

Dechromisation of Cu-Cr alloy in acid solutions containing Cl^- ^①

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Abstract: The phenomenon, characteristics and influence factors of dechromisation of a Cu-Cr alloy in acid solutions containing Cl^- were studied by means of metallographic observation, SEM/EDX, TEM and XRD. The mechanism of dechromisation of Cu-Cr alloy was discussed. The results show that dechromisation of the Cu-Cr alloy occurs at a certain temperature in solutions with H^+ and Cl^- simultaneously. The corrosion starts initially at the interfaces between Cu phase and Cr phase, then develops gradually into the centers of Cr phase. It is also revealed that dechromisation rates of the Cu-Cr alloy increase with increasing concentration of H^+ or Cl^- , and temperature of the solutions.

Key words: Cu-Cr alloy; dechromisation; H^+ ; Cl^-

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1 INTRODUCTION

It is very important to exploit a new kind of Cu alloys with excellent anti-corrosion performance because Cu alloy, as a kind of anti-corrosion materials applied for a long time, often undertakes leakage and serious corrosion in the early stage during its service^[1]. Cu-Cr alloy has high strength and excellent electric conductivity and heat conductivity, and it is applied widely to prepare functional devices in high strength, high conductivity fields. Although many attention was paid to the Cu-Cr alloy and a large number of works had been done^[2-12], study on its corrosion behavior in solutions has scarcely been reported.

In our experiments it has been found that Cu-Cr alloy conducted serious dechromisation in the HCl solutions. Some results about Cu alloys' dealloying have been reported already^[13, 14], but mainly concentrated on brass's dezincification and aluminum bronze's dealuminization, and none was about Cu-Cr alloys' dechromisation. Therefore, the study on dechromisation of Cu-Cr alloy is significant for understanding of Cu alloy's behavior in solutions with different pH values and extending Cu-Cr alloys' application.

The $\text{Cu}_{53}\text{Cr}_{47}$ alloy was employed in the present paper to study dechromisation behavior in different

solutions at different temperatures. The mechanism of dechromisation and its influence factors were also discussed.

2 EXPERIMENTAL

A Cu-Cr alloy containing 53% Cu and 47% Cr (mass fraction) was used to prepare samples with the size of 5 mm × 5 mm × 10 mm. The samples were polished, washed with water and degreased with alcohol. Then, the samples were immersed into solutions for corrosion. The composition of the solutions are as follows: 1) 3.5% NaCl solution; 2) H_2SO_4 solution with concentrations of 0.207 mol/L, 0.526 mol/L, 1.09 mol/L and 1.69 mol/L, respectively; 3) mixture solutions of 3.5% NaCl, and 0.207 mol/L, 0.526 mol/L, 1.09 mol/L and 1.69 mol/L H_2SO_4 , respectively; 4) mixture solutions of 1.09 mol/L H_2SO_4 , and 3.5%, 7.0%, 9.0% and 11.0% NaCl, respectively. For each kind of solutions, the tests were conducted at 20, 40, 60 and 80 °C. Tests were carried on a HHS-12 type electric thermostatic water container.

Rate of dechromisation was calculated according to the following equation:

$$v = \frac{d}{t} \quad (1)$$

where v is the dechromisation rate; d the thickness

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of dechromisation layer, and t the dechromisation time. Thickness of dechromisation layer was determined through metalloscope observation on sample's cross section. Dechromisation time was recorded from the beginning of bubble evolution.

Corrosion products in the solutions were analyzed with chemical methods. Micromorphology in micro-zones and compositions of phase were observed and analyzed by means of metalloscope, H800 TEM, KYKY-2800 SEM (with EXD) and D/MAX- γ B XRD (with graphite monochromator, K_{α} radiation). And the effects of the concentration of H⁺ and Cl⁻ as well as temperature on the Cu-Cr alloy's dechromisation were assessed by the orthogonal tests.

3 RESULTS

3.1 Conditions for dechromisation

Such phenomenon was seen in some solutions through macroscopical observation: plenty of gas was produced on the samples' surface with solutions turning into blackish green gradually, and the samples giving red copper color after rinsing. The chemical analysis indicated that the gas was hydrogen and the solutions contained a large number of Cr³⁺ and trace Cr²⁺. So corrosion with the above characteristics was conduced to be dechromisation.

Experimental results showed that dechromisation was not found in simple NaCl solutions or simple H₂SO₄ solutions with all given concentrations at all given temperatures even if immersion lasted for two weeks long. No Cr³⁺ was found through chemical analysis either. The dechromisation phenomenon was observed in some mixtures of NaCl and H₂SO₄ beyond a certain temperature as listed in Tables 1 and 2. It was found that dechromisation occurred after the immersion for 2 - 15 min in most solutions. Once dechromisation began, it developed quickly.

It can be concluded that dechromisation of Cu₅₃Cr₄₇ occurred when the alloy was immersed into solutions containing enough H⁺ and Cl⁻ at certain temperature. The higher the concentrations of H⁺ and Cl⁻, the lower the critical temperature at which dechromisation took place.

Table 1 Occurrence of decromisation of Cu₅₃Cr₄₇ in mixtures of NaCl and 1.09 mol/L H₂SO₄ (Immersion time 120 min)

Content of NaCl/ %	Occurrence			
	20 °C	40 °C	60 °C	80 °C
3.5	No	No	Yes	Yes
7	No	No	Yes	Yes
9	No	Yes	Yes	Yes
11	Yes	Yes	Yes	Yes

Table 2 Occurrence of decromisation of Cu - Cr alloy in H₂SO₄+ 3.5% NaCl solutions (Immersion time 120 min)

Concentration of H ₂ SO ₄ / (mol•L ⁻¹)	Occurrence			
	20 °C	40 °C	60 °C	80 °C
0.207	No	No	No	No
0.526	No	No	Yes	Yes
1.090	No	No	Yes	Yes
1.690	No	Yes	Yes	Yes

3.2 Dechromisation rate

On the basis of above experiments, the effects of the concentration of H⁺, Cl⁻ and temperature on the dechromisation rate were studied further. The dechromisation rates of the Cu-Cr alloy in some solutions are listed in Table 3. It can be seen that dechromisation rates are higher when the concentrations of H⁺ and Cl⁻ as well as the temperature increases.

Table 3 Dechromisation rates of Cu₅₃Cr₄₇ in some solutions

Composition of solution	Dechromisation rate/ (μm•min ⁻¹)		
	40 °C	60 °C	80 °C
1.09 mol/L H ₂ SO ₄ + 7% NaCl	-	1.65	2.58
1.09 mol/L H ₂ SO ₄ + 11% NaCl	1.56	2.48	2.91
3.5% NaCl+ 1.09 mol/L H ₂ SO ₄	-	1.08	2.14
3.5% NaCl+ 1.69 mol/L H ₂ SO ₄	1.13	2.25	2.74

3.3 Orthogonal tests

To explore further the effects of concentration of H⁺, Cl⁻ and temperature on dechromisation of the Cu-Cr alloy, orthogonal tests were carried out to understand the incubation time (the time needed for the Cu-Cr alloy to start dechromisation after the sample was immersed in the solution) of dechromisation of the Cu-Cr alloy, using L₄(2³) with three factors and two levels, and the data are listed in Table 4. In this table, factor A is the concentration of H⁺, factor B the concentration of Cl⁻, factor C the temperature. The results (Table 5) indicate that with increasing concentrations of H⁺, Cl⁻ and the temperature, incubation time becomes shorter. The polar difference R of the concentration of Cl⁻ is the biggest, which indicates that when the dechromisation occurs, within the range of the experimental condition, the concentration of Cl⁻ is the most important factor for reducing incubation time, and the temperature is less important.

Table 4 Level value of factors in orthogonal tests

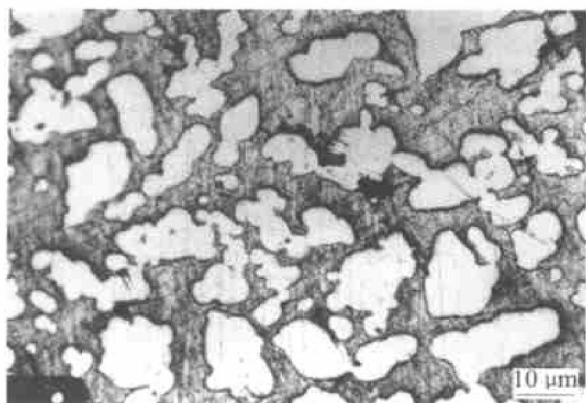
Level	Factor		
	A $c(\text{H}^+)/$ ($\text{mol}\cdot\text{L}^{-1}$)	B $c(\text{Cl}^+)/$ ($\text{mol}\cdot\text{L}^{-1}$)	C Temperature/ $^{\circ}\text{C}$
1	1.09	0.64	60
2	1.67	1.28	80

Table 5 Orthogonal tests results

Exprimment No.	Factor level			Incubation time/ s
	A	B	C	
1	1	1	1	610
2	1	2	2	170
3	2	1	2	200
4	2	2	1	196
I	780	810	806	Total time 1176
II	396	366	370	
I / 2	390	405	403	
II / 2	198	183	185	
Polar difference, R	192	222	218	

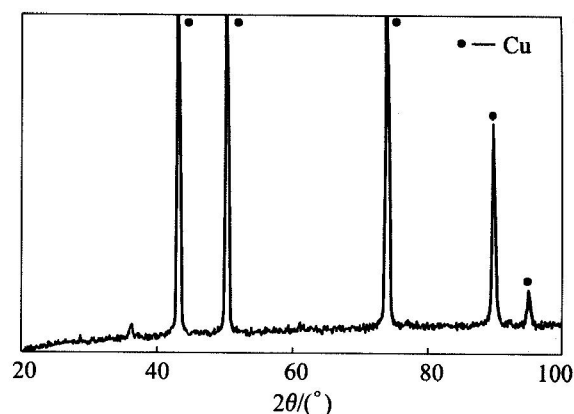
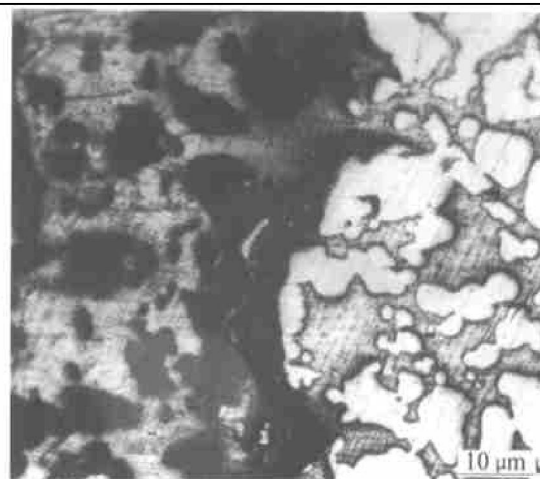
3.4 Results of phase analysis

Fig. 1 shows the microstructure of the Cu-Cr alloy. Combined with EDX results, it can be known that the Cu-Cr alloy is composed of Cu phase and Cr phase with the articulated Cr phase scattering in the Cu phase substrate.

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

The surfaces of dechromisation samples are scraped up to the interface between dechromisation area and inner original substrate area. The XRD pattern (Fig. 2) in dechromisation area in the depth of 100 μm from the surface shows no Cr phase existed. Observation on the interface of the two areas by met-

allograph microscope indicates that in dechromisation area many holes existed in Cu substrate (illustrated in Fig. 3). These holes are thought to be resulted from dechromisation. SEM observation discloses that corrosion is more serious at the boundary, and spreaded into Cr phases gradually to form a white and bright zone (illustrated in Fig. 4), while Cu substrate seldom dissolves. EDX analysis shows that Cr content of the white and bright zone is 32.51% (mass fraction), much lower than that in Cr phase (99.7%). In order to further observe the microphenomenon of corrosion, TEM analysis was conducted on dechromisation samples. The results show that in Cu substrate, dechromisation took place in Cr phases with the size of 10 ~ 100 nm (illustrated in Fig. 5), and the corrosion characteristic is the same as that from SEM observation. It means that the Cu-Cr alloy's dechromisation occurred at the interface between Cu phase and Cr phase initially, and then extended inward the Cr phase inside until Cr phase dissolved entirely.

**Fig. 2** XRD pattern of dechromisation area in depth of 100 μm from Cu-Cr alloy surface**Fig. 3** Interface morphology between Cu phase and Cr phase in dechromisation sample

4 DISCUSSION

It can be known from potential (φ) —pH dia-



Fig. 4 SEM image of dechromised sample

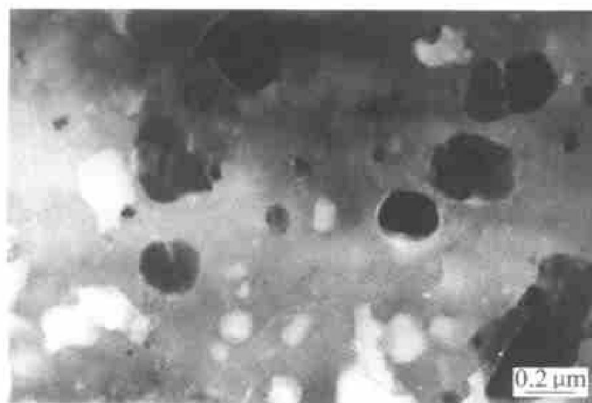
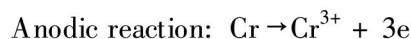


Fig. 5 TEM image of dechromised sample

grams that, $\Delta\varphi$ between Cu and Cr in acid solutions is about 1.2 mV. That is to say Cu-Cr alloys show a strong tendency of dechromisation in acid solutions theoretically. In fact dechromisation didn't occur in simple H_2SO_4 solution. The most probable reason was the passivation of Cr. It is well known that Cr is very easy to be oxidized and its electrode potential becomes more positive after being oxidized, so the dechromisation of Cu-Cr alloys becomes difficult due to passivation, and even becomes an unspontaneous process. When Cl^- exists in the solution, because of its small radius and strong penetrability, Cl^- can destroy the passivation film on the Cr surface. And increasing temperature can accelerate the atom's movement, which enhances the effect of Cl^- . So, when there was H^+ and Cl^- with some concentration in the solution, Cr was activated. Because the activity of activated Cr is superior to Cu, Cu and Cr in the solution composed a corrosion battery with Cr being the anode and Cu the cathode, and thus Cr was dissolved as Cr^{3+} in the solution. Dechromisation of Cu-Cr alloys became a spontaneous process.

Such experimental results mean that the concentrations of H^+ , Cl^- and temperature not only affect the activation of Cr but also affect the rate of dechromisation after activation. The electrochemical reactions of the Cu-Cr alloy in solutions can be described simply as the following:



As H^+ was the main depolarizer for the dechromisation of Cu-Cr alloys in acid solutions, its concentration would result in increasing of the initial electrode potential of the cathodic process, and would consequently cause dechromisation rate to increase. It's very easy for Cl^- to complex Cr^{3+} to form complex compounds ($[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$, $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ and $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_2 \cdot \text{H}_2\text{O}$, so increasing the concentration of Cl^- could promote anodic dissolve process thus accelerate dechromisation. Increasing temperature can accelerate dechromisation because more energy was provided. So dechromisation rates increased with increasing of H^+ and Cl^- concentrations and temperature.

It is concluded from the above experimental results that dechromisation occurred at the interface between Cu and Cr phase initially, and then extended to the Cr phase inside until Cr phase dissolved entirely. Cu-Cr alloys are composed of Cu phase and Cr phase, and these two phases almost undissolve each other. The atom diameters and crystal structures of Cu phase and Cr phase are different from each other, so at the interface between the two phases, atom arrangement is not continuous, with many holes existed, density being lower and diffusion resistance for atoms being shorter. At the same time, lattice distortion is bigger at the interface between the two phases, so atoms are more active and easy to move outward^[15]. It can be seen from Fig. 6 that atoms arrange loosely in semi-boundaries of Cu matrix, so Cr atoms moved firstly along semi-boundaries. The above facts result in the prior leaching of Cr at the interface. Then the Cr inside the alloy moved to the surface until the Cr phase dissolved entirely through the way such as original empty place and the place from which the Cr atom had moved out, however, Cu with higher electric potential was reserved.

Thus, it can be concluded that dechromisation of Cu-Cr alloys was selective dissolution, so cor-

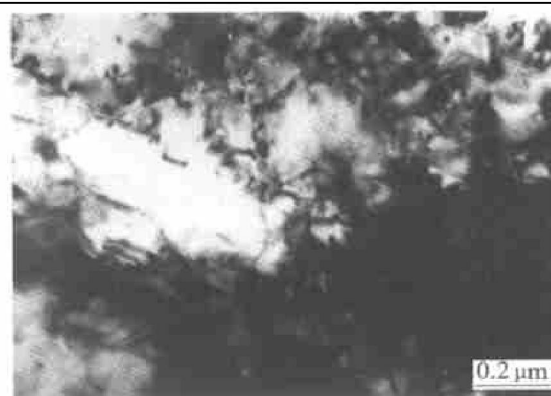


Fig. 6 TEM image of Cu substrate

trolling the solvent component, concentration and temperature could reasonably restrain entirely its occurrence.

5 CONCLUSIONS

1) Dechromisation of a Cu-Cr alloy occurs at a certain temperature when there are H^+ and Cl^- simultaneously in solutions. Under the condition of dechromisation of the Cu-Cr alloy, Cl^- and H^+ concentration and temperature can reduce the incubation time of dechromisation of the Cu-Cr alloy, and among them the concentration of Cl^- is the most important factor.

2) When the dechromisation occurs, gas is produced on the samples' surface with solutions turning into blackish green gradually, and the samples giving red copper color after rinsing. Dechromisation rate of the Cu-Cr alloy is higher when the concentrations of H^+ and Cl^- as well as the temperature increase.

3) Dechromisation corrosion of the Cu-Cr alloy is selective dissolution process, and it takes place at interface between Cr phase and Cu phase initially, then extends into Cr phase gradually, until Cr phase dissolves entirely.

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