

Improvement of anticorrosion and adhesion to magnesium alloy by phosphate coating formed at room temperature

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Abstract: A new surface protection process was developed to magnesium alloy against corrosion in aggressive environments. Firstly, a phosphate coating was formed on rinsed magnesium alloy. Then, powder painting was carried out on the phosphated magnesium alloy. Surface morphologies and phase compositions of the phosphate coating were investigated by X-ray diffraction (XRD) and scanning electron microscope (SEM). The results show that the phosphate coatings formed in bath containing earth additives at room temperature have dense and fine microstructure. The phosphate coating provides excellent paint adhesion to the magnesium alloy. Salt spray tests indicate that the corrosion resistance of the phosphate coating plus paint could meet the demand of magnesium alloy automobile components in aggressive environments.

Key words: anticorrosion; adhesion; magnesium alloy; paint; phosphate coating

1 Introduction

Magnesium alloy components have higher specific strength and lower environmental risks. The demand for light-weight products has grown recently due to the rapid development of automobile, aircraft, and 3C (computer, communication and consumer electronic) industry[1–6]. Under normal conditions, however, magnesium alloy components could not generally meet the demand of automobile components in aggressive environments. Researches on anticorrosion performance of magnesium alloys have been a hot topic nowadays[7–9].

Adhesion between paint and magnesium alloy is poor because of high electrochemical activity of magnesium. To improve the adhesion of magnesium alloy components, they were covered conversion coatings including earth conversion coatings[10–12], stannate coatings[13–14], phosphate-permanganate conversion coatings[15–17], manganese phosphate coating[18] and zinc phosphate coatings[19–24]. However, paints on magnesium alloys tend to produce local corrosion in aggressive environments. Investigations on how to avoid paint local corrosion of magnesium alloys are less.

In this study, the poor adhesion and local corrosion resistance of magnesium alloy were improved by phosphate coating. The influences of phosphate bath compositions on the surface morphologies, anticorrosion and adhesion of paint were studied as well.

2 Experimental

Cast AZ91D magnesium alloy samples (50 mm×50 mm×3 mm) were used. The compositions of the alloy are given in Table 1.

The process of surface treatments of magnesium alloys is listed in Table 2. Magnesium alloys were degreased in the alkaline bath and rinsed with distilled water. Afterward, they were treated in the phosphating bath. The composition of the phosphating bath is listed in Table 3. Then, samples were cleaned with overflowing distilled water. At last, FL-11 powder painting was carried out on the phosphate coating and dried.

Table 1 Compositions of AZ91D magnesium alloy (mass fraction, %)

Al	Zn	Mn	Ni	Cu	Ca	Si	K	Fe	Mg
8.77	0.74	0.18	0.001	0.001	<0.01	<0.01	<0.01	0.001	Bal.

Table 2 Process of surface treatments to AZ91D magnesium alloys

Stage	Operation	Composition (g/L)	Condition
1	Degreasing	Potassium hydroxide: 10.5	3–5 min, (60±2) °C
2	Overflowing rinsing	Distilled water	1 min
3	Phosphating	Phosphating bath	4 min, pH 2.2–2.4 (20±2) °C, (45±2) °C, (80±2) °C
4	Overflowing rinsing	Distilled water	1 min
5	Drying		10 min, (70±2) °C
6	Paint	FL-11 powder paint	Thickness: (20±2) μm
7	Drying		20 min, (160±2) °C

Table 3 lists chemical compositions of phosphating baths.

Table 3 Chemical compositions of phosphating baths (g/L)

Composition	Basic bath	Bath 1	Bath 2	Bath 3
Phosphoric acid	11.3	11.3	11.3	11.3
Zinc oxide	2.2	2.2	2.2	2.2
Sodium fluoride	2.3	2.3	2.3	2.3
Organic amine	1.2	1.2	1.2	1.2
Zinc nitrate	12.5	12.5	12.5	12.5
Alkyl phosphate	0	0.1	0.1	0.1
Hydrogen peroxide	0	0	1.0	0
Complex	0	0	0	1.6

Complex accelerator was mixture of sodium cerium and sodium chlorate with mass ratio of 1:25.

Surface morphology observations of phosphate coatings were conducted with scanning electron microscope (SEM). The phases in the phosphate coatings were analyzed by X-ray diffraction (XRD).

The potential—time curves were measured using platinum sheet as counter electrode (500 mm²). The working electrode was controlled by a saturated calomel electrode (SCE).

Adhesion tests were conducted according to ISO 2409. This method assessed the adhesion of paints on the substrates when a right-angle lattice pattern was cut onto the coating and penetrated to the substrate. The test results were classified to six grades. The classification of “0” indicates the best adhesion of the coating and that of “5” depicts the worst adhesion of the coating.

The first adhesion of the paint occurred when the coating was painted on the magnesium samples. The second adhesion of the paint came from the reaction when the painted magnesium samples were soaked in

water at (80±2) °C for 100 h.

The salt spray tests were conducted in SF850 salt spray cabinet (Atlas Electric Devices Company). The paints on AZ91D samples were in the size of 100 mm×100 mm×3 mm.

3 Results and discussion

3.1 Effects of phosphate bath compositions on coating formation time

The compositions of basic bath are: 11.3 g/L phosphoric acid, 2.2 g/L zinc oxide, 2.3 g/L sodium fluoride, 1.2 g/L organic amine, 12.5 g/L zinc nitrate. In Bath 1, Bath 2 and Bath 3, alkyl phosphate salt, hydrogen peroxide, sodium cerium and sodium chlorate were used to accelerate the coating formation reactions (Table 3).

Fig.1 shows the open circuit potentials of AZ91D samples in Basic bath, Bath 1, Bath 2 and Bath 3 at room temperature with time.

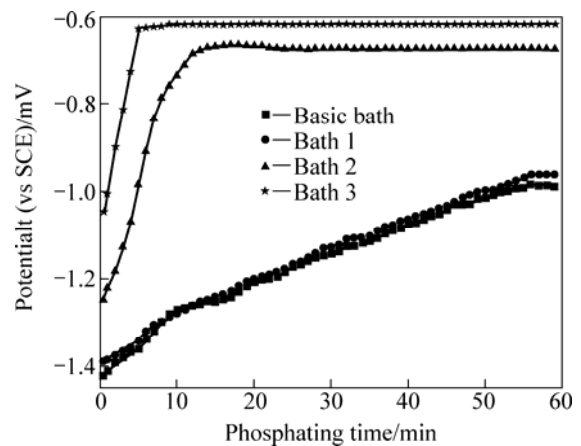


Fig.1 Potential—time curves of AZ91D magnesium alloys in Basic bath, Bath 1, Bath 2 and Bath 3

In Basic bath, the open circuit potential increased steadily. The potential was stabilized after 54 min of immersion. This meant that the coating formation finished after 54 min in Basic bath. The potential—time curve of magnesium alloys in Bath 1 was similar to that in Basic bath; the open circuit potential was stabilized after 57 min. Hence, alkyl phosphate salt could not effectively accelerate the coating reactions.

In Bath 2, the open circuit potential increased more rapidly and was stabilized after 14 min of immersion. This indicated that hydrogen peroxide effectively accelerated the reactions of the coating formation.

In Bath 3, the phosphating reaction proceeded at the highest speed. The open circuit potential increased significantly during the initial 5 min of immersion. Hence, complex accelerator (sodium cerium and sodium chlorate) in the phosphating bath could effectively

accelerate the phosphating reaction.

3.2 Effects of phosphate bath compositions on microstructure of phosphate coatings

The phosphate coatings were prepared in Bath 2 and Bath 3 at (20 ± 2) °C and (45 ± 2) °C, respectively, and the surface morphologies of phosphate coatings are shown in Fig.2.

It can be seen that the crystals of the phosphate coating obtained in Bath 3 are finer and more even than that in Bath 2 (Fig.2). In Bath 2, the coating formed at (20 ± 2) °C was porous and had cracked-mud microstructure (Fig.2(a)). However in Fig.2(b), the coating crystals formed at (45 ± 2) °C were not even.

In Bath 3, the complex accelerator contained sodium cerium and sodium chlorate accelerated effectively phosphating reaction (Figs.2(c) and (d)). The addition of complex accelerator made the zinc phosphate films dense and improved the integrality of zinc phosphate films. So, the phosphate coating formed in Bath 3 containing earth additive at room temperature had dense and fine microstructure.

Fig.3 shows the XRD pattern of the phosphate coating obtained from Bath 3 in 5 min at (20 ± 2) °C. It could be seen that the coating was composed of $Zn_3(PO_4)_2 \cdot 4H_2O$, $AlPO_4$ and Zn.

When magnesium alloy was soaked in the bath,

α -Mg phases dissolved and hydrogen was evolved. The formation of hydrogen resulted in the increase of local pH value at the interface of magnesium alloy and solution, which facilitated the precipitation of insoluble phosphate ($Zn_3(PO_4)_2 \cdot 4H_2O$, $AlPO_4$). During phosphating process, Zn^{2+} ions were also reduced to Zn and deposited on the magnesium alloy surface.

3.3 Effects of phosphate bath compositions on adhesion of paint to magnesium alloy

The first adhesion and second adhesion of the paint on the phosphatized magnesium alloy were measured by ISO 2409. The low grade “0” denoted the best adhesion. The adhesion demand of automobile components was grade “0” and grade “1”.

Painting Samples 1–4 were produced on the phosphate coating on the magnesium alloy obtained from Bath 2 at (20 ± 2) °C, Bath 2 at (45 ± 2) °C, Bath 3 at (20 ± 2) °C and Bath 3 at (45 ± 2) °C, respectively. The coating mass per area of the phosphate film for Samples 1–4 were 0.84, 8.57, 2.23 and 3.19 g/m². Fig.4 shows the adhesion grade of paint for the four samples. It could be seen that Samples 3 and 4 could meet the adhesion demand of automobile components. And Sample 3 showed the best adhesion in the tests of first adhesion and second adhesion.

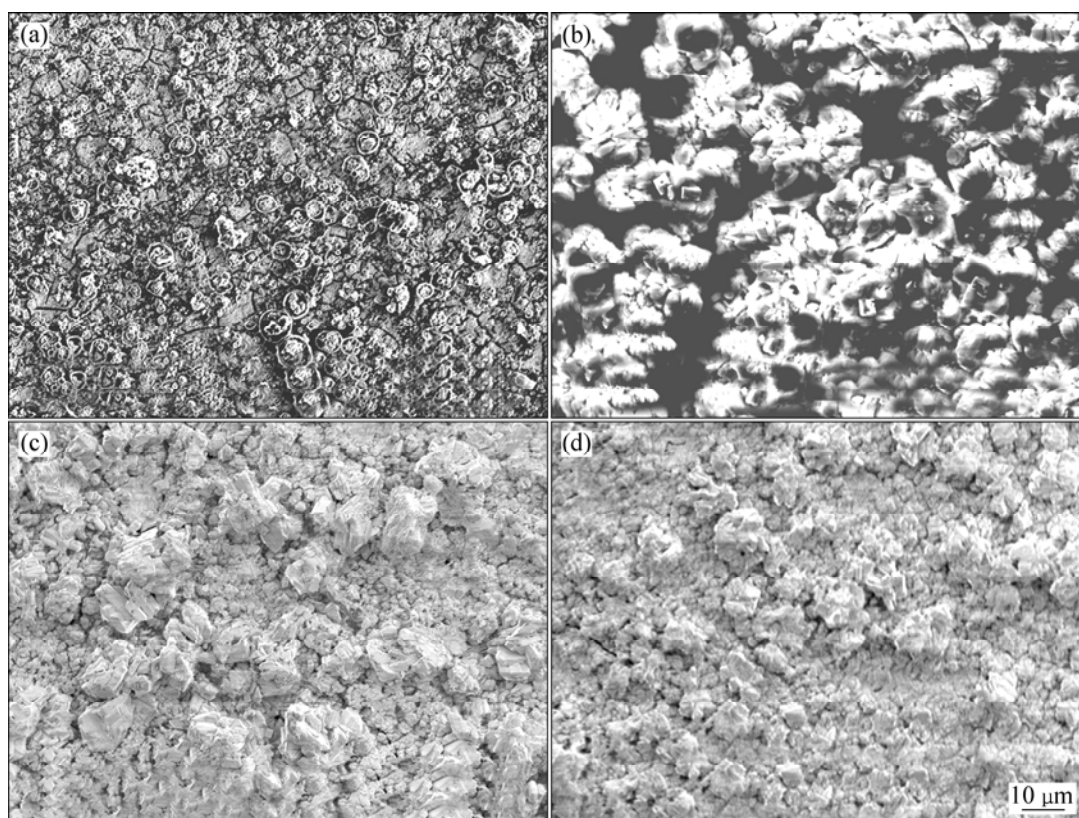


Fig.2 Surface morphologies of phosphate coating on AZ91D magnesium alloy: (a) Bath 2, (20 ± 2) °C; (b) Bath 2, (45 ± 2) °C; (c) Bath 3, (20 ± 2) °C; (d) Bath 3, (45 ± 2) °C

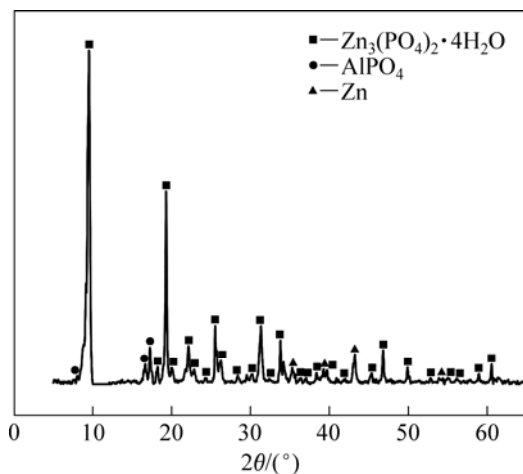


Fig.3 XRD pattern of phosphate coating obtained from Bath 3 in 5 min

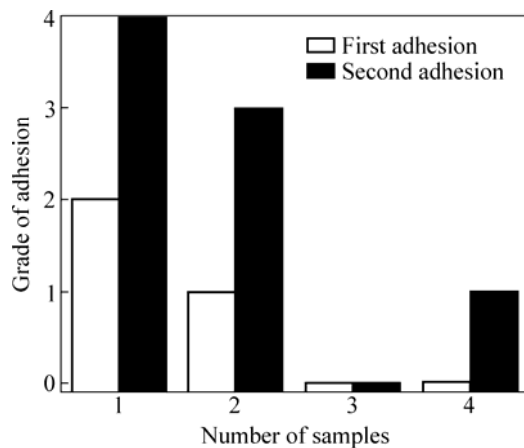


Fig.4 Adhesion of painted magnesium alloy with phosphate coating from Bath 2 at (20 ± 2) °C (Sample 1), Bath 2 at (45 ± 2) °C (Sample 2), Bath 3 at (20 ± 2) °C (Sample 3) and Bath 3 at (45 ± 2) °C (Sample 4)

3.4 Effects of phosphate bath compositions on corrosion resistance of phosphate coating for magnesium alloy

Salt spray test results of phosphate film and paint on magnesium alloy are depicted in Fig.5.

The paints on Samples 1 and 2 showed the local corrosion. The rust spots on the Samples 1 and 2 appeared in 220–340 h in salt spray test, and the rust pits grew as pitting corrosion.

Rust on Samples 3 and 4 emerged approximately in 650 h and exhibited uniform corrosion on the whole surface. Rust time of paints on the phosphate coating containing earth additives was about 3 times of that of paints the phosphate coating without earth additives in salt spray test. The paints on Samples 3 and 4 exhibited uniform corrosion, and the local corrosion was avoided by their uniform phosphate coating.

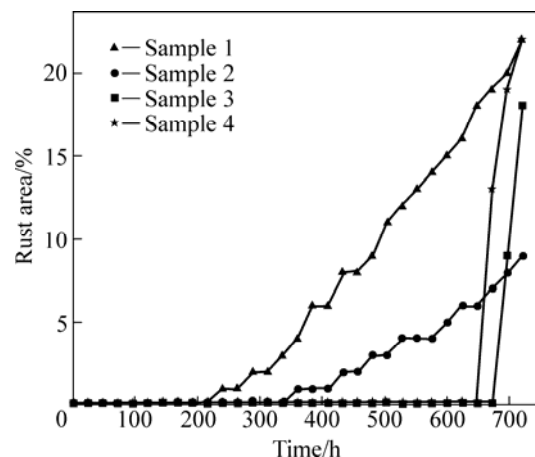


Fig.5 Rust areas of painted magnesium alloy with phosphate coating from Bath 2 at (20 ± 2) °C (Sample 1); Bath 2 at (45 ± 2) °C (Sample 2); Bath 3 at (20 ± 2) °C (Sample 3) and Bath 3 at (45 ± 2) °C (Sample 4)

4 Conclusions

1) An even phosphate coating were prepared in 5 min of immersion time at room temperature. The addition of complex accelerator made cracks of zinc phosphate films vanish and improved the integrality of zinc phosphate films.

2) The optimal composition of phosphate bath for obtaining more dense crystals at room temperature was: 11.3 g/L phosphoric acid, 2.2 g/L zinc oxide, 2.3 g/L sodium fluoride, 1.2 g/L organic amine, 12.5 g/L zinc nitrate, 0.1 g/L alkyl phosphate salt and 1.6 g/L complex accelerator (with ratio of cerium nitrate to sodium chlorate 1:25).

3) The first adhesion and second adhesion of the phosphate coating on magnesium alloy substrates were improved by the complex accelerator.

4) Salt spray test showed that paints on the phosphate coating containing earth additives exhibited uniform corrosion. Rust time of paints on the phosphate coating containing earth additives was about 3 times of that of paints on the phosphate coating without earth additives.

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