DEVELOPMENT OF NEW EROSION-CORROSION RESISTANT CUPRONICKEL ALLOYS①

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ABSTRACT Two series of erosion-corrosion resistant cupronickel alloys, 16Ni and 30Ni series, were developed. Erosion-corrosion resistant cupronickel alloys of 30Ni series was based on 70Cu-30Ni alloy and added Cr, Al and trace amount of boron. Erosion-corrosion resistant cupronickel alloys of 16Ni series was composed of about 16% Ni, 5% Mn and small amount of Fe, Cr, Al elements. Compared with 70Cu-30Ni and 90Cu-10Ni alloys, these new cupronickel alloys have high strength, hardness and corrosion resistance, their corrosive wear and erosion-corrosion resistance were greatly improved without affecting its corrosion resistance and mechanical formability. The effect and optimum content of alloying elements were discussed.

Key words cupronickel alloy erosion-corrosion erosion corrosive wear

1 INTRODUCTION

90Cu-10Ni(B10, CA706) and 70Cu-30Ni (B30, CA715) alloys were widely used as condenser tube, heat exchanger pipe and other sea structure materials for its heat conductivity, mechanical formability and high corrosion resistance in clean and polluted sea water. With the development of industrial technique, the erosion-corrosion resistance were needed to be improved for different applications. On one hand, the water flowing velocity in pipe was raised from 4~5 m/s to 15 m/s even to 40 m/s[1]; on the other hand, Sato[2] found that the surface shear stress of water at the inlet end of condenser tube is about double of that of further down the tube, and the water velocity passing a partial obstruction in the bore of a condenser tube such as in lodgment is four times as the overall velocity. Furthermore, the existence of solid state particle and corrosion media such as S^{2-}, NH_4^+ will also accelerate the impingement and corrosion of copper-base alloys.

From 1970s, the new erosion-corrosion resistant cupronickel alloy was begun to be designed and tested by adding Fe, Mn and Cr elements in 90Cu-10Ni and 70Cu-30Ni alloys in USA and other countries. Trace amount of boron can also improve 70Cu-30Ni alloy's strength, hardness, corrosion resistance[3]. But this improvement is very limited. In this work, the new erosion-corrosion resistant cupronickel alloys with high comprehensive properties were developed by adding small amount of B, Cr, Al and adjusting the content of Ni, Mn on the base of 90Cu-10Ni and 70Cu-30Ni alloys.

2 EXPERIMENTAL

2.1 Materials

According to the composition of newly designed erosion-corosion resistant cupronickel alloys, the electrolytic copper (99.99%), electrolytic nickel (99.99%), pure aluminum (99.9%), pure iron, pure chromium, pure manganese and copper-boron master alloy were put into a graphite crucible, 30Ni and 16Ni series of cupronickel alloys were made by vacuum induction furnace. 90Cu-10Ni and 70Cu-30Ni alloys were used as reference samples. The composition of cupronickel alloys is listed in Table 1. The ingot casting (d60 mm × 120 mm) was

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Table 1 Composition of erosion-corrosion resistant cupronickel alloys(%)

Alloy No.	Ni	Fe	Mn	Al	Cr	B	Cu
B31	28.02	1.12	1~3	0~1	0.55	0	Balance
B32	29.47	1.12	1~3	0~1	0.55	0.008	Balance
B11	17.13	1.18	3~6	0.5~2.5	0		Balance
B12	17.49	1.20	3~6	0.5~2.5	0.37		Balance
B13	16.88	1.33	3~6	0.5~2.5	0.82		Balance

forged at 950 ℃ into plate with 12 mm thickness, annealed for 30 min at 760 ℃, and then machined into different specimens.

2.2 Test methods

The mechanical properties were measured by tension and microhardness tester. The corrosion rate was measured at 60±2 ℃ in 25 g $FeCl_3$ + 100 ml HCl and 3.5% NaCl solutions by immersion test.

Corrosive wear tests in 3.5% NaCl solution were carried out in a pin-(Al_2O_3 ball of 6 mm diameter) on-ring apparatus. Wear loss of the alloys was calculated from the width and the depth of the worn track measured on the clean peripheral surface of the ring by using a profilometer after test.

Erosion tests in 3.5% NaCl and 3.5% NaCl + SiO_2(the mass ratio of liquid 3.5% NaCl and solid SiO_2 is 5∶1) solutions were carried out in slurry pot tester at room temperature. Eight cylindrical samples of 70 mm in length and 5 mm in diameter were attached respectively to symmetrically positioned frame at a speed of 3.3 m/s and 5.9 m/s. Erosion rate was calculated from the mass difference of samples before and after tests per hour.

The single pendulum scratch tests of B30, B32 and B12 specimens after immersion in 3.5% NaCl for 672 h(Cleaned with 1∶1 HCl) were carried out at single pendulum scratch tester. The specific energy was determined by the energy loss per groove volume[4].

3 RESULTS

3.1 Mechanical properties and fractography

Table 2 listed the mechanical properties of two series of erosion-corrosion resistant cupronickel alloys. From Table 2, it can be observed that compared with B30, the increments of yield stress $\sigma_{0.2}$ are 202 MPa(B31), 224 MPa(B32), 415 MPa(B11), 464 MPa(B12), 442 MPa(B13); the increments of ultimate tension stress σ_b are 134 MPa(B31), 162 MPa(B32), 371 MPa(B11), 425 MPa(B12), 433 MPa(B13); the increments of Brinell hardness are HB69(B31), HB104(B32), HB130(B11), HB142(B12), HB115(B13) respectively. The strength and hardness of B32 with boron were higher than those of B31 without boron; The strength and hardness of B12 with 0.37% Cr were higher than those of B11 and B13. All these indicated that the cupronickel alloy can be greatly strengthened by adding B, Cr and Al elements.

Table 2 Mechanical properties of erosion-corrosion resistant cupronickel alloys

Alloy No.	$\sigma_{0.2}$ /MPa	σ_b /MPa	δ /%	φ /%	HB
B30	186	399	44.0	25.0	105
B31	388	533	21.4	24.3	174
B32	410	561	16.0	22.0	209
B10	136	350	35.0	30.0	96.5
B11	601	770	16.0	25.4	235
B12	650	824	14.4	20.6	247
B13	628	832	10.4	18.5	230

From the fractographies of five erosion-corrosion resistant cupronickel alloys, it can be seen that the main characteristic is dimple(Fig. 1). Although the plasticity of erosion-corrosion resistant cupronickel alloys decreases to some extent, the adding of alloying elements can′t affect the mechanical forming of cupronickel alloys.

3.2 Corrosion rate

The corrosion rates of erosion-corrosion resistant cupronickel alloys in $FeCl_3$ + HCl and 3.5% NaCl solutions are listed in Table 3. Whether in $FeCl_3$+ HCl or in 3.5% NaCl solution, the corrosion rate of B31, B32 was lower than that of B30; the corrosion rate of B32 with boron was lower than that of B31 without boron. The corrosion rates of B11, B12, B13 decreased with the increase of Cr content, the corrosion rate of B11 was slightly higher than that of B30, which indicated that the corrosion resistance of erosion-corrosion resistant cupronickel alloys was improved to some extent.

Fig. 1 Fractographs of erosion-corrosion resistant cupronickel alloys
(a) —B32; (b) —B12

Table 3 Corrosion rate of erosion-corrosion resistant cupronickel alloys in $FeCl_3$+ HCl and 3.5% NaCl solutions (mm/a)

Alloy No.	3.5% NaCl(10^{-2})	$FeCl_3$+ HCl
B30	3.90	3.62
B31	3.14	3.09
B32	2.82	3.05
B11	4.32	3.66
B12	4.09	3.37
B13	3.71	3.25

3.3 Corrosive wear rate

Fig. 2 shows the dependence of corrosive wear rates of B10, B30, B32, B12 alloys on load. The corrosive wear rates of four cupronickel alloys increased almost in linearity with the load. The corrosive wear rates of B12, B32 were obviously lower than that of B10, B30 in the same load, and the slopes of corrosive wear rate of B32, B12 were also lower than that of B10, B30. From the corrosive wear test for B31, B11, B13, the same conclusion can be obtained.

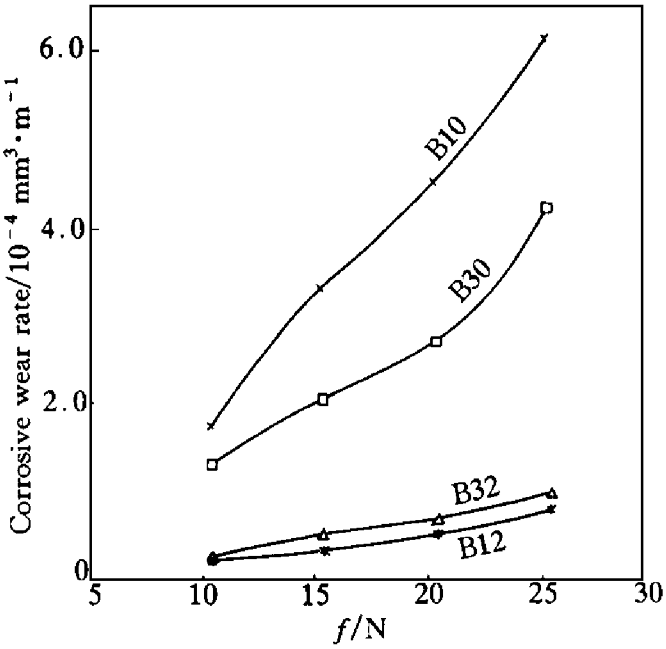

Fig. 2 Dependence of corrosive wear rate of cupronickel alloys in 3.5% NaCl solution on load(f)

3.4 Erosion rate

Table 4 shows the erosion rate of erosion-corrosion resistant cupronickel alloys in 3.5% NaCl and 3.5% NaCl+ SiO_2 solutions. Erosion rate of cupronickel alloys increased obviously when the flowing velocity rose from 3.3 m/s to 5.9 m/s. Erosion rate in 3.5% NaCl+ SiO_2 solution is about ten times of that in 3.5% NaCl solution for the same materials and at the same flowing velocity. The erosion rates of five erosion-corrosion resistant cupronickel alloys were also lower than that of B30, the erosion rate of B32 with boron was slightly lower than that of B31 without boron, the erosion rate of B12 with

0.37% Cr is the lowest one among B11, B12 and B13 alloys. As above mentioned, it can be concluded that the adding of B, Cr, Al elements can greatly improve the erosion-corrosion resistance of cupronickel alloys.

Table 4 Erosion rate of erosion-corrosion resistant cupronickel alloys in 3.5% NaCl and 3.5% NaCl+ SiO_2 solutions (mm/a)

Alloy No.	3.5% NaCl		3.5% NaCl+ SiO_2	
	3.3m/s	5.9m/s	3.3m/s	5.9m/s
B30	0.47	1.14	3.35	22.54
B31	0.33	0.64	2.70	19.20
B32	0.29	0.54	2.48	13.10
B11	0.35	0.75	2.86	16.20
B12	0.31	0.57	2.48	12.92
B13	0.32	0.65	2.55	13.84

4 DISCUSSION

4.1 Effect of alloying elements

While erosion-corrosion resistant alloys being developed, the corrosion resistance of materials must be firstly considered, and then the strength and hardness need to be improved by solid solution strengthening method or other methods without affecting its corrosion resistance and mechanical forming ability[5]. Meanwhile, the reformation of surface film should also be accounted.

The experimental results and the characteristic of B10, B30 alloys being regarded, the elements Fe and B should be chosen as additives because the adding of Fe and B can refine the grain size and improve the strength, erosion-corrosive wear resistance without reducing its corrosion resistance and mechanical workability[3].

So the following discussion was focused on the effect of Cr, Al and Mn.

4.1.1 Effect of Cr

The solubility of Cr in copper-base alloys is very small, and decreases with reduction of temperature. The solubility of Cr at 900 ℃ is 0.24%, but when the temperature was dropped down to 800 ℃, it was only 0.17%. So the strengthening effect by aging will be created in the process of continuous colling or aging treatment[6]. Cahn[7] found that this strengthening effect of aging was caused by the spinodal decomposition of α phase at high temperature into α_1 and α_2 phase which have different composition and the same structure, and this aging effect increases with the reduction of Ni content and the rising of Cr content. Furthermore, Cr also can prevent the grain growth of copper-base alloys, raise the re-crystallization temperature, and then improve the hardness and strength of copper alloys.

After aging treatment at 500 ℃ for 3h, the hardness of B30, B32, B12 was HB107, HB225, HB276, respectively. Compared with the hardness in Table 1, it is known that the hardness of B30 without Cr after aging treatment is almost the same as that before treatment, but the hardness of B32, B12 after aging treatment increases about HB20. All these show that the adding of Cr can strengthen cupronickel alloys. From Table 1, it is also found that the hardness of B13 with 0.82% Cr is less than that of B12 with 0.37% Cr. The reason may be that too much amount of Cr will produce a lots of precipitation, the grain of cupronickel alloys will grow large.

4.1.2 Effect of Al and Mn

It's well known that aluminum can form a thin film in the surface of alloys, and it is this film that can improve the corrosion resistance of alloys. So in the following we only discuss the strengthening effect of Al in cupronickel alloys. After investigating the phase diagram of Cu-Ni-Al systems, Alexander[8] found that the strengthening phase in Cu-Ni-Al was Ni_3Al. Clark[9] thought that aluminum can strengthen Cu-Ni alloys, the maximum strengthening effect can be obtained when the content ratio of Al and Ni is 1∶5; but the alloy under this condition will not fit for the structure material because of its low compact toughness. If this ratio is adjusted to 1∶8 or 1∶10 and 5% Mn is added, the designed alloy will possess high strength and high toughness. The effect of Mn is retarding the hardening of precipitation and improving its toughness.

In order to raise the strength of B10, the content of Ni was increased to 16% by considering the ratio of Al and Ni. Based on the above discussion, two series of erosion-corrosion resistant cupronickel alloys were developed. All experiments proved that these erosion-corrosion resistant cupronickel alloys do have high erosion-corrosion resistance.

4.2 Specific energy of surface layer

Fig. 3 shows the variation of specific energies of B30, B12 and B32 after immersing 672 h in 3.5% NaCl solution. It is observed that the specific energies of B30, B12 and B32 decrease with the increase of corroded groove volume, and gradually come to a constant. The specific energies of B12 and B32 are higher than that of B30. It is also seen that the erosion-corrosion resistance of erosion-corrosion resistant cupronickel alloys is higher than that of 70Cu-30Ni and 90Cu-10Ni alloys.

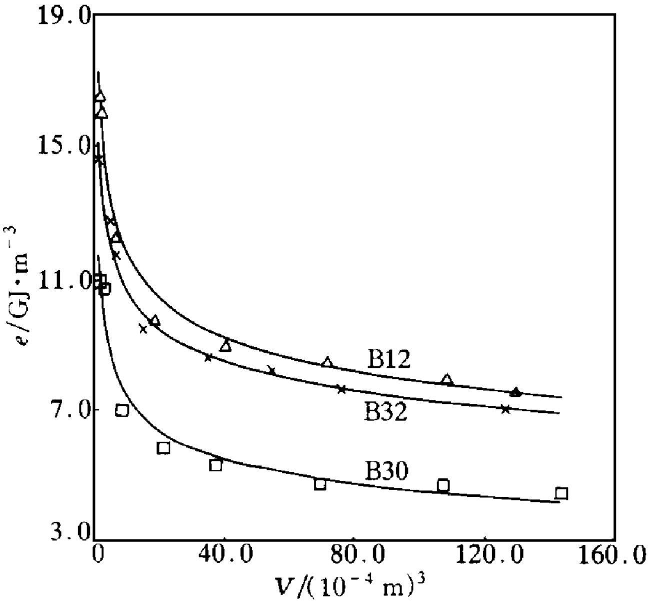

Fig. 3 Variation of specific energy *(e)* **of cupronickel alloys with the groove volume** *(V)*

The erosion-corrosion resistance is related to the surface behavior as well as the properties of material matrix. Efrid[10] determined the erosion-corrosion resistance of materials by the surface shear stress. But lately the single pendulum scratch test method was developed to replace the surface shear stress method. Actually speaking, the characteristic parameters, specific energy and surface shear stress, of these two methods not only have the same unit ($1\ N/mm^3 = 1\ J/mm^2$) but also represent the same scratch process of surface film. The higher the specific energy and surface shear stress, the higher the erosion-corrosion resistance of materials.

5 CONCLUSIONS

(1) The new erosion-corrosion resistant cupronickel alloys is developed by adding B, Cr, Al elements and adjusting the content of Ni, Mn on the base of 70Cu-30Ni and 90Cu-10Ni alloys.

(2) The erosion-corrosion resistance of erosion-corrosion resistant cupronickel alloys is greatly improved because of its high strength, hardness and good corrosion resistance.

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