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ScienceDirect
Trans. Nonferrous Met. Soc. China 25(2015) 654−660

Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Corrosion behavior of brass coinage in synthetic sweat solution

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Received 29 April 2014; accepted 10 September 2014

Abstract: Corrosion behavior of brass coinage was investigated in synthetic sweat solution by electrochemical measurement and surface analysis methods including scanning electron microscope (SEM) and energy dispersive X-ray spectrometer (EDX). It is indicated that chloride ions in sweat solution accelerate the anodic active dissolution of brass, which is the main reason of pitting corrosion and dezincification corrosion. Meanwhile, lactic acid and ammonia water also promote the anode reaction. The corrosion products on the surface are mainly composed of basic copper chloride, cuprous oxide, the complex consisting of urea in association with copper, and few lactate ion. The kinetics of pitting corrosion development obeys the following equation of $J_0=0.3735(t+185.93)^{-1/2}$, and the process is controlled by dissolution of salt deposited on pit surface.

Key words: brass coinage; dezincification; pitting corrosion; synthetic sweat solution

1 Introduction

Due to its magnificent color, brass is widely used in coinage and heat exchanger [1,2]. Tarnishing of coinage is a common phenomenon during circulation process. It shortens service life of coinage and reduces the collection value of commemorative coin.

There are many reasons for tarnishing of brass coinage, such as corrosive gas in air, the water molecule adsorbed on surface. As we know, coinage often contacts with skin during its usage process, so sweat left on coinage becomes one of the main reasons for tarnishing. Until now, there have been several reports about the corrosion of copper alloys for coinage in sweat solution. For example, COLIN et al [3,4] studied the corrosion product of copper/zinc/nickel, copper/nickel/zinc and nickel/copper alloys in synthetic sweat medium by means of surface analysis. It was found that the corrosion layers are composed of copper and nickel based compounds. For the alloys with a high copper content, the corrosion layers are mainly composed of copper (I) oxide in which chloride anions are included. For the alloys with a high nickel content, copper chloride hydroxide and nickel-compounds like nickel hydroxide and nickel oxide are detected in the corrosion layer. However, most of these reports centered at the analysis of corrosion production on metal surface, there was few study on the corrosion behavior of brass in sweat solution. Furthermore, the researches on localized corrosion of brass mostly focused on dezincification corrosion, few about pitting corrosion of brass [5,6]. However, to the best of our knowledge, it has widely used in China, in sweat solution until now.

Herein, the corrosion of brass coinage was investigated with electrochemical measurement and surface analysis methods. Based on the test results, the effects of the composition in synthetic sweat solution on the corrosion of brass were discussed, and the corrosion product and type of brass in sweat solution were analyzed. Furthermore, the corrosion process of brass in sweat solution was clarified.

2 Experimental

The material used in this work was *α* brass with a composition of copper 70 % and zinc 30 %, which was used for manufacturing coinage.

For the electrochemical test, the brass electrode was embedded into the epoxy resin with a geometrical

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Foundation item: Project (21276036) supported by the National Natural Science Foundation of China; Project (2009AA05Z120) supported by the National High-tech Research and Development Program of China; Project (2014025018) supported by the Liaoning Provincial Natural Science Foundation of China; Project (3132014323) supported by the Fundamental Research Funds for the Central Universities, China

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DOI: 10.1016/S1003-6326(15)63649-4

surface area of 1 cm^2 exposed to the corrosive environment. The electrode was abraded with emery paper to 2000 grade, degreased with ethanol and dried with blower before the experiment. The electrochemical tests were carried out in the four kinds of solutions shown in Table 1 at the temperature of (25±2) °C. The solution 1 in Table 1 is synthetic sweat solution [3].

Table 1 Composition of solution and methods of preparation

Solution No.	Composition of solution and methods of preparation
1	Sodium chloride 5 g/L, urea 1 g/L, lactic acid 1 g/L, pH value of solution is adjusted to 6.5 by adding 28 % ammonia
2	Sodium chloride 5 g/L, lactic acid 1 g/L, pH value of solution is adjusted to 6.5 by adding 28 % ammonia
3	Urea 1 g/L, lactic acid 1 g/L, pH value of solution is adjusted to 6.5 by adding 28 % ammonia
4	Sodium chloride 5 g/L

All electrochemical tests were carried out in a conventional three-electrode cell with Solartron 1280. Platinum plate was the counter electrode, and saturated calomel electrode (SCE) was the reference electrode.

Potentiodynamic polarization tests ranged from −0.2 V (more negative than the free corrosion potential (vs SCE)) to 1 V with the scan rate of 0.5 mV/s. The potentiodynamic cyclic anodic polarization tests commenced with the application of −0.03 V, more negative than the free corrosion potential. Subsequently, a potential scan started in the anodic direction with the scan rate of 1 mV/s until the potential reached 1 V (vs SCE), and then it was reversed in the backward direction with the same scan rate. Potentiostatic polarization test was carried out at the potential of 1 V.

Immersion test was carried out in synthetic sweat solution (solution 1 in Table 1) and the experimental temperature was (25±2) °C. In order to prevent the sweat from evaporating, the beaker filled with solution was covered with a protective plastic film. After 28 d of free corrosion, the samples were rinsed with distilled water and dried by ambient air. The corroded surface of the tested brass was inspected by scanning electron microscope (SEM) and optical microscope (OM), and the composition was revealed with X-ray diffraction (XRD), Fourier transform infrared spectrometer (IR), and energy dispersive X-ray spectrometer (EDX). In order to confirm the corrosion type of brass in sweat solution, the composition of the solution in which brass was immersed for 24 h was analyzed by atomic absorption spectroscopy (AAS).

3 Results and discussion

3.1 Corrosion type of brass in synthetic sweat

After 28 d of immersion, brownish yellow corrosion product can be observed on brass surface. Figure 1 presents the SEM micrographs of brass after immersion. It can be observed that the corrosion product film presents map cracking shape (see Fig. 1(a)), and the corrosion product is loose and porous (see Fig. 1(b)).

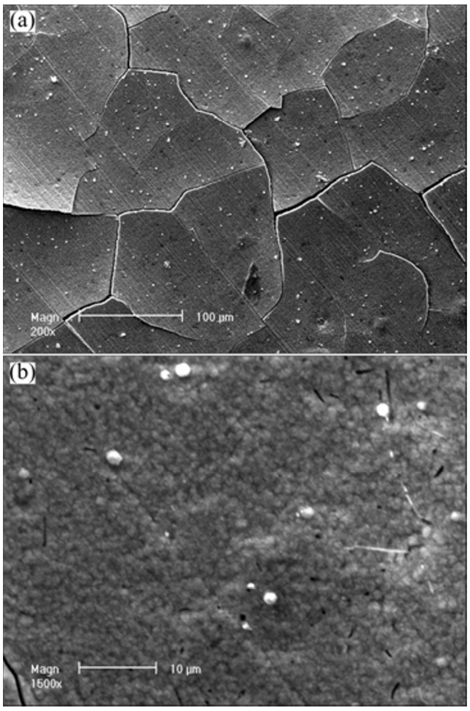

Fig. 1 SEM images of brass immersed in sweat solution for 28 d: (a) Cracking shape; (b) Corrosion product

After corrosion product on brass surface is removed, the cross section of brass is observed with OM, and its result is shown in Fig. 2. Several pits with depth of about 10 μm can be observed on brass surface. It is demonstrated that pitting corrosion occurs on brass surface in sweat solution.

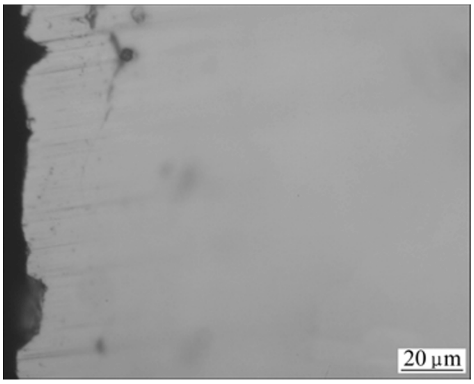

Fig. 2 Side view of brass immersed in sweat solution for 28 d