Research on Microstructure and Corrosion Behavior of Zinc-Magnesium Coating by Powder Impregnation

Qiuyuan Liu 1, Wendong Zhang 2, Juntao Jiang 3, Linjiang Yue 4, Wei Shen 4*, Xin Liu 1, Sheming Jiang 1 and Qifu Zhang 1

1 Laboratory of Advanced Coating Technology for Metals, China Iron and Steel Research Institute Group, National Engineering, Beijing 100081, China;
2 Linqu Inspection and Testing Center, Linqu, Shandong 262600, China;
3 Linyi Vocational University of Science and Technology, Linyi, Shandong, 276000, China;
4 Yancheng KE AO pack coating Research Institute, Yancheng KE AO Machinery Co., Ltd., Yancheng 224022, China.
Email: wells.shen@aliyun.com

Abstract. In order to improve the service life of railway fasteners under various environmental conditions, the Zn and Zn-Mg coating were prepared on the railway fastener gaskets by powder impregnation. XRD and SEM were used to characterize the phase composition, microstructure and morphology before and after the salt spray. The neutral salt spray test (NSST) and the electrochemical workstation were used to characterize the corrosion resistance of the two coatings. Results show that there was a large area of red rust on Zn coating after 480 hours of NSST, while there was no red rust on Zn-Mg coating after 1920 hours of NSST. The impedance of the Zn-Mg coating reached 1015.6 Ω·cm², about 3.65 times of the Zn coating. Zn-Mg coating current density was 3.27 μA·cm², which was only 21% of the Zn coating. MgZn₂ and Mg₂Zn₁₁ phases were easier to formed in Zn-Mg coating due to the infiltration of magnesium, forming a dense and protective layer, thereby greatly improved its corrosion resistance.

Keywords. Powder impregnation; Zn-Mg coating; salt spray test; corrosion resistance.

1. Introduction
Powder impregnation is a heat treatment process that diffuses zinc and alloy elements into the surface of iron and steel components under heating to form protective layers. It has excellent bonding performance, corrosion resistance, wear resistance and other characteristics, as well as a wide application prospect in the field of anti-corrosion engineering materials [1-3]. At present, the commonly used process is mechanical assisted powder zincification. The cylindrical or hexagonal zincification tank rotates inside the heating body. Generally, the processing of thermal diffusion coating can be realized in a sealed container in atmospheric environment. Compared with hot dip galvanizing, powder impregnating has no hydrogen embrittlement and better wear resistance. Therefore, powder impregnating has been widely used for the anti-corrosion of high-strength fasteners [4-8].

Railway fasteners are required to have excellent mechanical properties and anticorrosion ability. At present, the anti-corrosion of railway fasteners mainly adopts the technology of powder zincification and composite sealing treatment. As far as the current technology of powder zincification is concerned,
the salt spray resistance life of pure powder zincification is less than 200 hours. Therefore, sealing treatment must be carried out on the surface after galvanizing to improve its service life. After galvanizing and sealing, the salt spray resistance life can reach more than 500 hours [9-11]. However, under the conditions of wind and sand, erosion and vibration in the actual service environment, the sealing layer is easy to be worn off, resulting in premature corrosion of fasteners and failure and fracture. Zn-Mg coating has attracted the attention of many large iron and steel enterprises and scientific research institutions in the world because of its excellent corrosion resistance and notch self-healing [12-14], Japan's Kawasaki iron and Steel Company [15], Nippon Steel Company [16], Kobe Steel Institute [17], Germany's ThyssenKrupp [18], Korea's POSCO [19] and Europe's ArcelorMittal [20]. The production process and Zn-Mg coating’s anticorrosion ability have been studied and reported. At present, the methods for preparing Zn-Mg coatings mainly include aqueous solution plating [21], molten salt plating [22], hot dip plating [16] and vacuum plating [23]. There are no reports on the preparation of Zn-Mg coating by powder infiltration. Therefore, it is urgent to develop a new generation of powder Zn-Mg coating technology to achieve high corrosion resistance without sealing and meet the requirements of long service life for railway fasteners under various environmental conditions. Therefore, Zn-Mg coating was prepared on the surface of railway fastener gasket in this work.

2. Experimental

Zn-Mg coating was prepared by using multicomponent alloy carburizing furnace (model: YCKA200-70) designed and developed by Yancheng Keao Machinery Co., Ltd. The basis material is railway fastener gasket, the material is spring steel 60Si2Mn, and the size is ① 70 mm × 31 mm × 10 mm. See table 1 for the chemical composition of the gasket. The process flow of preparing Zn-Mg coating is as follows: shot blasting, preparation of infiltration agent, canning, powder impregnating and cooling. The penetrating agent used is self-made zinc-magnesium alloy powder, and the magnesium content is 1.8 wt%.

| Table 1. Main chemical elements of railway gasket (mass fraction, %). |
|---|
| Element | C | Mn | Si | P | S | Cr | Ni | Cu | Fe |
| Content | 0.56~0.60 | 0.60~0.90 | 1.50~2.00 | ≤0.035 | ≤0.035 | ≤0.35 | ≤0.35 | 0.25 | Bal. |

The morphology was observed by FEI Quanta FEG 650 (FE-SEM). The phase in the coatings was analyzed by XRD. YQ-25D shall be used according to the national standard GB/T 101225-2012 for corrosion test in artificial atmosphere. The salt spray solution is 5% NaCl solution, pH is 6.5~7.2, test temperature is (35±1)℃. The polarization curve and electrochemical impedance spectrum of the samples were measured by Gamry reference 600 electrochemical work station.

3. Results and Discussion

3.1. Phase Analysis of Two Coatings

Figure 1 shows the XRD spectra of the two coatings. The phase composition of Zn coating is mainly FeZn_{10.98}, FeZn_{10.87}, Fe_{12}Zn_{10}, FeZn_{6.67} and ZnO. Figure 1 (b) shows that the Zn-Mg coating is mainly composed of FeZn_{10.98}, FeZn_{6.67}, MgZn_2, Mg_{2.5}Zn_{11}, Mg_{2}Zn_7 and other alloy phases, which indicates that Mg atoms have penetrated and formed into intermetallic compounds with zinc. Previous studies have shown that MgZn_2 and Mg_{2.5}Zn_{11} phases are the main reasons for the improvement of corrosion resistance [24]. Morishita [25,26] pointed out that the above two intermetallic phases have lower anodic dissolution current than pure zinc, and the formed alloy layer attached to the surface can further improve the corrosion resistance.
Figure 1. XRD spectra of the two coatings.

Figure 2 shows SEM pictures of the surface and cross-section. Figure 2 (a) shows that Zn coating is uneven. The bond between the particles is very loose and there are many pores, which is unfavorable to the anti-corrosion resistance. Figure 2 (b) shows that the particle size on the surface of the Zn-Mg coating is relatively uniform, and there are no defects such as cracks. It can be seen from figure 2 (c) that the Zn coating has no defects such as voids and skip plating, but a certain number of cracks can be observed. During the cooling process of the sherdizing process, the thermal expansion coefficient of the Zn-Fe alloy layer and the substrate are different and the residual stress in the coating is relatively large, which leads to the appearance of cracks. Figure 2 (d) shows that the cross-sectional thickness of Zn-Mg coating is relatively uniform, the alloy layer is about 50 μm, and there are no defects such as skip plating.

Figure 2. SEM images of surface and cross of the two coatings.

3.2. Corrosion Resistance of Two Coatings
The NSST was carried out to study the anti-corrosion resistance of Zn-Mg coating, and the sample was taken out after 1920 hours. The results are shown in figure 3. No passivation was performed before the NSST.
It can be seen from figure 4 that after 180h of NSST, red rust began to appear on the surface of Zn coating; after 480h of NSST, red rust appeared on the surface of Zn coating in a large area; after 960 hours of NSST, its surface was full of red rust. White rust on Zn-Mg coating began to appear after 180 hours of NSST; after the NSST for 1200h, the white rust on surface of Zn-Mg coating increased, and the others hardly changed. After 1920 hours of NSST, there was no red rust on Zn-Mg coating. It can be seen that the anti-corrosion resistance has been greatly improved compared to Zn coating, and anti-corrosion resistance of Zn-Mg coating is better.

The sectional morphology of the two coatings after 1000 hours of NSST was observed by SEM, and the photos are as follows:

A comparative analysis of the cross-section of the Zn-Mg coating after 1000h of NSST is carried out. Pictures in figure 5 shows that corrosion of Zn coating after 1000 hours is more serious, while Zn-Mg coating is just infiltrated for 1000h. There is basically no change in the sectional morphology. Studies have shown that [18, 26, 27] the chemical composition of the corrosion products of the Zn-Mg coating are ZnO, Zn₅CO₃(OH)₆·H₂O, Zn₅(CO₃)₂(OH)₆, Zn₅(OH)₆Cl₂·H₂O, etc. Zn₅(OH)₆Cl₂·H₂O is an
insoluble colloidal substance. Its existence effectively cuts off the transmission of the permeated layer and external substances, and enhances the corrosion resistance of the Zn-Mg coating. Mg can promote the formation of protective ZnO in the Zn-Mg coatings, the alkaline zinc chloride and alkaline zinc carbonate are filled in the corrosion cracks to prevent further corrosion, which causes Zn-Mg coating to corrode. Magnesium in the alloy layer reacts with water to form hydroxides, which absorbs carbon dioxide in the air to form carbonates, reducing the pH of electrolyte solution on which and promotes the formation of dense protective corrosion products, thereby slowing down the corrosion process. The corrosion product is Zn₅(OH)₈Cl₂·H₂O with low conductivity, which covers the free surface and is perpendicular to the surface to form a dense and effective protective layer and effectively hinders the transfer of Cl⁻.

3.3. Electrochemical Characteristics
Two coatings were immersed in 3.5% NaCl neutral solution for 20 minutes and then subjected to AC impedance spectroscopy. The obtained AC impedance spectrum is shown in figure 4.

It can be seen from figure 6 (a) and table 2 that the impedance modulus |Z| of Zn coating is 1034Ω·cm², and the impedance modulus value of Zn-Mg coating |Z| is 3241Ω·cm². The capacitive reactance arc of Zn-Mg coating is larger than that of the Zn coating, which means the greater the resistance of the electrochemical reaction, that is, the greater the charge transfer resistance during the corrosion process, the stronger the corrosion resistance, indicating that the electrochemical reaction resistance of the Zn-Mg coating is higher. Anti-corrosion resistance of the Zn-Mg coating is far better than that of the Zn.

| Coating       | Rₛ / (Ω·cm²) | CPEₛ | Rs / (Ω·cm²) | CPEₛall | Rₛ / (Ω·cm²) | | Z |
|---------------|--------------|------|-------------|---------|-------------|-------|
| Zn coating    | 5.96         | 6.98×10⁻³ | 0.79 | 660       | 6.98×10⁻³ | 0.54 | 858 | 1034 |
| Zn-Mg coating | 11.81        | 5.76×10⁻³ | 0.90 | 2187      | 5.76×10⁻³ | 0.76 | 1088 | 3241 |

It can be seen from figure 6 (a) and table 2 that the impedance modulus |Z| of Zn coating is 1034Ω·cm², and the impedance modulus value of Zn-Mg coating |Z| is 3241Ω·cm². The capacitive reactance arc of Zn-Mg coating is larger than that of the Zn coating, which means the greater the resistance of the electrochemical reaction, that is, the greater the charge transfer resistance during the corrosion process, the stronger the corrosion resistance, indicating that the electrochemical reaction resistance of the Zn-Mg coating is higher. Anti-corrosion resistance of the Zn-Mg coating is far better than that of the Zn.

| Coating       | Jₑᵣᵣ / μA·cm⁻² | Eₑᵣᵣ / mV | Beta A/( V/decade) | Beta C/( V/decade) |
|---------------|-----------------|----------|---------------------|---------------------|
| Zn coating    | 15.81           | -946     | 0.077               | 0.393               |
| Zn-Mg coating | 3.270           | -925     | 0.066               | 0.148               |
Anti-corrosion resistance is mainly due to its existence environment and other dynamic factors. Therefore, its corrosion resistance mainly depends on its corrosion rate, and the current density of the coating in this corrosive environment can be obtained through the polarization curve. Thus, the corrosion rate can be calculated, as shown in table 3. Figure 6 (b) shows the polarization curves of two coatings in 3.5% NaCl solution. The corrosion potential of Zn-Mg coating is more positive compared with that of Zn coating because of the addition of magnesium; the Zn coating has a tendency to be more corrosive from the thermodynamics. However, magnesium ions tend to form compounds and are difficult to stably exist in the electric double layer, the addition of magnesium not only increases the overpotential of the cathode process, but the overpotential of the anode dissolution process is also higher than that of the Zn coating. Zn-Mg coating’s corrosion current density reduced, so the corrosion rate reduced, and the corrosion resistance is improved, so that the kinetic analysis of the Zn-Mg coating is less prone to corrosion. Comprehensive AC impedance spectroscopy and polarization curve analysis show that the corrosion resistance of Zn-Mg coating is far greater than that of Zn coating. The results of the salt spray corrosion test and the electrochemical test are consistent.

4. Conclusions
(1) Zn-Mg coatings have been prepared by powder infiltration. After 1920 hours of NSST, there was no red rust on its surface, which indicates that Zn-Mg coating has extremely high anti-corrosion resistance.

(2) XRD analysis results show that the main phases of Zn-Mg coating are MgZn2, Mg2Zn11 and other alloy phases, and the corrosion products form a dense and protective layer, which greatly improves anti-corrosion resistance of Zn-Mg coating.

(3) Based on electrochemical results, Zn-Mg coating has a smaller corrosion current density than Zn coating. Combining with the experiment results of NSST, Zn-Mg coating has better anti-corrosion resistance than Zn coating.

References
[1] Yan Y Z 2011 Study on The Application of High-Strength Bolts (Qingdao: Shandong University of Science and Technology).
[2] Zhang X M 2012 Present situation and development prospect of wind power fastener technology Metal Working (Hot Working) (13) 20-21+25.
[3] Zhong S G and Zhang X M 2009 Differences of high strength fastener for wind power and steel structure Metal Products (06) 62-65.
[4] Wortelen D, Frielings, Bracht H, et al. 2015 Impact of zinc halide addition on the growth of zinc-rich layers generated by sherardizing Surface and Coatings Technology 263 66-77.
[5] Shi W G, Du G L, Chen S Q, et al. 2014 The evaluation and application of sherardizing anti-corrosion technology in offshore oilfields China Offshore Oil and Gas (06) 102-105.
[6] Dong X L, Shi X J, Huang Y B, et al. 2016 Application status of corrosion protection technologies to threaded fasteners Electroplating and Finishing (9) 481-485.
[7] Gao C 2015 Sheradizing Process and Its Effect on Microstructure and Corrosion Resistance (Tianjin: Hebei University of Technology).
[8] Ferguson D 2006 Approaching zero discharge: in plant evaluation of zinc thermal diffusion coating technology, phase I Clean Technologies and Environmental Policy 8(3) 198-202.
[9] Zhou X J, Zhang S P, Zheng P H, et al. 2007 Study of Corrosion Resistance of Zinc Impregnation and Dacromet Coating Equipment Environmental Engineering 4(004) 10-13.
[10] Zhang T 2015 Anti-corrosion performance of zinc-aluminum composite coating on fasteners Corrosion and Protection 36(006) 560-562 568.
[11] Zhao L N, Tang Z Q, Chao Y C, et al. 2011 Effect of dipping sealant on the performance of zinc coating Plating and Finishing 33(010) 40-42.
[12] Hosking N C, Ström M A, Shipway P H, et al. 2007 Corrosion resistance of zinc-magnesium coated steel China Surface Engineering 49(9) 3669-3695.
[13] Prosek T, Persson D, Stoulil J, et al. 2014 Composition of corrosion products formed on Zn-Mg, Zn-Al and Zn-Al-Mg coatings in model atmospheric conditions Corrosion Science 86 231-238.

[14] Marder A R 2000 The metallurgy of zinc-coated steel Progress in Materials Science 45(3) 191-271.

[15] Schwerdt C, Riemer M, Köehler S, et al. 2004 Application related properties of novel ZE-Mg coated steel sheet Stahl und Eisen 124(9) 69-74.

[16] Nishimura K, Shindo H, Nomura H, et al. 2003 Corrosion resistance of hot-dip Zn-Mg galvanized steel sheet Tetsu to Hagane 89(1) 174-179.

[17] Kawafuku J, Katoh J, Toyama M, et al. 1991 Properties of zinc alloy coated steel sheets obtained by continuous vapor deposition pilot-line Proc 5th Automotive Corrosion and Prevention Conference p 43-50.

[18] Schwerdt C, Riemer M, Köehler S, et al. 2004 A study of the application related properties of novel Zn-Mg coated steel sheet produced in a continuous pilot line Proceedings of Galvatech, the Iron and Steel Institute of Japan.

[19] Ferkous H, Talhi B, Barj M, et al. 2009 Investigation of the ability of the corrosion protection of Zn-Mg coatings The Open Corrosion Journal 2 26.

[20] Michel B 2007 Introduction to novel steels for automobiles of Arcelor Transaction of Iron and Steel 1 18.

[21] Nakano H, Oue S, Kobayashi S, et al. 2004 Mg-contained Zn electroplating from aqueous solution containing quaternary ammonium salt Tetsu to Hagane 90(10) 801-806.

[22] Morishita M, Koyama K, Murase M, et al. 1996 Improvement in the corrosion resistance of zinc-plated steel by electrodeposition of magnesium from a molten salt ISIJ International 36(6) 714-719.

[23] Qiu X P, Liu X, Liu Q Y, et al. 2019 Effect of annealing on corrosion resistance of Zn-Mg coatings deposited by vacuum plating Chinese Journal of Vacuum Science and Technology 39(06) 460-465.

[24] Schwerdt C, Riemer M, Koehler S, et al. 2004 Application related properties of novel Zn-Mg coated steel sheet Stahl und Eisen 124(9) 69-74

[25] Morishita M, Koyama K, Murase M, et al. 1996 Improvement in the corrosion resistance of zinc-plated steel by electrodeposition of magnesium from a molten salt ISIJ International 36(6) 714-719.

[26] Morishita M, Koyama K, Mori Y 1997 Inhibition of anodic dissolution of zinc-plated steel by electrodeposition of magnesium from a molten salt ISIJ International 37(1) 55-58.

[27] Liu Q Y 2014 Study on Manufacture Technology and Corrosion Resistance of Zn-Mg Alloy Coatings by Evaporation (Baotou: Inner Mongolia University of Science and Technology).