

A two-stage conversion process for AZ31B corrosion

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Abstract— Permanganate phosphate coating is considered as one of the most promising alternative coatings to chromate conversion coating because of the similarity between permanganate and chromate. However, the permanganate phosphate coating always has net-work cracks. In this paper, a thick and crack-free permanganate phosphate coating was developed by a two-stage conversion process. Results of scanning electron microscope (SEM) with X-ray diffraction (XRD) analysis showed that some more corrosion resistant compounds appeared in the coating after a two-stage conversion treatment, which were not found in the single conversion coating. Moreover, the two-stage conversion coating has a higher thickness with few cracks. Furthermore, electrochemical tests and salt spray test further exhibited that the two-stage conversion coating had a better corrosion performance than either of the two single conversion coatings.

Keywords—AZ31; Conversion coating; Two stage process; Corrosion

I. INTRODUCTION

Two major obstacles have limited the expansion of Mg alloy use in transportation industry. The limited slip systems at room temperature leads to activation of deformation twinning which causes different yield strengths in tension and compression [1-2] (which is different from hydrostatic stress dependent strength different effect [3] seen in high strength steel). The high corrosion susceptibility of magnesium alloys extremely restricts their further application in automotive, aerospace industries and electronics [4]. Presently, the most widely used method in industries to provide the protection on magnesium and its alloys is generally the chromate conversion coating. However, the inevitable environmental and health

problems caused by hexavalent chromate leads to a real necessity of developing alternative conversion coatings. During the past 20 years, a few environmental friendly conversion coatings were proposed to be aimed at replacing chromate conversion coating, including metal phosphate coatings, rare earth coating, stannate coating, etc [5-8].

Compared to chromate conversion coating, permanganate phosphate coatings are more environmental friendly and could provide equivalent corrosion resistance and paint adhesion. In recent years, varieties of research related to phosphate permanganate coating have been made on magnesium alloys. Hawke et al. [9] developed a coating consisting of an agglomerate of well-formed crystals with the coating thickness of 4-6 μ m using a conversion bath containing KMnO₄ and NH₄H₂PO₄, which showed good corrosion resistance and paint base performance. Typically, permanganate phosphate coatings have severe cracks, through which corrosive species could readily reach the Mg substrate. Jian, etc. [10] reported that a phosphate-permanganate conversion coating without cracks was able to be fabricated in a strongly acidic solution which exhibited excellent corrosion resistance. However, this coating is too thin and too weak. To date, there are no work on magnesium alloys reporting a permanganate phosphate conversion coating that is both thick and crack-free.

In the present study, a two-stage conversion process is proposed to form a dense and thick phosphate-permanganate coating. The microstructure and corrosion resistance of this two-stage conversion coating was evaluated by SEM-EDS, electrochemical testing. Results showed that this two-stage conversion coating were both dense and thick that the corrosion resistance was improved compared to the single-step conversion coating.

II. MATERIALS AND EXPERIMENTS

A. Materials and surface preparation

Specimens of AZ31B [11-12] cast alloy with a size of 3×25.4×50.8 mm taken from a cylindrical ingot were utilized as the test material. These coupons were mechanically grinded to 1200# using emery paper, ultrasonic degreased in acetone, washed in ethanol and dried in air stream.

B. Conversion coating treatment and characterization methods

Potassium permanganate (15g/L KMnO₄), potassium dihydrogen phosphate (3g/L KH₂PO₄), manganese sulfate (4g/L MnSO₄) and ethylenediaminetetraacetic acid, namely EDTA (1g/L C₁₀H₁₆N₂O₈) were used to prepare the aqueous conversion bath. The two-stage conversion process was firstly conducted in a low pH bath and then was immediately treated by a high pH solution. Another two single stage coatings were also separately obtained as a comparison by a single low pH solution treatment (marked as LP treatment) and a single high pH solution treatment (marked as HP treatment).

The surface morphology, microstructure and chemical composition of the conversion coating were characterized using scanning electron microscopy (SEM) and energy-dispersive spectrometry (EDS). The potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements were performed in 3.5% sodium chloride (NaCl) using a potentiostat/galvanostat electrochemical system (Solartron SI 1287 and 1255B). Prior to the polarization scan and EIS measurement, each sample was immersed in the testing solution for 30min to reach a steady open circuit potential (OCP). The potentiodynamic polarization measurement was conducted by sweeping the potential from -100mV to +500mV vs the OCP at a scan rate of 1 mV/s. For EIS analysis, each spectrum was recorded at the OCP in frequencies ranging from 100 kHz to 10 mHz, with a sinusoidal signal amplitude of 10mV. All experimental data were presented in the form of the average± the standard deviation of three measurements.

The salt spray chamber test was performed according to the SAE J2334 standard. In this test, the coupons were placed at an angle of 15°-30° from the vertical direction in a chamber. One 24-hour cycle includes a 6 hours exposure in 100% condensing humidity at around 50°C, a 15 minutes exposure at 25°C to a fog containing 0.5 wt. % NaCl, 0.1%CaCl₂, 0.075% NaHCO₃ and a 17.75 hours exposure in a dry environment at 60°C (50% relative humidity).

III. RESULTS AND DISCUSSION

A. Surface morphology and coating composition analysis

Figure 1.1 shows the surface morphology of the coating obtained by the two-stage conversion process described above. Another two coatings, i.e. the most corrosion resistant from the low pH treatment and the most corrosion resistant from the high pH treatment, are also presented in the figure together with the bare alloy for comparison. In general, all the coatings displayed similar surface morphology with networks of shallow cracks except that some cracks in the two-stage

coating was slightly widened. The EDS analysis suggested that the second phase particles in the bare alloy were oxidized after the conversion process, as shown in the Table . And it can be seen from Figure that more oxidized second phase particles were seen in the coating from the high pH treatment (HP coating) than that from the low pH bath (LP coating). The fact that the second phase particles can be seen on the coating surface indicates that the coating was quite thin. The most interesting aspect of EDS results is that some manganese oxides were also detected in the two-stage conversion coating, as shown by the spot D in Figure (d). Manganese oxides (MnO/MnO₂/Mn₂O₃) are generally more corrosion resistant than MgO and Al₂O₃. Therefore, this two-stage conversion process has the potential to further improve corrosion resistance of the Mn-P coating, as compared to a single conversion process. Additionally, the thickness of each coating could be evaluated from the weight gain of the coated samples, as presented in Figure . It distinctly demonstrated that the two-stage conversion coating had the highest thickness and the HP coating film was the thinnest, indicating that the two-stage conversion process can be used to grow thick and corrosion resistant Mn-P coating on Mg alloys.

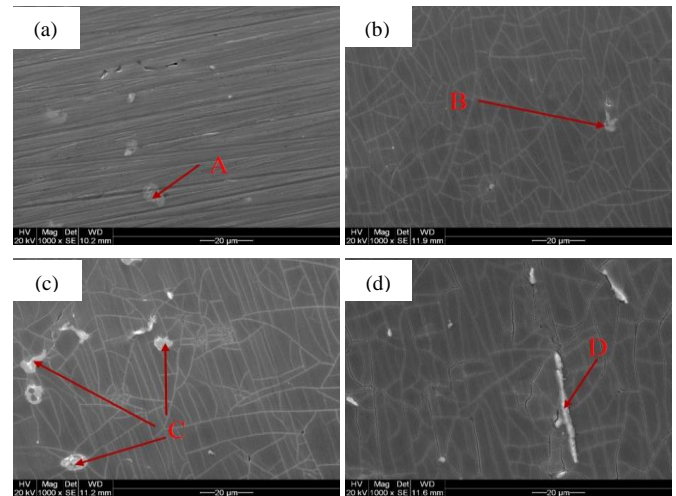


Figure 1.1 The surface morphology of (a) the bare alloy; (b) the coating obtained by low pH treatment (LP coating); (c) the coating obtained by high pH treatment (HP coating); (d) Two-stage coating.

Table 1 Chemical composition (atm.%) of the compounds as indicated in Figure 1.1

| Spot | Mg | Al | Zn | Mn | O |
|------|-------|-------|-------|-------|------|
| A | 90.65 | 6.88 | 2.47 | | |
| B | 90.50 | 3.69 | 3.81 | | 2.00 |
| C | 67.64 | 19.01 | 12.18 | | 1.16 |
| D | 50.45 | 9.45 | 2.31 | 25.04 | 9.79 |

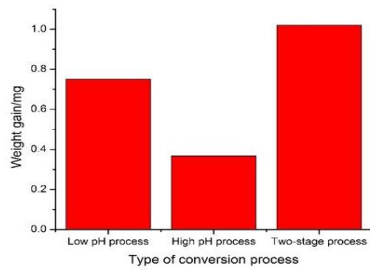


Figure 1.2 Weight gain of the samples after being treated by different conversion process

B. Electrochemical test

Figure shows the potentiodynamic polarization curves of the various conversion coated AZ31B in 3.5% NaCl solution. Generally, the cathodic polarization curve is related to the evolution of hydrogen and the anodic polarization curve represents the corrosion resistance of the coating. As can be seen in the figure below, both the anodic and cathodic polarization curves of the conversion coatings shifted toward the lower current direction (left) significantly compared to those of the bare alloy, indicating that both the anodic reaction and cathodic reactions were inhibited and hence the corrosion resistance of the AZ31B was effectively improved by the conversion coating. Moreover, it can be observed that a passive region (defined as the potential difference between the corrosion potential E_{corr} and the breakdown potential E_{break}) occurred in the anodic polarization branch of the coated samples. Among all coated samples, the HP coating exhibited the largest passive region of 432.2mV. From the polarization test results we can see that the HP coating and two-stage coating showed similar corrosion behavior and both were more corrosion resistant than the LP coating.

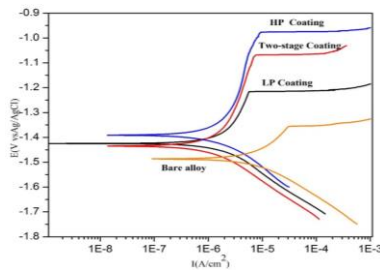


Figure 1.3 Polarization curves of the bare alloy and different conversion coated samples

Electrochemical impedance spectroscopy (EIS) was then used to further study the corrosion resistance of the coated samples. As can be clearly observed from the Bode plots (Figure) of various conversion coatings and the bare alloy, the two-stage conversion coating exhibited the highest impedance values in the low frequency range. The impedance generally represents the ability of the coating to resist the flow of electrical current. Higher impedance suggests a lower anodic dissolution rate. Therefore, from the point view of EIS results, the two-stage conversion coating shows the highest corrosion resistance.

From the results of the electrochemical tests, it can be concluded that the two-stage conversion process resulted in a thick and dense coating with better corrosion resistance than

the coating obtained by a single conversion process (LP coating and HP coating).

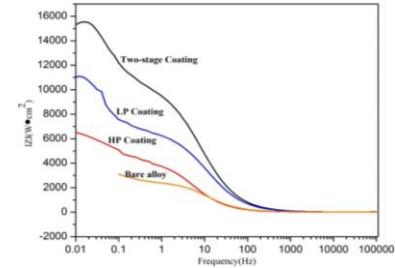


Figure 1.4 Bode plots of the bare alloy and different conversion coated samples

C. Salt spray test

To characterize long-term corrosion performances of the coated specimens, salt spray chamber test according to SAE J2334 standard was conducted for up to 168 hours. The edge of the examined samples were all sealed with epoxy to avoid the edge effect in the corrosion process. By visual examination of the conversion coated samples as shown in Figure 1.5, we observed that a few corrosion pits were seen on the surface of LP coated and HP coated samples after a test duration of 96 hours. In contrast, only several small corrosion pits were found on the surface of the two-stage conversion coated specimen. Furthermore, as the testing duration went up to 168 h, corrosion pitting on the LP coated and HP coated coupons became more severe with an increased number of pits. However, the corrosion of two-stage conversion coated coupon did not deteriorate so much with the increasing testing time.

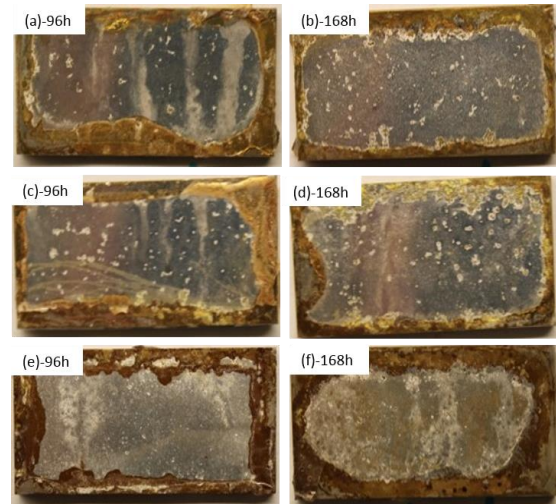


Figure 1.5 Salt spray test results conversion coated samples: (a)(b) LP coating; (c)(d) HP coating; (e)(f) Two-stage coating

IV. CONCLUSIONS

A two-stage conversion process, namely, the treatment in a low pH solution followed by an immediate treatment in a high pH solution, was developed to deposit a thick and dense protective surface coating on Mg alloy AZ31B. Results of SEM analysis, electrochemical tests and salt spray test exhibited that the two-stage conversion coating had better

corrosion performance than either of the two single conversion coatings.

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