# INFLUENCE OF THE MICROSTRUCTURE OF Cu–Ni ALLOY ON ITS CORROSION RESISTANCE①

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## ABSTRACT

The microstructures of two kinds of Cu–Ni alloys were observed by TEM. The results show that one of the alloys is a homogeneous solid solution. The other contains discontinuous precipitates at some grain boundaries, and the precipitate is a phase rich in Fe–Ni. By monitoring the corrosion potential ($E_{corr}$) in artifical seawater and exposure to natural seawater for a long time, it is found that the $E_{corr}$ of the former alloy steadily decreases, while the $E_{corr}$ of the latter decreases a little and fluctuates, and the corrosion rate of the former is clearly lower than that of the latter. Aanalyses of SEM and EDX show that the corrosion product film of the former is thin, uniform, compact and rich in nickel, and the film of the latter is thick, loose and covered with numerous deposits. Additionally serious intergranular corrosion occurs in the underlying substrate of the latter. The author proposes that the intergraular corrosion results from preferential dissolution of discontinuous precipitates at grain boundaries. In addition, the protective characteristics of corrosion product films are related not only to the enrichment of nickel but also to their compactness.

**key words:** Cu–Ni alloy microstructure corrosion resistance seawater corrosion potential corrosion product film

## 1 INTRODUCTION

The Cu–Ni (70 / 30) alloy has been successfully used for condenser tubes in marine engineering. It is generally believed that the corrosion resistance of the alloy depends on the ability of its surface corrosion product film to protect the underlying metal[1–4]. The factors which influence the corrosion product film are complicated, such as the Fe content and microstructure[5–6]. Stewart and La,Que[5] found that the corrosion resistance of the Fe solid-solutionized Cu–Ni alloy is superior to that of the Fe–precipitated Cu–Ni alloy, and further investigations into the influence of the microstructure of the alloy on its corrosion resistance have been carried out[6].

In this paper, observations of the microstructures of two kinds of Cu–Ni alloys similar in chemical composition, and insight into their corrosion behaviours are presented.

## 2 EXPERIMENTAL METHOD

The Cu–Ni alloy samples (200 mm × 1 mm × 25 mm) are denoted by A and B, and their compositions and mechanical properties are shown in Table 1.

The microstructure of the samples was analysed by TEM (2000FX). The corrosion potential was tested in artificial seawater (3.5% NaCl solution, pH 8.2–8.5). The solution was renewed every week. The samples were immersed in natural seawater (36 ° 03′N, 120 ° 25′E) for 1, 2 and 4 years. The main

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characteristics of natural seawater are listed in Table 2.

Corrosion products were analysed by SEM (JSM–840) with EDX(TN5500).

**Table 1 Compositions and mechanical properties of Cu–Ni alloys**

| No | chemical composition / wt.–% | | | | | | | | mechanical properties | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Cu | Ni | Fe | Mn | P | Si | Pb | others | $\sigma_b$ / MP | $\delta$ / % |
| A | 67.48 | 30.79 | 0.85 | 0.87 | 0.0001 | | | | 389 | 44.8 |
| B | bal. | 29.58 | 0.89 | 0.89 | | 0.19 | 0.0001 | Co < 0.01 | 392 | 36.5 |

**Table 2 Main characteristics of natural seawater**

| salinity* / $mg \cdot L^{-1}$ | $O_2$ / $mL \cdot L^{-1}$ | pH | $T$ / ℃ | | | $V_f^{**}$ / $m \cdot s^{-1}$ |
|---|---|---|---|---|---|---|
| | | | max. | min. | aver. | |
| 32.23 | 5.57 | 8.16 | 27 | 1.1 | 13.6 | 0.1 |

* —average salinity; * * —flow rate

## 3 RESULTS

### 3. 1 *Analyses of Microstructure*

Sample A was a homogeneous solid solution, except for some dislocations (Fig. 1a). Discontinuous precipitates were found at some grain boundaries (Fig. 1b). The precipitates were too small to allow structured information to be abtained by electron diffraction or X–ray diffraction. Popplewell, Hart and Ford[7] indentified them as a Fe–Ni rich phase (FCC). Berg and Delange[8] determined the lattice constant of the phase to be 3.58A. Because the composition of the precipitates cannot be obtained from the phase diagram of Cu–Ni–Fe, Richter and Pepperhoff[9] found that the Ni content of the precipitates is 60～70% with Mossbauer Spectroscopy. In addition, the Fe content was measured to be about 20% by Vogel[10].

### 3. 2 *Corrosion Potential Monitoring*

Fig. 2 displays the corrosion potential of two kinds of samples over time in artifical seawater. In the beginning, they had almost the same corrosion potential ($E_{corr}$). The $E_{corr}$ of sample A rapidly decreased and then steadily declined. The $E_{corr}$ of sample B was higher than that of sample A and unstable. After measuring the $E_{corr}$, samples A and B were analyzed by SEM (Fig. 3). The corrosion product film of sample A was uniform and compact (Fig. 3a), and its composition (wt. –%), shown by EDX, was Cu–57.98, Ni–34.43, Fe–1.71, Mn–0.75 and Cl–4.93. The film was rich in nickel and low in chlorine. The film of sample B was loose and displayed serious pitting (Fig. 3b), and the film contained (wt. –%) Cu–44.80, Ni–35.99, Fe–5.56, Mn–0.88 and Cl–1.09. The contents of Ni, Fe and Cl in the film of sample B were higher than in the film of sample A.

### 3. 3 *Corrosion Data and Corrosion Product Films*

The variation between the corrosion data

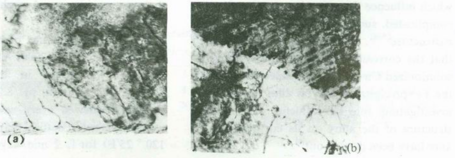

(a) (b)

Fig. 1 Microstructure of Cu–Ni alloys

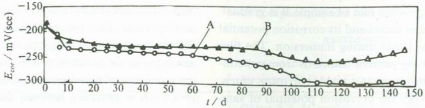
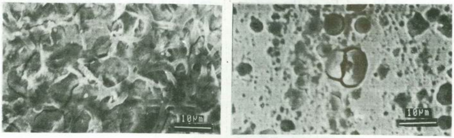


Fig. 2 corrosion potential ($E_{corr}$)–corrosion time ($t$) curves of Cu–Ni alloys (3.5%NaCl, pH 8.2~8.5)



(a) (b)

Fig. 3 Corrosion morphology of Cu–Ni alloys in artificial seawater

of samples A and B is great and becomes greater with the increase of exposure time in natural seawater (Fig. 4). Exposure results for 4 years indicate that the pitting of sample A was 0.66 μm in depth and was corroded through. The corrosion characteristics observed by SEM show that the film of sample A was of a layered structure and smooth with an inner layer which was uniform and rich in nickel and an outer layer which was rich both in nickel and iron and in chlorine or sulfur (Fig. 5a). In the case of sample B, enormous deposits covered the outer layer of the film, and intergranular corrosion was found in the underlying substrate (Fig. 5b). The deposits primarily contained copper and seawater impurities such as calcium, chlorine and sulfur. The composition (wt. −%) of the underlying substrate was Cu–68.84, Ni–29.00, Fe–1.21 and Mn–0.96, similar to the average composition of the alloy. However the content of nickel and iron at the grain boundaries surpasses the average content of Ni and Fe in the alloy.

## 4 DISCUSSION

Some researchers have applied electrochemical methods to study the corrosion behaviors of Cu–Ni alloys in artificial seawater. Stewart and La, Que[5] proposed that the free corrosion potential of Cu–Ni alloys generally remained between −200 mV and −250 mV, independent of the microstructure and Fe content (less than 3.5%). Efird[11] and Francis[12] found that a potential jump occured in 70 Cu–30Ni alloys in seawater but did not occur in 90 Cu–10Ni alloys. They attributed the jump to the change in corrosion product films such as the formation of the film rich in iron. Drolenga[6] pointed out whether there was a potential jump depended on the corrosion resistance of the alloy. When discontinuous precipitates were present, the alloy displayed potential jumps in the positive direction, and its corrosion product film was thin and uniform, so that it had good corrosion resistance. So far the cause for the potential jump has not been clarified. In the above experimental results, the corrosion product film of sample B is gradually enriched in nickel and its corrosion potential tends to be lower during immersion. The film can effectively prevent chlorions from penetrating, and this leads to a stable corrosion potential. Although the corrosion potential of sample B decreases a little with increasing immersion time, it rises and falls. The reason is that the segregation of Ni and Fe of the surface film from the underlying substrate results in the decrease of the corrosion potential, and the penetration of chlorions in the loose film makes the potential fluctuate.

The formation of corrosion product films on Cu–Ni alloys in seawater is affected by the original surface, microstructure and seawater environment. The corrosion product film of sample A forms uniformly on the film and is compact and rich in nickel. With the immersion, the film slowly deteriorates, and a new underlying film forms. The corrosion product layer of sample B forms by precipitation or redeposition of dissolved species[13], so that the film is poorly adherent, porous and loose. Discontinuous precipitates at some grain boundaries have different corrosion potentials from the surrounding substrate and they constitute a corrosion cell. The precipitates, rich in Ni and Fe, preferentially dissolve as an anodic electrode. Therefore, intergranular corrosion takes place. On the other hand the surface film of sample B cannot protect the underlying substrate since the porous and loose film could not prevent the penetration of chlorions. When the diffusion of oxygen in seawater is inadequate, the cathodic process is depolarized by reduction of dissolved cupric ions ($Cu^{2+}+2e \rightarrow Cu$). It is generally believed that the corrosion product film rich in nickel protects the underlying substrate. However, if the film is porous and loose, the penetration of chlorions increases the electronic conductivity of the film and so makes it lose its protective effect.

## 5 CONCLUSIONS

(1) The microstructures of two kinds of

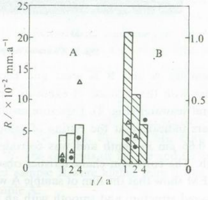
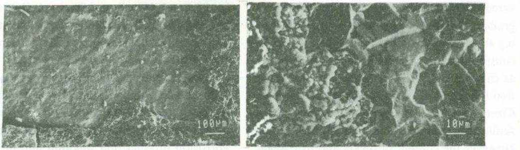


**Fig. 4 Corrosion rates ($R$) of Cu–Ni alloys in natural seawater for 124 d**

△—maximum pitting depth; ●—average pitting depth;

□, ▨—average corrosion rate



(a) (b)

**Fig. 5 Corrosion characteristics of Cu–Ni alloys in natural seawater**

Cu–Ni alloys, similar in compositions, are different, one alloy was a homogeneous solid solution and discontinuous precipitates were found at some boundaries of the other;

(2) With the increase of immersion time the corrosion potential of the homogeneous alloy decreases and the potential of the Fe–Ni precipitated alloy decreases a little and fluctuates. After 4 years immersion in seawater, the former corrodes less seriously, and the latter is corroded through;

(3) The corrosion product film of the homogeneous alloy has a layered structure, thin, uniform, compact and rich in nickel, while the film of the Fe–Ni precipitated alloy is thick, loose and covered with deposits. Additionally intergranular corrosion occurs to the underlying substrate of the Fe–Ni precipitated alloy. The protective characteristics of corrosion product films of Cu–Ni alloys depends on both compactness and nickel richness.

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Me-HCl-$H_2O$ system and followed by the removal of lead in other system can be used to solve this problem and in the meantime concentrate the lead into leached residues.

## 6 CONCLUSIONS

(1) The most important factors in the arsenic chlorination-leaching-distilling process for complex tin dusts are the amount and method of adding MeS and the amount and concentration of hydrochloric acid. The better targets are obtained in the optimal conditions: (a) the removed Pb, As, Zn and Ag are more than 95%, and the removed Sb and Fe are more than 88%; (b) the distilled arsenic is 95.35%; (c) the recovery of tin in residues and the total recovery of tin are 85.68% and 98.59% respectively; (d) the grade of tin concentrate is about 50%.

(2) The CR process is also suitable for treating other highly arsenic materials. Therefore it is of great significance in eliminating the arsenic harm.

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