MICROALLOYING EFFECT OF BORON ON COPPER-BASE ALLOYS①

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ABSTRACT The microstructure and properties of boron-modified copper-base alloys were investigated by tension, corrosion, corrosive wear and erosion tests. The results show that by adding boron in copper-base alloys, the strength and hardness of alloys increase, the plasticity decreases somewhat; the corrosion, corrosive wear and erosion resistance of boron-modified copper-base alloys improve obviously. The microalloying mechanism of boron in copper-base alloys was found.

Key words boron copper-base alloys microalloying

1 INTRODUCTION

It's well known that trace amount of special alloy elements can enhance the mechanical properties and corrosion resistance of metals and alloys, such as B, Nd, Ti, V in microalloyed steel[1], B in nickel and nickel-base alloys[2], B in intermetallic compounds (Ni_3Al, FeAl)[3,4] for increasing their strength and toughness; trace amount of boron in HSn70-1 brass for improving the selective corrosion resistance of naval brass etc[5]. The main reason was that the interaction among these trace elements and the atoms of matrix plays an important role in the properties of alloys.

HSn70-1, HAl77-2 brass, BFe30-1-1 cupronickel alloy were widely used as heat exchanger of condenser tube in power plants and sea ships because of their super conductivity and high corrosion resistance. The critical velocity of these three alloys in flowing sea water was separately 2, 3, 4.5 m/s, if the flowing velocity is greater than the critical velocity, the erosion failure will be severe[6]. In order to prolong the lifetime of condenser tube, the corrosion resistance and strength of these copper alloys must be improved without greatly affecting their machinability. In this paper, by adding trace boron in copper alloys, the microstructure and properties of the boronmodified copper-base alloys were investigated. The effect of boron on copper alloys and microalloying mechanism were found.

2 EXPERIMENTAL PROCEDURES

2.1 *Materials*

According to the designed composition of copper-base alloys, put the electrolytic copper (99.99%), electrolytic nickel (99.99%), pure zinc (99.9%), pure aluminium (99.9%), copper-arsenic (Cu-20%As) and copper-boron (Cu-5.1%B) intermediary alloy into a graphite crucible, four series (23 kinds) of copper-base alloys with different contents of boron were made by vacuum induction furnace. The chemical composition noted in the following is the analyzed content, not the added content which is the sum of analyzed content and the amount of loss in the melting. The content of boron was: Series H70 (70% Cu, 0.1%Al, Zn balance): 0, 0.002%, 0.010%, 0.031%, 0.032%, 0.049%; Series HAl77-2 (77%Cu, 2.4%Al, Zn balance): 0, 0.0021%, 0.0045%, 0.0059%, 0.0092%, 0.021%, 0.061%; Series HAl77-2A (77% Cu, 2.4%Al, 0.06%As, Zn balance): 0, 0.0023%, 0.0055%, 0.0077%, 0.031%,

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0.091%; Series BFe30-1-1(30%Ni, 0.7%Fe, 0.7%Mn, Cu balance): 0, 0.005%, 0.007%, 0.012%. The ingot casting (d60 mm × 120 mm) was forged into plate with 12 mm thickness at 760 ℃ for brass or 1 040 ℃ for cupronickel alloy, annealed for 30 min at 560 ℃ (brass) or 760 ℃ (cupronickel), and then machined into different specimens.

2.2 *Test Methods*

The microstructure was observed by microscope, and then the grain size of copper alloys was calculated. The mechanical properties were measured by tension and microhardness tester. The corrosion rate was measured at 60±2 ℃ in 50 g $CuCl_2$+42 ml/L HCl solution for brass and 25 g $FeCl_3 \cdot 6H_2O$+100 ml/L HCl solution for cupronickel alloy by immersion test.

Corrosive wear tests in 3.5%NaCl solution were carried out in a pin-(aluminium oxide Al_2O_3 ball of 6 mm diameter) on-ring apparatus. Wear loss of the alloys was calculated from the width and depth of the worn track as measured on the clean peripheral surface of the ring by using a profilometer after test. Erosion tests in 3.5%NaCl+SiO_2 (the weight ratio of liquid 3.5%NaCl and solid SiO_2 is 5∶1) solution were carried out in slurry pot tester at room temperature[7]. Eight cylindrical samples 70 mm in length and 5 mm in diameter were attached separately to symmetrically positioned frame at a speed of 3.3 m/s and 5.9 m/s. Erosion rate was calculated from the weight difference of samples before and after tests per hour.

3 RESULTS

3.1 *Grain Size*

Fig. 1 shows the dependence of the grain size of boron-modified copper-base alloys on content of boron after annealing. It is known that with the increase of boron in copper alloys, whether for brass or cupronickel alloy, the grain size of boron-modified copper alloys decreases. The grain size of series HAl77-2+B brass drops from 60 μm without boron down to 20 μm with 0.061%B, the grain size of series HAl77-2+As,B and BFe30-1-1+B (B30+B) alloys also decreases in some extent. All these results prove that trace amount of boron can refine the grain size of copper-base alloys.

3.2 *Brinell Hardness*

Fig. 2 shows the dependence of Brinell hardness of four series boron - modified copper

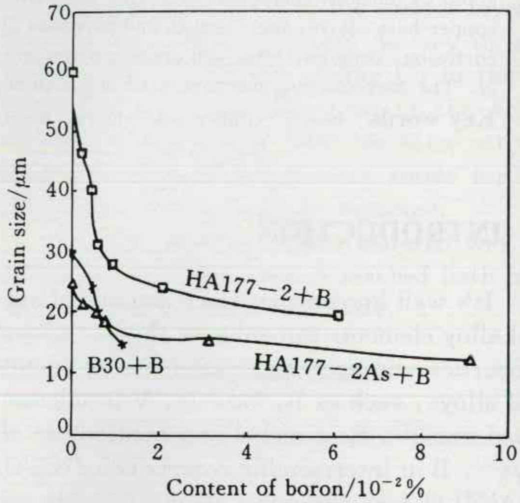

Fig. 1 Variation of grain size of boron-modified copper alloys with the content of boron

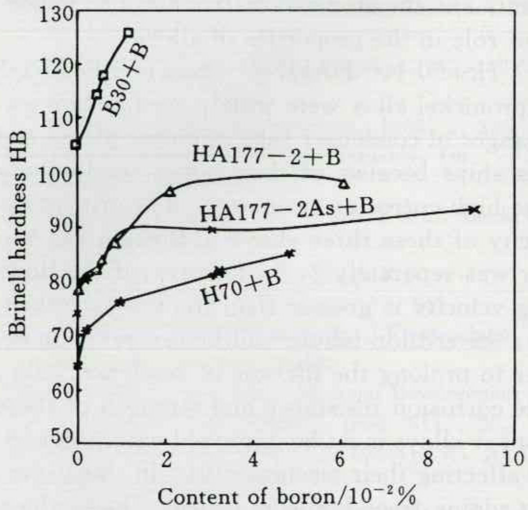

Fig. 2 Brinell hardness of boron-modified copper-base alloys

alloys on the content of boron. It is known that the variation of four series copper alloys' brinell hardness with the content of boron is almost the same whether for brass or cupronickel alloy. In the range of 0～0.01%, the hardness of copper alloys increases in linearity with the content of boron, but when the content of boron is more than 0.01%B, the hardness rises no more. The increment of hardness by adding trace boron is about 20～30 HB. The copper-base alloys were strengthened obviously by boron.

3.3 *Mechanical Properties*

From the results of tension tests of four series boron-modified copper-base alloys, it can be observed that with the increase of boron in the copper alloys, the ultimate tensile stress σ_b and yield stress $\sigma_{0.2}$ increase clearly, the maximum increment of σ_b is 50～60 MPa for three series brass and 40 MPa for cupronickel alloy; the maximum increment of $\sigma_{0.2}$ is 30～40 MPa for brass and 90 MPa for cupronickel alloy. Fig. 3 shows the dependence of the mechanical properties of series HAl77-2+B and series HAl77-2+As, B brass on the content of boron. It can be seen that the strength σ_b and $\sigma_{0.2}$ increase, the enlongation δ and reduction of area ψ only decrease slightly. This slight decrement in plasticity value δ, ψ can not affect greatly the boron-modified copper alloys' machinability. From the mechanical properties, it also can be observed the effectiveness of boron in strengthening the copper-base alloys.

3.4 *Corrosion Rate*

Fig. 4 shows the dependence of the corrosion rates of series HAl77-2+B and series HAl77-2+As, B alloys in $CuCl_2$+HCl solution for 152 h on content of boron. By adding boron to aluminium brass with and without arsenic, the corrosion rate decreases at first with the increase of boron, but when the content of boron is more than 0.0092% for series HAl77-2+B and 0.0077% for series HAl77-2+As, B alloys, the corrosion rate of boron-modified aluminium brass begins to rise somewhat. The corrosion rate of series HAl77-2+As, B alloys is less than that of series HAl77-2+B alloys at the same content of boron.

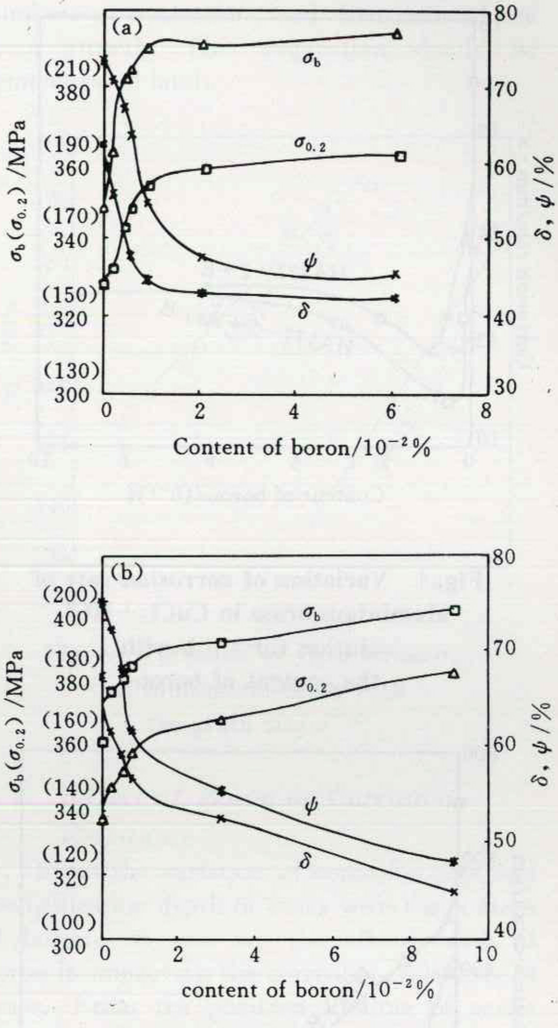

Fig. 3 Dependence of mechanical properties of aluminium brass on the content of boron

(a)—HA177—2+B;
(b)—HA177—2+As, B

Fig. 5 shows the dependence of the dezincification depth of series H70+B and HAl77-2+B alloys immersed in $CuCl_2$+HCl solution for 152 h on the content of boron. It can be seen that with adding boron to brass, the dezincification depth decreases rapidly with the content of boron. The variation of dezincification depth with the content of boron is consistent with that of corrosion rate.

From the experimental results of series

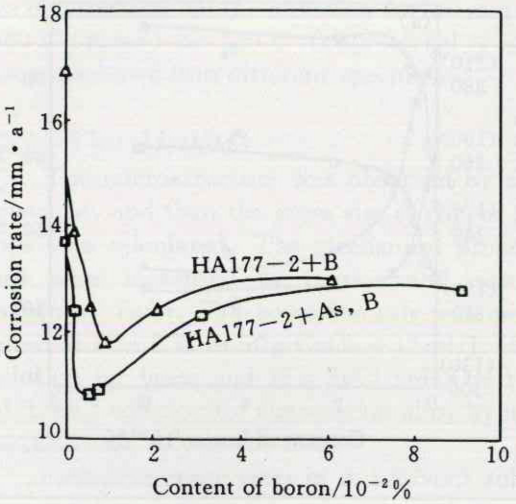

Fig. 4 Variation of corrosion rate of aluminium brass in $CuCl_2$+HCl solution for 152 h with the content of boron

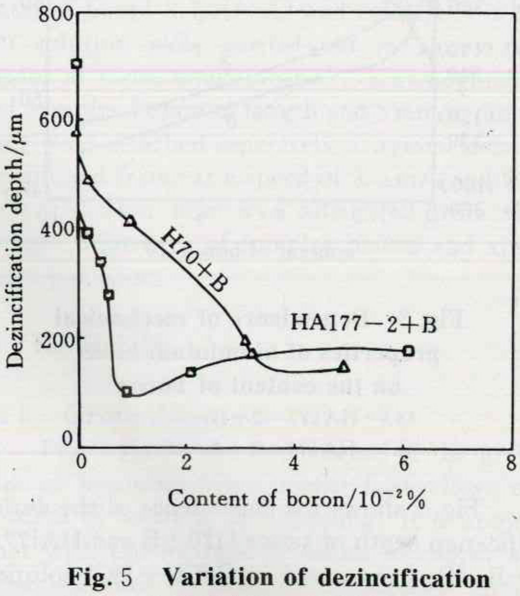

Fig. 5 Variation of dezincification depth of H70+B and HA177−2+B brass in $CuCl_2$+HCl solution for 152 h with the content of boron

BFe30-1-1+B alloys immersed in $FeCl_3$+HCl solution, it also can be observed that the adding of boron can improve the corrosion resistance of cupronickel alloy.

3.5 *Corrosive Wear Rate*

Fig. 6 shows the dependence of corrosive wear rate of cupronickel alloys on the content of boron and load. The corrosive wear rate of series BFe30-1-1+B alloys decreases almost in linearity with the content of boron, and increases with load. The reduction of corrosive wear rate between cupronickel alloys with and without boron increases with load, the corrosive wear rate of BFe30-1-1 alloy without boron is about twice of that with 0.012%B. From the corrosive wear tests for series H70+B, HAl77-2+B and HAl77-2+As, B brass, the same conclusion can be obtained.

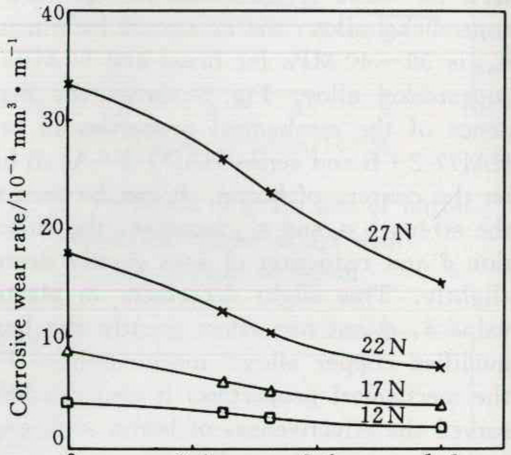

Fig. 6 Dependence of corrosive wear rate of BFe30-1-1+B alloys on the content of boron and load

3.6 *Erosion Rate*

Erosion rate of series HAl77-2+B and series HAl77-2+As, B brass in 3.5%NaCl+SiO_2 solution is shown in Fig. 7. Erosion rate of two series brass increases obviously with the flow velocity rising from 3.3 m/s to 5.9 m/s. On the other hand, erosion rate of two series aluminium brass, whether containing arsenic or not, decreases at first with the content of boron; but when the content of boron is greater than 0.01%, erosion rate of brass becomes unchanged with the increase of boron. At the same condition, erosion rate of series HAl77-2+As, B is a little less than that of series HAl77-2+B. Erosion rate of cupronickel alloys also decreases with the increase of boron.

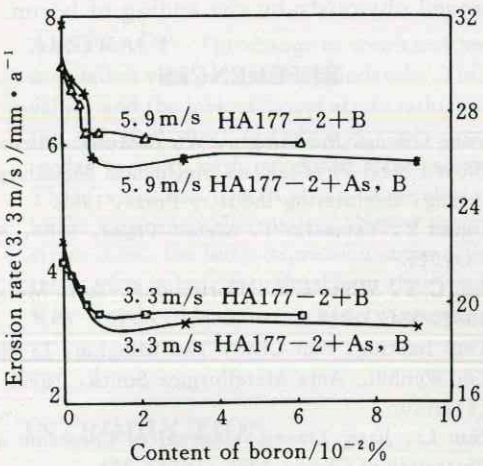

Fig. 7 Dependence of erosion rate of series HA177−2+B and HA177−2+As, B brass on the content of boron

4 DISCUSSION

4.1 *Effect of Boron on Mechanical Properties*

As mentioned above, the addition of boron can refine the grain size of copper-base alloys whether for brass or cupronickel alloy. The variation of yield stress $\sigma_{0.2}$ of series HAl77-2+B and HAl77-2+As, B brass with the grain size $d^{-1/2}$ is shown in Fig. 8. It can be seen that there is a linear relationship between $\sigma_{0.2}$ of two series brass and $d^{-1/2}$. This coincides with the Hall-Petch's formula. After drawing the variation of σ_b, HB for brass, $\sigma_{0.2}$ for cupronickel alloys with their grain size $d^{-1/2}$, we also find the linear relationship between them. All these prove that the strength and hardness can be improved by refining the grain size of copper-base alloys because of the adding of boron. The reason may be that the super fine boron or boride particles were used as the crystallization center, increased the numbers of nucleation, and then reduced the grain growth. This suggestion should be demonstrated later.

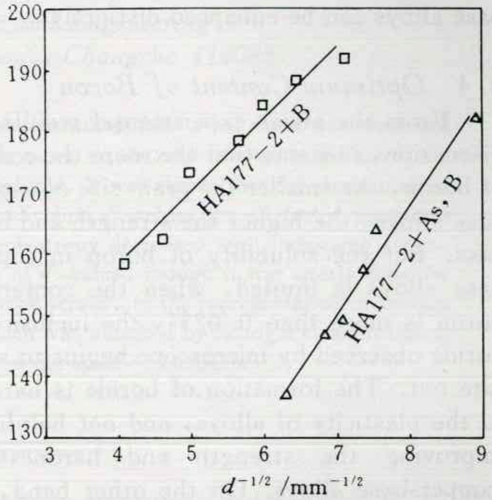

Fig. 8 Variation of yield stress $\sigma_{0.2}$ of aluminium brass with the grain size $d^{-1/2}$

4.2 *Effect of Boron on Corrosion Resistance*

From the variation of corrosion rate and dezincification depth of brass with the content of boron, we can see the effectiveness of boron in improving the corrosion resistance of brass. From the positron lifetime of series HAl77-2+B and HAl77-2+As, B brass before and after dezincification[8], it can be concluded that boron can diffuse into the grain boundary and divacancy of brass, reduce the mobility of grain boundary and divacancy which is the route of dezincification, slows down the dissolution rate of zinc, and then improves the corrosion resistance of aluminium brass.

4.3 *Effect of Boron on Corrosive Wear and Erosion Resistance*

The corrosive wear and erosion resistance is related to the hardness and corrosion resistance of materials. In ordinary circumstances, the high corrosive wear and erosion resistance can be obtained by increasing the hardness, strengthening the alloy and improving its corrosion resistance. The adding of boron not only strengthens the copper alloys, but also improves their corrosion resistance. So the corrosive wear and erosion resistance of copper-base alloys can be enhanced distinctly.

4.4 *Optimum Content of Boron*

From the above experimental results and discussion, it seems that the more the content of boron, the smaller the grain size of copper-base alloys, the higher the strength and hardness. But the solubility of boron in copper-base alloys is limited, when the content of boron is more than 0.02%, the inclusion of boride observed by microscope begins to separate out. The formation of boride is harmful to the plasticity of alloys, and not helpful to improving the strength and hardness of copper-base alloys. On the other hand, the boride which is the cathodic electrode in the corrosion process will accelerate the corrosion of copper alloys. Because too much content of boron will decrease the comprehensive properties of copper alloys, the content of boron in copper alloys shouldn't be too higher. From the experimental results, the optimum content of boron is about 0.01%B. For different kinds of copper-base alloys, the optimum content of boron may be different more or less.

5 CONCLUSIONS

(1) Boron can refine the grain size of copper-base alloys, and then strengthen the copper alloys but without adversely affecting on the plasticity of alloys.

(2) The corrosion, corrosive wear and erosion resistance of copper-base alloys were improved obviously by the adding of boron.

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