



Electrochemical properties of Pb-0.6 wt% Ag powder-pressed alloy in sulfuric acid electrolyte containing $\text{Cl}^-/\text{Mn}^{2+}$ ions



Shuai Wang, Xiang-yang Zhou, Ma Chi-Yuan, Bo Long, Hui Wang, Jing-Jing Tang, Juan Yang*

School of Metallurgy and Environment, Central South University, Changsha 410083, China

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ABSTRACT

In this study, Pb-0.6 wt% Ag powder-pressed alloy was fabricated and used as an insoluble anode for zinc electrowinning. The micromorphology, phase composition and elements distribution of the oxide layer formed on Pb-0.6 wt% Ag anode were studied. Additionally, the anodic reaction process, galvanostatic potential and oxygen evolution kinetics in $\text{Cl}^-/\text{Mn}^{2+}$ ions containing sulfuric acid electrolyte were investigated. Compared with the traditional Pb-0.6 wt% Ag cast-rolled alloy, Pb-0.6 wt% Ag powder-pressed alloy shows much lower anodic potential, self-corrosion current density, cell voltage and higher exchange current density in the same electrolyte. Due to a thin and uniform MnO_2 layer formed on the surface of powder-pressed alloy with the presence of Mn^{2+} ion in the electrolyte, the powder-pressed alloy presents a stable anodic potential. Consequently, the corrosion of powder-pressed Pb-0.6 wt% Ag anode was suppressed and the anode slime was decreased compared with Pb-0.6 wt% Ag cast-rolled anode.

1. Introduction

About 85% of the global zinc is produced by hydrometallurgy, in which electrowinning is one of the key steps (Antuñano et al., 2013; Chai et al., 2014; Chai et al., 2009). In the zinc electrowinning process, the current widely used insoluble anode is Pb-Ag (0.5–1 wt%) alloy because of its high corrosion resistance and stability in sulfuric acid electrolyte. Before the occurrence of oxygen evolution reaction (OER) (Bestetti et al., 2001; Lafront et al., 2010; Shkarji et al., 2011), Pb-Ag anode surface is covered by non-conductive PbSO_4 layer due to the dissolving of lead. With the increasing of electrode potential, the PbSO_4 layer is gradually oxidized to conductive PbO_2 layer, inhibiting the further corrosion of Pb (Pérez-González et al., 2012). Then, sustainable and stable OER occurs on the anode in the electrolyte (Nguyen and Atrens, 2009; Zhang et al., 2009). Although the equilibrium potential of OER is about 1.229 V, this reaction only occurs when a much higher potential (about 2 V) is applied. The OER overpotential and anodic potential depend on the electrocatalytic activity of anodes. Nevertheless, the commercial Pb-Ag alloy still shows some shortcomings, such as poor mechanical properties, insufficient conductivity and high cell voltage (Zhu et al., 2010).

In order to improve the electrochemical properties of Pb-Ag alloy, many strategies have been reported, such as changing the alloy composition, designing porous alloy, depositing or coating active layer on the surface of Pb-Ag alloy and so on. Among them, the fabrication of Pb-

Ag alloy by powder metallurgy is believed to be an effective technique. Research has shown the application of Pb-Ag powder-rolled alloy can improve the creep resistance and decrease the amount of Pb impurities in the deposited zinc (Taguchi et al., 2013). However, the electrochemical experiments were carried out in pure sulfuric acid electrolyte, and the anodic potential of Pb-Ag powder-pressed alloy did not reduce compared with that of Pb-Ag cast-rolled alloy. Besides, the electrolysis duration was only 5 h, which is not compatible with the practical industrial production.

Studies have shown that not only the phase composition and structure of anodes, but also the impurities of electrolytes play significant roles in the performance of Pb-Ag anodes (PT and Asselin, 2009). In the zinc electrolytic cell, Cl^- and Mn^{2+} are two typical ions in the electrolyte solution and can greatly influence the electrowinning of zinc (Schmachtel et al., 2008). Although Cl^- ions can reduce the oxygen evolution potential, the corrosion of anode will be dramatically accelerated (Lashgari and Hosseini, 2013; Lee et al., 2011). Mn^{2+} ions in the electrolyte can be easily oxidized to MnO_2 during the electrowinning process, which can cause short circuit upon the electrolyzing and increase the amount of anode slime, resulting in the impoverishment of Mn^{2+} ions and the loss of anodes.

In this study, Pb-0.6 wt% Ag alloy was fabricated through powder pressing method followed by a sintering process. Its electrochemical properties were evaluated in a simulated industrial zinc electrowinning electrolyte with Cl^- and Mn^{2+} ions. The effects of Cl^- and Mn^{2+} ions

* Corresponding author.

E-mail address: j-yang@csu.edu.cn (J. Yang).

on the electrochemical behaviors of Pb-0.6 wt% Ag powder-pressed alloy were investigated. The micromorphology, elements distribution and phase composition of the oxide layer formed on the Pb-0.6 wt% Ag powder-pressed anode after galvanostatic electrolysis at a current density of 50 mA/cm² for 72 h were obtained and compared with those of the traditional Pb-Ag cast-rolled alloy by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD), respectively.

2. Experimental

2.1. Sample preparation

Powder mixtures of Pb and Ag with a mass ratio of 99.4:0.6 were mechanically ball milled (mechanical alloying process) for 8 h at room temperature using a high-energy planetary ball mill in Ar atmosphere. The powder mixtures were then uniaxially die-compacted under a pressure of 300 Mpa. Finally, the Pb-0.6 wt% Ag bulk was sintered under H₂/Ar (H₂:Ar = 10:90). The sintering conditions were as follows: (i) Heating to 300 °C with a heating rate of 3 °C /min; (ii) Keeping at 300 °C for 5 h; (iii) Cooling to room temperature naturally. The obtained Pb-0.6 wt% Ag alloy were cut into cubic samples (10 mm × 10 mm × 5 mm) using a wire-cut machine. The diagrammatic sketch of the mould and the flowchart of experimental process are shown in Fig. 1.

2.2. Measurements

Before the electrochemical tests, Pb-0.6 wt% Ag powder-pressed alloy and Pb-0.6 wt% Ag cast-rolled alloy coated by denture base resins with a working area of 10 mm × 10 mm were connected to a plastic isolated copper wire. Then the electrodes were polished with SiC abrasive paper and rinsed in deionized water for testing. The assembly diagram of experimental sample is shown in Fig. 2.

Electrochemical experiments, including chronopotentiometry, cyclic voltammetry (CV), galvanostatic polarizations, electrochemical impedance spectroscopy (EIS) and linear scanning voltammetry (LSV), were conducted on electrochemical workstation (PARSTAT 4000) in 160 g/L H₂SO₄ electrolytes containing Cl⁻ (500 mg/L) and Mn²⁺ (2 g/L) ions which were introduced into the electrolyte through the addition of MnSO₄·H₂O and HCl, respectively. All the electrochemical tests were carried out in a glass three-electrode system. The fabricated Pb-0.6 wt% Ag powder-pressed alloy and Pb-0.6 wt% Ag cast-rolled alloy were utilized as working electrode. Mercurous sulphate electrode (MSE: 0.64 V versus SHE) and platinum plate (2 cm × 3 cm) were used as the reference and counter electrodes, respectively. All potentials in this study were given versus the reference electrode. The distance between the working electrode (anode) and the counter electrode was fixed at 3 cm. Fig. 3 shows the diagrammatic sketch of three-electrode system

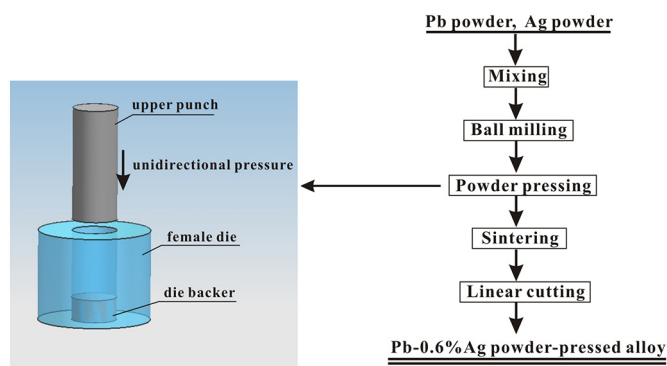


Fig. 1. The diagrammatic sketch of the mould and process flow diagram of Pb-0.6%Ag powder-pressed alloy.

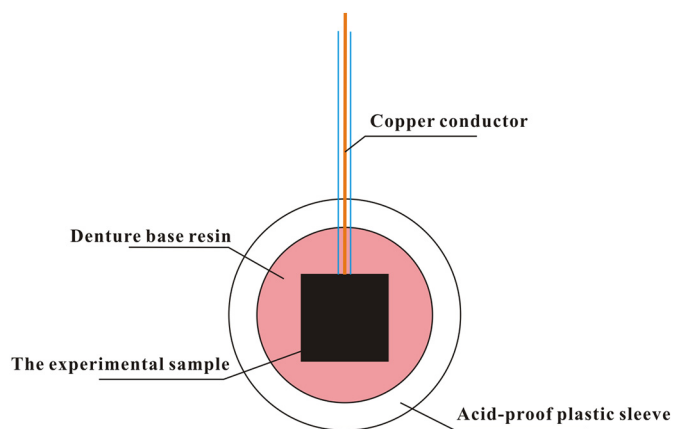


Fig. 2. Assembly diagram of experimental samples.

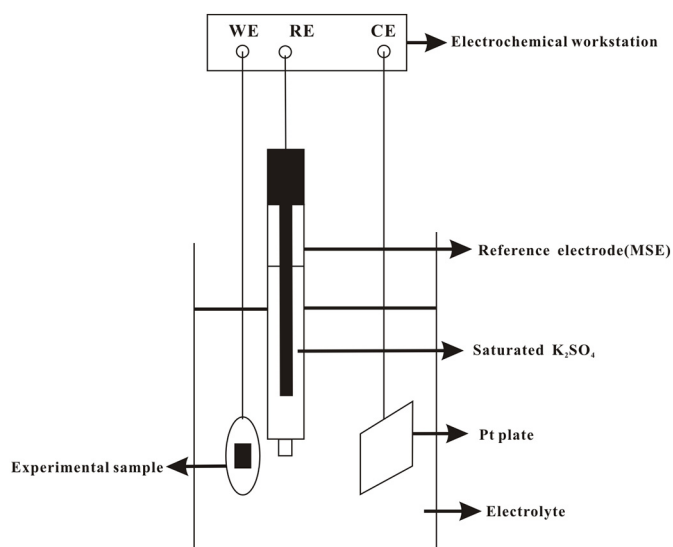


Fig. 3. Schematic plot of electrochemical test.

for electrochemical tests.

Chronopotentiometry was used to remove oxides on the surface of anode at a current density of -5 mA/cm^2 lasting for 2 h. Then CV was performed in a potential range from -1.4 V to $+1.9 \text{ V}$ at a scanning rate of 20 mV/s . Galvanostatic polarization was carried out at 50 mA/cm^2 for 72 h. Thereafter, EIS was conducted at 1.3 V with an amplitude of 10 mV in a frequency range of 10^5 – 10^{-2} Hz . Finally, LSV was proceeded at a constant scan rate of 5 mV/s from $+1.1 \text{ V}$ to $+1.7 \text{ V}$.

After galvanostatic electrolysis, the anodes were taken out from electrolyte, washed with deionized water and dried for 72 h at room temperature. Then, the microscopic surface morphology, element distribution and phase composition of anodic layers were characterized by using a scanning electron microscope (SEM, QuantaFEG250, American) equipped with energy dispersive X-ray spectroscopy (EDS) and X-ray powder diffractions (XRD) (Rigaku-TTRIII, Japan).

3. Results and discussion

3.1. Cyclic voltammetry

In order to research the process of oxidation and reduction reaction on fresh electrode, cyclic voltammetric experiments of Pb-0.6 wt% Ag powder-pressed alloy and Pb-0.6 wt% Ag cast-rolled alloy were carried out. As shown in Fig. 4a, an anodic oxidation peak and an anodic oxidation branch present in the forward scan, labeled as O1 and O2.

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