



Preparation of copper–silver alloy with different morphologies by a electrodeposition method in 1-butyl-3-methylimidazolium chloride ionic liquid

SUN JIE, MING TING-YUN* , QIAN HUI-XUAN and LI QI-SONG

School of Environmental and Chemical Engineering, Shenyang Ligong University, Shenyang 110159, People's Republic of China

*Author for correspondence (1350548424@qq.com)

MS received 3 December 2018; accepted 21 May 2019

Abstract. Electrodeposition of a copper–silver alloy based on a 1-butyl-3-methylimidazolium chloride (BMIC) ionic liquid was studied. The electrochemical behaviour of copper and silver ions was characterized by cyclic voltammogram. The morphologies and phase compositions of copper–silver alloy coating under different electrodeposition conditions were investigated by scanning electron microscopy and X-ray diffraction. The results show that copper–silver alloys with different micro-morphologies can be obtained under different potential conditions in BMIC. Co-deposition of the copper–silver alloy followed a two-step reduction process, the first step is the reduction of the cupric ion to the cuprous ion and the second step is the simultaneous reduction of the cuprous ion and the silver ion to form an alloy. A dendritic alloy can be obtained at -0.60 V, a bract alloy can be obtained at -0.80 V and a granular alloy can be obtained at -1 V. The coating particle size at 60°C was smaller than the particle size obtained at 40°C . The Cu–Ag alloy prepared by electrodeposition in ionic liquids consists of single-phase copper and single-phase silver.

Keywords. Ionic liquid; electrodeposition; metals and alloys; copper–silver alloy; morphology; thin films.

1. Introduction

In recent years, ionic liquids have been widely used in the fields of water treatment, atmospheric treatment and metal electrodeposition due to their advantages of wide electrochemical window, stable physical and chemical properties and green environmental protection [1,2]. In the field of electrodeposition of metal copper and copper alloys in ionic liquids, researchers have also conducted related studies, such as electrodeposition of a copper–zinc alloy in choline acetate and 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide [3,4], electrodeposition of an aluminium–zirconium–copper ternary alloy in triethylamine hydrochloride [5], electrochemical behaviour of the electrodeposition process on a copper–lithium alloy in 1-butyl-3-methylimidazolium tetrafluoroborate ionic liquids [6] and electrochemical behaviour of a copper–manganese alloy in *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethylsulphonyl) imide ionic liquids [7]. In these studies, many beneficial results have been obtained with regard to the electrochemical behaviour of different copper alloys. In addition, investigations showed that the BMIC ionic liquid was very suitable for the electrodeposition of metals and alloys [8,9].

As copper–silver alloy coating which has important applications in the field of catalysis, there have been few studies on electrodepositing copper–silver alloys in ionic liquids.

Rajagopal *et al* [10] conducted electrochemical behaviour studies of copper–silver alloy electrodeposition in a triethylammonium acetate ionic liquid. Reyna-González *et al* [11] studied the electrochemical behaviour and nucleation growth mechanism of copper–silver alloy electrodeposition in 3-butylpyridinium bis(trifluoromethanesulphonyl) imide. From the results of these studies, it can be seen that the morphology of the copper–silver alloy obtained in the fixed electrodeposition system is relatively simple, while the copper–silver alloy is often used as a catalyst, which may limit the application of the alloy plating.

In this paper, electrodeposition of the copper–silver alloy with different micromorphologies has been carried out in a 1-butyl-3-methylimidazolium chloride (BMIC) ionic liquid. The electrochemical behaviour, microstructure and phase composition of the copper–silver alloy were studied by cyclic voltammetry (CV), scanning electron microscopy (SEM) and X-ray diffraction (XRD).

2. Experimental

The electrochemical behaviour of the copper chloride and silver nitrate was determined by using a CV curve method based on a BMIC ionic liquid. Electrodeposition of the

copper–silver alloy under different conditions was carried out on a brass substrate according to the results of CV. All ionic liquids used were 6 h of vacuum distillation at 60°C first, and then vacuum drying for 24 h at 90°C. And the copper chloride and silver nitrate metal salts were also vacuum dried for 24 h at 90°C before experiment. In addition, electrodeposition experiments were carried out under the protection of nitrogen gas.

CV and electrodeposition experiments were performed by a CS350 electrochemical workstation. A conventional three-electrode cell was used with a graphite electrode as the counter electrode, a silver wire as the reference electrode, a glassy carbon (GC) electrode (CV) and a brass plate (electrodeposition experiments) as the working electrode. Acetone, anhydrous ethanol and deionized water were used to clean all the electrodes before testing. In addition, working electrodes were polished to mirror smoothness by using different types of sandpapers. The morphology and phase composition of coatings were characterized by S-3400 SEM and D/max-RB XRD.

3. Results

3.1 Analysis of redox behaviour of copper ions and silver ions

Figure 1 shows the CV of BMIC–CuCl₂·2H₂O (0.1 mol l⁻¹)–AgNO₃ (0.1 mol l⁻¹). It can be seen that there exist two peaks labelled as C1 and C2 in the part of the reduction curve. C1 corresponds to the reduction of Cu²⁺/Cu⁺ and C2 is the reduction peak of the co-deposition of the copper–silver alloy [12–14]. This indicates that the reduction of the copper and silver ions is carried out in two steps. The first step is the reduction of the cupric ion (Cu²⁺) to the cuprous ion (Cu⁺) and the second step is the simultaneous reduction of the cuprous

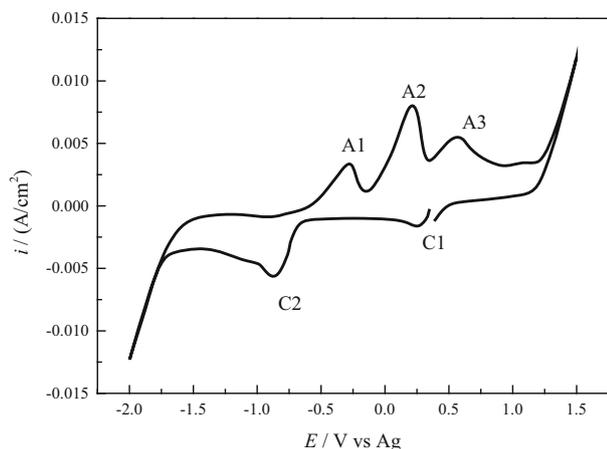


Figure 1. CV in BMIC–0.1 mol l⁻¹ CuCl₂·2H₂O–0.1 mol l⁻¹ AgNO₃ on a GC electrode at 60°C with the sweep rate of 100 mV s⁻¹ from open current potential to negative and then positive.

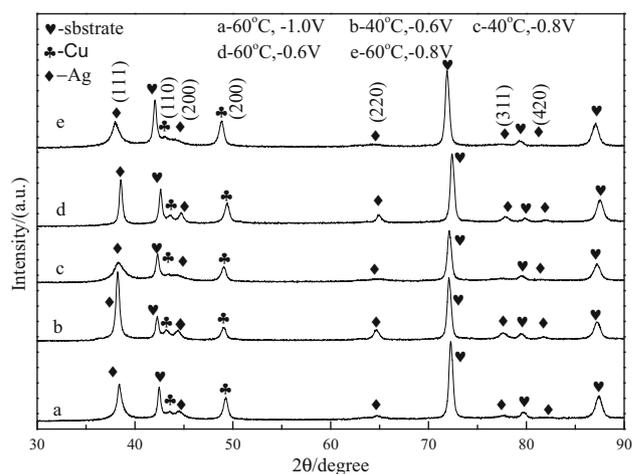


Figure 2. XRD spectra of electrodeposition layers under different electrodeposition conditions.

ion (Cu⁺) and the silver ion (Ag⁺) to form an alloy. There are three oxidation peaks labelled as A1, A2 and A3 in the oxidation curve. A1 corresponds to the oxidation of Cu⁰/Cu⁺, A2 corresponds to the oxidation peak of the copper–silver alloy and A3 corresponds to the oxidation peak of Cu⁺/Cu²⁺ [11,15].

3.2 Analysis of phase composition

Figure 2 shows the XRD test results of electrodeposition coating under different deposition conditions. Comparing the standard cards PDF1-1164 and PDF1-1241, the XRD patterns of the electrodeposited copper–silver alloy under different deposition conditions are composed of the diffraction peaks of the brass substrate, copper and silver. Silver grows mainly along the five-crystal planes of (111), (200), (220), (311) and (420), and copper grows mainly along the (110) and (200) crystal planes. These results show that the co-deposition of copper–silver alloys is a separate metal copper phase and a single-metal silver phase rather than a copper–silver alloy phase, which is consistent with the results of Rajagopal *et al* [10].

3.3 Analysis of micromorphology

Figure 3 shows the micro-morphologies of copper–silver alloy electrodeposition coating under different conditions. It can be seen that when the temperature is 40°C, as the deposition potential is increased from –0.60 to –1.00 V, dendritic, bract and granular coatings are sequentially formed. When the temperature is increased to 60°C, there is also a similar trend of the microscopic morphology. However, at the same deposition potential, the coating particle size at a temperature of 60°C is always smaller than the particle size obtained at 40°C. This result shows that an appropriate increase in temperature

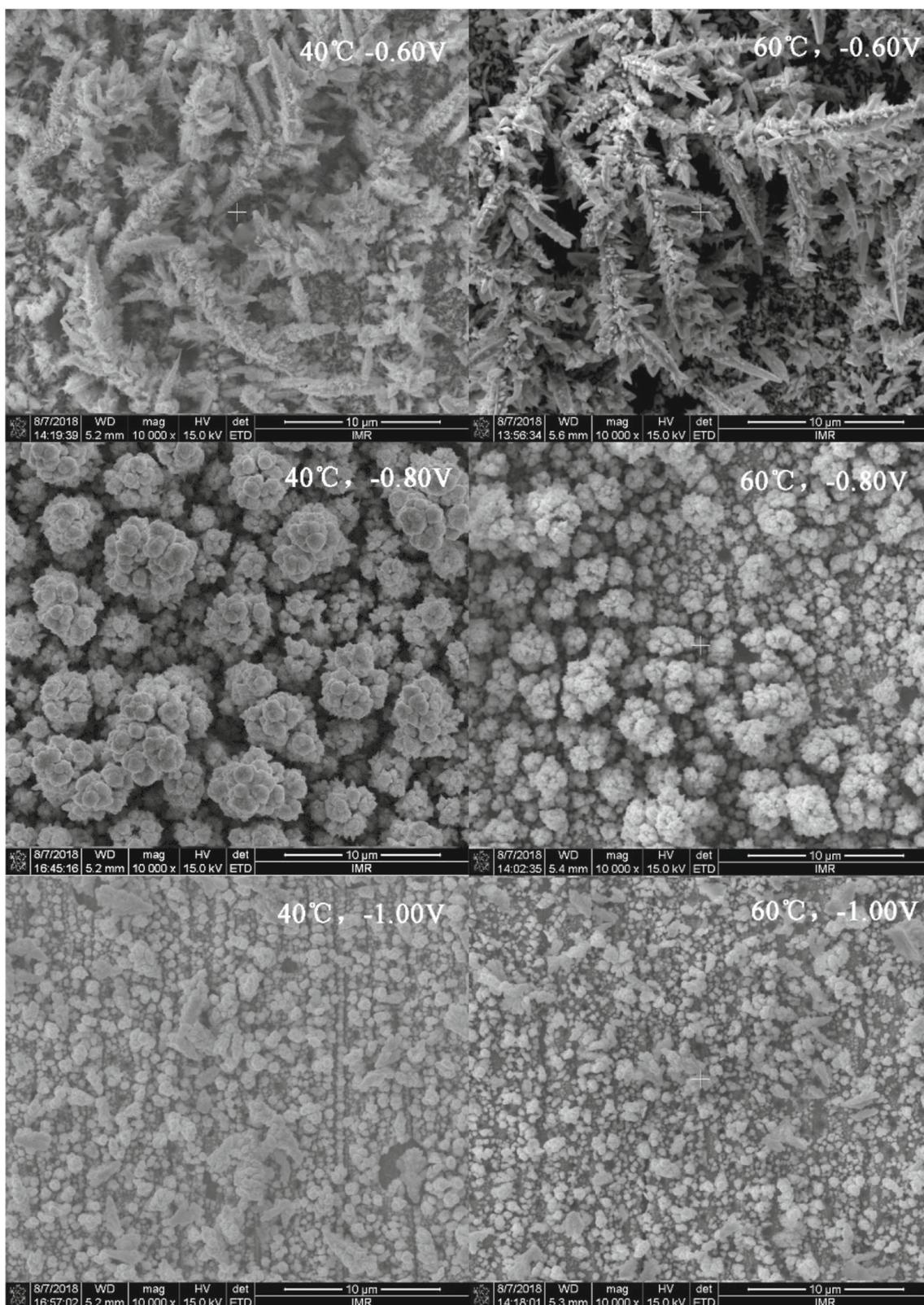


Figure 3. Micromorphology of copper-silver alloy electrodeposition under different conditions.

and deposition potential contributes to a more uniform and fine coating.

4. Conclusion

Electrodeposition of a copper–silver alloy can be carried out in a BMIC ionic liquid. The reduction of the copper–silver ions in the ionic liquid needs to be first reduced to cuprous ions by copper ions, and then the cuprous ions and silver ions are simultaneously reduced to form a copper–silver alloy. Electrodeposition of copper–silver alloys under different conditions can obtain alloy coatings with different micromorphologies and different sizes. Properly increasing the deposition potential and temperature contributes to the preparation of better quality alloy coatings. The copper–silver alloy consists of copper and silver phases.

References

- [1] Sun J, Ming T Y, Qian H X, Zhang M K and Tan Y 2018 *Chem. J. Chinese Univ.* **39** 1497
- [2] Ji S S, Yang P X, Zhang J Q, Lian Y, Zhang J and An M Z 2014 *Mater. Lett.* **133** 14
- [3] Peter D V, Alicja S, Edward M, Jan F and Koen B 2013 *Electrochim. Acta* **108** 788
- [4] Rouse C, Beaufile S and Fricoreaux P 2013 *Electrochim. Acta* **107** 624
- [5] Suneesh P V, Ramachandran T and Satheesh Babu T G 2018 *Mater. Today: Proc.* **5** 16640
- [6] Yang P X, Zhao Y B, Su C N, Yang K J, Yan B and An M Z 2013 *Electrochim. Acta* **88** 203
- [7] Chen P Y, Deng M J and Zhuang D X 2009 *Electrochim. Acta* **54** 6935
- [8] Debabrata P and Ramana G R 2014 *Mater. Chem. Phys.* **143** 564
- [9] Franz S, Barzi E, Turroni D, Glionna L and Bestetti M 2015 *Mater. Lett.* **161** 613
- [10] Rajagopal V, Velayutham D, Suryanarayanan V, Kathiresan M and Ho K C 2018 *J. Taiwan Inst. Chem. Eng.* **87** 158
- [11] Reyna-González J M, Reyes-López J C and Aguilar-Martínez M 2013 *Electrochim. Acta* **94** 344
- [12] Barrado E, Rodríguez J A, Hernández P and Castrillejo Y 2016 *J. Electroanal. Chem.* **768** 89
- [13] Suryanto B H R, Gunawan C A, Lu X Y and Zhao C 2012 *Electrochim. Acta* **81** 98
- [14] Fu C P, Zhou H H, Peng W C, Chen J H and Kuang Y F 2008 *Electrochem. Commun.* **10** 806
- [15] Ashraf B and Volkmar N 2015 *Electrochem. Commun.* **51** 113