Dealloying of $\text{Cr}_{48.24}\text{Cu}_{51.76}$ Alloy in H_2SO_4 Solution and the Effect of Ultrasonic Vibration

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Abstract: Dealloying of $\text{Cr}_{48.24}\text{Cu}_{51.76}$ alloy in H_2SO_4 solution was investigated by using static immersing corrosion, the effect of ultrasonic vibration on dealloying of the alloy in H_2SO_4 solution was studied by optical microscope, X-ray diffraction, scanning electron microscope, transmission electron microscope and X-ray fluorescence spectrometer techniques, and the dealloying mechanism was discussed. The results show that dechromisation corrosion of $\text{Cr}_{48.24}\text{Cu}_{51.76}$ alloy happens in H_2SO_4 solution with certain temperature and concentration, the ultrasonic vibration can decrease temperature and concentration of H_2SO_4 solution that when the dechromisation occurs, increase the dechromisation rate, and weaken the microstructure of dechromisation layer. And yet, ultrasonic vibration scarcely has an effect on the dechromisation mechanism.

Key words: $\text{Cr}_{48.24}\text{Cu}_{51.76}$ alloy, dechromisation, H_2SO_4 solution, ultrasonic vibration.

1. Introduction

CrCu alloy is an excellent material for preparing components such as high strength and high conductivity devices and vacuum switch contacts due to its higher compressive strength and excellent electric conductivity [1-3]. With the rapid development of modern industry, applications of CrCu alloy in the correlative fields expands [4, 5]. According to report that CrCu coating successfully protected NARLOY-Z from corrosion under flowing corrosive gas at high temperature [6]. Research on the corrosion resistance of CrCu alloy has already attracted researchers' attention [7-9]. In our recent work, it is observed that dealloying corrosion of CrCu alloy occurs in acid solutions under a certain condition. So far, the investigations of dealloying Cu alloys are mainly focused on dezincification of brass and dealuminization of aluminum bronze, but few reports were about CrCu alloys' dechromisation. Because many of Cu alloy workpiece service in the eroding and vibrational medium, and the solutions for industrial application often contain H_2SO_4 . Therefore,

this article studied the condition and mechanism of dechromisation corrosion of $\text{Cr}_{48.24}\text{Cu}_{51.76}$ alloy in H_2SO_4 solution and investigated the effect of ultrasonic vibration on dechromisation corrosion. These results provide some reference data to the research and application of dealloying corrosion of CrCu alloy.

2. Experiment

The experimental material is $\text{Cr}_{48.24}\text{Cu}_{51.76}$ alloy (mass fraction, %), and its size is $\Phi 5 \times 5$ mm. Every surface of samples was polished with 1200[#] metallic sand papers, washed with water and dried. Then, the samples were immersed into H_2SO_4 solutions with different concentrations and temperatures for corrosion. To test the effect of ultrasonic vibration on dechromisation of $\text{Cr}_{48.24}\text{Cu}_{51.76}$ alloy, the experiment is carried out in CQ50 ultrasonic cleaning machine and its vibrational frequency is 0 kHz, 20 kHz, 40 kHz, respectively. In this study the dechromisation of above mentioned samples was observed, the incubation time of dechromisation was tested for samples in different states in H_2SO_4 solution and the lowest concentration and temperature of H_2SO_4

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solution at which dechromisation took place, and the dechromisation rate was calculated:

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

where, h represents thickness of dechromisation layer (the thickness was measured from the cross-section of the sample by optical microscope), t represents the dechromisation time (timed from air bubble separating out in the samples' surface and its datum is the mean value of three measured results). Surface components and microstructure after corrosion were observed and analyzed by means of ADVANTXP-381 X-rays fluorescent spectrograph, Axiovert200MAT optical microscope, D/MAX-rB X-ray diffractometer (with graphite monochromator, K_α radiation), H800 transmission electron microscope and S-3400N SEM (Scanning electron microscope) with EDS (energy dispersive spectrometer).

3. Results and Discussion

3.1 Dechromisation Corrosion

Fig. 1 shows the microstructure of $\text{Cr}_{48.24}\text{Cu}_{51.76}$ alloy. It can be seen that the microstructure of $\text{Cr}_{48.24}\text{Cu}_{51.76}$ alloy consists of Cu matrix and particulate Cr phases. When $\text{Cr}_{48.24}\text{Cu}_{51.76}$ alloy samples was immersed in a certain concentration and temperature of H_2SO_4 solution to stay for some time (off chrome incubation period), the sample surface produce a lot of bubbles, the color of the sample surface change gradually from light gray to copper color and H_2SO_4 solution gradually become deep dark green. According to the analysis of Table 1 by a fluorescence spectrometer, the Cr content of the sample surface significantly reduces, only 2.41% (mass fraction, %). XRD (X-ray diffraction) (Fig. 2) shows that the sample surface is not present with Cr phase. Thus it can be concluded that the phenomenon is $\text{Cr}_{48.24}\text{Cu}_{51.76}$ alloy dechromisation corrosion, and the higher the H_2SO_4 solution concentration and temperature are, the more prone to take off de-chrome corrosion of $\text{Cr}_{48.24}\text{Cu}_{51.76}$ alloy will be occurred.

Fig. 1 Microstructure of $\text{Cr}_{48.24}\text{Cu}_{51.76}$ alloy.

Table 1 Composition of sample's surface of the $\text{Cr}_{48.24}\text{Cu}_{51.76}$ alloy immersed in H_2SO_4 solution (mass fraction, %).

Sample	Cu	Cr	Others
Original	51.54	48.32	0.14
Dechromisation	97.24	2.41	0.35

Fig. 2 X-ray diffraction patterns.

It can be known from the potential-PH chart that the electrode potential of Cr metal is lower than that of Cu metal in the acid region, and the potential difference between the electrodes is approximately 1.2 V. That is to say, CrCu alloy shows a strong tendency of selective corrosion in acid solutions theoretically. It can be concluded that Cu and Cr in the solutions compose a corrosion battery with Cr being the anode and Cu being the cathode, and the dechromisation corrosion happens. It can be described simply as:

The gas produced on the sample is H_2 , Cr^{3+} stay in solution, and porous copper remains in the alloy matrix.

In fact, the dechromisation corrosion of $\text{Cr}_{48.24}\text{Cu}_{51.76}$ alloy doesn't immediately occur in lower temperature and concentration H_2SO_4 solution. This may be caused by the passivation of Cr. After passivation, the electrode potential of Cr increases [10], and the tendency of dechromisation corrosion of $\text{Cr}_{48.24}\text{Cu}_{51.76}$ alloy decreases. As the acid can dissolve the metal surface oxide film, the movement of atoms can be accelerated to promote the destruction of the passive film as the temperature increases. Therefore, only when the concentration and the solution temperature of H_2SO_4 solution meet certain conditions, the passive film of chromium surface can be damaged, and the dechromisation corrosion of $\text{Cr}_{48.24}\text{Cu}_{51.76}$ alloy can occur, and the higher H_2SO_4 solution concentration and temperature are, the more prone to take off dechromisation of $\text{Cr}_{48.24}\text{Cu}_{51.76}$ alloy will be occurred.

3.2 The Microstructure of Dechromisation Layer

It can be seen from macro-observation that the dechromisation samples' surface without ultrasonic vibration is compact, whereas the dechromisation samples' surface under ultrasonic vibration is coarse,

and the greater the frequency of ultrasonic vibration, the rougher the surface of the specimen will be. The microstructure of dechromisation layer of samples under different states was shown in Fig. 3, it shows that Cu phase exists in the dechromisation district, Cr phase fell out and some hollows remained. The pore size of the chromium layer without ultrasonic vibration is small, much smaller than the size of Cr phase of the original organization; while the pore size of chromium layer under 40 kHz ultrasonic oscillation is larger, as big as that of Cr phase in the original microstructure. The SEM observation (Fig. 4) reveals that there are more pores in the chromium layer microstructure under ultrasonic vibration, and the densification is poor; the dechromisation corrosion of $\text{Cr}_{48.24}\text{Cu}_{51.76}$ alloys without ultrasonic vibration preferentially first occurs around the interface of Cu phase and Cr phase, then gradually extends to the center of Cr phase until Cr phase falls out completely. This shows that the ultrasonic vibration can deteriorate the off chrome layer organization $\text{Cr}_{48.24}\text{Cu}_{51.76}$ alloy, but the ultrasonic oscillation has little effect on dechromisation corrosion mechanism of $\text{Cr}_{48.24}\text{Cu}_{51.76}$ alloy.

Fig. 3 Morphology of dechromisation layer of $\text{Cr}_{48.24}\text{Cu}_{51.76}$ alloy in $4.23 \text{ mol}\cdot\text{L}^{-1}$, 60°C H_2SO_4 solution: (a) 0 kHz; (b) 40 kHz.

Fig. 4 SEM images of dechromisation area of $\text{Cr}_{48.24}\text{Cu}_{51.76}$ alloy in $4.23 \text{ mol}\cdot\text{L}^{-1}$, 60°C H_2SO_4 solution: (a) 0 kHz; (b) 40 kHz.

Since $\text{Cr}_{48.24}\text{Cu}_{51.76}$ alloy consist of almost immiscible phase Cu and Cr phases, the atomic arrangement at the junction surface of these two phases is not continuous and the density is low. Therefore, the movement resistance of atoms in the interface is small resulting in the easily accessible movement from the interface to the outside. So the dechromisation corrosion priority occur in a two-phase Cu and Cr junction surface. For microstructure of dechromisation layer, without ultrasonic vibration, the size of the hole left by the Cr phase in the removal of the chromium layer is smaller than the size of the Cr phase in the original microstructure. This indicates that Cu atoms take up the position of Cr atoms. Under ultrasonic vibration, the activity of Cr atom increases, that may make the moving rate of Cr atoms from center to outside is larger than that of Cu atoms, resulting in larger pore size in dechromisation layer under ultrasonic oscillation and lower dense in off chrome layer microstructure, which remains to be further explored.

3.3 The Lowest Concentration and Temperature in H_2SO_4 Solution When Dechromisation Occurs

Fig. 5 shows the relationship between concentration and temperature of H_2SO_4 solution when the dechromisation occurs in different states. It can be seen that the higher concentration of H_2SO_4 solution when dechromium of $\text{Cr}_{48.24}\text{Cu}_{51.76}$ alloy occurs, the lower the temperature of the solution. At the same temperature or concentration, the concentration or temperature of H_2SO_4 solution can be reduced by ultrasonic oscillation when the dechromisation of $\text{Cr}_{48.24}\text{Cu}_{51.76}$ alloy occurs, and the greater the frequency of ultrasonic vibration, the more obvious of the effect will be. The results show that when the temperature is $60\text{ }^\circ\text{C}$, the concentration is $4.23\text{ mol}\cdot\text{L}^{-1}$ without ultrasonic vibration during dechromisation. However, at the same temperature, the concentrations are $3.96\text{ mol}\cdot\text{L}^{-1}$ and $3.82\text{ mol}\cdot\text{L}^{-1}$ during dechromisation under 20 kHz and 40 kHz ultrasonic

vibration, respectively. When the concentration is $3.34\text{ mol}\cdot\text{L}^{-1}$, the temperature is $80\text{ }^\circ\text{C}$ during dechromisation without ultrasonic vibration. However, at the same concentration, the temperatures are $75\text{ }^\circ\text{C}$ and $72\text{ }^\circ\text{C}$ during dechromisation under 20 kHz and 40 kHz ultrasonic vibration. The results of the test (Fig. 6) show that ultrasonic oscillations can shorten the incubation time of dechromisation and increase the dechromisation rate of $\text{Cr}_{48.24}\text{Cu}_{51.76}$ alloy. This means that the ultrasonic vibration can increase the tendency of dechromisation and accelerate the dechromisation process of $\text{Cr}_{48.24}\text{Cu}_{51.76}$ alloy.

Ultrasonic vibration can bring strong liquid vibration to accelerate breakage of passivation layer, abbreviate the incubation time of dechromisation, and

Fig. 5 Relationship between temperature and concentration of H_2SO_4 solution when the dechromisation occurs at different conditions.

Fig. 6 Dechromisation incubation time and dechromisation corrosion rate of $\text{Cr}_{48.24}\text{Cu}_{51.76}$ alloy in

4.23 mol·L⁻¹, 60 °C H_2SO_4 solution.

reduce the concentration and temperature of H_2SO_4 solution when dechromisation of $\text{Cr}_{48.24}\text{Cu}_{51.76}$ alloy occurs. Meanwhile, ultrasonic vibration penetrates into the bare cracks of the interface of Cu phase and Cr phase, which leads to vibration of Cr atoms, accelerates the Cr atom to move out, and increases the dechromisation rate. Hence, it is helpful for the dechromisation corrosion of the alloy.

4. Conclusions

The dechromisation corrosion of $\text{Cr}_{48.24}\text{Cu}_{51.76}$ alloy can occur when the concentration and the solution temperature of H_2SO_4 solution meet certain conditions, and the higher the H_2SO_4 solution concentration and temperature are, the $\text{Cr}_{48.24}\text{Cu}_{51.76}$ alloy more prone to take off dechromisation corrosion occurred.

Ultrasonic vibration can reduce the concentration and temperature of H_2SO_4 solution when dechromisation of $\text{Cr}_{48.24}\text{Cu}_{51.76}$ alloy occurs, shorten the incubation time of dechromisation and increase the dechromisation rate, benefiting the occurrence of dechromisation corrosion in the alloy.

The ultrasonic oscillation can reduce the density of off chrome layer and has little effect on dechromisation corrosion mechanism of $\text{Cr}_{48.24}\text{Cu}_{51.76}$ alloy.

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