

Electrochemical evaluation of zinc and magnesium alloy coatings deposited on electrogalvanized steel by PVD

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Abstract: Zinc alloy coating attracted much attention due to its high anti-corrosive properties. Particularly, zinc alloy coatings containing magnesium was considered a promising metallic alloy due to a remarkable improvement of corrosion resistance. The proper magnesium content for Zn–Mg alloy coatings was studied. The samples were prepared using thermal evaporation method. The influence of Zn–Mg alloy coating on corrosion resistance was evaluated using immersion test, potentiodynamic test, and galvanic test in 3% NaCl solution at room temperature. The results show that the corrosion resistance of Zn–Mg alloy coatings is strongly dependent on magnesium content. Corrosion potential decreases with increasing magnesium content, whereas current density increases up to 15% magnesium content, and passivity region was found only in Zn–Mg coatings.

Key words: magnesium; zinc; corrosion resistance; physical vapor deposition; coating; electrochemistry

1 Introduction

Metallic coatings containing zinc (Zn) have been commercially used to improve the corrosion resistance of various steel construction materials. These coatings provide anti-corrosive barriers and offer galvanic protection to steel substrates applied in automotive and building. When Zn-coated steel is exposed to a corrosive environment, the active Zn tends to produce corrosion products like ZnO or Zn(OH)₂ [1–6]. These low conductive corrosion products can act as anti-corrosive barriers against corrosive environments. A function of sacrificial anode is expected by the active Zn coating when a bare steel substrate is exposed to a corrosive environment.

However, as severe corrosive environmental issues garner great attention, the development of Zn coating method with better corrosion resistance is required. Although an undamaged Zn coating on steel has good corrosion resistance, this good protection cannot be expected in severely corrosive environments without increasing thickness in the conventional coating method. Thus, coatings offering better galvanic or sacrificial protection for steel are desired without increasing Zn coating thickness. To this end, Zn–Mg alloy coatings were studied to extend the lifetime of steel constructions

and save cost, and great effort has been exerted to optimize Zn coating composition by alloying it with Mg [7–13].

In this study, Zn–Mg alloy coatings were deposited onto electrogalvanized (EG) steel substrate by the PVD method. After that, the influence of the Zn–Mg alloy coating on corrosion resistance was evaluated using immersion test, potentiodynamic test, and galvanic test in a 3% NaCl solution at room temperature.

2 Experimental

2.1 Specimen preparation

The vacuum evaporation method was used to prepare Zn–Mg alloy coatings on an EG steel sheet. The thickness of Zn–Mg coatings was approximately 2.7 μm. Figure 1 shows a schematic diagram of the experimental setup. The deposition conditions are shown in Table 1. EG substrates were ultrasonically cleaned in a bath of trichloroethylene for 10 min. After the substrate was placed on the cathode, the chamber was pumped up to pressure of 6.67×10^{-4} Pa. The substrates were pre-cleaned to remove the surface contamination using argon ion for 5 min at a bias voltage of –400 V at pressure of 93.33 Pa and the content of magnesium was controlled by the power of a heating coil at 5%–25% (mass fraction).

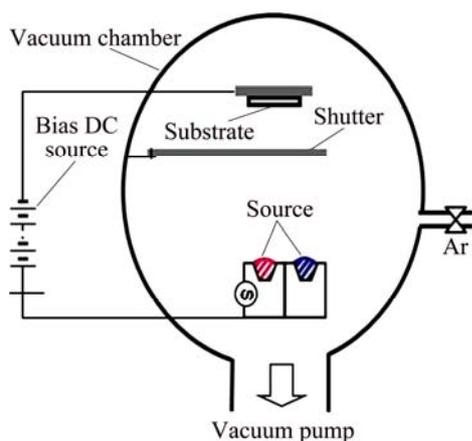


Fig. 1 Schematic diagram of vacuum deposition apparatus

Table 1 Deposition condition of Zn–Mg coating

Substrate	Argon pressure/ Pa	Bias voltage/V	Mg content/%	Evaporation metal
Electro galvanized steel sheet	6.6×10^{-2}	0	5, 10, 15, 20, 25, 30	99.99 % magnesium and zinc

2.2 Corrosion test

An immersion test was carried out to evaluate the corrosion behavior of Zn–Mg alloy coatings (pure Zn, Zn–5%Mg, Zn–10%Mg, Zn–15%Mg, Zn–20%Mg, and Zn–25%Mg). Corrosion potential (φ_{corr}) was measured using a sodium saturated calomel electrode (SSCE) in 3% NaCl solution for 400 h. A potentiodynamic test was conducted to examine the effect of magnesium on the corrosion resistance of Zn–Mg alloys in 3% NaCl solution by Potentio-stat (CMS 100 System; Gamry Instruments, USA). An SSCE and a platinum electrode were used as reference electrode and counter-electrode, respectively. The φ_{corr} was anodically polarized from -200 to $+1000$ mV with scanning rate of 1 mV/s. Experimental measurements of galvanic corrosion current and potential were carried out in 3% NaCl solution at room temperature and the test time was 10 h. The distance between the reference electrode and the working electrode was kept at 10 mm.

3 Results and discussion

3.1 Sacrificial anodic protection of Zn–Mg alloy coatings

The open-circuit potential plot of Zn–Mg alloy coatings illustrated with potential versus immersion time is shown in Fig. 2. Typical potential–time curves were obtained for all specimens by immersion tests in 3.0% NaCl solution. The open-circuit potential of the Zn–Mg alloy coatings initially shows an active potential under

-1.2 V and increases rapidly to -1.0 V with exposure time. The potential keeps at -1.0 V within 150 h, and then increases gradually up to -0.65 V. These variations of potential indicate that all Zn–Mg coatings consist of one outer layer and an inner double layer [13–16].

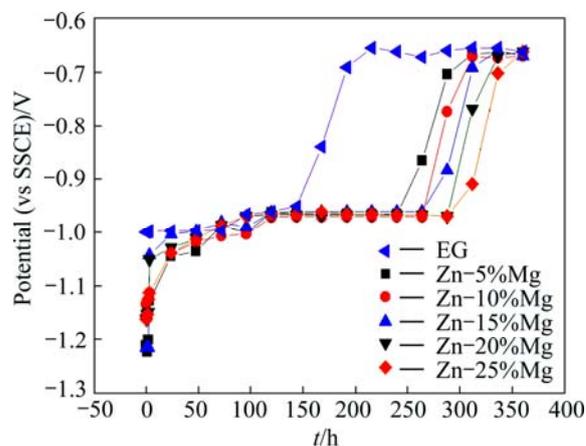


Fig. 2 Potential–time curves during corrosion of Zn–Mg alloy coatings in 3.0% NaCl solution at room temperature

Of note, the inner double layer, but not the outer layer, contributes to enhancing the corrosion resistance of the conversion coating. This finding can be considered an effect of the sacrificial anode of the Zn–Mg and Zn coating.

Figure 3 shows a schematic diagram of the corrosion process of Zn–Mg alloy coating over time. In the first stage, magnesium, which remains without forming Zn–Mg alloys on the top layer, makes the potential of the Zn–Mg alloys more active for about 100 h, after which the Zn–Mg alloy layer deteriorates in response to the corrosive attacks. At that time, a mixed potential, which consists of the potential of Zn and Zn–Mg alloy, is close to the Zn potential and continually supplies electrons to protect an Fe substrate as a sacrificial anode as shown in the second stage. Finally, in the third stage, with the consumption of almost zinc, the corrosion potential is close to that of the Fe substrate.

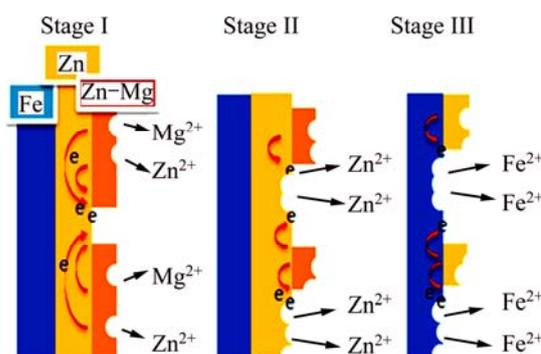


Fig. 3 Schematic diagram of corrosion mechanism of Zn–Mg alloy coating on electro galvanic steel sheet

3.2 Electrochemical properties of Zn–Mg alloy coatings

The anodic polarization tests were conducted in 3.0% NaCl solution (Figs. 4 and 5), and the respective values of φ_{cor} , I_{cor} , and passive current are shown in Table 2. From the polarization tests, we find out that as the magnesium content increases in the Zn–Mg coating surface, φ_{cor} tends to be active due to the addition of active magnesium, but I_{cor} shows a low corrosion current density in the typical range of 10% to 15% magnesium content. These phenomena, in that range, can

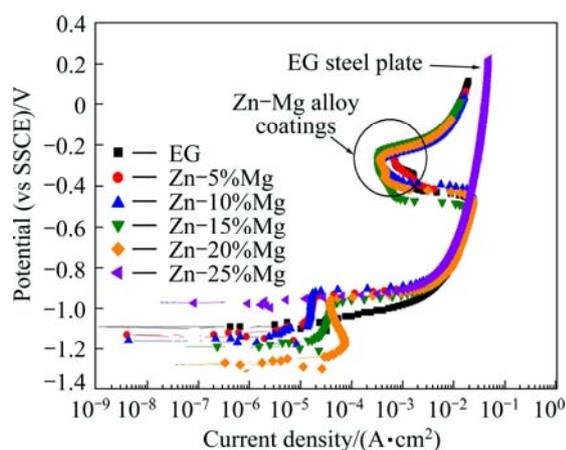


Fig. 4 Anodic polarization curves of Zn–Mg alloy coatings and EG steel plate in 3.0% NaCl solution at room temperature

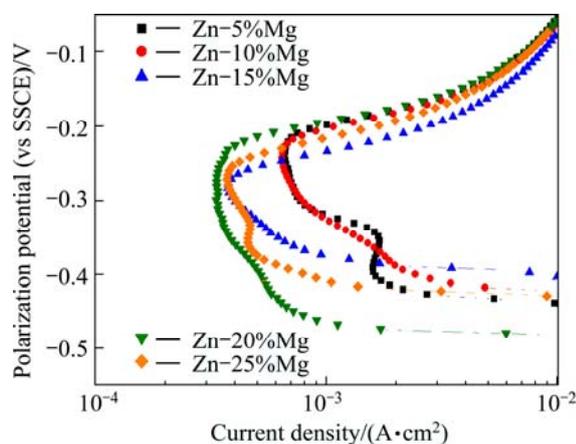


Fig. 5 Passivity curves for Zn–Mg alloy coatings in 3.0% NaCl solution at room temperature

Table 2 Results of anodic polarization test

Mg content/%	φ_{corr} (vs SSCE)/V	I_{corr} ($\mu\text{A}\cdot\text{cm}^{-2}$)	Passive current/($\mu\text{A}\cdot\text{cm}^{-2}$)
5	-1.08	3.60	6.54
10	-1.12	1.33	6.51
15	-1.15	1.07	3.71
20	-1.21	4.01	3.27
25	-1.27	5.45	3.75
Hot-dipping galvanized steel	-0.97	2.21	–

be considered that almost of the magnesium on the surface is in the form of Zn–Mg alloy. These Zn–Mg alloys develop lower corrosion rates with lower electric conductivity. On the other hand, with 20% or 25% magnesium content, extra magnesium, which cannot form Zn–Mg alloy on the top layer, has higher corrosion density since it readily reacts with the electrolyte.

Figures 4 and 5 represent the effects of magnesium on anodic polarization curves of Zn–Mg alloy coatings and hot-dipping galvanized steel sheets. As shown in Fig. 4, the curves of Zn–Mg alloy coatings show passivity in the potential range of -0.4 to -0.1 V. However, the curve of EG coating has no passivity in any potential range. The only difference between the two kinds of specimens is whether or not they contain magnesium. As such, it can be considered that magnesium contributes to passivity on Zn–Mg alloy coatings.

3.3 Galvanic corrosion

Figures 6 and 7 show the evolution of both galvanic potential and current obtained from the couple between the bare steel plate and the Zn–Mg alloy coatings with an area ratio (Zn–Mg alloy coating/bare steel plate) close to 0.1 and 10 h immersion. In each experiment, the galvanic potential follows an approximate parabolic growth up to 3 h and then remains stable. Its values decrease with the increasing of magnesium content in the alloy coatings from -0.66 V up to -0.78 V. On the contrary, the galvanic currents increase with the increase of magnesium content but level off after 6 h, and the fluctuation of the galvanic currents can be interpreted as competition between the initiation and ceasing of corrosion in various areas. It is possible that corrosion stops in a corroded area but is initiated in a new area.

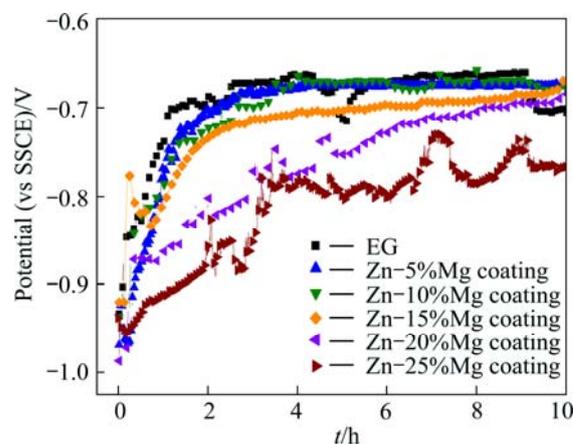


Fig. 6 Evolution of galvanic potential corresponding to coupling between Zn–Mg alloy coating and steel base metal ($S_{\text{Zn-Mg}}/S_{\text{steel}}=10\%$; $S_{\text{steel}}=1\text{ cm}^2$)

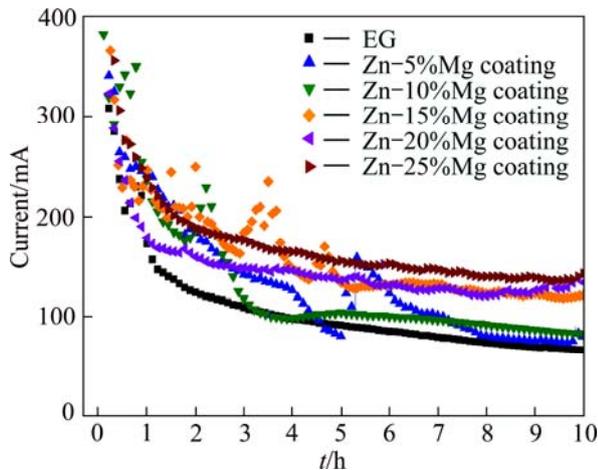


Fig. 7 Evolution of galvanic current corresponding to coupling between Zn–Mg alloy coatings and steel base metal ($S_{\text{Zn-Mg}}/S_{\text{steel}}=0.1$; $S_{\text{steel}}=1 \text{ cm}^2$)

4 Conclusions

1) The potentials of Zn–Mg alloy coatings in the immersion test initially indicated low potential for a few hours. Zn–Mg alloy coating on EG steel in that period plays an important role in improving corrosion resistance by delaying the exposure of the EG steel surface to the corrosive environment. Exposed EG surfaces participate in protecting base metal by supplying a protective current to a corroded area. At that time, the mixed potential depends on the amount of remaining Zn.

2) In anodic polarization tests in 3% NaCl solution, at room temperature, the corrosion resistance of the Zn–Mg alloy coatings strongly depended on the magnesium content. φ_{corr} decreased with magnesium content increasing, whereas current density increased up to 15% magnesium content and a passivity region was found in Zn–Mg coatings only. Specimens containing 15%–25% magnesium had lower passivity currents. Zn–Mg coatings contribute to the enhancement of the protection of EG steel through an anti-corrosive Zn–Mg layer.

3) The galvanic potential decreased with the increases of magnesium content and then leveled off. Its value was lower with magnesium content increasing, whereas the galvanic currents increased. Maintaining low galvanic potential increased galvanic current, which acts as a protection current.

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电镀锌钢材表面物理气相沉积 Zn–Mg 合金镀层的电化学性能

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摘 要: 锌合金镀层由于具有较强的耐腐蚀性能而得到广泛的关注, 特别是 Zn–Mg 合金镀层, 其耐腐蚀性能能得到显著提高。采用气相沉积方法制备不同镁含量的 Zn–Mg 合金镀层, 研究 Zn–Mg 合金镀层中镁含量对其耐腐蚀性能的影响。在 3%NaCl 溶液中进行浸泡试验、动电位测试和电偶腐蚀试验, 研究不同 Mg 含量镀层的耐腐蚀性能。结果表明, Zn–Mg 合金镀层的耐腐蚀性能与 Mg 含量显著相关, 镀层的腐蚀电位随着 Mg 含量的增加而降低, 但是腐蚀电流密度却升高, 直至 15%Mg 含量; 在 Zn–Mg 合金镀层中存在钝化区。

关键词: 镁; 锌; 耐腐蚀性能; 物理气相沉积; 镀层; 电化学

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