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Influence of microstructure and surface condition on antifouling property of 90Cu-10Ni alloy in seawater ①

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[Abstract] Through the experiment of natural seawater exposure corrosion, the antifouling properties of the plate specimens of 90Cu-10Ni alloy were studied, which were processed by different deformations, annealing treatments and surface treatments. The results indicate that after exposure corrosion for half a year, the antifouling properties of the specimens are quite different. The specimens processed by suitable deformations, annealing treatment at 650 ℃ and pretreatment of surface film possess both good corrosion resistance and antifouling properties. However, the specimens processed by different deformations and annealing treatment at 450 ℃ possess lower corrosion resistance, although they are also treated by the pretreatment of surface film; their antifouling properties change with different deformations. The relationships among the corrosion morphology and microstructure with the antifouling property of 90Cu-10Ni alloy are observed under the scanning electron microscopy (SEM).

[Key words] 90Cu-10Ni alloy; seawater corrosion; antifouling; deformation; annealing
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1 INTRODUCTION

Copper and its alloys are widely used in marine engineering because of their good corrosion resistance as well as excellent antifouling ability in marine environment[1,2]. The 90Cu-10Ni alloy (CDA706) is well known to be the best one. Study about seawater corrosion of the alloy was concentrated on the formation of corrosion film when the alloy was exposed to seawater[2~6]. Different mechanisms of antifouling ability of Cu alloys elucidated and published by LaQue[7] and Efird[8]. The former considered that only those Cu alloys with corrosion rate greater than 0.8 mpy (about 20 μm/a) possess antifouling ability, and the latter proposed a new viewpoint that it is cuprous oxide film that provides the antifouling ability. Meanwhile, a lot of articles were published in literature to study the influence of temperature, flowing rate, contamination and other environment factors of seawater on corrosion of the alloy[9~11]. The present project studied 19 kinds of Cu and Cu alloys exposed in seawater for 1, 2, 4, 8 years not only in their corrosion resistance but also in antifouling ability of the alloys[12]. The results show that in most of the cases the viewpoint of cuprous oxide having antifouling ability is correct but it needs analysis in detail because of the complicated fouling and antifouling behavior of the metal and the alloys. For the 90Cu-10Ni alloy it seems that the antifouling behavior is influenced by the material type i. e. tube or plate. It is suggested that the property is related with the microstructure of the alloys as well as their surface condition. This phenomenon has not been reported in literature till now.

The present paper deals with the phenomenon by different process deformation and heat treatment to 90Cu-10Ni alloy plate and by immersing the specimens in seawater for a long time. It is possible to light on the relationships among the corrosion morphology and microstructure with the antifouling property of the alloy.

2 EXPERIMENTAL

The ingot of 90Cu-10Ni alloy rolled out in plates with different deformation amounts and was annealed of 650 ℃ and 450 ℃ respectively. Then, they were exposed to seawater in Yulin sea area of China for corrosion experiment. The chemical factors of the seawater could be seen elsewhere[10]. After half a year they were taken from the exposure fields and treated according to standard method[9]. Before above-mentioned treatment the marine organism attachment on the specimens were recording by inspection and taking photos so that we could recognize the antifouling behavior of the alloys. For further investigation, small pieces were cut out from the specimens (plate size 100 mm × 200 mm) without pickling. Graphite powder spraying treatment was conducted for the corrosion film of the small pieces in order to ensure their electrical conductivity. The piece specimens were observed by scanning electron microscopy (SEM) and energy dispersive of X-ray analysis (EDXA). The instruments used are JSM840 by JEOL Co. fitted with TN5500 (EDXA) by Tracer Co.

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The electron acceleration voltage of SEM and EDXA was 15 kV.

The chemical composition and the process technology of the specimens are listed in Table 1 and Table 2.

Table 1 Chemical composition of 90Cu-10Ni alloys studied in present project (%)

Alloy	Cu	Mn	Sn	Ni
90Cu-10Ni alloy	Bal.	0.65	0.013	9.80
Alloy	Fe	Mg	Si	Zn
90Cu-10Ni alloy	1.18	0.085	0.075	0.05

Table 2 Process technology (deformation and heat annealing) of alloy specimens

Specim No.	Deformation	Annealing condition
112	35%	650 ℃, 1 h
116	35%	650 ℃, 1 h
122	18%	650 ℃, 1 h
212	35%	450 ℃, 10 h
214	35%	450 ℃, 10 h
222	18%	450 ℃, 10 h

Specim No.	Surface pretreatment	Antifouling status*
112	Yes	Good (20% attach)
116	No	Good (20% attach)
122	No	Bad (90% attach)
212	Yes	Bad (100% attach)
214	No	Good (50% attach)
222	No	Bad (80% attach)

* The attachment organisms appeared in this experiment were mainly hydroxides.

3 RESULTS AND DISCUSION

As is well known that the specimens with different processing technologies possess different microstructures. Figs. 1 and 2 are the typical their metallographs taken by SEM. Fig. 1 shows the microstructure of specimen No. 112, which is disperse distribution structure of second phases. To contrast, Fig. 2 shows the structure of specimens No. 212 etc., which is obviously the chain-like second phase precipitated on grain boundary of the alloy. From the alloy structure as shown in Figs. 1 and 2, it is not difficult to predict the corrosion resistance of the 90Cu-10Ni alloy of in seawater.

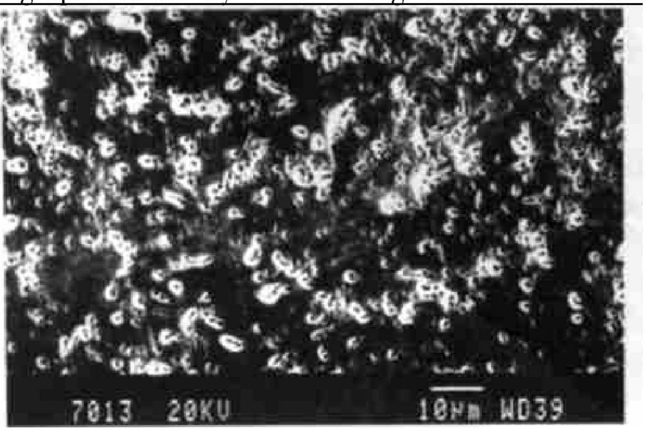

Fig. 1 Metallograph of speciment of No. 112 by SEM

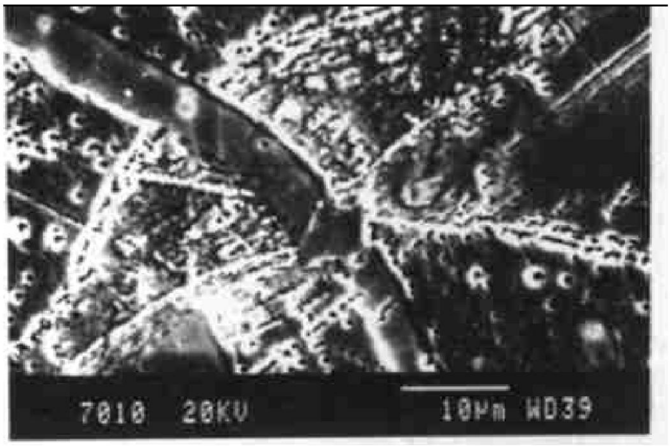

Fig. 2 Metallograph of specimen No. 212 by SEM

The antifouling results of the specimens which were exposed in seawater of Yulin sea area for half a year, are shown in Table 2. Some of the results are also shown in Figs. 3 and 4, respectively. The results indicate that the differences among the antifouling properties of the specimens are significant.

By using EDXA to analyze the composition of the corrosion layer formed on the surface of specimens, one can discover the reason why the antifouling property is related to the microstructure of the alloys. Based on the antifouling mechanism of not Cu ions but cuprous oxide film, Cu alloys can be divided into two kinds, i. e. those with good antifouling property and those lost this property very soon when they are immersed in seawater.

Table 3 gives a part of the analysis results of corrosion product of the specimens analyzed by EDXA. At first, one can see that composition characteristic of

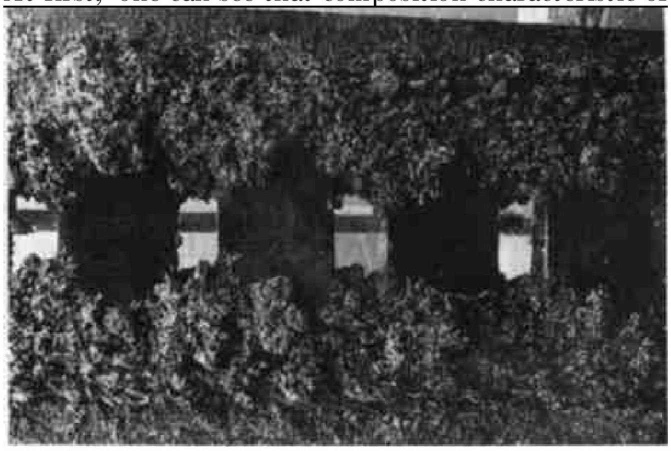

Fig. 3 Specimens No. 116 (the left two) and No. 112 (the right two) with good antifouling property

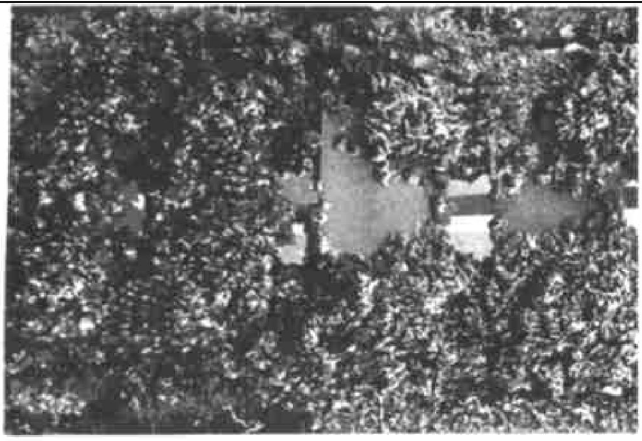

Fig. 4 Specimens No. 212 (the left two) and No. 214 (the right two) with poor antifouling property

specimen No. 112 is Ni enrichment in its corrosion product film. The content of Ni is even as much as 37% (much more than the nominal concentration 10%). Most of Cu alloys lose their antifouling ability with their corrosion resistance increasing when they are immersed in seawater, which are covered with the corrosion product film on their surface gradually. The process of corrosion resistance increasing is that the alloying elements diffuse from alloy matrix toward the surface film as it is exposed in seawater, forming a new alloying surface film called surface realloying[11]. As the composition of the surface film changes, the proportion of cuprous oxide in the film becomes less and less so that the alloy, lose their antifouling ability gradually[12]. Fortunately, it is not the case of specimen No. 112 listed in Table 3. Even though the corrosion film of specimen No. 112 is enriched in Ni, the Cu content is still more enough in the surface cuprous oxide film to possess good antifouling property. So the deformation and the surface pretreatment of specimen No. 112 can make the alloy possess double excellent properties both in corrosion resistance and in antifouling.

Specimen No. 116 is almost in the same condition as No. 112. Table 3 shows that both Cu and Ni contents in surface layer of the specimen are as high as 48% and 22%, respectively. The Cl content is a little high but much lower than the proportion of Cl: Cu in atacamite. It still possesses good antifouling property because of the cuprous oxide film existed on its surface.

In the case of specimen No. 212, things are completely different. Cu alloys exposed in seawater could form corrosion product layer dominated by atacamite, which can shield the antifouling ability of cuprous oxide film. Analysis result of specimen No. 212 listed in Table 2 is the atacamite composition characterized by an atomic ratio of 22: 44 of Cu and Cl which has the same chloride ion content as $Cu_2(OH)_3Cl$ (Cu: Cl= 2: 1). So it is impossible to contain cuprous oxide in the corrosion product film and it is inevitable to lose antifouling ability. Specimen No. 122 is also as the same type of antifouling property as specimen No. 212. The reason is probably that the last time deformation is too low to get suitable structure like specimen No. 112, although they both have been annealed in the same temperature afterwards. The alloys of this type possess medium corrosion resistance. The surface pretreatment technology can not work on specimen No. 212. This is obviously due to the chain-like precipitate structure assisted in the alloy.

As the basic salt film (such as atacamite) peeling off new surface of the alloy emerged, then the property of the specimen changed. It could become good antifouling material again[8]. That is the case of specimen No. 214.

In Table 3, the composition of specimen No. 214-1 is nearly close to that of the alloy matrix,

Table 3 Composition analysis of corrosion surface for various specimens exposed to seawater for half a year (%)

Detec. points	Cu	Ni	Fe	Mn	Cl	Al	Ca	S	Si	Mg
112-1	36.0	37.5	8.3	1.6	2.3	1.7	1.5	3.5	6.5	1.2
112-2	43.6	27.7	7.4	0.6	3.4	5.3	1.1	4.7	2.4	2.0
116-1	48.9	22.5	9.7	0.2	6.8	1.6	1.5	3.6	3.1	1.9
212-1	54.3	20.0	3.4	1.2	14.6	–	2.0	1.7	2.8	–
212-1	44.9	17.9	3.2	1.2	22.0	–	2.7	2.9	5.3	–
212-2	60.1	13.2	2.4	0.9	19.0	–	1.0	1.2	2.2	–
212-2	49.3	11.8	2.2	0.9	28.5	–	1.3	2.0	4.2	–
122-1	28.9	40.5	9.6	2.4	6.9	1.2	2.2	3.4	2.3	2.7
122-1	23.0	35.2	8.8	2.4	10.1	2.2	2.9	5.4	4.3	5.8
214-1	88.6	6.8	1.0	0.5	0.9	0.5	0.3	0.4	0.6	0.5
222-1	96.9	1.5	0.4	0.0	0.6	–	–	0.3	0.4	–

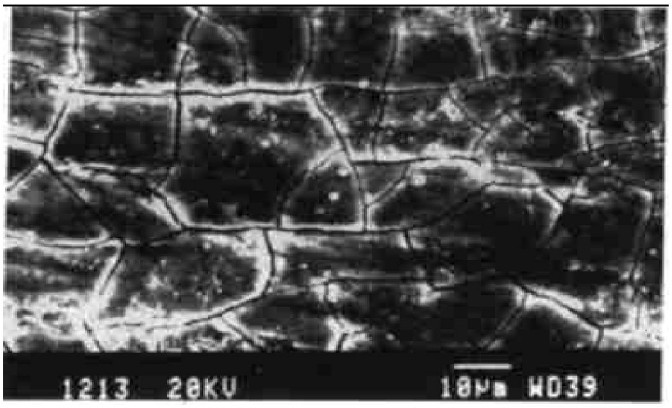

Fig. 5 Corrosion film morphology of specimen No. 112 by SEM

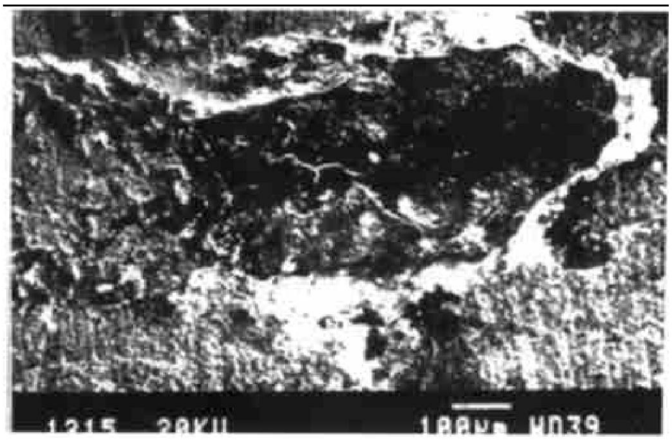

Fig. 6 Morphology of place of fouling organism attached by SEM

so the antifouling property of the specimen is just as good as that of the original alloy. Finally specimen No. 222 should be mentioned too. Because it suffered serious corrosion the surface of the specimen was deposited Cu crystals (see No. 222-1 in Table 3). The fouling organisms just attached on the surface of the red Cu. It seems that this deposited crystal does not possess good antifouling property. The reason should be detected further.

4 CONCLUSION

The 90Cu-10Ni alloy plates processed by different deformation content and annealed by different temperature were exposed to seawater of Yulin sea area for half a year. The specimens exhibited different antifouling properties as well as different corrosion resistance. The specimen with 35% last deformation content, annealed at 650 ℃ for 1 h and surface film pretreatment possesses the best corrosion resistance and antifouling property. The double excellent properties are due to Ni enrichment cuprous oxide film formed on the surface of specimen.

The specimen with the same process technology but different annealing technology, i. e. annealed at 450 ℃ for 10 h exhibits poor properties both in corrosion and in fouling. Other specimens have their own properties according to definite corrosion film condition and the correspondent mechanisms of antifouling property.

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