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Preparation of black Cu-Sn alloy with single phase composition by electrodeposition method in 1-butyl-3-methylimidazolium chloride ionic liquids

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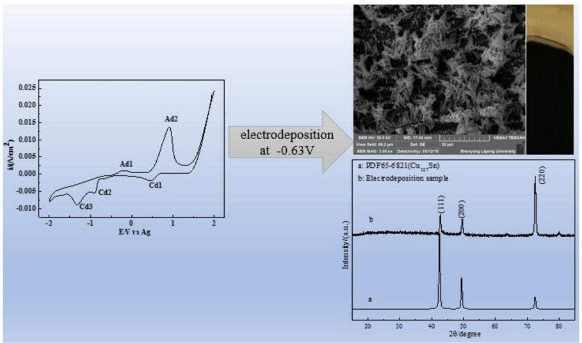
HIGHLIGHTS

- Black and cypress leaf-like Cu-Sn coating was prepared by electrodeposition.
- A new peak locating at −0.5 V ~ −1.0 V in CV belonged to reduction of copper ion and tin ion.
- The phase composition of alloy is $Cu_{13.7}Sn$.

GRAPHICAL ABSTRACT



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ABSTRACT

Black Cu-Sn alloy coating was prepared from 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) ionic liquids by electrodeposition method. The electrochemical behaviors of different electrodeposition systems were investigated by cyclic voltammetry. The micromorphology of the black coating was investigated by scanning electron microscopy (SEM) coupled with energy dispersive spectrometer (EDS) and X-ray diffraction (XRD). The results showed that black coating was cypress leaf-like material. The electrochemical behavior in [BMIM]Cl-$CuCl_2·2H_2O$-$SnCl_2·2H_2O$ ionic liquids showed the peak located at −0.5 V ~ −1.0 V belonged to the reduction peak of copper-tin alloy co-deposition. The element compositions of coating were Cu and Sn, and the phase composition of the coating was $Cu_{13.7}Sn$.

1. Introduction

Copper-tin alloy coating is widely used in industry owning to its outstanding mechanical strength, hardness and corrosion resistance. At present, the preparation of Cu-Sn alloy coating is usually performed in aqueous electroplating solution. The effects of composition of solution, parameters and other factors on the composition [1–4], elastic [5], corrosion resistance [6], hardness [7] and phase composition [8] of Cu-Sn alloy coating were studied. It can be seen from these studies that the copper-tin alloy coating with good properties can be electrodeposited in aqueous solution, but at the same time, the characteristics, such as complicated process conditions, complex composition of the bath, low utilization of current and difficultly in treating the subsequent waste liquid are existed.

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In recent years, the application of ionic liquids in electrodeposition field has attracted more and more attention. Silicon [9], iridium [10], aluminum [11] and other metals can be electrodeposited successfully from 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl) imide ($Py_{1,4}$[TFSI]), 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF_4) and hydrophobic perfluoro-3-oxa-4,5 dichloro-pentansulphonate [$CF_2ClCFClOCF_2SO_3^-$] based ionic liquids, respectively. A large number of studies have shown that the electrodeposition bath of metals and alloys and the process conditions in ionic liquid system are simple [12–14].

The researchers used different methods and systems to obtain copper-tin alloys with different colors, different morphologies and different phase compositions [1–4,6,7,15,16]. In this paper, the electrodeposition of black copper-tin alloy with single phase composition in 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) ionic liquid has been carried outside the glove box in order to border the electrodeposition application of ionic liquid. The electrochemical behavior of copper(II), tin(II) and copper(II)-tin(II) existing in [BMIM]Cl ionic liquid has been studied. The morphology, element compositions and phase composition of copper-tin alloy have been studied.

2. Experimental details

1-Butyl-3-methylidazolium chloride ([BMIM]Cl) ionic liquid was used as basic liquid. Electrolytes were obtained by adding $CuCl_2{\cdot}2H_2O$ and $SnCl_2{\cdot}2H_2O$ into [BMIM]Cl, respectively. Cyclic voltammetry (from 2 V to -2 V and then to 2 V) and electrodeposition experiments were carried out with CS350 electrochemical workstation and the measured temperature was 35 °C without stirring. A traditional three-electrode cell was used in these experiments with silver wire (diameter is 1 mm) used as reference electrode, graphite electrode used as counter electrode, glass carbon (GC, diameter is 3 mm, CV) electrode and brass (electrodeposition experiments) used as working electrodes. The micromorphology of coating was investigated by VEGA3 scanning electron microscopy (SEM) and the phase composition of coating was studied by D/max-RB X-ray diffractometer (XRD).

3. Results and discussion

3.1. Electrochemical behaviors of Cu(II), Sn(II) and Cu(II)-Sn(II) in [BMIM]Cl ionic liquid

Fig. 1 shows the cyclic voltammetry curves of [BMIM]Cl (a), [BMIM]Cl-0.1 mol/L $SnCl_2{\cdot}2H_2O$ (b), [BMIM]Cl-0.1 mol/L $CuCl_2{\cdot}2H_2O$ (c) and [BMIM]Cl-0.1 mol/L $CuCl_2{\cdot}2H_2O$-0.1 mol/L $SnCl_2{\cdot}2H_2O$ (d), respectively. From the [BMIM]Cl cyclic voltammetry curve (shown in Fig. 1a), it can be seen that the electrochemical stability window is about −1.50 V to 1.50 V, that is, the electrochemical window of [BMIM]Cl is 3 V. An oxidation peak can be observed at 0V-0.50 V, and the formation of this oxidation peak is due to the characteristic of strong water absorption of [BMIM]Cl, which can absorb water molecules in the atmospheric environment during the test [17,18].

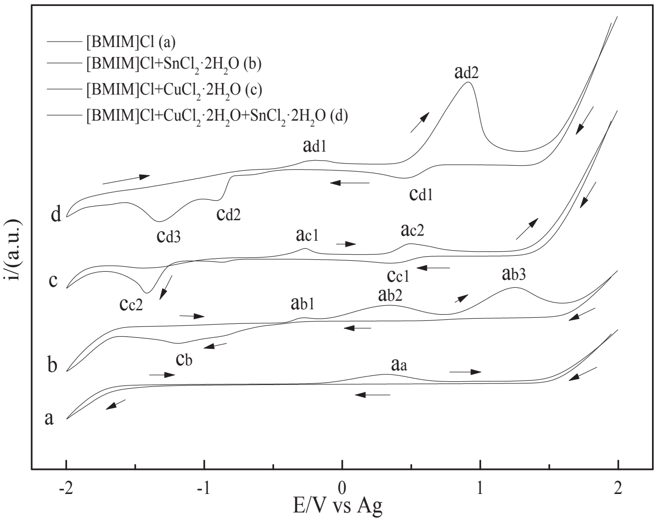

Fig. 1. Cyclic voltammetries in different systems at sweep rate of 50 mV/s on GC electrode.

From the [BMIM]Cl-0.1 mol/L $SnCl_2{\cdot}2H_2O$ curve (shown in Fig. 1b), it can be seen that there exists only one reduction peak at −0.5 V ~ -1.5 V, which means that the reduction of Sn^{2+} is one step reduction process, $Sn^{2+}\rightarrow Sn^0$. At the oxidation part of cyclic voltammetry curve, there are two oxidation peaks at 0 V–0.5 V and 1.0 V–1.5 V, respectively. Comparing with curve a, the peak located at 0 V–0.5 V belongs to the oxidation of H_2O and the peak located at 1.0 V–1.5 V is caused by tin oxidation, $Sn\rightarrow Sn^{2+}$.Besides, a small oxidation peak located at −0.25 V can be seen. This is because after the metal chloride is added, the metal is reduced by electrodeposition, the content of chlorine ions in the system increases, and the chlorine atoms are formed under the oxidation of some chlorine ions. That is peak located at −0.25 V resulting from the reaction $2Cl^-\rightarrow 2Cl\rightarrow Cl_2$.

The cyclic voltammetry curve (shown in Fig. 1c) of [BMIM]Cl-0.1 mol/L $CuCl_2{\cdot}2H_2O$ shows that there are two reduction peaks located at 0.45 V–0.55 V and −1.25 V ~ -1.5 V, respectively. This phenomenon shows that the reduction process of Cu^{2+} can be divided into two step reduction processes. The peak located at 0.45 V–0.55 V is caused by $Cu^{2+}\rightarrow Cu^+$, and the other peak located at −1.25 V ~ -1.5 V can be assigned to $Cu^+\rightarrow Cu^0$ [19]. The two oxidation peaks located at −0.25 V ~ 0 V and 0.50 V–0.75 V show that the oxidation of copper can be also divided into two step oxidation processes. That is, the reaction of $Cu^0\rightarrow Cu^+$ occurs at −0.25 V ~ 0 V and the other reaction of $Cu^+\rightarrow Cu^{2+}$ occurs at 0.50 V–0.75 V. In addition, the peak located at −0.25 V ~ 0 V also contained the reaction of chloride ions oxidation.

From the [BMIM]Cl-0.1 mol/L $CuCl_2{\cdot}2H_2O$-0.1 mol/L $SnCl_2{\cdot}2H_2O$ curve (shown in Fig. 1d), it can be seen that there are three reduction peaks located at 0.25 V–0.55 V, −0.5 V ~ -1.0 V and −1.0 V ~ -1.5 V, respectively. Comparing with curve b and curve c, the peak located at 0.25 V–0.55 V is caused by the reaction of $Cu^{2+}\rightarrow Cu^+$ and the peak located at −1.0 V ~ -1.5 V is caused by the reaction of $Cu^+\rightarrow Cu^0$. It is worthy to note that the peak located at −0.5 V ~ -1.0 V belongs to neither reduction of copper(II) existing alone nor reduction of tin(II) existing alone. Therefore, this peak can be considered the reduction peak of copper(II) and tin(II) co-deposition. In the subsequent positive scanning, it can be seen that there are two oxidation peaks located at −0.25 V-0V and 0.50V-1.20 V, respectively. Combining with the analysis of curve b and curve c, the oxidation peak located at −0.25 V ~ 0 V belongs to $Cu^0\rightarrow Cu^+$ and $2Cl^-\rightarrow 2Cl\rightarrow Cl_2$. The oxidation peak located at 0.50V-1.20 V is the oxidation peak formed by the dissolution of $Cu^+\rightarrow Cu^{2+}$ and co-deposited Cu-Sn [20]. It is worth noting that the oxidation peak of H_2O can't be seen in b, c and d. However, this does not mean that the oxidation of water doesn't exist in b, c and d. It mainly because of the oxidation of H_2O overlap with the oxidation of metal.

3.2. Morphology and phase composition of Cu-Sn alloy coating

Fig. 2 shows the macrograph and micromorphology of coating obtained by electrodeposition in [BMIM]Cl-0.1 mol/L $CuCl_2{\cdot}2H_2O$-0.1 mol/L $SnCl_2{\cdot}2H_2O$ ionic liquids at −0.63 V and 35 °C for an hour. As shown in Fig. 2, the coating shows black, and shape of coating looks cypress leaf-like material. The EDS surface scanning was carried out and the results showed that the elements composition of the coating are Cu and Sn.

Fig. 3 shows the phase composition of the coating after electrodeposition at −0.63 V for 1 h. In Fig. 3, curve a is the standard card