ELSEVIER Science Press
Available online at www.sciencedirect.com
ScienceDirect
Trans. Nonferrous Met. Soc. China 25(2015) 199−205
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

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

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Received 21 February 2014; accepted 1 July 2014

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.

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DOI: 10.1016/S1003-6326(15)63596-8

Table 1 Composition of electroplating bath and processing parameters

Zn electrolyte		Bi electrolyte			Deposition parameter		
ρ(NaOH)/($g\cdot L^{-1}$)	ρ(ZnO)/($g\cdot L^{-1}$)	$c(Bi(NO_3)_3\cdot 5H_2O)$/($mol\cdot L^{-1}$)	c(Tartaric acid)/($mol\cdot L^{-1}$)	c(KOH)/($mol\cdot L^{-1}$)	Current density/($mA\cdot cm^{-2}$)	Deposition time/min	Agitation speed/($r\cdot min^{-1}$)
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.

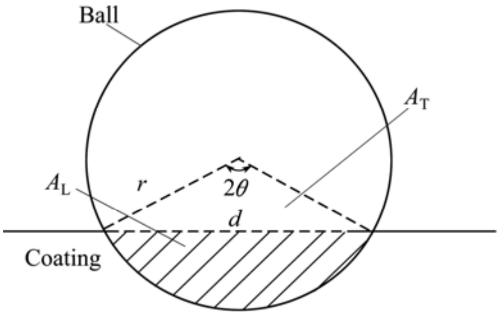

Fig. 1 Diagram for derivation of wear volume loss in wear testing

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

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

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

Hence, the wear volume loss is

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

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.

$$K=\frac{V_{loss}}{SF} \tag{3}$$

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]:

$$\mathrm{RTC}_{hkl}=\frac{I_{hkl}/I_{hkl}^0}{\sum(I_{hkl}/I_{hkl}^0)}$$

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

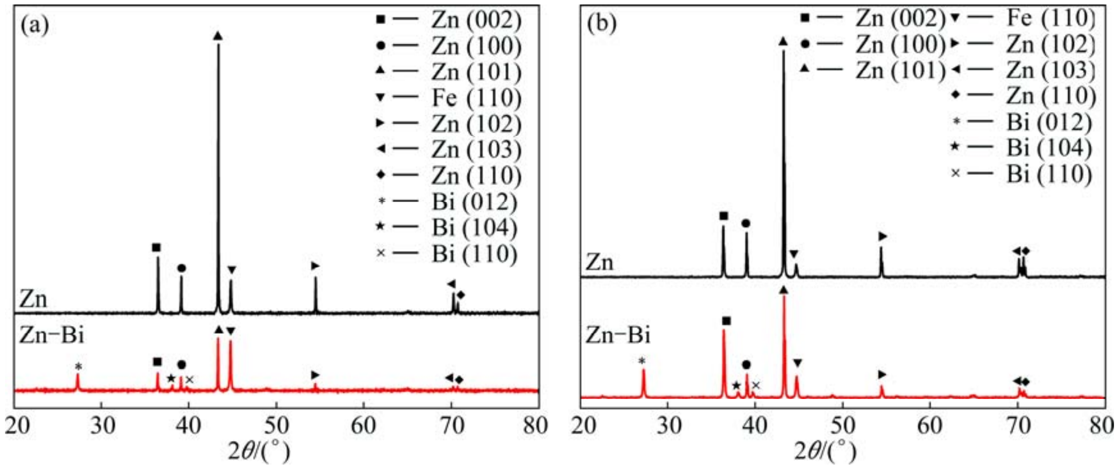

Fig. 2 XRD patterns of Zn and Zn−Bi composite coatings deposited at 20 mA/cm^2 (a) and 30 mA/cm^2 (b)

Table 2 Relative texture coefficient (RTC) of Zn coatings

No.	Orientation	20 mA/cm^2			30 mA/cm^2		
		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/cm^2			30 mA/cm^2		
		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 MoS_2 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

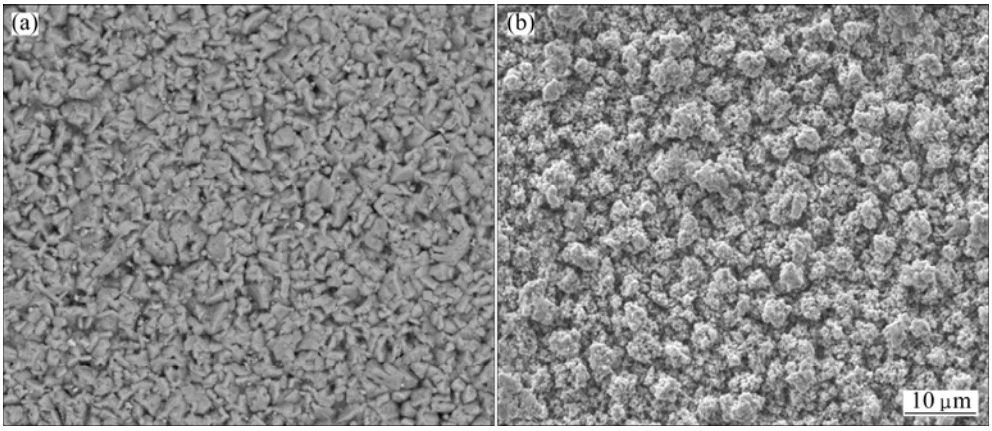

Fig. 3 Top surface morphologies of Zn coating (a) and Zn−Bi coating (b) deposited at 30 mA/cm^2

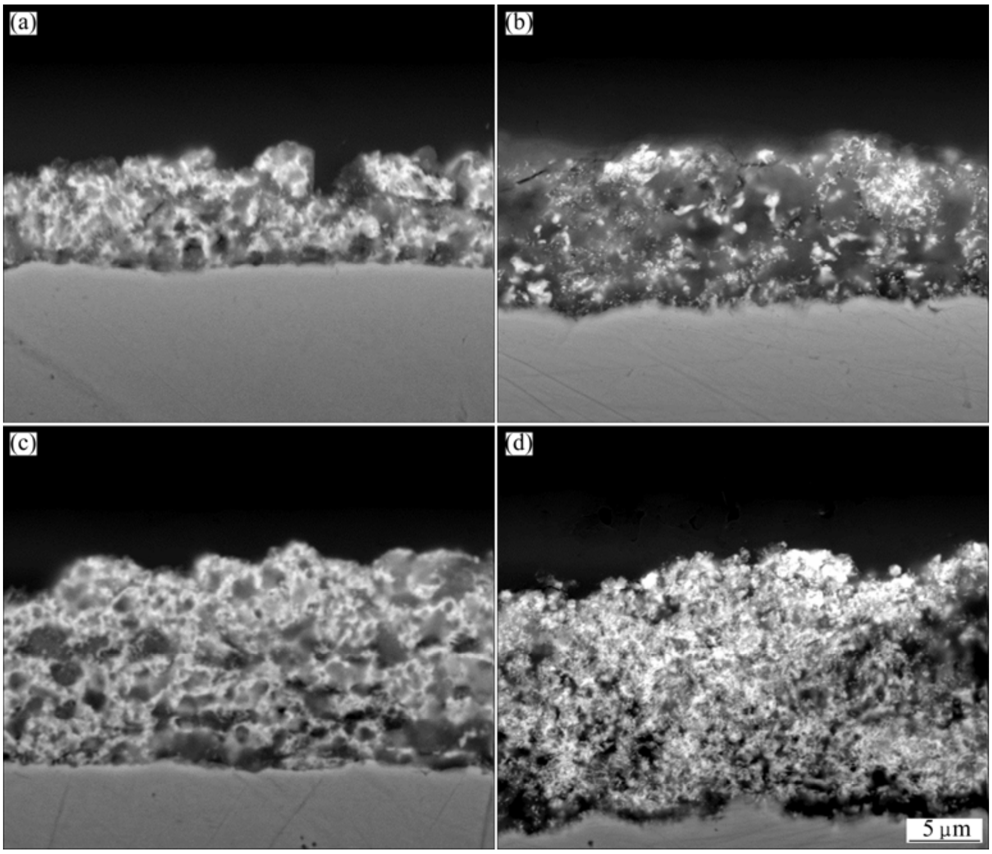

Fig. 4 Cross-sectional morphologies of Zn (a, b) and Zn−Bi (c, d) coatings at different current densities: (a, c) 20 mA/cm^2; (b, d) 30 mA/cm^2

Table 4 EDS results of Bi content electrodeposited in Zn−Bi coating at different current densities

Coating	x(Bi)/%
Zn−Bi coating deposited at 20 mA/cm²	1.38±0.29
Zn−Bi coating deposited at 30 mA/cm²	3.18±0.41

promote more Bi ions deposition. SHI et al [17] also reported that the content of codeposition of SiC in the Ni−Co coating was increased with increasing the current density up to 20 mA/cm². By increasing the current density, there was a tendency for more particles to deposit on the substrate.

3.4 Mechanical properties

3.4.1 Microhardness

The microhardness of the coatings deposited at two current densities is shown in Fig. 5, showing a significant improvement of hardness by addition of Bi. The average microhardness of Zn coating deposited at the 20 and 30 mA/cm^2 are HV 102 and HV 108, respectively. With Bi addition, the microhardnesses increase to HV 183 and HV 200, respectively. The hardness is increased by almost 2 times with just the addition of 1 mL Bi electrolyte into 70 mL of Zn bath solution.

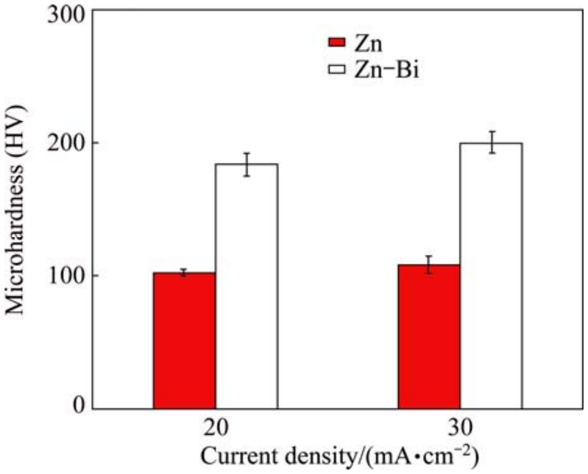

Fig. 5 Microhardness of Zn and Zn−Bi coatings deposited at different current densities

In comparison, only a small increase of microhardness at the higher current density for the Zn−Bi composite coatings is found, even though the Bi contents are quite different with different current densities. This implies that Bi content is not the only influential factor for the mechanical property. This result also shows the same trend with the addition of Bi into the Cu coating in our previous study [18].

It is known that several factors influence the mechanical properties of composite coatings, including dispersion strengthening due to the Orawan mechanism, and grain-refinement effect. The second phase of Bi is insoluble with the Zn metal, which is well dispersed in the Zn matrix and hinders the dislocation movement in the alloy [19]. The grain refinement strengthening mechanism follows the Hall−Petch relationship. As shown in Fig. 3, a fine grained structure formed with the addition of Bi into Zn coating. The higher density of grain boundaries could impede the movement of dislocation, and thus enhance the microhardness [16,20]. PARAVEEN and VENKATESHA [16] also reported that the addition of TiO_2 into Zn coating enhanced the microhardness due to the fine grained structure of the deposit.

3.4.2 Wear testing

Figure 6 shows the volume loss and wear rate of the coatings deposited at different current densities. The volume loss or wear rate of the Zn−Bi composite coating is lower compared with that of the Zn coating, indicating that the Zn−Bi coating has a better wear resistance compared with the Zn coating.

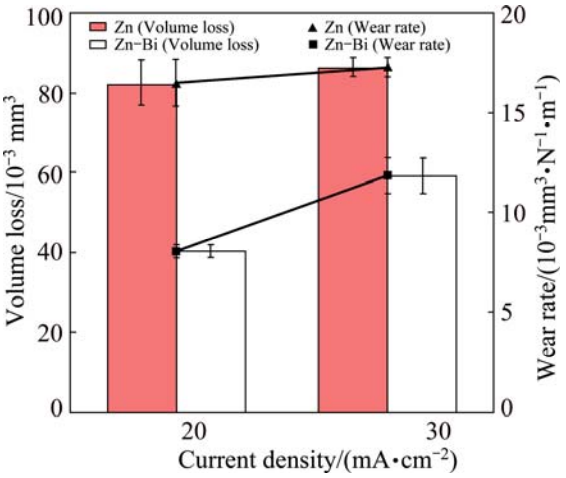

Fig. 6 Volume loss and wear rate of Zn and Zn−Bi coatings at different current densities

Figure 7 represents the wear tracks of Zn and Zn−Bi composite coatings. The widths of wear tracks of Zn and Zn−Bi composite coatings were ~660 μm and 525 μm, respectively. Many plough lines were observed on the surface of the Zn coating. In contrast, the wear tracks on the Zn−Bi composite coatings were narrower and the plough lines were shallower, indicating that the Zn−Bi composite coatings had improved the wear resistance.

According to the Archard’s law [21], the volume loss during the sliding wear is proportional to the work done by the friction force and inversely to the hardness of the contact surface. Hence, the higher microhardness of the coating had a lower volume loss. The microhardness of the Zn−Bi coatings as indicated earlier, proved that the lower wear volume loss of composite coating came from the higher microhardness.

An opposite effect was found with the coating

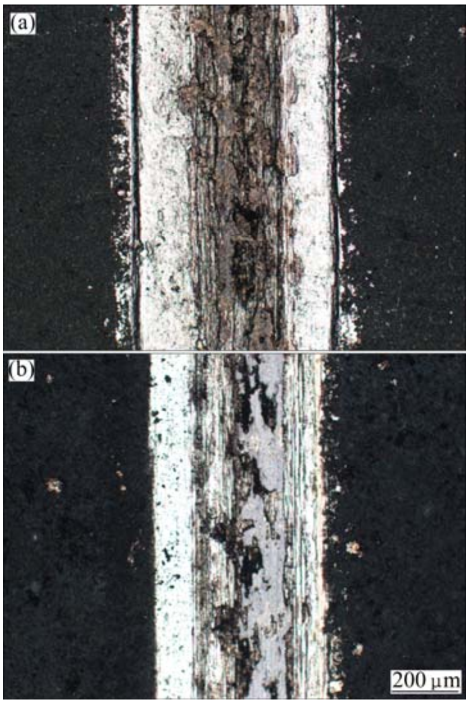

Fig. 7 Wear tracks on coatings deposited at 20 mA/cm² for 30 min: (a) Zn coating; (b) Zn−Bi coating

deposited at different current densities. At the higher current density of 30 mA/cm^2, both Zn and Zn−Bi coatings showed a slightly higher microhardness than those deposited at 20 mA/cm^2. However, the volume loss did not show improvement, implying that other factors such as microstructure may also play a role in the wear performance [22]. It is interesting to note that there are two opposing properties which are ductility and hardness that could influence the wear value [22]. A softer surface normally contains higher ductility and greater plastic deformation to reduce the wear volume loss. On the other hand, increasing the hardness enhances the wear resistance by retarding the dislocation motion. However, the increment of the hardness decreases the ductility of the material at the same time.

4 Conclusions

The Zn−Bi composite coating was prepared by ionic co-discharge deposition. The coating possesses a finer grained microstructure with dispersive Bi phase. The Bi content could be adjusted by controlling the deposition current density and time. The mechanical properties including hardness and wear resistance are improved significantly. The incorporation of Bi also enhances the deposition rate.

Acknowledgements

The authors would like to thank the technical staff and research group members in the Department of Chemical and Materials Engineering, the University of Auckland, for their valuable assistance. See Leng TAY appreciates the financial support from the Bright Spark Unit, University of Malaya.

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离子共放电沉积法制备 Zn−Bi 复合镀层及其性能

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摘 要：采用离子共放电沉积法制备 Zn−Bi 复合镀层并对其性能进行研究。结果表明，Bi 可以有效地抑制电镀过程中 Zn 晶粒的生长，有利于镀层晶粒的细化，从而使得 Zn−Bi 复合镀层与纯锌镀层相比具有优异的力学性能。该方法制备的 Zn−Bi 复合镀层，其显微硬度是纯锌镀层的 2 倍,同时具有更高的耐磨性。

关键词：Zn−Bi 复合镀层；离子共放电沉积；电镀；力学性能

(Edited by Xiang-qun LI)