Research Article

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Influence mechanism of pulse frequency on the corrosion resistance of Cu–Zn binary alloy

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Abstract: In this work, the influence of pulse frequency on the corrosion resistance of Cu–Zn binary alloy has been investigated by using electrochemical workstation, scanning electron microscope and X-ray diffraction. The results have shown that after the electric pulse treatment, the average grain size in the microstructure of high-zinc binary brass decreased and the corrosion resistance increased. The thickness of dezincification layer decreased from 49.8 to 30.8 μm . The diameter of capacitive reactance arc increased from 741.1 to 2898.0 μm . The corrosion potential increased from -0.2719 to -0.2378 V, and the corrosion current density decreased from 6.3147×10^{-6} to 4.6971×10^{-7} A cm^{-2} by one magnitude order.

Keywords: corrosion resistance, pulse frequency, brass, γ phase

1 Introduction

Due to the excellent cold and hot workability, cutting performance, conductivity and thermal conductivity, brass has been widely used in automobile production, aircraft manufacturing and electric component [1–3]. The service life of workpieces has been reduced by the dezincification of brass especially in the aqueous solution with the gas of O_2 , CO_2 , H_2S , SO_2 and NH_3 . It has attracted much attention from the researchers in the world on how to further eliminate the dezincification and to improve the service life of workpieces [4–6]. Literature have expressed that the

corrosion resistance of brass can be improved by the trace elements of Boron and Arsenic. But the solid solubility of B in brass has been restricted, and excessive B has precipitated and concentrated distribution as the form of boride. On the other hand, due to the corrosion, brass resistance reduced, workpieces failed prematurely and the environment could be polluted by the element of As [7,8].

The electric pulse treatment (EPT) has the characteristics of simple equipment, easy to operate and no pollution to the environment. The progress of metal solidification could be controlled and the solidification structure of metals could be refined by EPT; therefore, the comprehensive performance of alloys improved [9,10]. The literature [11] has expressed that after EPT, the corrosion potential of silicon brass increased, the corrosion current density decreased and the corrosion resistance increased. In this work, the influence of pulse frequency on the corrosion resistance of Cu–Zn binary alloy has been examined by the method of adjusting the pulse frequency, based on the cluster theory and the existing research results of the solidification process of liquid metal.

2 Experiment materials and methods

Brass alloy (Zn: 52 wt%, Cu bar) was used as the experiment material for the present study. First, the graphite crucible was preheated to 800°C, and the furnace with silicon carbide rods was heated to 1,150°C. When Cu and Zn were melted, the temperature was held for 5 min. The melt was then poured into a permanent mold. After solidification, the original samples were obtained. After EPT with different pulse frequencies, the residual melt was poured, and the experimental samples were obtained. The graphite electrode was inserted vertically into the alloy melt of 3 cm depth. The electric pulse frequencies were 3, 8 and 15 Hz. The pulse voltage was 500 V, and the treatment time was 30 s. When the samples solidified and cooled, the samples were sealed by epoxy resin for metallography, and corrosion tests were prepared.

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Figure 1: Microstructure of brass alloy with and without EPT (a) original sample, (b) 3 Hz, (c) 8 Hz and (d) 15 Hz.

3 Results and discussions

The metallographic microstructure of brass alloy with and without EPT was observed by a scanning electron microscope and ZEISS Axiovert2000MAT metallurgical microscope, and the results are presented in Figure 1. The average grain size of brass alloy with and without EPT is presented in Table 1.

Based on Figure 1 and Table 1, the average grain size of original samples was 576.4 μm. The γ phase was star shaped and distributed aggregately on the grain boundary. The grain size of samples with EPT and the γ phase decreased and dispersed, and the brittleness of brass alloy also decreased. The average grain size of sample (b) with 3 Hz EPT was 362.5 μm, which is 62% of the original samples and decreased more obviously. The size of γ phase has changed smaller and the amount has changed less and distributed uniformly. The average grain size of sample (c) with 8 Hz EPT and sample (d) with 15 Hz EPT increased, which were 88% and 91% of the original samples, and the γ phase became fish bone shape and increased.

The polarization curve and the AC impedance spectroscopy of the samples with and without EPT were tested in 3.5% NaCl solution by an electrochemical workstation corrosion resistance test system (IVIUM Stat.XRi). The

platinum was used as the auxiliary electrode of 1×1 cm in size. The reference electrode was the standard calomel electrode. The scan speed was 0.5 mV/s and the open circuit potential ranged from -250 to 1,000 mV in the polarization curve tests. The sine-wave amplitude modulation was 10 mV and the frequency was 100 kHz–0.01 Hz in EIS AC impedance spectroscopy testing. The results are presented in Table 2.

The steady-state polarization curves of samples with and without EPT are given in Figure 2. It can be seen that the polarization curve of the cathode was smooth, while the polarization curve of anode was flat, suggesting the smaller electrode reaction and resistance of the polarizability. The two characteristic regions, the active dissolution region and the transition region of active deactivation, were presented in the polarization curve of cathode of all the four samples. The free corrosion potential of samples with EPT was higher than those without EPT, and the corrosion current density of samples with EPT was lower, implying that the ability of passivation of the samples with EPT obviously improved.

Table 1: The average grain size of brass alloy with and without EPT

Pulse frequency/Hz	0	3	8	15
Grain size/μm	576.4	362.5	504.7	525.6

Table 2: The free corrosion potential and corrosion current density of brass alloy with 500 V EPT

Samples	Free corrosion potential (V)	Corrosion current density (A cm^{-2})
Original	-0.2719	6.3147×10^{-6}
3 Hz	-0.2378	4.6971×10^{-7}
8 Hz	-0.2505	2.7545×10^{-6}
15 Hz	-0.2525	1.3559×10^{-6}

Based on Figure 2 and Table 2, the free corrosion potential and corrosion current density of samples with EPT increased and decreased, respectively. After EPT, the free corrosion potential of brass alloy samples with 3 Hz increased by 3.41%, and the corrosion current density decreased by one magnitude order. Therefore, it can then be concluded that the corrosion resistance of brass alloy has significantly increased. In this experiment, the corrosion resistance of 3 Hz brass alloy sample is the best.

The corrosion resistance of samples in corrosion medium can be indicated by the diameter of the capacitive reactance arc in EIS. A bigger diameter of the capacitive reactance arc was usually related to a better corrosion resistance of the samples. The EIS of brass alloy samples is shown in Figure 3. It can be seen that after EPT, the diameter of capacitive reactance arc increased by four times from 741.1 to 2898.0 μm , suggesting the enhanced corrosion resistance of the aluminum brass with EPT.

According to the literature, three mechanisms describe the dezincification corrosion, namely, the preferential dissolution and resolution deposit mechanism, the double-space mechanism and the seepage mechanism. To

Figure 2: Polarization curves of brass alloy with and without EPT. **Figure 3:** Impedance spectroscopy of brass alloy with and without EPT.

further explore the internal relations between the changes in the corrosion resistance and phase structures, the X-ray diffraction tests were carried out, and the results are shown in Figure 4. It can be concluded from Figure 4 that the β phase (CuZn) and γ phase (Cu_5Zn_8) were found in the samples without corrosion. The β phase disappeared, the γ phase decreased and the Cu phase precipitated with corrosion.

The distribution of elements on electrochemical corrosion surface of brass samples was detected and the results are shown in Figure 5. It can be seen that the Zn content decreased and the Cu content was constant. In summary, dezincification of the original brass alloy sample was in progress. The findings show that Zn dissolved first as the anode in the corrosion progressed and double space occurred. The double space then diffused into the brass alloy under the concentration gradient in brass alloy, and Zn diffused to the surface of brass alloy, therefore, leading to the preferential dissolution of Zn.

The profile morphology of corrosion layer in brass alloy with electrochemical corrosion is shown in Figure 6. It can be seen that the dezincification layer of the original brass samples was porous (Figure 6a); and for the samples with 3 Hz EPT, the surface of matrix was covered tightly and uniformly.

The findings show that dezincification occurred on the boundary between β and γ phases during the corrosion, and the β phase was then corroded as anode. The corrosion of the γ phase did not occur until the porous shape was formed on the corrosion layer, and the corrosion rate was related to the quantity of the galvanic couple [12]. The nucleation rate of the brass alloy melt obviously improved by EPT and the quantity of galvanic

Figure 4: Phase analysis of brass alloy with and without EPT (a) without corrosion and (b) with corrosion.

couple decreased, therefore, efficiently inhibiting the dezincification progress. The undercooling of brass alloy melt improved by EPT, thus the size of atomic cluster decreased and the quantity increased. Additionally, the critical dimension of nucleation decreased during the nucleation process. The morphology, size and distribution of the γ phase can be ameliorated by EPT, and the rate of dezincification obviously decreased.

The profile morphology of corrosion layer in brass alloy was contrasted and analyzed, and the results are given in Figure 7. The thickness of corrosion layer in brass alloy is given in Table 3. It can be seen that the average thickness of corrosion layer (the deep gray in surface) in the original samples was $49.8\mu\text{m}$, and in the sample (b) with 3 Hz EPT it was $30.8\mu\text{m}$, which was 61.8% of the original samples. Therefore, the thickness

Figure 5: Element distribution analysis of brass alloy with and without corrosion (a) original sample and (b) with corrosion.

Figure 6: Profile morphology of brass alloy with and without EPT (a) original sample and (b) 3 Hz.

of corrosion layer decreased obviously by 3 Hz EPT, and the corrosion resistance of brass efficiently improved.

According to the structure model of liquid metallic clusters which was proffered by Bing [13], for the most stable cluster r_0 in molten metal, its existence probability was bigger than others which were correspond by other magic numbers. But the cluster, which was embryo in the progress of liquid metal solidification, depends on the relationship between cluster size and undercooling. Only the cluster that corresponds to the size r_{0max} of minimum undercooling can change into the critical nucleus [14,15]. For this solidification system of brass in this experiment, the outer shell of Zn atom cluster has distorted repeatedly in brass alloy sample with EPT. Thus, the potential of the other outer shells decreased and the connection with surrounding atoms increased, and the barrier between atom and clusters decreased. Therefore, the combination of the surrounding atoms and clusters is promoted, and the nucleation rate increased. The crystal structure of brass alloy samples

Table 3: The thickness of the corrosion layer in brass alloy with and without EPT (μm)

Corrosion layer	1	2	3	4	5	Average thickness
Origin	48.7	46.9	49.6	52.1	51.7	49.8
3 Hz	34.8	32.5	27.7	27.2	26.5	30.8

is distributed uniformly; thus, Zn atom is distributed uniformly. The quantity of galvanic couple decreased, and the progress of dezincification efficiently inhibited.

The electromagnetic force occurred in the brass alloy melt with EPT. With the increasing temperature of brass alloy melt with EPT and with the effect of electromagnetic force, the non-dendrite and dendritic microstructures were produced. The non-dendrite and dendritic microstructures then grow as the particles of nucleation; thus, increasing the nucleation rate. Meanwhile, the brass alloy melts were compressed and shocked by the electromagnetic force.

Figure 7: The morphology of corrosion in brass alloy with and without EPT (a) original sample and (b) 3 Hz.

The fresh dendrites dropped from the cavity into the brass alloy melt, and fresh crystal nucleus was produced in the cavity. The nucleation rate of brass alloy melt increased and the solidification structure thinned in the repetitive progress. In conclusion, the Zn atom cluster was distributed uniformly in the brass solidification system with EPT. The γ phase decreased and dispersed. The dezincification rate decreased, and the corrosion resistance of brass alloy increased.

4 Conclusions

- (1) The thickness of corrosion layer in brass alloy with EPT decreased. The average grain size of sample with 3 Hz EPT decreased by 62% to $362.5\mu\text{m}$, and the γ phase changed little. The surface of the matrix was covered tightly and uniformly. The average thickness decreased by 61.8% to $30.8\mu\text{m}$.
- (2) The corrosion resistance of brass alloy increased by 3 Hz EPT. The free corrosion potential increased by 3.41% to -0.2378 V . The free corrosion current density decreased by one magnitude order to $4.6971 \times 10^{-7}\text{ A cm}^{-2}$. The diameter of the capacitive reactance arc increased by 3 times to $2898.0\mu\text{m}$.

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