Properties of Zn−Bi composite coatings prepared by ionic co-discharge deposition

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Abstract: Zn−Bi composite was synthesized by ionic co-discharge deposition and its properties were investigated. The results show that the Zn−Bi composite with the incorporation of Bi has a finer grain size than the pure Zn coating and improves the mechanical properties. The microhardness is increased by approximately two times simply by adding a small amount of Bi electrolyte into a Zn bath solution. A lower volume loss of the Zn−Bi composite coating compared with the pure Zn coating also indicates that the Zn−Bi coating has a better wear resistance.

Key words: Zn−Bi composite coating; ionic co-discharge deposition; electroplating; mechanical properties

1 Introduction

Zn coatings are the most commonly used non-noble metal coatings to protect the substrate by cathodic control. About half of the product Zn in the world is used for protection of corrosion. It is widely used because of its relatively low price, adequate supply, flexibility in application, ease to control the thickness of coating, good cathodic protection to steel, and the ability of combining with other elements to form special alloy coatings for special properties [1,2].

Composite coatings contain a dispersion of second phase, usually in the form of particles, to improve material properties such as hardness, wear resistance, self-lubrication, and corrosion resistance [3−5]. Various types of Zn composite coatings such as Zn−Al_2O_3 [6], Zn−MoS_2 [7], Zn−TiO_2 [8], and Zn-yttria stabilized zirconia (YSZ) [9] have been studied recently. Researchers found out that the Zn composite coatings enhanced mechanical properties and showed better sacrificial protection ability on steels than the pure Zn coating [8].

There are a number of methods to produce metal matrix composites in electroplating. One of the conventional ways is adding solid particles into the bath solution with vigorous agitation to form a homogenous distribution of fine-particles. It is an important factor in determining the properties of composite coatings [10].

A novel method called an ionic co-discharge process is introduced to obtain a homogenous dispersion. This method is to have different ions in the electrolyte and allow them to discharge to the cathode at the same time. If the metals do not dissolve each other or form intermetallic compounds, a two or more phases composite coating will be formed. The details were reported in our previous study [11].

In the present study, Zn−Bi composite coatings were developed, and their phase structure, microstructure, microhardness and wear property were characterized. Zn and Bi are two insoluble metals in their solid state; the two-phase composite is therefore expected to form.

2 Experimental

Mild carbon steel plate with the dimensions of 15 mm×25 mm was used as substrate. Before electroplating, the substrate was ground with the sand paper to a grit of 1200, and then degreased in ethanol. The pre-treatment of the substrate also included activation by acid pickling with 1 mol/L HCl for 60 s. The electrolyte solution and electroplating parameters are listed in Table 1.

Table 1 Composition of electroplating bath and processing parameters

Zn electrolyte		Bi electrolyte			Deposition parameter		
ρ(NaOH)/ (g·L^{-1})	ρ(ZnO)/ (g·L^{-1})	c(Bi(NO$_3$)$_3$·5H$_2$O)/ (mol·L^{-1})	c(Tartaric acid)/ (mol·L^{-1})	c(KOH)/ (mol·L^{-1})	Current density/(mA·cm^{-2})	Deposition time/min	Agitation speed/(r·min^{-1})
100	10	0.2	0.2	2.5	20 and 30	30	300

The Zn and Bi bath solution was prepared separately. 1 mL of 0.2 mol/L Bi electroplating solution was added into 70 mL of Zn electrolyte to make Zn−Bi composite. The pure Zn coating was also electroplated for comparison.

The morphology and Bi concentration in the Zn−Bi coatings were measured by a scanning electron microscope (SEM) with an energy dispersion spectroscopy (EDS) attachment. The phase structure of the coatings was determined by X-ray diffraction (XRD). The coating hardness was measured by a microhardness tester (Leco M400) with a Vickers diamond indenter. The applied load was 50 g with a holding time of 10 s. At least 5 measurements under the same conditions were conducted, and the average value was used as the microhardness (HV). The standard deviation was also calculated.

The wear property of the coatings was tested by NANOVEA Tribometer where a ceramic ball of 6 mm in diameter acted as friction counterpart. The test was conducted with a load of 1 N and sliding speed of 100 r/min at room temperature with the relative humidity of ~50%. The wear volume was calculated based on Fig. 1.
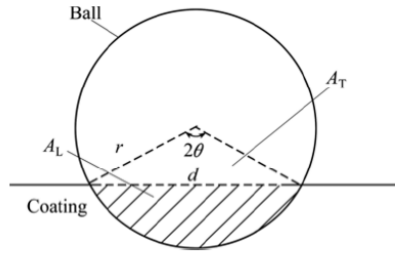
Fig. 1 Diagram for derivation of wear volume loss in wear testing

$$\sin\theta = \frac{d}{2r}, \quad \theta = \sin^{-1}\left(\frac{d}{2r}\right).$$

The area is subtended by 2θ, $A_\theta = \pi r^2 \dfrac{2\theta}{2\pi} = r^2 \sin^{-1}\left(\dfrac{d}{2r}\right).$

Area of the triangle $A_T = \dfrac{1}{2}d\sqrt{r^2 - \left(\dfrac{d}{2}\right)^2} = \dfrac{d}{4}\sqrt{4r^2 - d^2}.$

The shaded worn away area is

$$A_L = A_\theta - A_T = r^2 \sin^{-1}\left(\frac{d}{2r}\right) - \frac{d}{4}\sqrt{4r^2 - d^2} \quad (1)$$

Hence, the wear volume loss is

$$V_{loss} = A_L L = L\left[r^2 \sin^{-1}\left(\frac{d}{2r}\right) - \frac{d}{4}\sqrt{4r^2 - d^2}\right] \quad (2)$$

where L is the length of the wear track; r is the radius of the ball used for wear testing (6 mm); d is the wear track width.

$$K = \frac{V_{loss}}{SF} \quad (3)$$

where K is wear rate; S is the sliding distance; F is the applied load.

The wear track was measured with the optical microscope (Olympus BX60M), and the wear volume loss and wear rate were also calculated by Eqs. (2) and (3), respectively.

3 Results and discussion

3.1 Phase structure and orientation

Figure 2 shows the XRD patterns of Zn and Zn−Bi coatings deposited at 20 and 30 mA/cm^2 for 30 min. The two main peaks of the Zn coatings were Zn (101) and Zn (100). There were no different phases in the Zn or Zn−Bi coatings with different current densities. However, co-deposition of Bi into Zn matrix showed the Bi phase and changed the grain texture. Upon incorporation with Bi, the Zn (101) peak was decreased at both current densities. However, Zn (002) was slightly enhanced under the current density of 30 mA/cm^2.

The relative texture coefficients of Zn and Zn−Bi electrodeposition are shown in Tables 2 and 3, respectively. The relative texture coefficient (RTC) of the Zn coatings was calculated using the following equation [12,13]:

$$RTC_{hkl} = \frac{I_{hkl}/I_{hkl}^0}{\sum(I_{hkl}/I_{hkl}^0)}$$

where I_{hkl} and I_{hkl}^0 are the diffraction intensities of the hkl plane measured in the diffractogram of the deposit and the standard Zn powder sample. SEN et al [14] reported that a plane was namely as preferred orientation
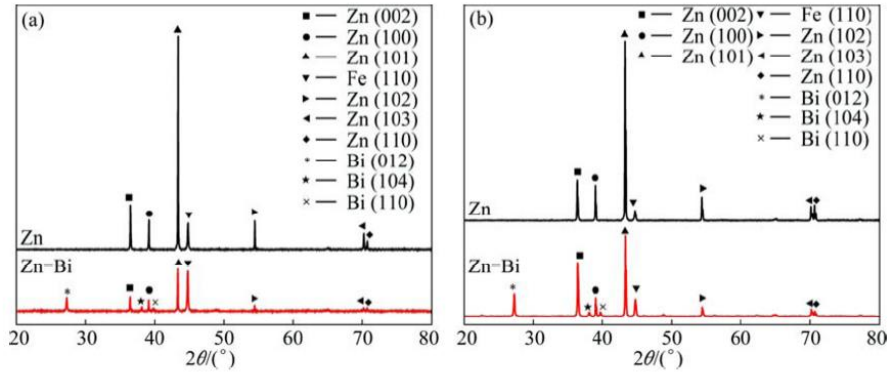
Fig. 2 XRD patterns of Zn and Zn−Bi composite coatings deposited at 20 mA/cm² (a) and 30 mA/cm² (b)

Table 2 Relative texture coefficient (RTC) of Zn coatings

No.	Orientation	20 mA/cm²			30 mA/cm²		
		I_{hkl}	I^0_{hkl}	RTC_{hkl}	I_{hkl}	I^0_{hkl}	RTC_{hkl}
1	Zn (002)	3146	15362	0.328	3038	21443	0.251
2	Zn (100)	8190	11614	1.128	9173	16142	1.006
3	Zn (101)	29012	28919	1.605	39968	40206	1.759
4	Fe (110)	555	602	1.475	357	477	1.324
5	Zn (102)	3517	8190	0.687	3753	11496	0.578
6	Zn (103)	2128	7311	0.466	2085	10186	0.362
7	Zn (110)	2314	6154	0.601	2919	8518	0.606

Table 3 Relative texture coefficient (RTC) of Zn−Bi coatings

No.	Orientation	20 mA/cm²			30 mA/cm²		
		I_{hkl}	I^0_{hkl}	RTC_{hkl}	I_{hkl}	I^0_{hkl}	RTC_{hkl}
1	Bi (012)	1183	1183	1.268	1901	1901	1.359
2	Zn (002)	5155	5425	1.205	9572	9538	1.363
3	Bi (104)	237	423	0.710	397	691	0.781
4	Zn (100)	2586	4124	0.795	2523	5616	0.610
5	Bi (110)	355	439	1.025	570	691	1.121
6	Zn (101)	10226	10226	1.268	10488	11870	1.200
7	Fe (110)	1521	1521	1.268	1019	1019	1.359
8	Zn (102)	1318	2907	0.575	1382	3490	0.538
9	Zn (103)	1082	2603	0.527	1400	3698	0.514
10	Zn (110)	811	2180	0.472	916	2471	0.504

if its texture coefficient was greater than 1.0. Based on this calculation, two similar preferred crystal orientations of Zn (100) and Zn (101) occurred at different current densities. Upon addition of Bi, the preferred crystal orientations changed to Zn (002) and Zn (101). A similar trend has also been reported with the incorporation of MoS₂ particles into Zn electrolyte where the preferred

crystal orientation changed from Zn (002) to Zn (101) and Zn (112) [7].

3.2 Microstructure characterization

Figure 3 depicts the top-view morphology of Zn and Zn−Bi coatings. The irregular microstructure shape was observed on the pure Zn coating. In the presence of Bi, a

finer and round structure formed in the Zn−Bi composite coating. This might be due to the fact that Bi provided more nucleation sites and inhibited the growth of Zn metal. Hence, Zn−Bi composite coating showed a fine-grained structure. Similar results were also reported in the case of incorporation TiO_2 [15,16], or MoS_2 [7] into Zn electrodeposition.

The cross-sectional microstructures of Zn and Zn−Bi coatings are shown in Fig. 4. A thicker coating was deposited in the composite coating compared with the pure Zn electrodeposition. The thicknesses of Zn−Bi composite coating deposited at 20 and 30 mA/cm^2 were (10.6±0.4) and (16.9±0.9) μm, and (7.5±0.7) and (14.1±1.4) μm for Zn coating, respectively, indicating that Bi ions enhanced the deposition rate.

3.3 Chemical analysis

Table 4 shows EDS analysis of the Bi content electrodeposited in the Zn coating at different current densities for the same deposition time of 30 min. The Bi content in the coating increased with the current density. This implies that the higher current density would
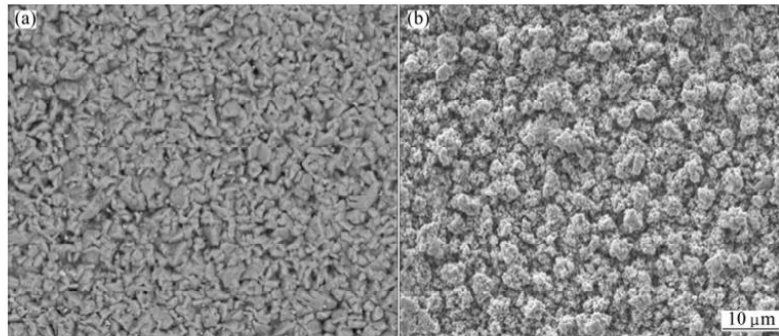

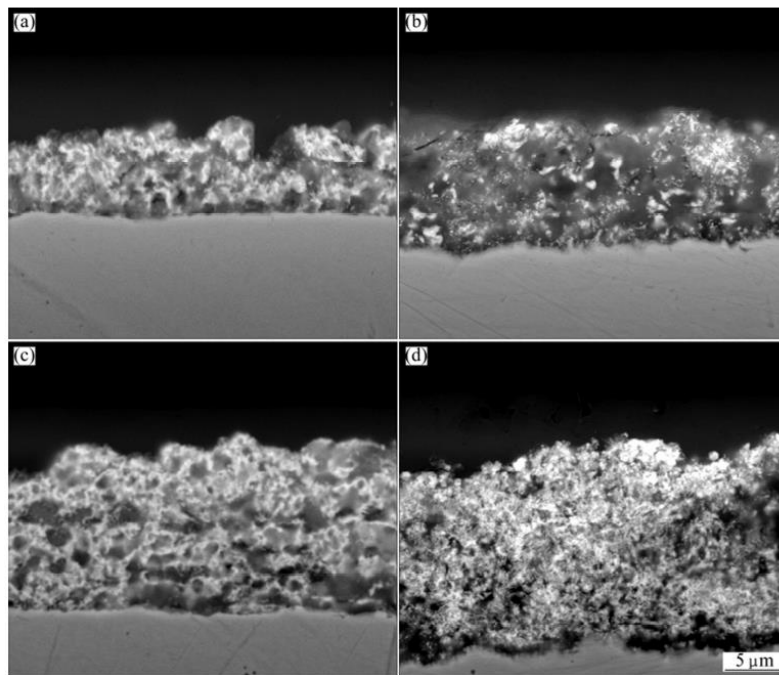Fig. 3 Top surface morphologies of Zn coating (a) and Zn−Bi coating (b) deposited at 30 mA/cm^2

Fig. 4 Cross-sectional morphologies of Zn (a, b) and Zn−Bi (c, d) coatings at different current densities: (a, c) 20 mA/cm^2; (b, d) 30 mA/cm^2

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