cu-30Ni alloy film

1—intermittent immersion for 24 months;
2—immersion for 35 d

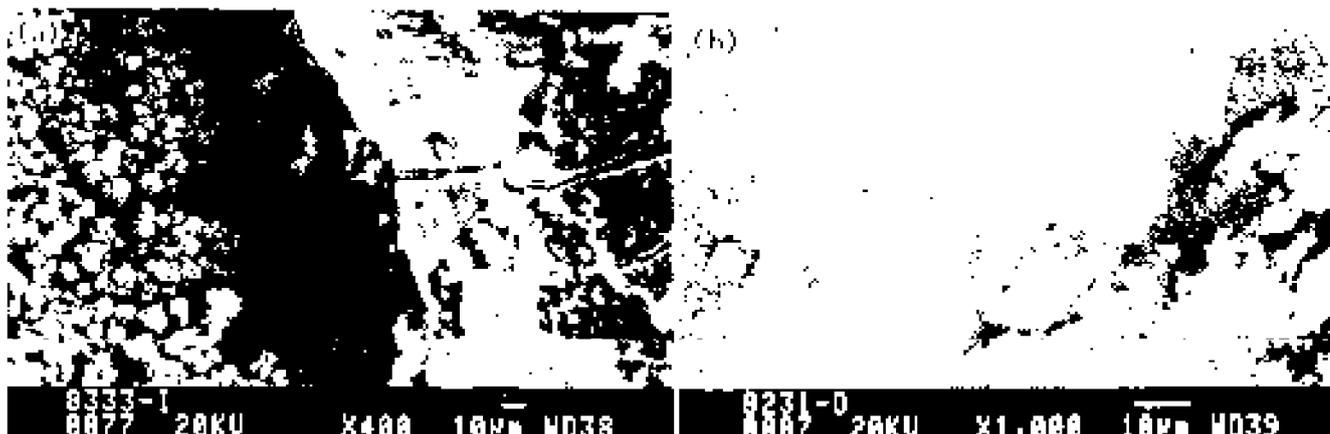
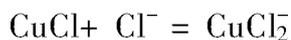


Fig. 4 Corrosion morphology of 70Cu-30Ni alloy intermittently immersed for 48 months



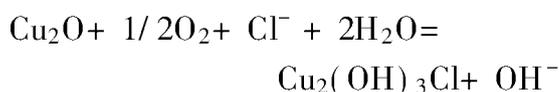
There are different potentials between the deformed grains with residual strain and high density of dislocations and recrystallized grains in seawater, so they compose corrosion cell. Because the distance of electronic transfer at the interface of deformed and recrystallized grains is short, corrosion develops in preference along the grain boundaries, resulting in intergranular corrosion. The deformed grain produces deformation potential which changes both the overpotential of ionic release and the adsorption of ions on the electrode surface and thus influences the cathodic process^[10]. Dislocations of the deformed grain as diffusion channels accelerate the corrosion of the deformed grain and so intergranular corrosion develops quickly.

Since short distance of the transportation of electric charge is preferred at the interface of deformed and recrystallized grains, the control step of anodic dissolution in Tafel zone depends on the diffusion of Cl^- to the surface of the alloy or CuCl_2^- to seawater^[10].

When the concentration of CuCl_2^- on the surface of the alloy is high enough, CuCl_2^- would hydrolyse to form Cu_2O ^[11]:



The Cu_2O film precipitates on the surface of the alloy, and Cu_2O is further oxidized to form $\text{Cu}_2(\text{OH})_3\text{Cl}$:



The diffusion of Cl^- or CuCl_2^- through the film gradually makes the film porous and loose. The residual strain and high density of dislocations accelerate the diffusion of ions and the formation of cracks in the film, which makes the film scale off and the intergranular corrosion appears in the matrix. Therefore, although the intermittent immersion favors the formation of protective product films and can be used as a pretreatment method for 70Cu-30Ni alloy, it can not prevent intergranular corrosion resulted from the inhomogeneous microstructure.

4 CONCLUSIONS

(1) Incompletely recrystallized 70Cu-30Ni alloy intermittently immersed in seawater forms protective corrosion product film which is uniform, rich in Ni and Fe and high in seawater elements such as O, Ca, Al, etc. The intergranular corrosion of the matrix appears where the surface film scales off.

(2) The passive corrosion product film formed on the alloy intermittently immersed in seawater is more protective than that immersed in NaCl solution in laboratory, which is related to the oxygen content provided.

(3) The microstructure of incompletely recrystallized 70Cu-30Ni alloy consists of deformed and recrystallized grains. Because there is potential difference between two kinds of grains, corrosion develops in preference along the grain boundary of the two kinds of grains. Besides, the intermittent immersion can not prevent the intergranular corrosion resulted from the inhomogeneous microstructure.

REFERENCES

- 1 Gilbert P T. Materials Performance, 1982, 21(2): 47.
- 2 IJsseling F P, Krougman J M, Drolenga L J P. In: 5th Internal Congress on Marine Corrosion and Fouling. Barcelona, (Corrosion), 1980: 146.
- 3 Drolenga L J P, IJsseling F P, Kolster B H. Werkstoffe und Korrosion, 1983, 34: 167.
- 4 Nagata K, Atsumi T, Yonemitsu M. Sumitomo Light Metal Technical Reports, 1992, 33(4): 20.
- 5 Francis R. British Corrosion Journal, 1983, 18(1): 35.
- 6 Ross R W. Materials Performance, 1979, 18(7): 15.
- 7 Cigna R, Gusmano G, Zama M. Materials Chemistry and Physics, 1989, 23: 311.
- 8 Hu Zhongyi. Surface Analyses, (in Chinese). Shanghai: Fudan University Press, 1989: 6.
- 9 Eiselstein L E, Syrett B C, Wing S S, Caligiuri R D. Corrosion Science, 1983, 23: 223.
- 10 Zhu Xiaolong. PhD Thesis, (in Chinese). Harbin Institute of Technology, 1996: 85.
- 11 Moreau A. Electrochimica Acta, 1981, 26: 1609.

(Edited by Li Jun)