

Influence of NaCl on dechromization of Cu-Cr-Al alloy in H₃PO₄ solution

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Abstract: The dechromization of Cu-Cr-Al alloys was investigated by a static immersing corrosion test. The influence of NaCl on the dechromization was analyzed by electrochemical test, scanning electron microscopy, optical microscopy and X-ray fluorescence spectroscopy. The results show that the dechromization of Cu-Cr-Al alloys will take place in a H₃PO₄ solution of 11.32 mol/L at 55 °C. And the corrosion process occurs initially at the interface between Cu and Cr phase, and then extends inward Cr-phase inside. The addition of NaCl into H₃PO₄ solutions can shorten the dechromization incubation time, decrease the dechromization temperature and concentration of H₃PO₄ solution, and increase the tendency of dechromization. But, the NaCl scarcely has an effect on the form and structure of chromium depleted-layer.

Key words: dechromization; Cu-Cr-Al alloy; H₃PO₄ solution; NaCl

1 Introduction

Cu-Cr alloy is widely applied in functional materials and parts with high conductivity and high strength due to its high intensity and excellent heat and electrical conductivity[1–4]. With the extending application fields of Cu-Cr alloys, Cu-Cr alloys are potential in use as corrosion-resistant parts applied in environmental and chemical engineering. The research on their corrosion behavior in solutions has been attracting great attention of many researchers[5–7]. Recently, we studied the corrosion behavior of a Cu-Cr alloy in H₃PO₄ solution and concluded that it is dechromization phenomenon that would occur, not decopperation if the temperature and concentration of H₃PO₄ solutions are compatible. Some results about dealloying of Cu-Cr alloys have been reported[8–10], which mainly contained dealloying conditions and effect factors. Furthermore, they concentrated on HCl and H₂SO₄ solutions. H₃PO₄ solution is a common kind of acid solutions used in industry. Adding NaCl into the solutions can deteriorate corrosion-resistant properties of

Cu alloys[11–12]. Many research papers on Cu alloys in H₃PO₄ solutions have been published. However, study on the dechromization corrosion of Cu-Cr alloy in H₃PO₄ solutions and the effect of NaCl in the solution on corrosion behavior has scarcely been reported. The addition of Al element into Cu-Cr alloys could increase the strength and anti-oxidation of alloys[13]. Therefore, in this work, the dechromization corrosion behavior of Cu-Cr-Al alloy, and the effects of NaCl in H₃PO₄ solutions on the dechromization incubation time, and the microstructure of dechromization layer were discussed.

2 Experimental

Cu-Cr-Al alloy containing 50.12%Cu, 48.02%Cr, 1.07%Al, 0.32%Si, 0.45%Ni and 0.03% others (mass fraction) was used to prepare samples with the size of 5 mm×5 mm×10 mm. These samples were polished with silicon carbide paper up to 1200[#] grit, washed by water, dried and then immersed into H₃PO₄ solutions with different NaCl contents for dechromization experiments. Some parameters of dechromization of the Cu-Cr-Al alloy were measured, such as the incubation

time of dechromization (the duration from the beginning of the sample immersed into the solution to air bubble coming into being), the temperature and the lowest concentration of the H_3PO_4 solutions. Tests were carried out in a HHS-12 type electric thermostatic water container.

The anodic polarization curves of the alloy in H_3PO_4 solutions were traced by CH1660A electrochemical instrument with a saturated calomel electrode as the reference electrode and a platinum piece as the counter electrode at a scan rate of 0.5 mV/s. The microstructure and characteristics of the dechromization layer were observed by Neophot21 optical microscope, KYKY-2800 SEM (with EDS), and XP-2TM stylus profilometer. In addition, the compositions of Cu-Cr-Al alloy surface before and after corrosion were analyzed by ADVANTXP-381 X-ray fluorescence spectrometer.

3 Results and discussion

3.1 Dechromization of Cu-Cr-Al alloys

The original microstructure of Cu-Cr-Al alloy shown in Fig.1 is constituted by a bright white Cr phase and Cu solid state solution (named Cu phase). As shown in Fig.1, the irregular shaped grains of Cr phase scatter in the Cu phase substrate.

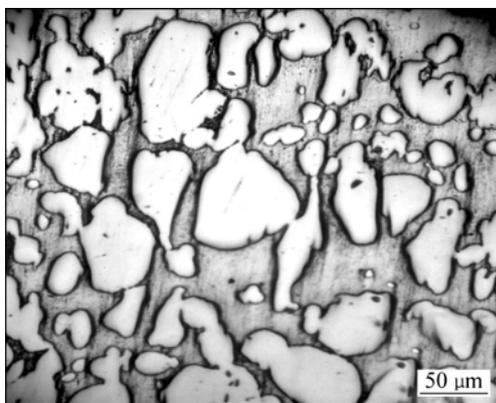


Fig.1 Original microstructure of Cu-Cr-Al alloy

One of the samples was immersed in 50 mL H_3PO_4 solution of 11.32 mol/L, at 55 °C, and others were immersed in the similar H_3PO_4 solutions but containing 0.15 g NaCl. It could be observed that the surfaces of the two kinds of samples become pure copper color. When the solution turns into blackish green, plenty of gases appear. The elements on the sample surface were analyzed by X-ray fluorescence spectrometer. Experimental results (Table 1) show that the majority of elements is Cu and the content of Cr decreases obviously and the content of Al is reduced a little. The microstructure of the surface layer of samples is mainly Cu matrix phase (illustrated in Fig.2), which indicates

that the corrosion characteristics results from the dechromization. SEM analyses indicate that the dechromization of Cu-Cr-Al alloy occurs initially at the interface between Cu phase and Cr phase, and then extends inward the Cr-phase inside until Cr phase dissolves entirely (illustrated in Fig.3). These results could also be confirmed by EDS analysis. Yet NaCl scarcely has an effect on the microstructure of dechromization layer.

Table1 Compositions of surface of samples immersed in H_3PO_4 solutions (mass fraction,%)

Sample	Cu	Cr	Si	Ni	Al	Others
Original	50.12	48.01	0.32	0.45	1.07	0.03
Dechromization without NaCl	95.16	2.67	0.33	0.43	0.94	0.47
Dechromization with NaCl	95.04	2.70	0.36	0.41	0.89	0.60

3.2 Influence of NaCl on incubation time of dechromization of Cu-Cr-Al alloy

During the experiments, it can be observed that the dechromization occurs after Cu-Cr-Al alloy is immersed in H_3PO_4 solutions for some time (incubation time of dechromization). Fig.4 shows the relationship between the content of NaCl and the incubation time of

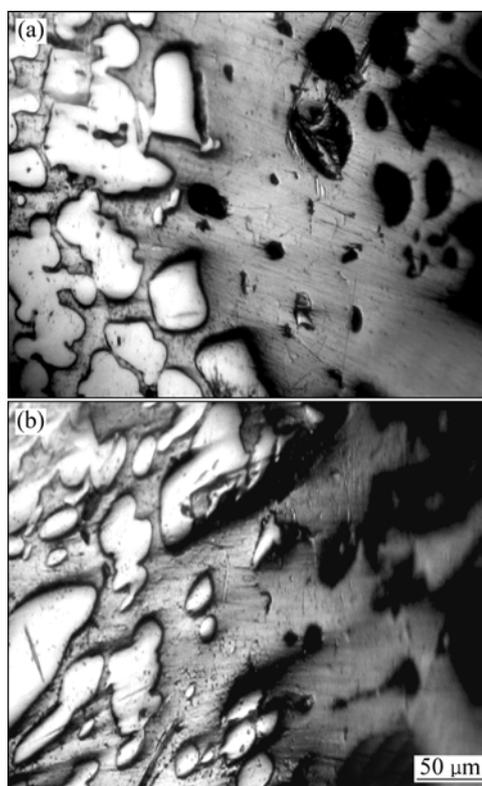


Fig.2 Microstructures of dechromized layer of Cu-Cr-Al alloy under different conditions: (a) Without addition of NaCl; (b) With addition of NaCl

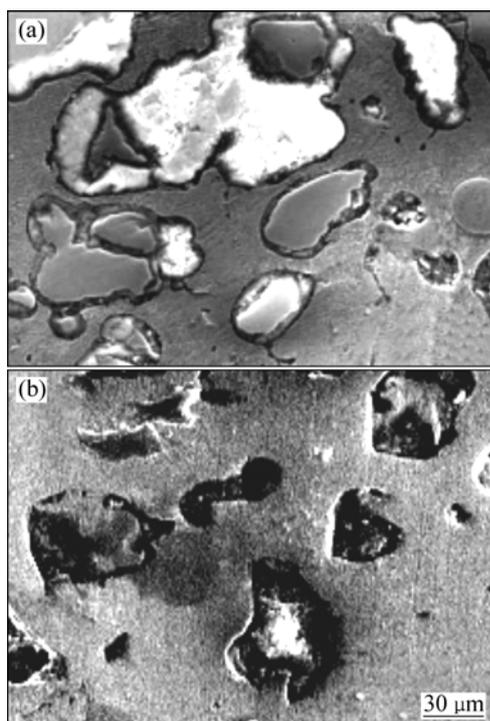


Fig.3 SEM images of dechromized zone of Cu-Cr-Al alloy under different conditions: (a) Without addition of NaCl; (b) With addition of NaCl

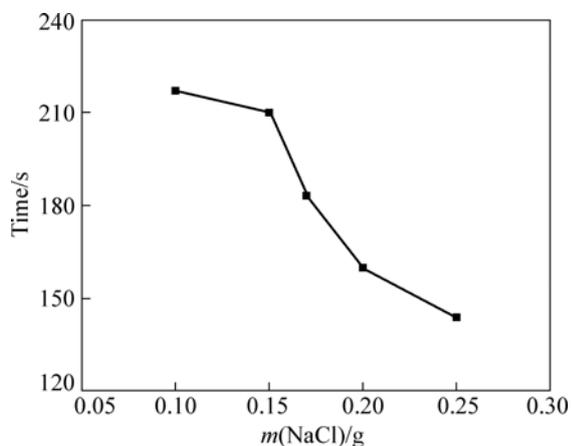


Fig.4 Relationship between content of NaCl and incubation time for dechromization of samples in 10.27 mol/L H_3PO_4 solution at 60 °C

dechromization in 20 mL H_3PO_4 solution of 10.27 mol/L at 60 °C. It can be seen that NaCl can reduce incubation time of dechromization and when the mass of NaCl ranges from 0.10 to 0.25 g, the incubation time decreases with increasing the content of NaCl.

3.3 Influence of NaCl on concentration and temperature for dechromization of Cu-Cr-Al alloy

Fig.5 shows the relationship between the content of NaCl and the concentration and temperature of H_3PO_4

solutions when the dechromization happens on the surface of the samples. It can be found that when the temperature (or concentration) is a constant, NaCl can reduce the concentration (or temperature) of H_3PO_4 solutions for dechromization of the Cu-Cr-Al alloy. The experimental results show that the more the content of NaCl in the solutions is, the lower the concentration or the temperature of H_3PO_4 solutions is needed for the dechromization. In a word, addition of NaCl in H_3PO_4 solutions could increase the tendency of dechromization of the Cu-Cr-Al alloy.

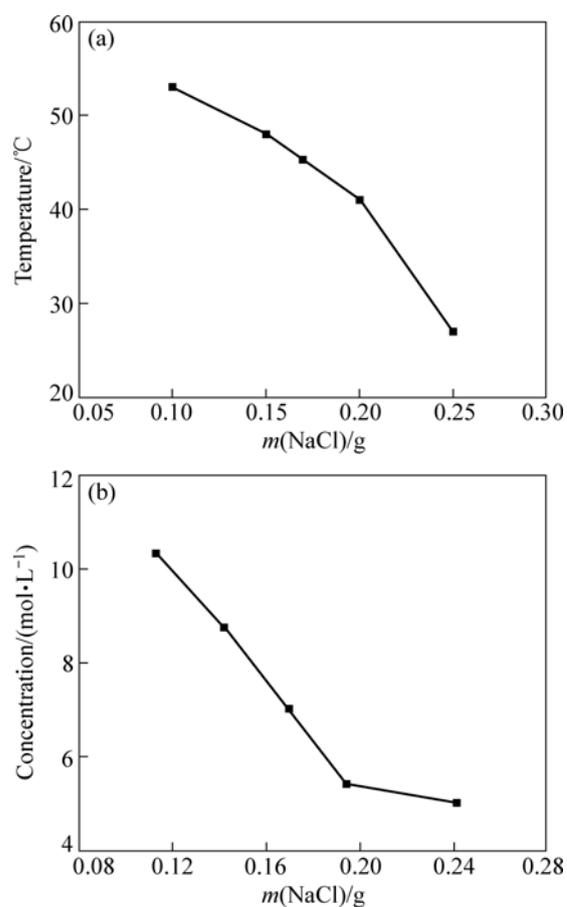


Fig.5 Relationship between content of NaCl and concentration and temperature of H_3PO_4 solutions in dechromization: (a) NaCl content vs temperature(10.27 mol/L, 20 mL); (b) NaCl content vs concentration of H_3PO_4 (50 °C, 20 mL)

3.4 Influence of NaCl on corrosion potential and corrosion current of Cu-Cr-Al alloy

In order to further discuss the effect of NaCl on the corrosion behavior, the surface electrochemical polarization and roughness of Cu-Cr-Al alloy in H_3PO_4 solutions were tested. Fig.6 shows the polarization curves. It can be seen that when NaCl is added in the H_3PO_4 solution, the corrosion potential becomes more negative and the corrosion current density increases. The results from X-ray fluorescence spectroscopy (Fig.7) show that the surface of sample after being immersed in

H_3PO_4 solutions with NaCl changes much coarser compared with that of sample after being immersed in H_3PO_4 solutions without NaCl. It can be concluded that NaCl could increase the corrosion sensibility of the alloy in H_3PO_4 solutions.

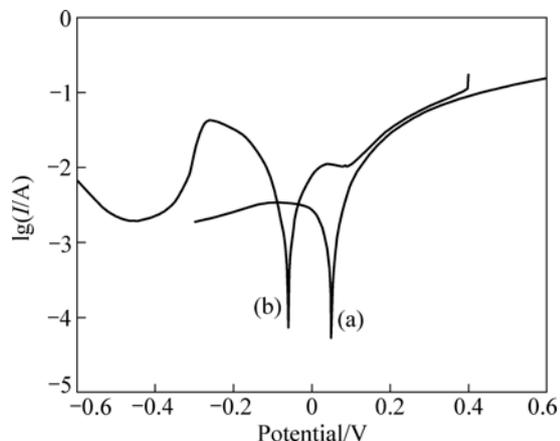


Fig.6 Polarization curves of Cu-Cr-Al alloy in 50 mL H_2SO_4 solution of 1.60 mol/L at 20 °C: (a) Without NaCl; (b) With addition of 20 g NaCl

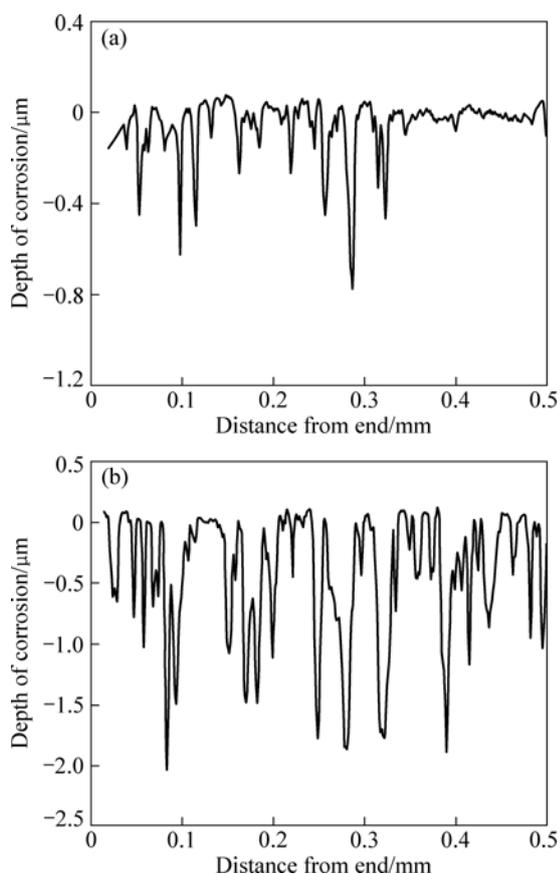
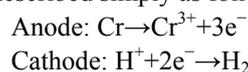


Fig.7 Roughness of sample surface after being immersed in 50 mL H_3PO_4 solution of 1.60 mol/L at 20 °C for 5 h: (a) Without NaCl; (b) With addition of 20 g NaCl

3.5 Discussion

Cu-Cr-Al alloy is composed of Cu phase and Cr phase, in which the two phases are almost undissolved in

each other[14]. It can be seen from the plots of the potential pH that in the acid region, the electrode potential of Cu metal is higher than that of Cr metal, and thus the ionization of Cu metal is more difficult than Cr metal. It can be confirmed that Cu and Cr in the H_3PO_4 solutions compose a corrosion battery with Cr being the anode and Cu being the cathode, and the electrochemical reactions of the Cu-Cr-Al alloy in H_3PO_4 solutions can be described simply as follows:



It would be expected that when Cu-Cr-Al alloy is immersed in H_3PO_4 solutions under a certain conditions, the corrosion of Cr phase is much easier than Cu phase and the dechromization occurs easily. However, it is well known that the Cr exposed in the air is very easy to be oxidized, and a steady passivation film formed on the surface could protect Cr phase from oxidization. So, in fact, the dechromization of Cu-Cr-Al alloys is more difficult. Therefore, the dechromization occurs after the Cu-Cr-Al alloy is immersed in H_3PO_4 solutions for some time (incubation time) until the passivation film on the Cr surface is dissolved. As soon as the dechromization occurs, Cr^{3+} created from the Cr phase surface goes into the solution and thus the surface is almost covered by copper element.

Generally, an acid solution could dissolve the passivation film on metal surface. The higher the concentration and the temperature of acid solutions are, the faster the passivation film dissolves. For Cl^- has a smaller radius and strong penetrability[15–16], the addition of NaCl in H_3PO_4 solutions can provide Cl^- , which could accelerate deterioration of the passivation film on the Cr surface. In addition, Cl^- could react with Cr^{3+} to form complex compounds, such as $([\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O})$, $([\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O})$ and $([\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_2 \cdot \text{H}_2\text{O})$. So, the addition of NaCl in H_3PO_4 solutions could promote anodic dissolving process, and thus accelerate dechromization of the Cu-Cr-Al alloy. As a result, the incubation time of dechromization is shortened, the temperature and concentration of H_3PO_4 solutions for dechromization decrease, and the tendency of dechromization increases. Besides, Al dissolved completely in the Cu substrate has a little effect on dechromization corrosion.

4 Conclusions

1) The addition of NaCl in H_3PO_4 solutions could shorten the dechromization incubation time of Cu-Cr-Al alloy, decrease the temperature and concentration of H_3PO_4 solutions for the Cu-Cr-Al alloy to dechromize, and increase the tendency of dechromization, but it has a little effect on the microstructure of chromium

depleted-layer.

2) Cl^- in H_3PO_4 solutions could facilitate the dechromization of the Cu-Cr-Al alloy. So, avoiding Cl^- into the H_3PO_4 solutions is benefit for protecting the Cu-Cr-Al alloy from the dechromization corrosion.

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