Corrosion behavior of novel imitation-gold copper alloy with rare earth in 3.5% NaCl solution

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ABSTRACT

A novel imitation-gold copper alloy with rare earth was designed and prepared. The corrosion behavior of the alloy immersed in 3.5% NaCl solution and its anti-tarnish property in the salt spray for different days has been studied. The designed alloy (CuZnAlNiMeRe) has more excellent anti-tarnish property and lower corrosion rate than those of currency coinage materials of H7211 alloy (used in China). A uniform and compact of corrosion film has been formed after the designed alloy immersed in 3.5% NaCl solution. The corrosion current densities I_{corr} of the alloy decreased while the polarization resistance R_p increased with time. The capacitance of the corrosion product film C_{film} of the alloy decreased while the charge transfer resistance R_{ct}. The Warburg diffusion impedance W_R and the resistance of the equivalent circuit R increased with time.

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1. Introduction

Copper and copper-based alloys are widely used in many environments and applications, such as coinage and ornamental parts, due to their corrosion resistance, noble, variety and beautiful colors, remarkable cast-ability (e.g. for church bells and statuaries) and good processing (e.g. for coinage). Other applications include in electricity and electronics, heat exchangers and condensers, transportations, roofing, air conditioning systems, plumbing goods, agriculture and water treatment.

Many copper-based imitation-gold alloys have been developed. The typical ones are Cu–Zn alloys [1], Cu–Al alloys [2,3] and Cu–Ni alloys [4], which have different k-gold colors. The imitation-gold copper alloys with 24 k-gold color are more commonly accepted by the costumers. In order to obtain imitation-gold copper alloy with 24 k-gold color, the zinc elements should be used. However, dezincification in brass may be readily observed with naked eyes because the alloy develops a reddish color, which contrasts with its original yellowish color [5]. Generally, there are two types of dealloying. Uniform or layer dealloying commonly occurs in high zinc alloys where the outer layer is dealloyed and becomes dark while the inside is not affected [6]; plug dealloying is typified by the presence of the dealloyed dark plugs in the unaffected matrix of low zinc alloys [7].

On its exposure to the atmosphere or solution, clean copper transforms from salmon-pink to a progressively darker brown and finally to an esthetically pleasing green. The surface layer causing the green color is commonly known as patina, and is the natural green film formed on copper and its alloys after prolonged the exposure.

In the present work, a novel imitation-gold copper alloy with 24 k-gold color has been designed and prepared. The anti-tarnish property in the salt spray and corrosion behavior of the designed alloy immersed in 3.5% NaCl solution for different days has been studied by means of EIS, potentiodynamic polarization, scanning electron microscopy and energy dispersive X-ray analysis (SEM–EDAX).

2. Experimental procedures

A new imitation-gold copper alloy (1#) with 24 k-gold color was prepared by induction melting and mold casting. Its composition was shown in Table 1. The surface defects of the ingots were first removed by mechanical milling. The ingot was then rolled from a thickness of 35 mm into strip of 4 mm thick, then cool-rolled to 2 mm thickness. The strip was annealed at 963 K for 1 h. The specimens with dimensions of 2 mm × 10 mm × 10 mm were cut from the strip and mechanically polished with glazing machine. An area of 1 cm² on the surface of a specimen was exposed, while the other part was sealed with paraffin for electrochemical measurement. Those with diameter of 25 mm were punched from the strips for measurement of anti-tarnish

Table 1
The compositions of designed alloy (wt.%).

Alloying elements	Cu	Al	Ni	Me	Re	Zn
Content (%)	74.2	0.8	0.5	0.3	0.10	Bal.

properties, and ones with dimensions of 50 mm × 25 mm × 2 mm were cut from the strip for measurement of corrosion rate. The corrosion medium was 3.5% NaCl solution whose pH is 6.5 prepared using analytical NaCl and distilled water. To find the trend of corrosion with time, the specimens were immersed in the solution for 1 d, 2 d, 4 d, 6 d, 8 d, 15 d and 30 d, respectively. Electrochemical performance of the specimens has been carried out thereafter. One kind of currency coinage material of H7211 imitation-gold copper alloy with 24 k-gold color was investigated comparatively.

The weights of the specimens both before and after the corrosion tests were measured by TG328A analytical balance with accurate of 0.1 mg. The corrosion rate of the specimen, R (mm/y) was determined by [8–10]:

$$R = \frac{87.6 \times \Delta m}{\rho St} \tag{1}$$

where $\Delta m = m - (m_t + m_0)$, m (mg) is the weight of the specimen before corrosion, m_t (mg) is weight of the corrosion specimen after the corrosion product removed using 1:1 hydrochloric acid solution, m_0 (mg) is weight loss of a non-corroded specimen immersed in the 1:1 hydrochloric acid solution, ρ (g/cm^3) is density of specimen, S (cm^2) is surface area of the specimen, and t (h) is time that the specimen was immersed in the solution. Besides corrosion products were removed by hydrochloric acid solution, non-corroded matrix alloy was removed, therefore the weight loss of a non-corroded specimen (m_0) immersed in hydrochloric acid solution should be measured to correct the corrosion rate of the specimen (R).

The electrochemical measurements were carried out using IM6ex (from Germany) frequency response analyzer. The designed alloy with an area of 1 cm^2 was used as a working electrode. A saturated calomel electrode (SCE) and large area platinum were served as the reference and the counter (auxiliary) electrode, respectively. All electrochemical measurements were performed after the open circuit potential (OCP) was stabilized. The AC voltage signal amplitude was 10 mV and the frequency was between 100 kHz and 1 mHz. The EIS data were analyzed by Zview software. The potentiodynamic polarization measurements were performed from −200 mV to 600 mV at a scan rate of 2 mV/s, and the data were analyzed by CHI660C software.

Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX) were preformed to characterize the corrosion products, using a Sirion200 field emission SEM equipped with EDAX GENESIS 60.

3. Results and discussion

3.1. Corrosion rate

Table 2 lists the average corrosion rate of the designed alloys and H7211 alloys in the NaCl (35 g/L) solutions. It shows that the average corrosion rate of the designed alloys is much less than that

Table 2
The average corrosion rates of the designed alloys and H7211 alloys.

Alloys	Corrosion rate (mm/a)
H7211	0.04664
Designed alloy (1#)	0.01304

of the H721alloy. The electrode potential of rare earth is less than Cu substrate, so the addition of rare earth can reduces the self-corrosion potential of the alloy. Oxides of rare earth and other corrosion products formed a compact layer, which was tightly bonded to the Cu substrate so as to improve the corrosion resistance of designed alloy [11]. And the polarization resistance grew significantly because of the compact layer, which results that corrosion current decreased. The compact layer also prevented dezincification effectively [12].

3.2. Anti-tarnish properties

The tarnish properties of the designed alloy (1#) and H7211 alloy in the salt spray (NaCl: 35 g/L) have been carried out and shown in Fig. 1. The color difference of alloys increased with the times of testing cycle. In whole testing period, the color difference of designed alloy was always less than that of H7211 alloy. When the alloy was tested in the salt spray, addition of Al, Me and rare earth should form a thinner compact layer bonding to substrate and prevented the further corrosion in the alloy, so that the color difference of alloy increased less. Therefore, the designed alloy has more excellent anti-tarnish property than that of H7211 alloy.

3.3. AC impedance studies

The EIS was performed to test the corrosion behavior of the designed imitation-gold copper alloy. Fig. 2 shows both Nyquist and Bode impedance spectrum of the specimen immersed in 3.5% NaCl solution for different days. The similar patterns of the impedance spectra of the alloy immersed in 3.5% NaCl solution for different days present. A linear-like pattern of the impedance spectra in the high frequency and the semicircle structure of the impedance spectra in the low frequency appear. Hybrid controlling process of concentration polarization combined with electrochemical polarization took a key effect on the corrosion of the sample as it was immersed in 3.5% NaCl solution. With the increase of immersing time, diameter of semicircle in the high frequency increases. To better understand the impedance, Bode representations of the impedance spectra shown in Fig. 2a were plotted in Fig. 2b. Fig. 2b shows the relationship between the logarithmic values of the impedance and the logarithmic value of the frequency. The value of log |Z| are low and relatively constant in the high frequency (higher than 4.5), which is a typical response of a resistor to AC, corresponding to solution resistance. In the medium frequency region (log f of 4.5 to −0.5), the relationship between log |Z| and log f

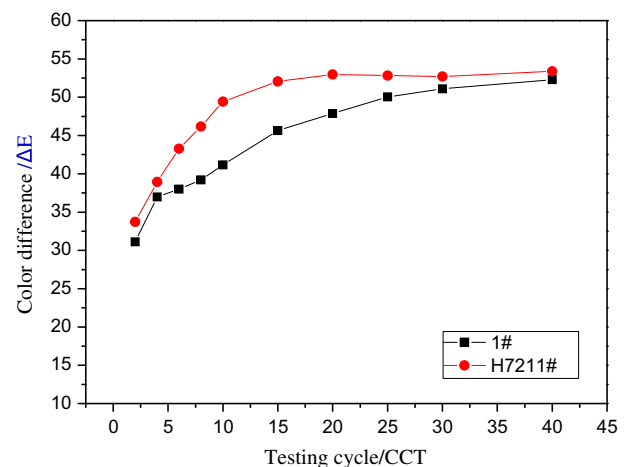**Fig. 1.** The tarnish properties of the designed alloy (1#) and H7211 alloy.