Physiochemical Characterization of Sn-Zn Coatings Electrodeposited from an Acidic Chloride Bath in the Absence of Complexing Agent

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ABSTRACT. The purpose of this study is to identify the Zn^{2+} ions concentration at Sn-Zn coating which could be produced in the absence of a complexing agent. The electrolytic bath comprised of $SnCl_2$ and $ZnCl_2$. The ionic mole ratio Zn^{2+}/Sn^{2+} of the electrolytic bath studied were 1:2, 1:1, 2:1, 4:1 and 10:1. Pure Zn and Sn electrodeposits were also prepared. The deposition process was performed at constant current of 5 mA and deposition time of 120 min. The electrodeposits were analyzed using X-ray diffraction (XRD) and scanning electron microscopy (SEM). It was found that in the absence of complexing agent, even an electrolytic bath with Zn^{2+}/Sn^{2+} ionic ratio of ten folds could not produce Zn-rich of Sn-Zn electrodeposits. Further, a unique method has been introduced to characterize the electrodeposits i.e. using the metal-air electrochemical cell. In this method, the electrodeposits were coupled with an air electrode in an alkaline electrolyte (6 M KOH) and discharged at 1 mA. Specific metallic element content will produce a distinct discharge profile thus enables it to be used in characterizing alloys or composites.

1. INTRODUCTION

Sn-Zn alloy coatings offer high corrosion protection for steel, good frictional properties and ductility, and good solder ability [1,2,7,8]. They also have low electrical contact resistance and are not subjected to bimetallic corrosion [3,5]. Sn-Zn alloy coatings also serve as substitutes for toxic cadmium and allergenic nickel coating at the end of the last century [3,4,6].

Tin and zinc can in principle be co-deposited from a simple salt solution containing both ions. However, since their standard electrode potentials are substantially wide apart (-0.76 V for Zn and -0.14 V for Sn), the electrodeposited layer is Sn-rich by default. Optimum zinc content required for effective corrosion protective layer is 20-30 wt.% [3]. Numerous electrolytic baths have been investigated to deposit Zn-rich Sn-Zn coatings [4,9-16].

In this study, we report the galvanostatic electrodeposition of Sn-Zn coating using simple acidic electrolytic bath comprising a mixture of tin chloride ($SnCl_2$) and zinc chloride ($ZnCl_2$) without the inclusion of complexing agent such as the gluconate, tartrate, citrate or cyanide baths. The purpose is identify the zinc ions concentration (Zn^{2+}) at which a rich-Zn Sn-Zn coating could be produced in the absence of a complexing agent. Further, we are using a unique method to distinguish whether a Sn-Zn coating is either a Sn-rich or a

Zn-rich i.e. by employing the coating as an anode in a metal-air electrochemical cell. Metal-air cell is popularly dubbed as a breathing battery as it requires oxygen from the ambient air to operate. As the system is supplied with unlimited supply of oxygen from the ambient air, any variation in its discharge profile is attributed to the anode i.e. the electrodeposited Sn-Zn coating in this case.

2. EXPERIMENTAL METHOD

The standard bath composition for Sn, Zn and Sn-Zn alloy deposits are given in Table 1. A copper clad laminate printed circuit board (PCB), patterned by the photolithography process employing a negative photoresist, was used as the substrate. The electrochemical cell consisted of tin plate (99.99% purity) as the working electrode (except for pure zinc deposits where a zinc plate (99.99%) was used) and copper substrate as the counter electrode. The copper substrate was clamped by an acrylic board holder with a fixed displacement (d) of 20 mm between the two electrodes. The holder possessed a circular window (11.5 mm in diameter)for deposition to take place on the copper substrate. The deposition current was fixed at 5 mA for a duration of 120 minutes. The surface morphology and chemical composition of the deposit was evaluated by a scanning electron microscope (SEM) and Energy-dispersive X-ray Spectroscopy (EDX); JSM-5600,JEOL,Japan). X-ray diffractometry (XRD) Empyrean PAN alytical was used to identify the phases of Sn-Zn alloy deposited. Metal-air cell was fabricated by pairing the electrodeposits with a commercial air electrode sheet in 60 ml of 6 M potassium hydroxide electrolyte. The cell was discharged at constant current of 1 mA using the AUTOLAB PSTAT.

Table 1 Basic electrolyte composition for the electrodeposition

Sample	$SnCl_2$ Molarity/Volume	$ZnCl_2$ Molarity/Volume	Mole ratio Zn^{2+}/Sn^{2+}	Remarks
A	1 M/60 ml	-	-	Sn electrodeposits
B	-	1 M/60 ml	-	Zn electrodeposits
C	1 M/30 ml	1 M/30 ml	1:1	
D	0.5 M/30 ml	1 M/30 ml	2:1	
E	1 M/30 ml	0.5 M/30 ml	1:2	
F	0.5 M/30 ml	2 M/30 ml	4:1	
G	0.5 M/30 ml	5 M/30 ml	10:1	

3. Results and Discussion

3.1 X-ray diffraction patterns

Fig. 1 shows that the changes in the XRD patterns of Sn as zinc ions were introduced into the electrolytic bath. It is evident that the electrodeposits were Sn-rich by merely referencing with the XRD patterns obtained from the Sn and Zn coatings. Even at zinc ions mole ratio of 10, the electrodeposits was still a Sn-rich coating. An EDX measurement on this sample (10:1), revealeda zinc content of only 2.6%. However, note that at 10:1 electrolytic bath composition, the entire XRD patterns shifted towards low 2θ angle. This could probably due to the incorporation of zinc alloying element into the space lattice of tin and thus changes the unit cell parameters (Vegard's law). The radius of zinc atom (142 pm) is slightly less than that of tin (145 pm).Therefore, this could suggest that in order to obtain a Zn-rich Sn-Zn electrodeposits in the absence of complexing agent, the zinc to tin ionic mole ratio of the electrolytic bath should be in excess of ten folds.
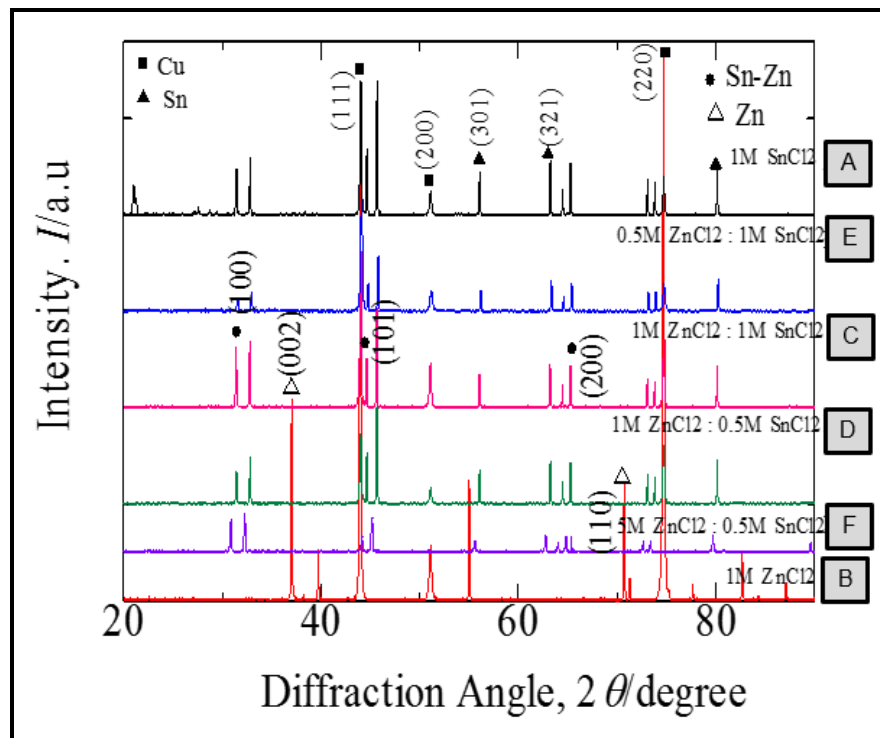
Fig. 1 XRD patterns of Sn and Zn by fixed deposition at 120 min and 5 mA, (a) 1 M SnCl$_2$,(b) 1M ZnCl$_2$, (c) 1M ZnCl$_2$: 1M SnCl$_2$, (d) 1M ZnCl$_2$: 0.5M SnCl$_2$, (e) 0.5M ZnCl$_2$: 1M SnCl$_2$ and (f) 5M ZnCl$_2$: 0.5M SnCl$_2$

3.2 Surface morphology

The surface morphology observations were conducted to support the XRD results. One distinct feature of tin electrodeposits are their porous nature, unlike zinc electrodeposits which is dense. Thus, all samples of Sn-Zn coatings appear to be Sn-rich as they possess similar morphology to that of pure tin electrodeposits.

3.3 Metal-air cell characterization

This is a unique method proposed to distinguish or to verify a metal element content. Electronegative metals such as aluminum, zinc, iron and tin have been utilized as anode for metal-air cell. Despite the general features of a metal-air system, each element possesses distinctive properties such as the open circuit potential, operating potential and multiple plateaus in the discharge curve. As such, any variation in the metallic composition could be identified and reflected on its discharge curve. Fig. 3 shows the discharge profiles of Sn, Zn, and Sn-Zn coatings. The best profile is shown by zinc electrodeposits (curve B) since zinc is much more electronegative than tin (curve A). There is no particular trend as the zinc ions content was increased from 0.5 M to 2 M. However, when the zinc ions content was increased by ten folds (5 M, curve G), the discharge duration was extended markedly and becomes compatible to the pure zinc deposits. On the other hand, its discharge plateau (the flat region prior to the abrupt voltage drop) remained unchanged. These observations support our conjecture that the metal-air electrochemical system could be used to characterize metallic composition of alloys or composites. Therefore there seems a substantial incorporation of zinc elements into the Sn-Zn deposits from the 5 M bath (10:1) but not reflected distinctively in the X-ray diffractograms.
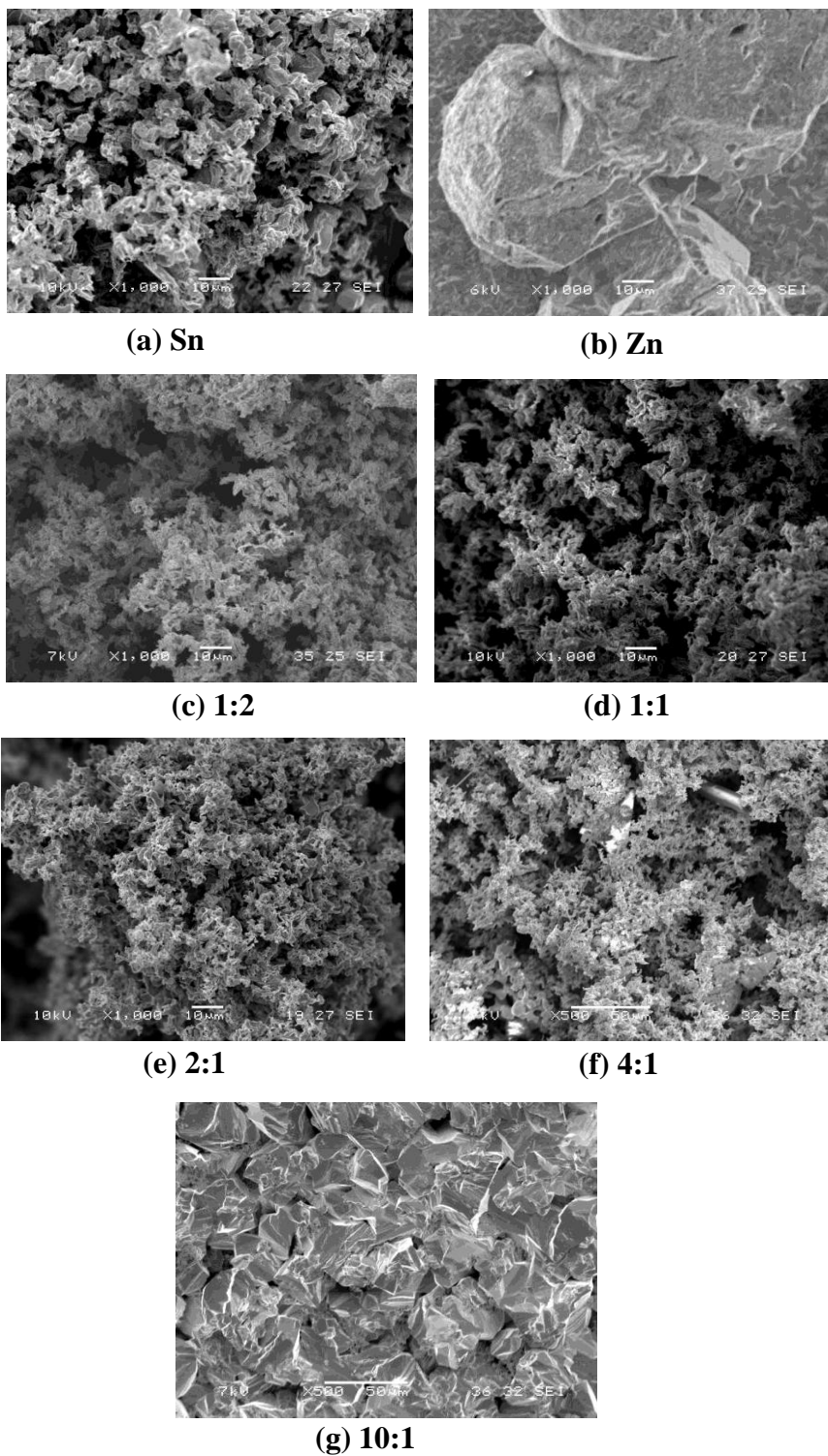
(a) Sn

(b) Zn

(c) 1:2

(d) 1:1

(e) 2:1

(f) 4:1

(g) 10:1

Fig. 2 SEM images of Sn and Zn by fixed deposition at 120 min and 5 mA, (a) 1 M $SnCl_2$ (b) 1M $ZnCl_2$, (c) 0.5M $ZnCl_2$: 1M $SnCl_2$, (d) 1M $ZnCl_2$: 1M $SnCl_2$, (e) 1M $ZnCl_2$: 0.5M $SnCl_2$, (f) 2M $ZnCl_2$: 0.5M $SnCl_2$, and (g) 5M $ZnCl_2$: 0.5M $SnCl_2$
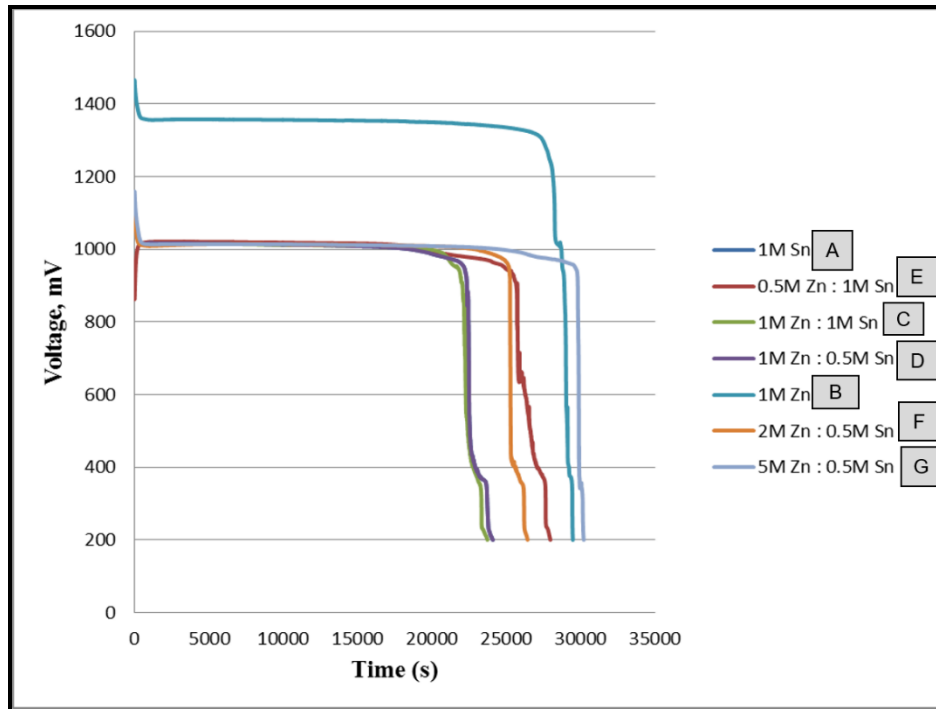
Fig. 3 Discharge profiles of metal-air cells employing the Sn, Zn and Sn-Zn electrodeposits rated at 1 mA, (a) 1 M $SnCl_2$ (b) 1M $ZnCl_2$, (c) 1M $ZnCl_2$: 1M $SnCl_2$, (d) 1M $ZnCl_2$: 0.5M $SnCl_2$, and (e) 0.5M $ZnCl_2$: 1M $SnCl_2$, (f) 2M $ZnCl_2$: 0.5M $SnCl_2$, and (g) 5M $ZnCl_2$: 0.5M $SnCl_2$

4. SUMMARY

As anticipated, the electrodeposition of Sn-Zn coatings employing simple acidic electrolytic bath ($SnCl_2$/$ZnCl_2$) in the absence of complexing agent resulted in Sn-rich electrodeposits. Even an electrolytic bath with zinc to tin ionic mole ratio of ten folds could only produce electrodeposits with zinc content of 2.6 wt.%. We introduced a metal-air electrochemical system in characterizing the metallic element content of alloys or composites.

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