

Bi-Cu film deposition in aqueous solutions

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Abstract: The relatively uniform bismuth-copper film was electrodeposited between -15 and -20 mV in the sulfate electrolyte containing 4 mmol/L bismuth ion and 2 mmol/L copper ion. Only copper was electrodeposited at -5 mV. The dendritic bismuth-copper film was electrodeposited under -20 mV. The cathodic current became constant between -20 and -400 mV. Therefore, bismuth-copper electrodeposition changes from charge transfer controlling to diffusion controlling at -20 mV. On the other hand, the uniform bismuth-copper film was electrodeposited between -5 and -35 mV in the methanesulfonate electrolyte containing 4 mmol/L bismuth ion and 2 mmol/L copper ion. The dendritic bismuth-copper film was electrodeposited under -35 mV. The potential region for good electrodeposition in methanesulfonate electrolyte is wider than that in sulfate electrolyte. Therefore, it is easy to control electrodeposition conditions by using methanesulfonate electrolyte.

Key words: electrodeposition; lead-free electrolyte; Bi-Cu film; current efficiency

1 Introduction

Lead has been used in many industrial fields because of its characteristics such as good ductility, large corrosion resistance and low melting point[1–5]. However, the use of lead is limited because it is harmful to the human body and the environment. In addition, it is difficult to use lead by ELV[6], RoHS and WEEE directives that went into effect by the EU.

Though bismuth is more brittle than lead[7], it has a low melting point near that of lead and other characteristics are also similar to those of lead. Therefore, the demerit of the embrittlement is expected to improve by the addition of dissimilar metals. In this work, we investigated the effects of the electrodeposition conditions such as applied potential and the composition of electrolytic solution on the morphology, crystal orientation and current efficiency of the bismuth-copper deposits.

2 Experimental

$\text{Bi}_2(\text{SO}_4)_3$, CuSO_4 and H_2SO_4 were dissolved in distilled water to prepare the electrolytic solution with Bi

ion of 4 mmol/L and Cu ion of 2 mmol/L at 298 K. In addition, Bi ion concentration of 4 mmol/L was limited to be dissolved in H_2SO_4 solution ($\text{pH}=0$), therefore, Bi ion concentration was fixed to 4 mmol/L. The electrodeposition and cathodic polarization measurement were conducted in above solutions. This electrolyte was adjusted to pH 0 by H_2SO_4 . To prepare the nitrate electrolyte, $\text{Bi}(\text{NO}_3)_3$ and $\text{Cu}(\text{NO}_3)_2$ were used, and the pH of the electrolyte was adjusted to 0 by HNO_3 . For the methanesulfonate bath, $\text{Bi}(\text{OH})_3$ and $\text{Cu}(\text{OH})_2$ were used, and the pH was adjusted to 0 by $\text{CH}_3\text{SO}_3\text{H}$. After that, Ar gas bubbling was conducted for 1 h to remove dissolved oxygen in the electrolyte.

The three-electrode method was utilized. The cell consisted of a Pt coil counter electrode, a Ag/AgCl (saturated KCl) reference electrode and a Au plate working electrode. In addition, during the experiment, all polarization measurements and electrodeposition processes were controlled by personal computer, and the solution was stirred at a constant speed smoothly; furthermore, Ar gas bubbling was conducted.

The controlled potential electrolysis was conducted in Bi-Cu mixed solution by using three kinds of adjusted solutions. The electric charge was 5 C and bath temperature was 298 K.

In addition, the electrodeposited films were evaluated by SEM observation, roughness measurement and ICP analysis.

3 Results and discussion

Electrodeposition potential in the controlled potential electrolysis was judged by results of each cathodic polarization measurement. Results of cathodic polarization measurement are shown in Fig.1.

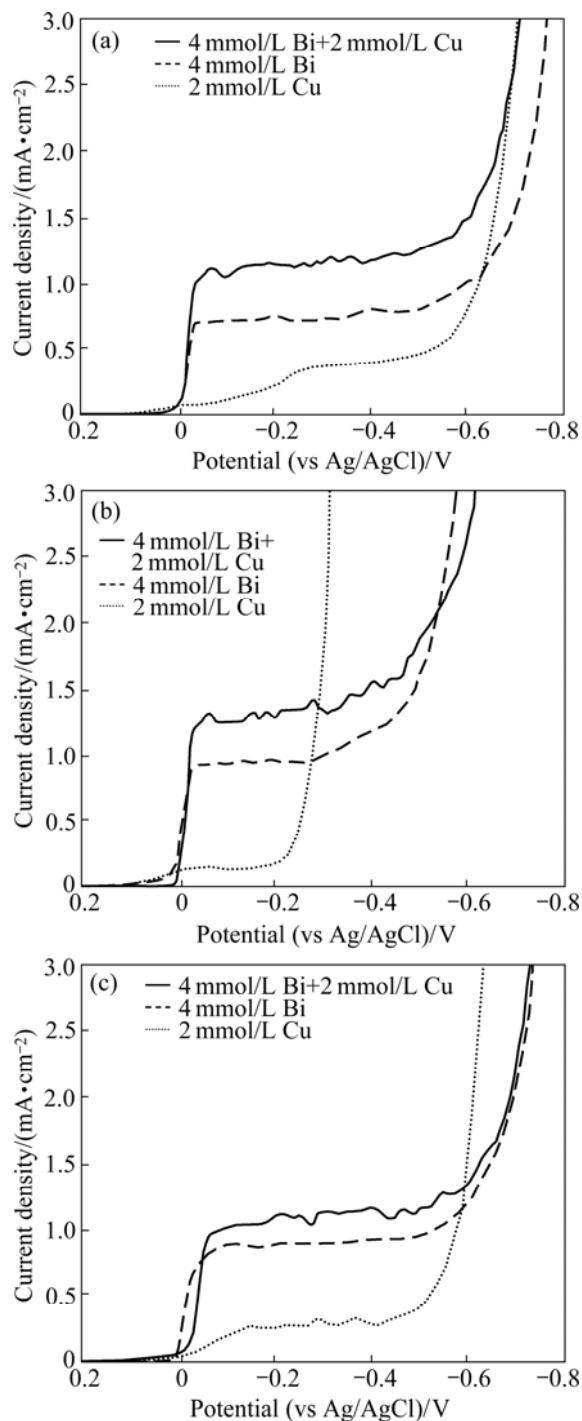


Fig.1 Cathodic polarization curves in H_2SO_4 (a), HNO_3 (b) and $\text{CH}_3\text{SO}_3\text{H}$ (c)

In Bi alone solution, the reduction current density increased from ca. -5 mV. The reduction current density became constant between ca. -25 mV and ca. -400 mV. It entered limiting current region by Bi(III) diffusion-limited at potential lower than -25 mV. After that, it increased rapidly from -600 mV. Gray deposit was found on the electrode surface by observation at ca. -5 mV. As mentioned above, it was considered that Bi electrodeposition reaction started from ca. -5 mV. In addition, H_2 generated on the electrode at ca. -600 mV, and the rapid increase started in current density.

In Cu alone solution, cathodic current started to flow from ca. 50 mV. A reddish electrodeposition was found on the electrode surface by observation at ca. 50 mV and H_2 bubble generated on the electrode at ca. -500 mV.

As mentioned above, it was considered that Cu electrodeposition reaction started from ca. 50 mV and then accelerated, and the current density was maintained at almost constant value because it entered limiting current region by Cu(II) diffusion-limited at potential lower than ca. -220 mV. After that, current density gradually increased from ca. -500 mV, and it increased rapidly from ca. -600 mV.

In Bi-Cu mixed solution, current density increased rapidly from ca. -5 mV, and then it became almost constant because it entered limiting current region by Bi(III) and Cu(II) diffusion-limited at potential lower than ca. -30 mV. After that, cathodic current increased rapidly by H_2 generation from ca. -600 mV.

From the above-mentioned result, compared with the current density in each Bi or Cu solution, it was found that current density increased in mixed solution. Therefore, it is considered that co-deposition of Bi and Cu ions is possible.

Based on the above result, controlled potential electrolysis was conducted at -5 , -15 and -20 mV, which are considered the deposit potentials of Bi ion. The results are shown in Figs.2(a)–(c).

In Bi alone solution, current density increased from ca. -5 mV and then became constant at potential lower than ca. -25 mV because of Bi(III) diffusion-limited. Furthermore, it increased rapidly from ca. -500 mV by H_2 evolution. Bi electrodeposition was found on the electrode surface by observation at ca. -5 mV. As mentioned above, it is considered that Bi electrodeposition reaction starts from ca. -5 mV.

In Cu alone solution, cathodic current started to flow from ca. 100 mV, and then kept almost constant because of the Cu(II) diffusion-limited at potential lower than -50 mV. After that, current density increased rapidly from ca. -250 mV by H_2 evolution.

In Bi-Cu mixed solution, current density increased rapidly from ca. -5 mV and then became constant because

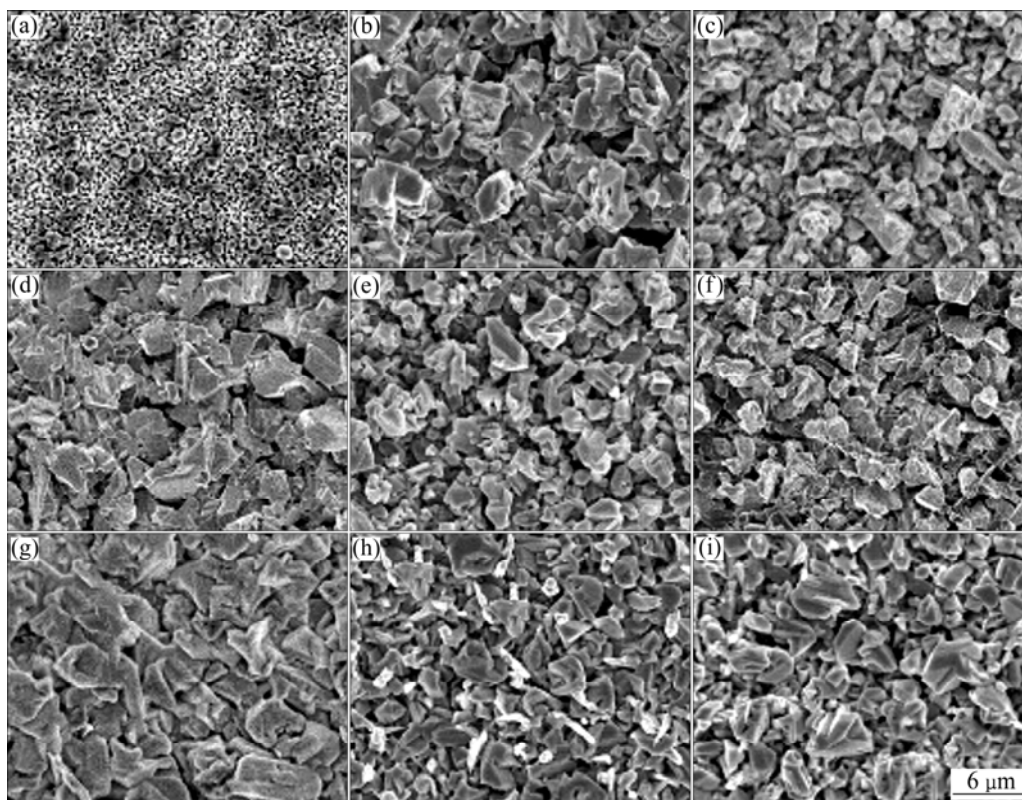


Fig.2 SEM images of surface of films deposited on Au plate at 298 K from various acid solutions containing 4 mmol/L Bi(III) and 2 mmol/L Cu(II) at various cathodic potentials: (a) H_2SO_4 solution, -5 mV; (b) H_2SO_4 solution, -15 mV; (c) H_2SO_4 solution, -20 mV; (d) HNO_3 solution, -5 mV; (e) HNO_3 solution, -15 mV; (f) HNO_3 solution, -25 mV; (g) $\text{CH}_3\text{SO}_3\text{H}$ solution, -5 mV; (h) $\text{CH}_3\text{SO}_3\text{H}$ solution, -15 mV; (i) $\text{CH}_3\text{SO}_3\text{H}$ solution, -35 mV

it entered limiting current region by Bi(III) and Cu(II) diffusion-limited at potential lower than ca. -30 mV. After that, cathodic current increased rapidly from ca. -500 mV by H_2 evolution.

From the above-mentioned result, compared with current density in each Bi or Cu solution, it was found that current density increased in mixed solution. Therefore, it is considered that co-deposition of Bi and Cu ions is possible.

Based on the above results, controlled potential electrolysis was conducted at -5 , -15 and -25 mV. The surface morphologies of the films are shown in Figs.2(d)–(f).

In Bi alone solution, current density increased from ca. -5 mV and then became constant at potential lower than ca. -40 mV because of Bi(III) diffusion-limited. Furthermore, it increased rapidly from ca. -600 mV by H_2 evolution. Bi electrodeposition was found on the electrode surface by observation at ca. -5 mV. As mentioned above, it is considered that Bi electrodeposition reaction starts from ca. -5 mV.

In Cu alone solution, cathodic current started to flow from ca. 0 mV, and then kept almost constant because of the Cu(II) diffusion-limited at potential

lower than -80 mV. After that, current density increased rapidly from ca. -500 mV by H_2 evolution.

In Bi-Cu mixed solution, current density increased rapidly from ca. -5 mV and then became constant because it entered limiting current region by Bi(III) and Cu(II) diffusion-limited at potential lower than ca. -40 mV. After that, cathodic current increased from ca. -600 mV rapidly by H_2 evolution.

From the above-mentioned result, compared with current density in each Bi or Cu solution, it was found that current density increased in mixed solution. Therefore, it is considered that co-deposition of Bi and Cu ions is possible.

Based on the above results, controlled potential electrolysis was conducted at -5 , -15 and -25 mV. The surface morphologies of the films are shown in Figs.2(g)–(i).

Figs.2(a)–(c) show surface images of the films electrodeposited in H_2SO_4 solution; Figs.2(d)–(f) show those in HNO_3 solution and Figs.2(g)–(i) show those in $\text{CH}_3\text{SO}_3\text{H}$ solution. In addition, Table 1 lists the Bi-Cu films composition and the current efficiency evaluated by ICP analysis.

The relatively uniform Bi-Cu film was electro-

Table 1 Current efficiency for various types of electrolyte (vs Ag/AgCl)

Electrolyte	Potential/ mV	x(Bi)/ %	x(Cu)/ %	Current efficiency/%
H ₂ SO ₄	−5	2.9	97.1	51.7
	−15	63.2	36.8	96.1
	−20	62.8	37.2	90.6
	−50	62.7	37.3	32.2
HNO ₃	−5	69.2	30.8	85.0
	−15	66.1	33.9	90.9
	−20	60.8	39.2	83.9
	−50	64.8	35.2	49.6
CH ₃ SO ₃ H	−5	66.3	33.7	89.2
	−15	64.4	35.6	90.6
	−20	62.2	37.8	86.7
	−50	62.3	37.7	85.1

deposited between −15 mV and −20 mV in H₂SO₄ solution containing 4 mmol/L Bi ion and 2 mmol/L Cu ion. The surface roughness of the deposits at −15 mV was 0.17 μm. According to the ICP analysis results, it was found that the film electrodeposited between −15 and −20 mV had high current efficiency (Min. 80%). The composition ratio of Bi to Cu in the films was 6:4. On the other hand, the film electrodeposited at −5 mV had low current efficiency and the Cu content was mainly dominated. Furthermore, the film electrodeposited below −50 mV had low current efficiency (Max. 50%), because the film dropped off during electrolysis due to dendrite electrodeposition. From these results, it is considered suitable to deposit Bi-Cu film at electrodeposition potential in charge transfer controlling region, not in diffusion-limited region.

In HNO₃, the relatively uniform Bi-Cu film was electrodeposited between −5 and −25 mV. But the surface roughness of the deposits at −15 mV was 0.47 μm. From the ICP analysis results, it was found that the film electrodeposited between −5 mV and −25 mV had high current efficiency (Min. 80%). The composition ratio of Bi to Cu in the films was 6:4. Furthermore, the film deposited below −50 mV had low current efficiency (Max. 50%) because the film dropped off during electrolysis due to dendrite electrodeposition. From these results, it is considered that suitable potential for producing good Bi-Cu film is charge-transfer controlling potential region but not diffusion-limited one.

On the other hand, the uniform Bi-Cu film was electrodeposited between −5 and −35 mV in CH₃SO₃H

solution containing 4 mmol/L Bi ion and 2 mmol/L Cu ion. The dendritic Bi-Cu film was electro-deposited under −35 mV. The surface roughness of the deposits at −15 mV was 0.09 μm and the value is the lowest among the electrolytes in this investigation. From the ICP analysis results, it was found that the film electrodeposited between −5 and −100 mV had high current efficiency (Min. 80%). The composition ratio of Bi to Cu in the films was 6:4 and the ratio was almost constant in this condition. The film composition was independent of the potential, but it would depend on ion concentration ratio in the electrolyte.

From these results, the good Bi-Cu films were obtained in charge-transfer controlling potential region.

4 Conclusions

1) In the case of good surface morphology on the films, the film composition was almost constant, and was independent of the electrolyte. The film composition was also independent of the potential, but it would depend on ion concentration ratio in the electrolyte.

2) In the methanesulfonate electrolyte and the sulfate one, deposits were a flat film. On the other hand, in the nitrate one, it was a rough film.

3) The electrodeposition potential region for preparing the good surface morphology in methanesulfonate electrolyte was wider than that in sulfate one or nitrate one. Therefore, it was easy to control electrodeposition conditions by using methanesulfonate electrolyte.

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