



Study on corrosion resistance of zinc alloy coating of mechanical plating by electrochemical method

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ABSTRACT

Electrochemical method was utilized to study the corrosion resistance of zinc alloy coatings. These coating, plated by mechanical plating, include pure zinc coating, Zn-Al coating, Zn-Mn (5:1) coating, Zn-Mn-Al (5:1:1) coating. The parameters in Stern-Geary formula were obtained by several tests. According to these parameters, corrosion electric current was calculated. The corrosion resistances of these zinc alloy coatings were compared by corrosion electric current. Results indicate that the corrosion resistance of Zn-Al coating was the best in these zinc alloy coatings. And the sequence of these coatings ranged from high corrosion resistance to low corrosion resistance was as follow, Zn-Al > Zn-Mn-Al (5:1:1) > Zn > Zn-Mn (5:1).

Keywords: mechanical plating; electrochemical; corrosion resistance; zinc alloy coating

INTRODUCTION

Mechanical plating can plate metal to the surface of workpiece to form coating by mechanical energy produced by medium impact [1]. Mechanical plating process need not heating and electric field don't act directly in this process. Therefore, less energy and metal powders were needed in this process [2]. It was reported in literatures [3-6] that the power consumption of mechanical plating is only five percent of electroplating. And zinc consumption in mechanical plating process is only thirty to fifty percent of hot dip galvanizing. Consequently, the cost of mechanical plating is far less than electroplating and hot dip plating. Because the pure zinc coating is comparatively monotonous and the corrosion resistance of pure zinc coating is inferior to that of some alloy coatings, more and more alloy coating were studied by researchers of all the world [7-9]. In this study, electrochemical method was utilized to study the corrosion resistance of zinc alloy coatings made by ourselves. The corrosion resistances of different series of zinc alloy coatings were compared. The relationship of corrosion metal content and corrosion resistance was studied.

EXPERIMENTAL SECTION

Reagents and Instruments

Reagents. NaCl solution (3%); ethanol;

Instruments. LZ3-200-type function recorder; HDV-7 transistor potentiostat; Platinum electrode; calomel electrode; volumetric flask(1000ml, 2000ml); electrolyzer (self-made, the electrolyzer used in this experiment was shown in Figure 1);

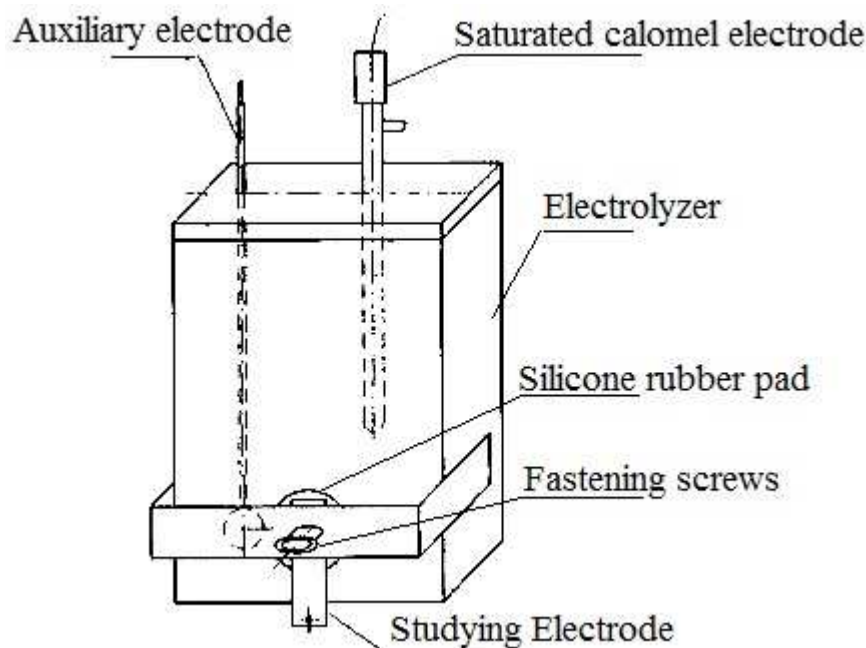


Figure 1. The schematic diagram of the electrolyzer used in this experiment

Experimental principle

There were many electrode reactions on the metal surface in corrosion process. The whole electrode system was a coupling system containing two or many electrode reactions [10]. Therefore, electrochemistry can be used to study the corrosion resistance of metal [11, 12]. Electrode potential and electric current density were the main parameters to be measured by electrochemical method when studying corrosion resistance of metal. Electric current density indicated the electrochemical reaction speed per unit area on metal surface. In electrochemical theory, Stern formula and Tafel formula were used in this experiment. At 1905, Tafel proposed that between electric current I closing to single electrode reaction speed on metal surface and metal potential E , their relationship obeyed empirical formula [13], shown as Formula (1).

$$E = a + b \log I \quad (1)$$

Corrosion speed formula was shown as Formula (2). When applied polarization was large, it can be deduced by Formula (2) that the relationship of impressed electric current and electrode polarization were straight on the ΔE - $\log i$ semi-logarithmic coordinates and meet Tafel relationship.

$$I = I_{corr} \left\{ \exp\left[\frac{2.303(E - E_{corr})}{b_a}\right] - \exp\left[-\frac{2.303(E - E_{corr})}{b_c}\right] \right\} \quad (2)$$

At 1957, according to electrochemical reaction kinetics and mixed potential theory, Stern and Geary deduced linear polarization formula, also called Stern-Geary formula, shown as formula (3).

$$i_{corr} = \frac{b_a b_c}{2.3(b_a + b_c)} \cdot \frac{1}{Rp} \quad (3)$$

where b_a , b_c were Tafel constants of anode and cathode polarization respectively.

It can be seen from the formula that if R_p , b_a and b_c were obtained, i_{corr} can be calculated by Stern-Geary formula. The value of i_{corr} was inversely proportional to metal corrosion resistance. Therefore, the corrosion speeds of different metals can be compared according to the value of i_{corr} [14]. A three-electrode system, consisting of a research electrode, a reference electrode and an auxiliary electrode, was used in specific electrochemical measurements [15].

Experimental methods

Measurement of R_p . According to Stern-Geary formula, galvanostatic by-point method was utilized to determine polarization potential. A series of electric currents, $I_1, I_2, I_3, \dots, I_n$, $I_n = nI_1$, were applied on the samples in step approach. After each adjustment of applied electric current, the values of polarization potential were recorded every two minutes. From this, a line can be drawn and its slope was the value of R_p , $R_p = \Delta E / \Delta I$, ($E < 10\text{mV}$).

Measurement of b_a and b_c . It can be known by Tafel empirical formula and corrosion speed formula that

$$b_a = \left(\frac{dE_a}{d \log i_a} \right)_{E \gg E_{\text{corr}}}$$

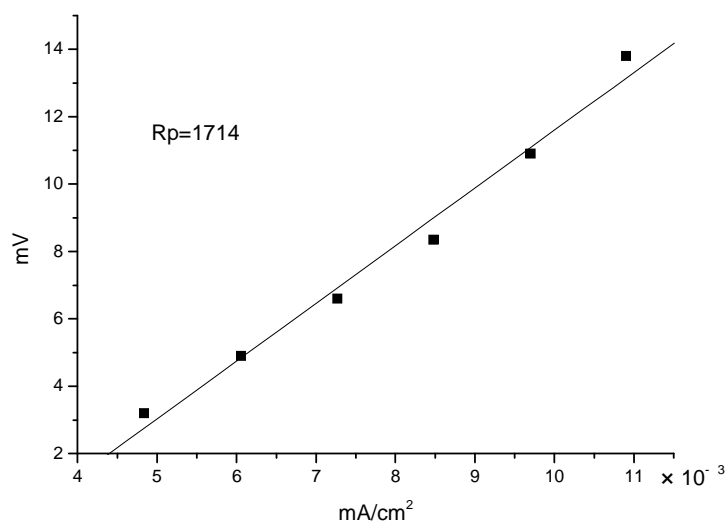
$$b_c = \left(\frac{dE_c}{d \log i_c} \right)_{E \ll E_{\text{corr}}}$$

Galvanostatic by-point method was also used to determine anode polarization potential and cathode polarization potential. Applying methods of electric current was similar to that used in determining R_p . Electric currents, $I_1, I_2, I_3, \dots, I_n$, $I_n = nI_1$, were applied on the samples in step approach. Every step was 0.5mA. After each adjustment of applied electric current, the values of polarization potential were recorded when the electric current was stable. The intervals of recording were different. At normal condition, the intervals of the first four points, about 10-15 minutes, were longer than followed points, about five minutes. Then, corresponding E-log*i* diagram was drawn on Cartesian coordinate paper and its slope was obtained by calculating. The average value of three groups of data was the value of b_a .

The method of measuring b_c was similar to that of measuring b_a . The different point was that polarization current was set to be negative and galvanized sheet became electrode to be studied.

RESULTS AND DISCUSSION

According to the test principle, the values of polarization potential were recorded at same intervals. Polarization curves of different series of coating were drawn and the values of R_p were obtained from polarization curves. The value of b_a and b_c were obtained from E-log*i* curves. Then, the values of R_p , b_a and b_c were put into Stern-Geary formula and then the value of i_{corr} was obtained by calculating. Polarization curves of Zn-Mn (5:1) were shown in Figure 2. E-log*i* curves of Zn-Mn (5:1) were shown in Figure 3. Due to limited space, polarization curves and E-log*i* curves of other zinc alloy won't be shown in this paper. The electrochemical test results of zinc alloy coating were listed in Table 1.



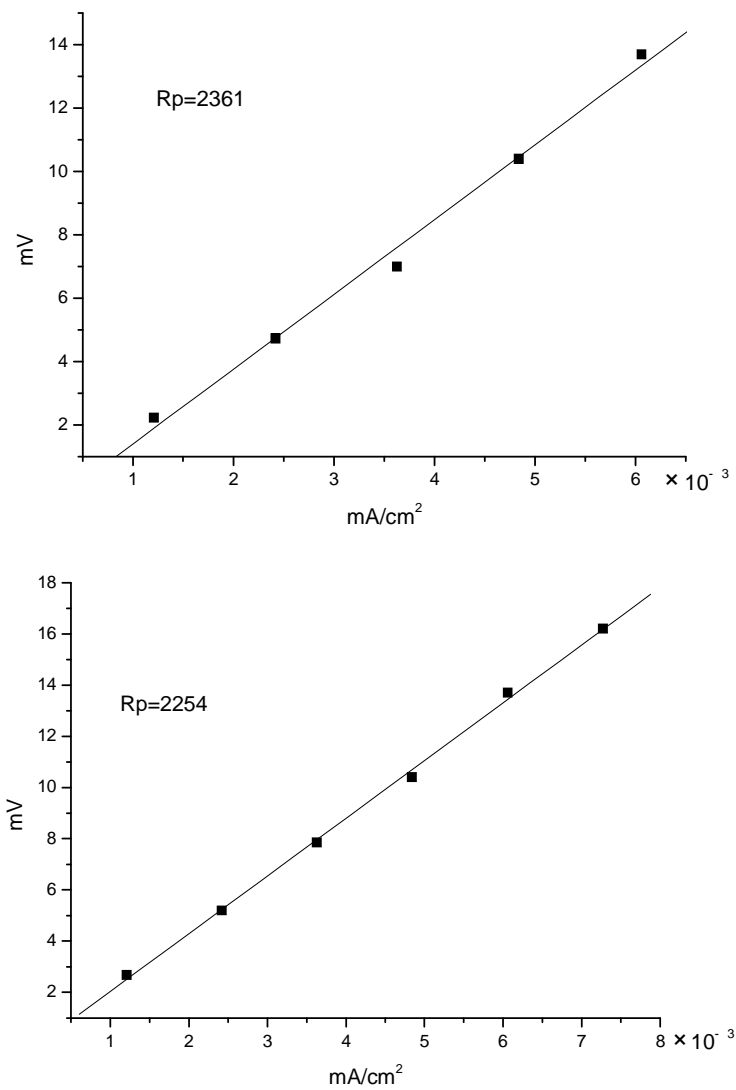


Figure 2. Polarization curves of three Zn-Al parallel samples

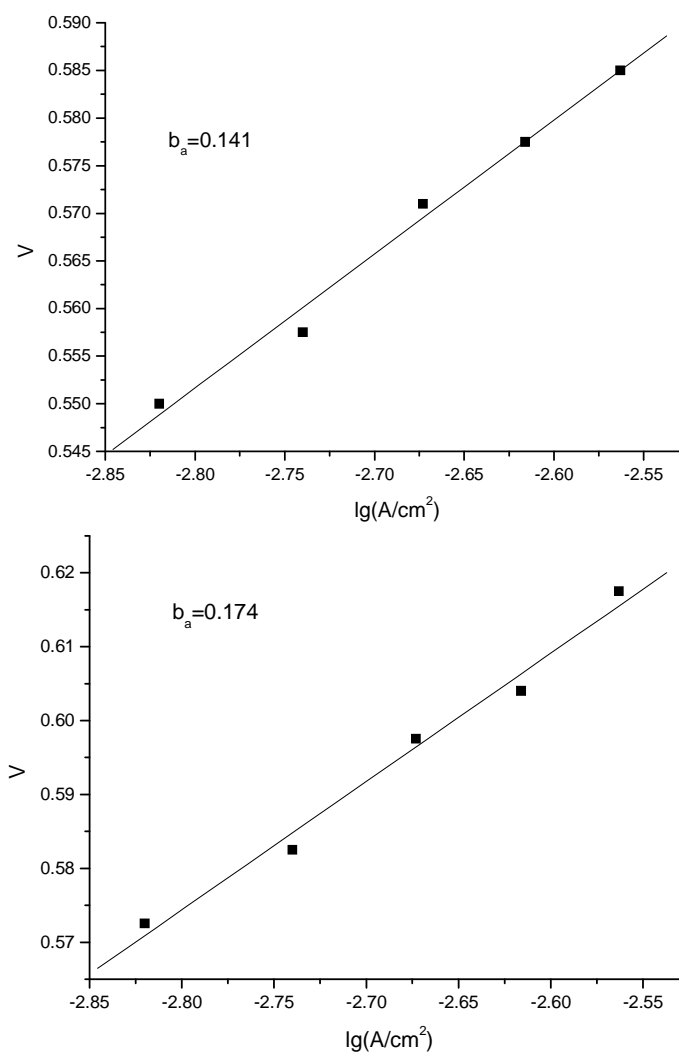


Figure 3. E-logi curves of three Zn-Al parallel samples

Table 1. Electrochemical test results of zinc alloy coating

Samples	Manganese content (%)	Rp(Ω) Test values	Rp Average values	b _a (V) Test values	b _a Average values	-b _c (V) Test values	-b _c Average values	i _{corr} (mA)
Pure Zn		1024	1037	0.316	0.290	0.116	0.121	0.0358
		1117		0.298		0.129		
		969		0.256		0.118		
Zn-Al		1714	2110	0.178	0.164	0.116	0.121	0.0143
		2361		0.141		0.129		
		2254		0.174		0.118		
Zn-Mn (5:1)	2.21	667	727	0.174	0.178	0.116	0.121	0.0431
		786		0.187		0.129		
		728		0.172		0.118		
Zn-Mn-Al(5:1:1)	2.51	887	962	0.277	0.275	0.116	0.121	0.0380

It can be indicated that the corrosion current density of Zn -Al alloy coating was the smallest among all these zinc alloy coatings. Therefore, the corrosion resistance of Zn -Al coating was the best. When Zn-Mn series of coatings were compared with each other, it can be found that if a little aluminum was added into Zn-Mn alloy coating, the corrosion current density of the coating would decrease. This can lead to increasing of corrosion resistance.

CONCLUSION

In this study, electrochemical method was utilized to study the corrosion resistance of zinc alloy coatings. The parameters in Stern-Geary formula were obtained by several tests. According to these parameters and their polarization curves, corrosion electric current was calculated. The corrosion resistances of these zinc alloy coatings were compared with each other by corrosion electric current. Results indicate that the corrosion resistance of Zn-Al

coating was the best in these zinc alloy coatings. And the sequence of these coatings ranged from high corrosion resistance to low corrosion resistance was as follow, Zn –Al> Zn-Mn-Al (5:1:1)>Zn> Zn-Mn (5:1). These series of tests verified that aluminum can improve the corrosion resistance of zinc alloy. These experiments have guiding significance for mechanical plating applications in industry.

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