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ORIGINAL PAPER

Conversion coating treatment for AZ31 magnesium alloys by a phytic acid bath

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Abstract A phytic acid chemical conversion bath was applied to a sample of AZ31 magnesium alloy in this study; a transparent conversion coating formed subsequently on the sample surface. The test results of this coating with a scanning electron microscope (SEM) showed that there exist compact coatings on the surface of treated magnesium alloy. With the analyses of electronic probe microscopy (EPMA) and IR spectrum, a further study of this coating indicated that the coating was mainly composed of phytate and oxide or hydroxid. Furthermore, The electrochemical tests showed that the phytic acid bath conversion treatment enhanced the corrosion resistance of AZ31 magnesium alloys. The optimal pH of the phytic acid bath was 9.00–10.00.

Keywords Magnesium alloy · Phytic acid · Corrosion

1 Introduction

Magnesium alloys are of great importance at present and future fields of engineering for their attractive combination of low density and high strength/weight ratio. However, since magnesium is intrinsically active in the environment, the corrosion resistance of magnesium alloys is generally inadequate, which limits their application. Nowadays, in order to improve the corrosion resistance of magnesium alloys, surface treatment technologies, such as chemical conversion, are commonly applied. DOW (developed by the DOW chemical Co.) and JIS (H8651) are the most popular chemical conversion treatment technologies for magnesium alloy [1, 2]. But both methods introduce chromate ions in the solutions, which are progressively restricted due to its high toxicity to the environment.

Actually, many researchers have developed more environmental-friendly alternatives, such as permanganate bath, phosphate-permanganate bath, stannate bath, and rare earth metal salts (REMS) bath [3–8]. But all the baths include heavy metal icons. Phytic acid ($C_6H_{18}O_{24}P_6$), an inartificial and innoxious, organic large molecular compound, consists of 24 oxygen atoms, 12 hydroxyl groups, and 6 phosphate carboxyl groups. The peculiar structure of phytic acid has powerful complex capability with many metal ions. If the metal atoms on the surface of magnesium or magnesium alloys can react with the active groups of phytic acid to form chelate compounds, the complex compounds deposit on the surface of magnesium alloys to form a chemical conversion layer which could insulate the contact of magnesium alloy base and environmental media. The corrosion resistance of magnesium and its alloys could be improved.

Our study is aiming at developing an environmentally friendly conversion treatment. In this article, a phytic acid chemical conversion bath for AZ31 magnesium alloy was developed. Furthermore, the composition and morphology of coatings were examined, the electrochemical stability of the treated magnesium alloy was investigated, and the formation process of the coatings was speculated.

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2 Experimental

2.1 Chemical treatment

The treatments described in this study were performed on 4 × 4 × 0.2 cm die cast plates of AZ31 magnesium alloy, with chemical composition (wt%): Al 2.80%, Zn 0.80%, Mn 0.38%, Si < 0.05%, Cu < 0.025%, Fe < 0.004%, Ni < 0.001%, and Mg Balance. The chemical conversion on magnesium alloy was investigated on the samples using the following sequence of operations:

(1) The surfaces of the specimens were polished with abrasive paper (grade 360, 600, 1000, and 2000), rinsed with distilled water, degreased with ethanol and dried by air.

(2) Alkaline cleaning

Sodium hydroxide, NaOH: 10.0 g dm^{-3}; sodium carbonate, Na_2CO_3 15.0 g dm^{-3}; Na_2SiO_3 10.0 g dm^{-3}; triethanolamine 5.0 g dm^{-3}
Temperature: 333 ± 5 K; time: 3–10 min; post treatment: water rinse

(3) Acid picking

Nitric acid (68%), HNO_3 20.0–50.0 g dm^{-3}; magnesium nitrate, $Mg(NO_3)_2$ 100.0–200.0 g dm^{-3}; ethanol (97%), 200.0–400.0 g dm^{-3}
Temperature: 293 ± 5 K; time: 10–20 s; post treatment: water rinse

(4) Chemical conversion

Phatic acid, 20.0 g dm^{-3}, pH: 8.0–10.0 (adjusted by NaOH)
Temperature: 298 ± 5 K; time: 0.5–3 min; post treatment: hot air drying

2.2 Surface analysis

A scanning electron microscope (SEM, model JSM-5600LV) was used to observe the morphology of the chemical conversion coatings. The elementary distribution and the phase of the coatings were analyzed by electronic probe microanalysis (EPMA, model EMPA-1600). The compositions and chemical valence state of the elements in the conversion coatings were measured using Infrared spectrum (IR, Model EQUINOX55).

2.3 Measurement of corrosion resistance

The electrochemical stability was tested by potentiostatic test and potentiodynamic polarization in 0.05 mol L^{-1} NaCl solution at room temperature. The untreated and chromate-treated AZ31 magnesium alloy acted as contrast samples. The electrochemical experiments were performed on a traditional three-electrode system with a platinum wire as counter-electrode and a saturated calomel as reference electrode (SCE). The tests were carried out using a Princeton Potentiostat/Galvanostat Model 2273 with a scan rate of 0.5 mV s^{-1}.

3 Results

3.1 Morphology of the coatings

After treatment with the phytic acid bath, the surface of the magnesium specimen was covered with transparent conversion coatings. Figure 1 showed the morphology of the coatings observed by SEM. Obviously, the coating was compact, only a few stains exist on the surface. Even if the amplification increased to 5,000, no apparent cracks were observed on the surface.

3.2 Distributions of the coating elements

Table 1 showed the element compositions of the coating elements analyzed by EPMA. The coatings was mainly composed of Mg, Al, Zn, O, P, and C element, and the presence of P showed that phytic acid was involved in the formation of the coatings. P element was considered the indicator of phytic acid molecule, for its content could hardly change during the analytical process. Calculation

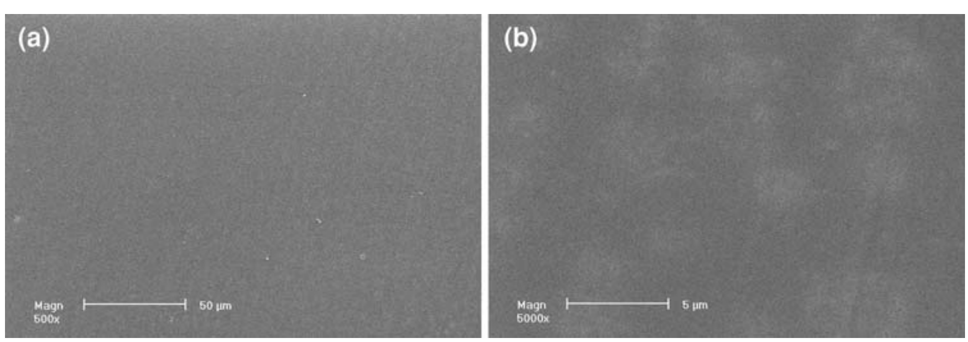

Fig. 1 SEM photographs of the phytic acid conversion coatings on magnesium alloy **a** ×500, **b** ×5,000

Table 1 Composition of phytic acid coating on magnesium alloy

Elements contents	Mg	Al	Zn	O	P	C
Wt (%)	87.500	1.460	1.152	6.979	0.986	1.923
Mol (%)	83.724	1.258	0.410	10.145	0.740	3.723

showed that mol ratio of O, C, and P elements in the coatings was: O:C:P = 13.7:5.03:1, while their ratio in phytic acid molecule was O:C:P = 4:1:1. Hence, we concluded that besides phytic acid, oxide also existed in the coatings.

Distributions of the coating elements were analyzed using electronic probe microanalysis (EPMA). Figure 2 showed EPMA maps of Mg, Al, Zn, O, P, and C at the same position of the coating. The distribution images of the elements, resembling the micrograph obtained by SEM, also presented compact structure. According to the distribution pattern of Mg and Al, the stains on the coatings were mainly composed of Al elements, which were caused by the nonuniformity of alloy composition. O, P, and C elements distributed uniformly on the whole surface showed that a compact coating was formed on the metal.

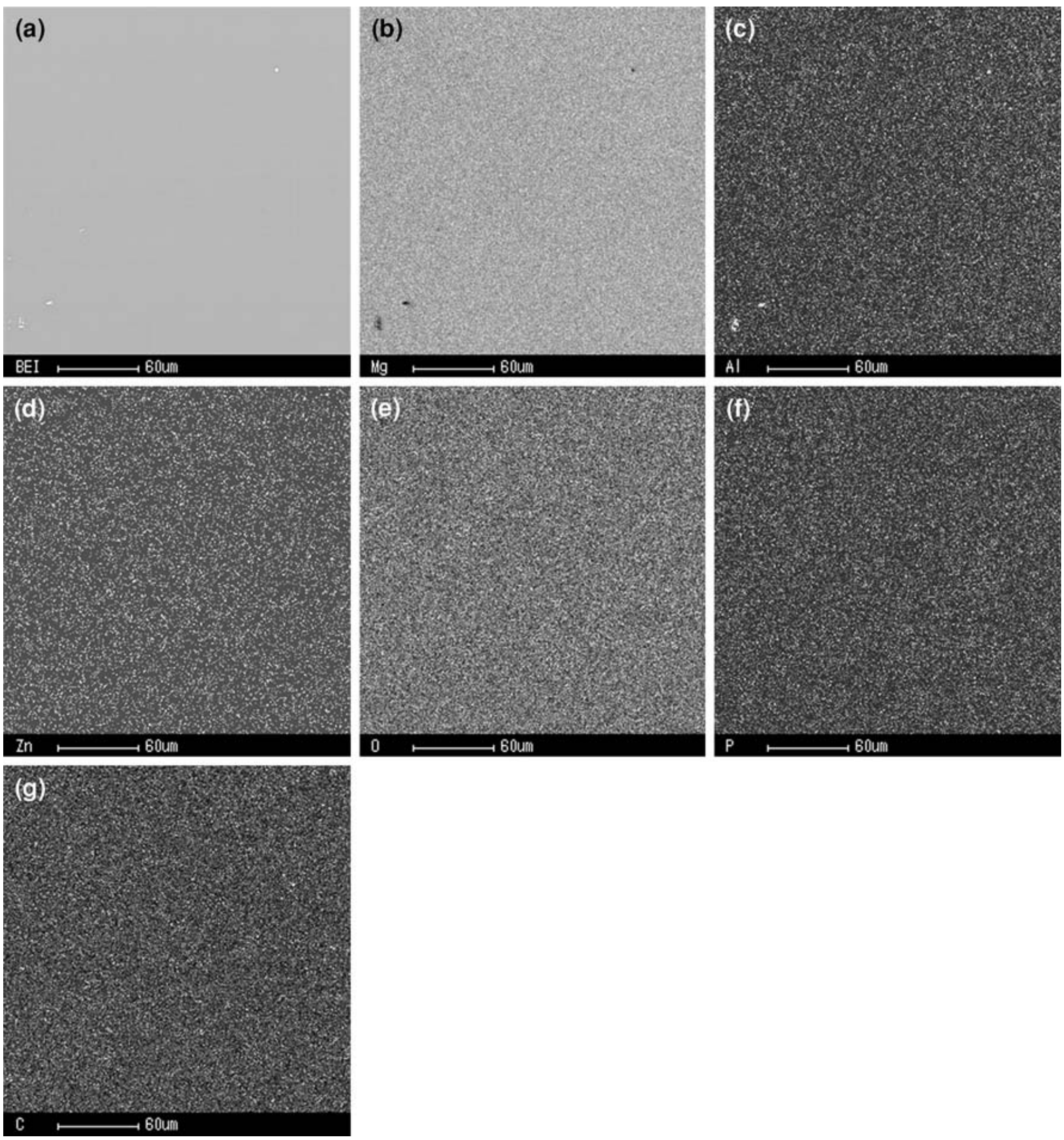

Fig. 2 Distribution of the phytic acid conversion coating elements on magnesium alloy by EPMA: **a** BEI chart, **b** distribution of Mg, **c** distribution of Al, **d** distribution of Zn, **e** distribution of O, **f** distribution of P, and **g** distribution of C

3.3 IR spectrum studies of the chemical coatings

To obtain a better understanding of the compositions and chemical state of the elements in the conversion coatings, IR was performed to analyze the conversion coatings. Figure 3 shows the IR test results obtained for the AZ31 magnesium alloy and phytic acid, respectively. It was found that compared with the spectrum of phytic acid, the IR tests of phytic acid coating shifted toward left, and a new spectrum appeared at 600 cm^{-1}. As the characteristic peak of PO_4^{3-} was 1,100–1,000 cm^{-1} and 650–540 cm^{-1} and, and HPO_4^{2-} and $H_2PO_4^{-}$ was 1,100–1,000 cm^{-1}, the $H_2PO_4^{-}$ in the phytic acid was changed to HPO_4^{2-} or PO_4^{3-} during the conversion process. The analysis showed that the coatings were mainly composed of phytate and oxide or hydroxid.

3.4 Potentiostatic tests

Figure 4 shows the curves of current density versus time for the untreated magnesium alloys specimens (abbreviated to Blank), chromate-treated specimens (treated by JIS H 8651 MX-1, which was similar to DOW No. 1, abbreviated to Cr) and conversion-coated specimens treated with a phytic acid solution (abbreviated to phytic acid) potentiostatic polarized at −1.35 V. As can be observed in Fig. 5, it could be found that the Phytic acid coatings have the smallest current density. When the test time was less than 500 s, the current density of phytic acid coatings was maintained in a very low value. While the test time exceeded 500 s, the current density of phytic acid coatings began to rise. All these were because of the fact that the compact coatings were formed on the metal surface, which restrained the diffusion of Cl^{-} to the metal. However, with an increase in time duration the coatings could also be destroyed, which resulted in the increase of current density.

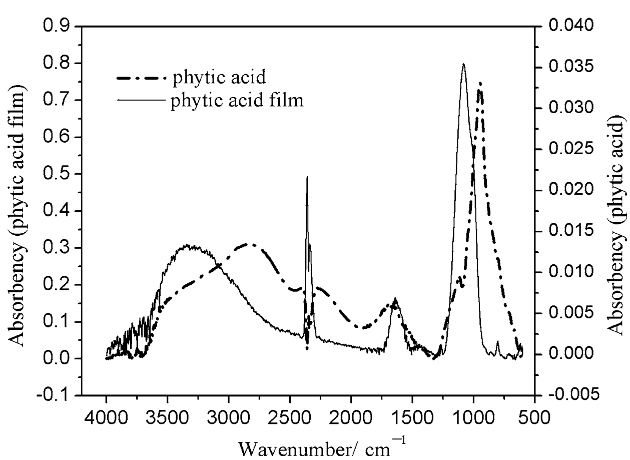

Fig. 3 Infrared spectrum of phytic acid and the phytic acid conversion coatings on magnesium alloy

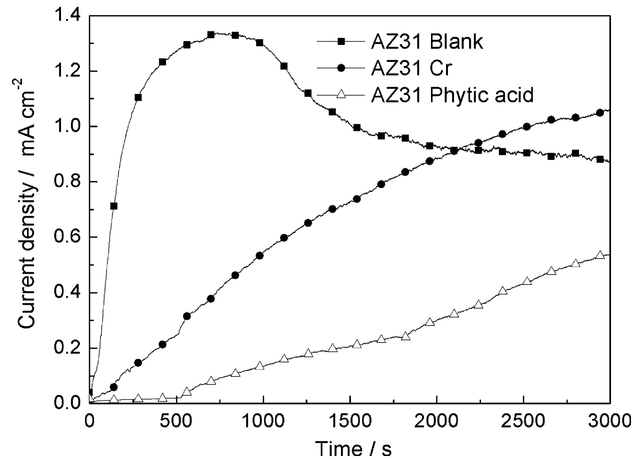

Fig. 4 Potentiostatic current transient curves for AZ31 magnesium alloy samples treated by phytic acid bath, chromate bath, and untreated in 0.05 mol L^{-1} NaCl electrolyte at the applied potential of −1.35 V

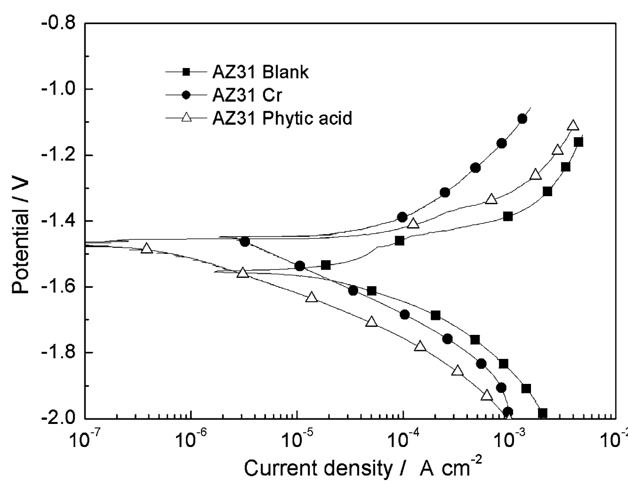

Fig. 5 Polarization plots for AZ31 magnesium alloy samples treated by phytic acid bath, chromate bath, and untreated in 0.05 mol L^{-1} NaCl electrolyte

3.5 Potentiodynamic polarization studies

Figure 6 showed the polarization curves of blank, Cr, and phytic acid coatings. From the polarization curves, it can be seen that the open-circuit potentials of these three specimens were $-1.46V_{SCE}$, $-1.33V_{SCE}$, and $-1.31V_{SCE}$, respectively. Compared with the blank samples, the open-circuit potentials of phytic acid-treated sample increased to 88 mV and corresponded to that of Cr sample. Simultaneously, compared with that of the untreated specimen, the current density of the treated specimens at the same potential decreased markedly. All these indicated that the phytic acid conversion treatment enhanced the corrosion resistance of AZ31 magnesium alloys.

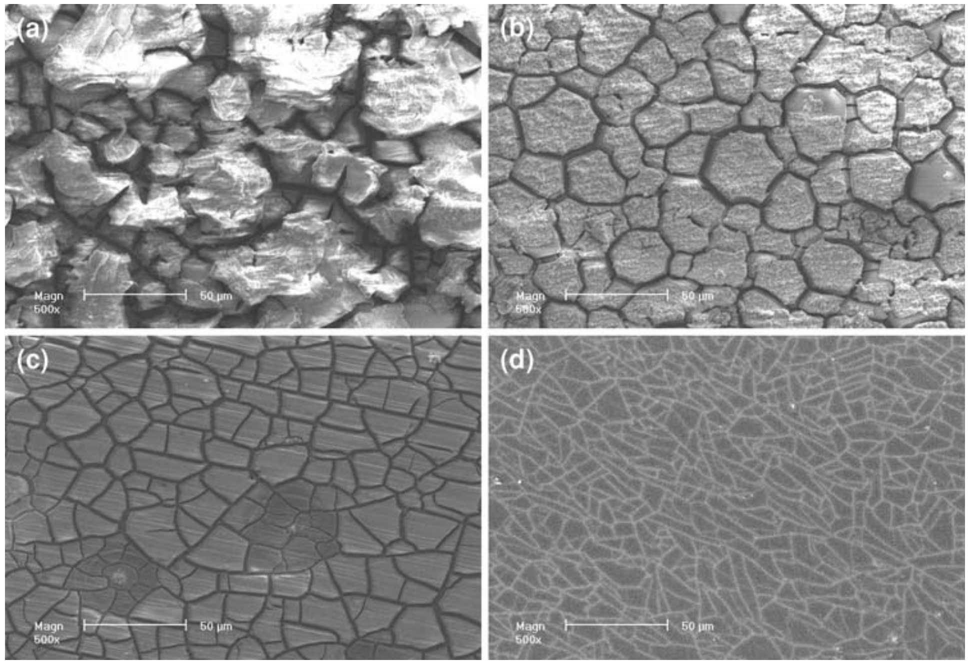

Fig. 6 SEM photographs for AZ31 magnesium alloy after immersion in 20.0 g L^{-1} phytic acid solution at different pH (×500) **a** pH = 1.13, **b** pH = 3.56, **c** pH = 6.59, and **d** pH = 8.06

4 Discussion

Phytic acid ($C_6H_{18}O_{24}P_6$), an inartificial and innoxious organic large molecular compound, consists of 24 oxygen atoms, 12 hydroxyl groups and 6 phosphate carboxyl groups [9, 10]. The ionization equations of phytic acid in the water were as follows.

$$RH_{12} + H_2O \leftrightarrow RH_{11}{}^{-} + H_3O^{+} \quad (1)$$

$$RH_{11}{}^{-} + H_2O \leftrightarrow RH_{10}{}^{2-} + H_3O^{+} \quad (2)$$

…

($R{=}C_6H_6O(PO_3)_6$)

The formation for the conversion coatings can be speculated as following. The alloying elements Mg, Al, and Zn would dissolve in the medium. The anodic reaction was the dissolution of metallic elements, where M represented Mg, Al, or Zn in the alloy.

$$Mg - 2e \rightarrow Mg^{2+} \quad (3)$$

The cathode reaction of the magnesium alloy was the reduction of the hydrogen ion H^{+}.

$$2H_3O^{+} + 2e \rightarrow 2H_2O + H_2 \uparrow \quad (4)$$

Finally, magnesium ion reacted with hydroxyl and phytic acid.

$$Mg^{2+} + 2OH^{-} \rightarrow Mg(OH)_2 \quad (5)$$

$$Mg(OH)_2 \rightarrow MgO + H_2O \quad (6)$$

$$RH_{10}{}^{2-} + Mg^{2+} \rightarrow MgRH_{10} \quad (7)$$

The pH of phytic acid solution (20.0 g L^{-1}) was 1.13. The pH was not adjusted during the conversion process. The reaction was too acutely to form integrated coatings on the surface. The SEM photographs of magnesium alloy immersed in the 20.0 g L^{-1} phytic acid solution with different pH (1.13, 3.56, 6.59 and 8.06) were shown in Fig. 6. As can be observed in Fig. 6, it could be found that the visible cracks appeared on the metal surface in the bath with low pH. The cracks became weakened with pH increasing. These indicated that the compact coatings could not form on the surface of magnesium alloy if the pH value was too low. So, during the process of conversion treatment, adjusting pH was necessary. Furthermore, if pH > 12.00, the coatings could hardly formed in a short time, and if pH < 9.00, the phytic acid bath would be denatured easily. The optimal pH range of phytic acid bath was 9.00–10.00.

5 Conclusion

The conversion coatings obtained with the phytic acid chemical conversion method improved the corrosion resistance of AZ31 magnesium alloy. The results of this study were as follows:

(1) After treatment in the bath, a transparent coating could be formed on AZ31 magnesium alloy. Observation via SEM, the coating was found to be compact.
(2) Analyzed by EMPA and IR spectrum, it could be concluded that the conversion coating formed by phytic acid bath was mainly composed of phytate and oxide or hydroxid, etc.
(3) The electrochemical tests showed that the phytic acid bath conversion treatment enhanced the corrosion

resistance of AZ31 magnesium alloys. The optimal pH of the phytic acid bath was 9.00–10.00.

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