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ALUMINUM ALLOYS: DEVELOPMENT, CHARACTERIZATION AND APPLICATIONS

Poster Session

STUDY ON INHIBITORS OF COPPER AND COPPER-NICKEL ALLOY IN LiBr SOLUTION

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Abstract

The effects of LiOH, Na_2MoO_4, and BTA on the corrosion behaviors of copper and copper-nickel alloy in 60% LiBr solution was studied by AC impedance measurements. Results indicated that LiOH, BTA, and Na_2MoO_4 could inhibited the corrosion of copper and copper-nickel alloy in LiBr solution respectively. When they were used together, the inhibition efficiency was higher than that of used one of them. They behaved a synergistic effect on inhibiting the corrosion of copper and copper-nickel alloy in 60% LiBr solution. It presented that when the concentration of LiOH, Na_2MoO_4 and BTA was 0.10mol/L, 150mg/L and 150mg/L, respectively, they behaved the highest inhibition efficiency on the corrosion of copper and copper-nickel alloy in 60% LiBr solution.

Introduction

LiBr solution is the working medium of LiBr absorption chiller. However, LiBr solution is a strong alkaline corrosion medium. The concentration of it in LiBr absorption chiller is between 50% and 65%, and the corrosion of metal materials is very serious. The problem of corrosion will short the service life, and also may cause the LiBr absorption chiller halt. Therefore, the studies of absorption chiller corrosion were aroused wild attention. The methods of corrosion control were mainly two ways. One was adopting corrosion resistant materials, and another was adding inhibitor into LiBr solution. The cost of corrosion resistant materials was high, so that the inhibitors was the study focus for a long time[1,2]. In this paper, the electrochemical behaviors of copper and copper-nickel in 60% LiBr solution with various inhibitors were studied by AC impedance technology.

Experiments

The test solution was 60% LiBr, LiOH, Na_2MoO_4 and BTA were analytical reagent, and the orthogonal distribution table was shown in Table 1. The test materials were copper and copper-nickel alloy, and the chemical compositions of them were list in Table 2. Specimens were processed into size 10 x 30 x 1 mm, and keep working area 10 x 10 mm, the other part were sealed with silicone resin. Specimens were polished by water sand paper step by step to 1000#, and then cleaned by deionized water and absolute ethanol.

Table 1: Orthogonal array of cooperate of inhibitors

No.	LiOH (mol/L)	Na_2MoO_4 (mg/L)	BTA (mg/L)
1	0.07	50	200
2	0.1	50	100
3	0.15	50	150
4	0.07	100	150
5	0.1	100	200
6	0.15	100	100
7	0.07	150	100
8	0.1	150	150
9	0.15	150	200
10	0	0	0

Table 2: Chemical composition of specimens (wt%)

Test material	Ni	Fe	Mn	Pb	Zn	P	Cu
Cu	-	-	-	-	-	0.002	99.97
Cu-Ni alloy	9.5	1.3	0.7	0.033	0.037	-	88.43

Electrochemical impedance measured by three electrodes system, with copper and copper nickel alloys as working electrode, the platinum electrodes as auxiliary electrode and saturated calomel electrode (SCE) as reference electrodes. Experiments were conducted under the condition of 100 C, and the system maintained anaerobic condition by nitrogen. Experimental apparatus used Princeton Model EG&G 283 potentiostat.

Results and Discussions

1. The corrosion behavior of copper in LiBr solution

1.1 Comparison of the inhibition performance

The AC impedance spectra measured in 60% LiBr solution with 0.07mol/L LiOH, 150 mg/L BTA and 150 mg/L Na_2MoO_4, respectively, are shown in Figure 1. The size of capacitive reactance arc indicated that the inhibition effect of LiOH on copper was the best, BTA was the second and Na_2MoO_4 was the worst.

119.37	26.818612	7160.2		423.87
106.45	31.839978	4495.6		346.13
93.459	38.41294	3257.7		262.27
79.354	44.072995	2024		190.2
61.648	43.008666	1376.2		146.11
47.797	36.216791	993.06		110.1
37.392	30.490173	442.37		86.658
29.236	24.497916	428.81		67.023
23.569	19.801826	255.74		52.153
19.337	15.890487	165.31	434.67	40.375
15.513	12.873445	94.4	282.34	29.9
12.64	10.538606	54.426	192.41	22.517
10.387	8.3620699	34.986	128.22	17.097
8.9136	6.3033954	24.733	85.592	9.1402
7.0794	5.4830578	14.073	57.193	6.7965

Figure1: Nyquist impedance diagram of best value for copper in 60%LiBr solution with various inhibitors

The reaction of copper in alkaline conditions[3, 4] and the standard electrode potential[5] were shown as below:

Anode：$2Cu + 2OH^- \rightarrow Cu_2O + H_2O + 2e \quad E^0=-0.361V$ (1)

$Cu + 2OH^- \rightarrow Cu(OH)_2 + 2e \quad E^0=-0.224V$ (2)

$Cu(OH)_2 \rightarrow CuO + H_2O$

Cathode：$2H_2O + 2e \rightarrow 2OH^- + H_2$ (3)

There are trace oxygen reduction reaction at the beginning:

$O_2+2H_2O+4e \rightarrow 4OH^- \quad E^0=0.401V$ （4）

Because Br^- was a highly corrosive ion in high temperature and high concentration of LiBr solution and OH^-, Br^- would spread to the surface of electrode firstly, the following reactions might occur on the electrode surface[6]:

$Cu + Br^- \rightarrow CuBr + e \quad E^0 = 0.05V$ (5)

It can be seen that OH^- not only inhibited the cathode reaction, but also was beneficial to the formation of Cu_2O, CuO oxidation film. Reaction (1), (2) and (5) were competitive reactions, and they caused the formation of Cu_2O, CuO and CuBr film on copper surface. The insoluble CuBr film could fall off easily, and had no protection to the matrix metal[7]. So that Br^- could permeate this film and corrode the metal matrix.

Because Cu^+ and BTA could form a complete Cu (I) - BTA and Cu_2O protective film on copper surface, which could inhibit the active dissolution of copper effectively.

Na_2MoO_4 had certain inhibition effect on copper, but it wasn't as well as LiOH and BTA. This might be because of Na_2MoO_4 relied on the redox products participate in the formation of passive film to inhibit the active dissolution of copper. However, the solubility of Na_2MoO_4 in LiBr solution was very low, and the inhibition performance on copper was not very well.

1.2 Compositional formulation

Experiments had proved that appropriate concentration of LiOH, BTA and Na_2MoO_4 could inhibit the corrosion of copper to a certain extent in 60%LiBr solution, but they all have some defects. In order to further improve the corrosion resistance of copper in 60% LiBr solution, compound inhibitors were studied.

Figure 2 was the nyquist plots of copper in 60%LiBr solution with compound inhibitor according to Table 1. It could be seen that the polarization impedance values were increased by all the compound inhibitors. This indicated that a protective film formed on the surface of copper by the compound inhibitors and the dissolution of copper was retarded. Compared the curves in Figure 2, the compositional formulation (8) was the optimum, and the composition of the compound inhibitor was 0.1 mol/L LiOH + 150 mg/L Na_2MoO_4 + 150 mg/LBTA.

The inhibition effects of LiOH, BTA, Na_2MoO_4 and the compound inhibitor could be compared by calculating the values of the surface film capacitance C. The value of C was smaller, the surface film was denser[8]. Therefore, the value of was smaller, also hinted the inhibition effect was better.

The value of C could be calculated by the following formula[9]:

$$C = \frac{1}{2\pi f_{\theta\max} \cdot |Z|_{\theta\max}}$$

Where in, $f_{\theta max}$ and $Z_{\theta max}$ was f and |Z| according to the phase angle θ_{max}.

The values of the surface film capacitance C with LiOH, BTA, Na_2MoO_4 and compound inhibitor(8) were listed in Table 3.

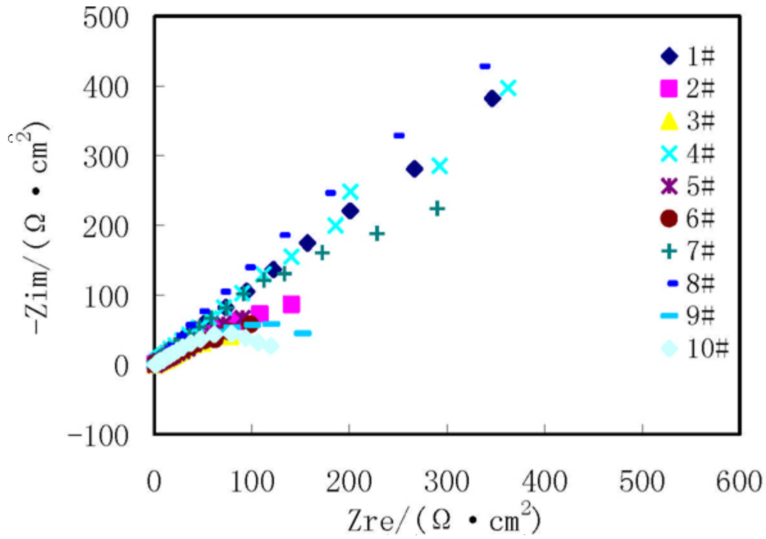

Figure 2: Nyquist plots for copper in 60% boiling LiBr solution with various concentrations of mixing inhibitors

Table 3: The value of C of Copper in boiling Lithium Bromide solution with different inhibitors

LiOH	BTA	Na_2MoO_4	Compound inhibitor(8)
235.2μF	960.6μF	4593.8μF	138.9μF

The data in table 3 showed that the protective film capacitance C value of copper in 60%LiBr solution with compound inhibitor(8) was 138.9μF. However, the value of C was 235.2μF, 960.6μF and 4593.8μF when the solution containing 0.07mol/L LiOH, 150mg/L BTA and 150mg/L Na_2MoO_4, respectively. It indicated that the inhibition effect of compound inhibitor(8) was better than LiOH, BTA and Na_2MoO_4 used individually. This proved that three inhibitors had synergistic effect, and the compound inhibitor could form a denser protective film on copper surface. The inhibition efficiency of compound inhibitor on copper was higher than that of three inhibitors.

2 Copper-nickel alloy

2.1 Comparison of the inhibition performance

The AC impedance spectra measured in 60%LiBr solution with 0.07mol/L LiOH , 150 mg/L BTA and 150 mg/L Na_2MoO_4, respectively, are shown in Figure 3. It showed that all three kinds of inhibitor could increase the polarization resistance and improve the anti-corrosion performance of copper-nickel alloy in LiBr solution. The curves also indicated that the inhibition effect of LiOH on copper-nickel was the best, BTA was the second and Na_2MoO_4 was the worst, this was the similar to that of copper.

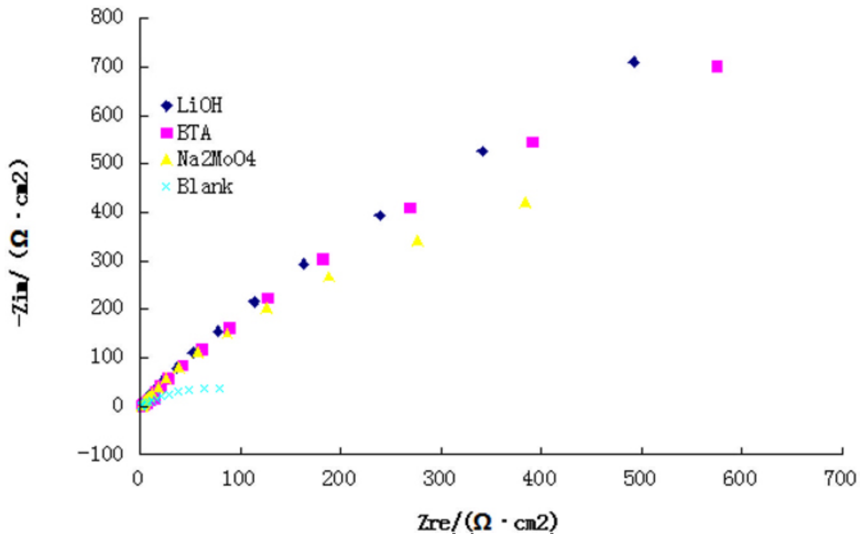

Figure 3: Nyquist plot for cupronickel in boiling 60% LiBr solution with various inhibitors

Copper-nickel alloy contained 9.5% nickel. Anode reactions included not only copper oxidation reactions but also nickel oxidation reactions[3-6]:

$Ni + 2OH^- \rightarrow Ni(OH)_2 + 2e \quad E^0 = -0.69V$ (6)

$Ni + 2OH^- \rightarrow NiO + 2H_2O + 2e$ (7)

The redox products could form a complete passive film containing copper compounds and nickel compound. So that the element nickel in alloy could enhance the corrosion resistance of copper-nickel alloy in LiBr solution.

2.2 Compositional formulation

Figure 4 was the nyquist plots of copper-nickel alloy in 60%LiBr solution with compound inhibitor according to Table 1. It could be seen that the polarization impedance values were increased by all the compound inhibitors. This indicated that a passive film had formed on the surface of copper-nickel alloy by the compound inhibitors and the dissolution of copper-nickel alloy would be retarded. Compared the curves in Figure 4, the inhibition effect of the compositional formulation(8) was the optimum, and the composition of the compound inhibitor was 0.1 mol/L LiOH + 150 mg/L Na_2MoO_4 + 150 mg/LBTA.

The values of the surface film capacitance C with LiOH, BTA, Na_2MoO_4 and compound inhibitor(8) were listed in Table 4.

Table 4: Values of C of copper-nickel alloy in 60%LiBr solution with various inhibitors

LiOH	BTA	Na_2MoO_4	Compound inhibitor(8)
122.6μF	224.8μF	1326.3μF	108.2μF

The data in Table 4 showed that the protective film capacitance C value of copper-nickel in 60%LiBr solution with compound inhibitor(8) was 108.2μF. While the value of C was 122.6μF, 224.8μF and 1326.3μF when the LiBr solution containing 0.07mol/L LiOH, 150mg/L BTA and 150mg/L Na_2MoO_4, respectively. It also indicated that the inhibition effect of compound inhibitor(8) was better than LiOH, BTA and Na_2MoO_4 used individually. It could be concluded that three inhibitors had synergistic effect, and the compound inhibitor could form a denser protective film on copper-nickel alloy surface. The inhibition efficiency of compound inhibitor on copper-nickel alloy was higher than that of three inhibitors. Compared Table 4 to Table 3, it could be seen that the values of C for copper-nickel alloy were all lower than that for copper corresponding to each of the studied inhibitors. It also proved that the corrosion resistance of copper-nickel alloy was better than copper in LiBr solution.

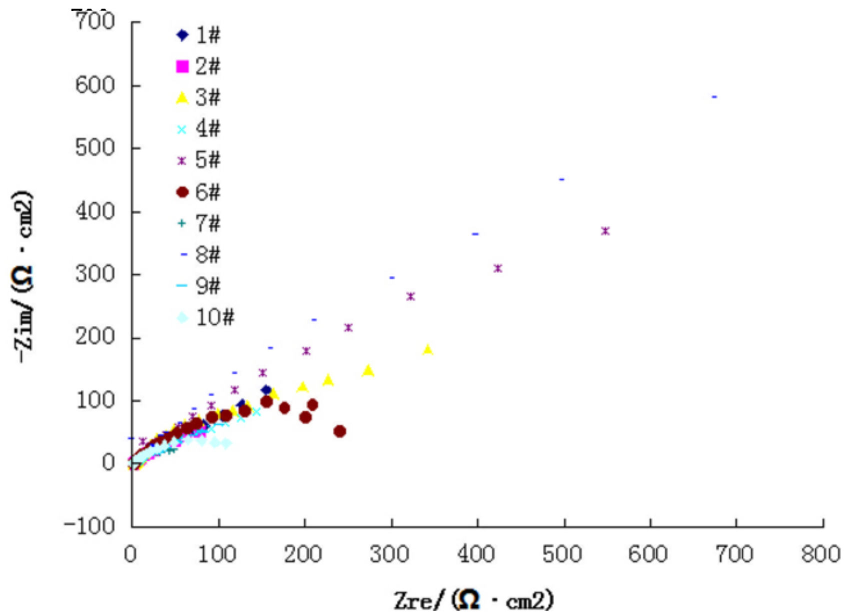

Figure 4: Nyquist plot for copper-nickel alloy in 60%LiBr solution with various concentrations of mixing inhibitors

Conclusions

(1) Both LiOH and BTA could retard the corrosion of copper and copper-nickel alloy in 60%LiBr solution markedly.

(2) The compound inhibitors containing LiOH, Na_2MoO_4 and BTA could form a denser passive film on the surface of copper and copper-nickel alloy, which would inhibit the corrosion of copper and copper-nickel alloy in 60%LiBr solution. The optimal compositional formulation was 0.10mol/L LiOH, 150mg/L Na_2MoO_4 and 150mg/L BTA.

(3) The inhibition efficiency of compound inhibitor on copper and copper-nickel alloy in 60%LiBr solution was higher than that of LiOH, Na_2MoO_4 and BTA used individually, and three inhibitors had a synergistic effect.

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