Effect of pH on Phytic Acid Conversion Coating on AZ31B Magnesium Alloy

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Abstract: The influences of pH on the formation process, corrosion resistance and microstructure, chemical state of the phytic acid conversion coatings on AZ31B magnesium alloy were investigated by electrochemical measurements, hydrogen evolution method, scanning electron microscopy (SEM) and the energy dispersive X-ray spectroscopy (EDS), respectively. The results show that the reaction rate of magnesium alloy with phytic acid was fastest under pH=1, followed by pH=2 and pH=6 during the formation process of the conversion coatings. The coating surface formed under pH=1 was fragmentized and had some big cracks. Some cracks were also on the surface of the coating formed under pH=2 and the cracks were small and uniform. The sample was entirely covered under pH=6 and the conversion coating was thin. The conversion coating mainly consisted of the compounds of magnesium, aluminum, zinc, oxygen and phosphorus. The conversion coating formed under pH=2 had higher corrosion resistance than that of the conversion coatings formed under pH=1 and 6 and the treated samples with phytic acid has better corrosion resistance than untreated sample.

Keywords: phytic acid; pH value; magnesium alloy; conversion coating; corrosion resistance

1. Introduction

Magnesium alloys are considered to be engineering materials with promising future in the automotive, aeronautic, electronic and recreational industries, owing to their low density, high specific strength, and good castability, machinability and weldability [1-4]. However, magnesium and its alloys are electrochemically active as a result of susceptible to corrosion in various environments, which greatly limits their further use. In order to enhance corrosion resistance of magnesium alloys, one of the most effective methods is to form a conversion coating on the magnesium alloy surface. In general, conversion coating behaving as barrier protects metal from corrosive environment. Conversion coating has been received increasing attention during the past years. [5-12]. The treatment solution of conventional chemical conversion contains chromium oxide or dichromate (hexavalent chromium) in practice [8]. The solution containing hexavalent chromium compounds is harmful to environment, which has been restricted and forbidden to be used in many countries. There is a great need for the development of less harmful treatment methods. Phytic acid, an inartificial and innoxious organic macromolecule compound, consists of 24 oxygen atoms, 12 hydroxyl groups and 6 phosphate carboxyl groups [13]. The peculiar structure of phytic acid makes it has powerful chelating capability with many metal ions. The metal atoms or cations on the surface of 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 coating which could insulate the contact of magnesium alloy base and environmental media. The corrosion resistance of magnesium and its alloys could be improved.

There were some literatures about phytic acid conversion coatings on magnesium alloys in recent years [14-18]. The influence of phytic acid concentration on performance of phytic acid conversion coating on the AZ91D magnesium alloy was discussed in detail [14].

The corrosion resistance of the conversion coatings formed under different concentration, pH value, temperature and time was investigated roughly by electrochemical measurements and hydrogen evolution method [15-18]. Pan F S et al. studied the effect of technical parameters on phytic acid conversion coating on AZ61 magnesium alloy [15]. The results show that the phytic acid conversion coating formed in 0.5mg/ml phytic acid solution (pH=5) for 20 min immersion at room temperature had best corrosion resistance. The studies of Gao Lili et al. [17] showed that the pH value of the solution was the main influencing factor that the phytic acid conversion coating was formed on Mg-Li alloy, and optimum process parameters were confirmed as follows: solution concentration was 20g/L, pH value was 6, treating temperature was 35 ℃ and treating time was 10 min. Jianrui Liu et al. found that the phytic acid conversion coating had good corrosion resistance in immersion test of 3.5% sodium chloride solution when AZ91D magnesium alloy was treated in the solution containing 0.5 ~1% phytic acid at 25~60 ℃ and pH 3~5 for 30~60 min [18].

The aforementioned studies indicate the pH value of phytic acid has significant influence on the properties of the conversion coatings on magnesium alloys. But the effect of pH value of phytic acid on the forming process of the conversion coatings on magnesium alloys and the corrosion resistance of conversion coating on AZ31B magnesium alloy have been less studied. In this study, the effect of the pH value on phytic acid conversion coating on AZ31B magnesium alloy has investigated.

2. Experimental Procedures

2.1 Sample preparation

The substrate material used in this study was AZ31B magnesium alloy (Mg-2.91%Al- 0.85%Zn-0.4%Mn - 0.21%Si) with the size of 7× 4× 1 mm. The samples were degreased in 10% sodium hydroxide and then rinsed in deionized water to remove all the alkali before the conversion treatment.

Phytic acid is a chemical reagent, purity≥50%, and the other materials are all analytical reagent, purity≥99%. The conversion coatings were prepared by immerging AZ31B magnesium alloy samples in the phytic acid solution containing 5 g/L phytic acid at 40 ℃ and pH=1, 2 and 6 for 1 h ,respectively. The pH values of conversion solutions were adjusted with triethylamine. The samples with a chemical conversion coating were taken out from the treatment solution, washed with distilled water and then dried at room temperature.

2.2 Measurements

The forming process of the conversion coating on AZ31B magnesium alloy in phytic acid solution at 40 ℃ was evaluated through open circuit potential (OCP) experiments and hydrogen evolution method. The corrosion resistance of the phytic acid conversion coating in 3.5% sodium chloride solution at room temperature was evaluated through potentiodynamic polarization curves experiments and hydrogen evolution method. Open circuit potential (OCP) and potentiodynamic polarization curves measurement were carried out using a CHI604C electrochemical workstation. A three electrode cell with sample that surface area was 2.68 cm2 as the working electrode, saturated calomel electrode (SCE) that was interfaced to the solution via a salt bridge as the reference electrode and platinum sheet as the counter electrode in this test. Before the potentiodynamic sweep experiments, the samples were immersed into electrolyte for about 10 min. The sweeping rate was 10 mV/s for all measurements and the scanning voltage range was determined by the rest potential according to the open circuit potential-time curve. The values of the corrosion potential (Ecorr) and the corrosion current density (icorr) were calculated using special analysis software. The surface morphology was observed using a TESCAN VEGA II scanning electron microscopy (SEM). The element compositions of coating were examined by the energy dispersive X-ray spectroscopy (EDS).

Magnesium is a very active metal element. The low potential leads it to react easily with phytic acid and water to produce hydrogen. When a magnesium alloy contacts with the solution, the main reaction in solution is as following:

$$Mg + RH_{12} = MgRH_{10} + H_2 \uparrow \quad (1)$$

$$R = C_6H_6O_6(PO_3)_6$$

$$Mg + 2H_2O = Mg(OH)_2 + H_2 \uparrow \quad (2)$$

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According to the reaction (1) and (2), there is 1 M H_2 formed and escaped out of solution when 1 M magnesium reacted. The H_2 can be collected in a container with scale to be measured. So the forming process of the conversion coatings on magnesium alloys in phytic acid solution and the corrosion resistance of conversion coating in 3.5% sodium chloride solution can be evaluated through the rate of hydrogen evolved. The rate of hydrogen evolved can be calculated based on the following formula:

$$\nu_{H_2} = \frac{V}{S \times t} \quad (3)$$

Where, ν_{H_2} stands for the average rate of hydrogen evolved, ml·min-1 (h^{-1})·cm^{-2}; V is the hydrogen evolution volume, ml; S is the surface area of the sample, cm^2; and t is the time of immersion test, min or h.

The schematic diagram of the set-up for measurement of the hydrogen evolution method is shown in Fig. 1 [17, 18]. The sample was put into the center of the beaker with phytic acid solution or 3.5% sodium chloride solution. The water level in the buret was adjusted to a known scale before the immersion test. The funnel was vertically laid above the sample. The hydrogen formed in the process of immersion test was collected in the above volume of the funnel. The volume of hydrogen evolved was recorded. According to (3), the hydrogen evolution rate could be calculated. The forming process of the conversion coating and the corrosion rate of the conversion coatings could be evaluated based on the change of the hydrogen evolution rate.

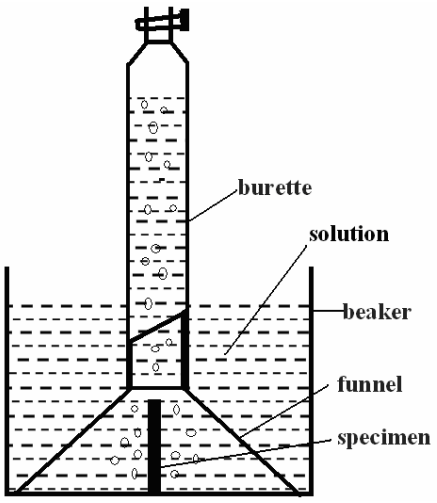

Figure 1. Schematic diagram of the set-up for measurement of the hydrogen evolution rate.

3. Results and discussions

3.1. The formation process of phytic acid conversion coating

The open circuit potential (OCP) values of AZ31B samples as a function of time in phytic acid solution with different pH values are shown in Fig. 2. When pH=1, the OCP for samples initially increased from -1640 mV to -1250 mV, reaching the maximum after 5 s immersion. It may result from the formation of phytic acid conversion coating and magnesium hydroxide corrosion products [19]. Then it decreased following possible attack of the metal because the hydrogen ions were more. It stabilized at approximately -1470 mV after 2000 s immersion. In comparison, in the other two solutions under pH=2 and 6, the variation of the OCP values was fluctuant, and it stabilized at approximately -1300 and -1420 mV after 8000 s immersion, respectively.

The curves of hydrogen evolution rate during the formation of conversion coatings in phytic acid with different pH values are shown in Fig. 3. It can be seen that when AZ31B sample was treated in the solution under pH=1, the hydrogen evolution rate changed rapidly and it decreased with the immersion time increased. The reason might be that this solution consisted of a great amount of hydrogen ions, which led to the quick reaction of magnesium alloy with phytic acid to produce a lot of hydrogen. With immersion time increased, the conversion coating formed and covered the surface of AZ31B sample gradually. The conversion coating could inhibit the corrosion of sample and the hydrogen evolution rate also decreased.

Besides, when pH=6, the hydrogen evolution rate was the slowest among three solutions. The reason might be that when pH value was high, the electrochemical reaction that magnesium ions and hydrogen was formed was not easy to start. The hydrogen evolution rate was mediacy under pH=2.

3.2 Morphology and composition of conversion coatings

Fig. 4 shows the SEM surface micrographs and EDS spectra of AZ31B samples treated in phytic acid solu-

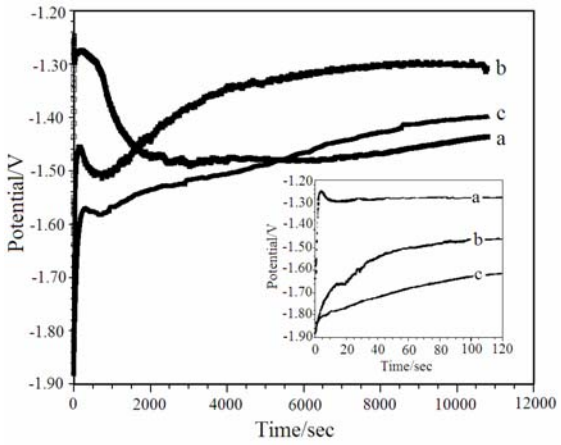

Figure 2. OCP of AZ31B magnesium alloy as a function of time in phytic acid solution: (a) pH=1, (b) pH=2, (c) pH=6.

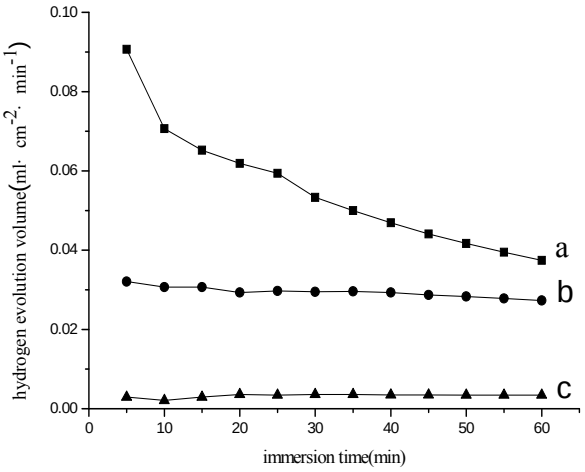

Figure 3. The curves of hydrogen evolution rate during the formation of conversion coatings on AZ31B in phytic acid with different pH: (a) pH=1, (b) pH=2, (c) pH=6.

tions with different pH values. It is seen that the sample was partly covered under pH=1 and the coating was fragmentized with some big cracks because of hydrogen evolution, which is about 2.5 μm in width. Some cracks were also observed on the surface of the conversion coating formed under pH=2, but the cracks were small and uniform, the width of the cracks is approximately 1 μm. The EDS results showed that the coatings were composed of magnesium, aluminum, zinc, oxygen and phosphorus elements. The EDS signals of oxygen and phosphorus suggest the presence of phytic acid on the surface of AZ31B sample. Although when pH=6, the magnesium alloy sample was entirely covered, there were some micro-cracks on the conversion coating surface, which is

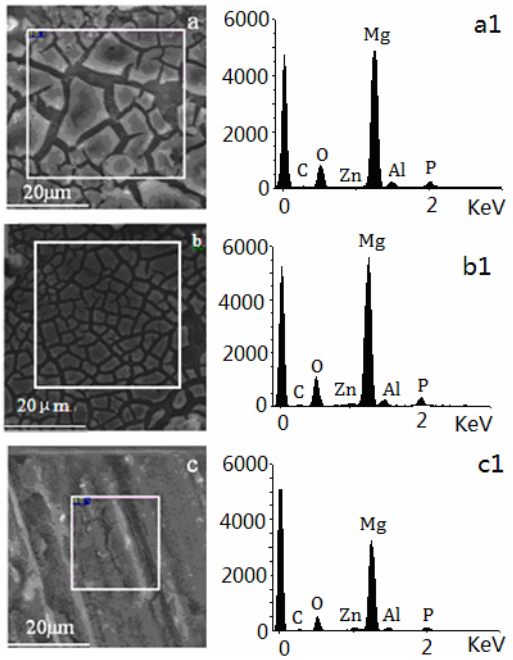

Figure 4. The SEM images (a–c) and EDS analysis (a1–c1) of conversion coatings in phytic acid solutions with different pH values:(a and a1) pH=1; (b and b1) pH=2; (c and c1) pH=6.

approximately 0.4 μm in width. And the quantity of oxygen and phosphorus was fewer than that of pH=1 and 2 from EDS signals, that is to say, the conversion coating formed in the solutions with pH=6 was thin.

3.3 The corrosion resistance of conversion coating

The potentiodynamic polarization curves of AZ31B samples with conversion coatings in 3.5% sodium chloride solution are shown in Fig. 5. The corrosion potentials (E_{corr}) and corrosion current densities (i_{corr}) of the samples were summarized in Table 1. The results indicate that the conversion coating formed under pH=2 has better corrosion resistance than that of the conversion coatings formed under pH=1 and 6. The reason might be that when magnesium alloy was treated in the solution under pH=1, magnesium could intensely react with phytic acid to produce a lot of hydrogen. The rapid release of hydrogen prevented from the formation of conversion coating on the surface of AZ31B sample. The conversion coating did not cover the surface of sample completely, which reduced its corrosion resistance. In the conversion solution under pH=6, the electrochemical

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reaction that magnesium ions and hydrogen were formed was not easy to start. So the conversion coating was thin and could not offer an effective corrosion resistance [18]. And there was a gentle reaction between magnesium and phytic acid under pH=2, which was in favor of forming effective surface coating. So the corrosion resistance of AZ31B sample could be improved. Furthermore, it can be seen that the E_{corr} of the samples after treatment with phytic acid solution under pH=1, 2 and 6 were significantly shifted positively about 77 mV, 204 mV and 10 mV compared to the untreated sample and the corrosion current density i_{corr} decreased about one orders than that of the untreated sample. This means that the treated samples with phytic acid has better corrosion resistance than untreated sample.

The hydrogen evolution rate curves of AZ31B samples with conversion coating in 3.5% sodium chloride solution are shown in Fig. 6. It can be seen that the change of the hydrogen evolution rate for the conversion coating formed in the treatment solution under pH=2 was relatively smooth, which was about 0.025 ml/(h·cm^2). For the conversion coatings formed under pH=1 and 6, the hydrogen evolution rate was 0.07 and 0.11 ml/ (h·cm^2), respectively. That is to say, the conversion coating

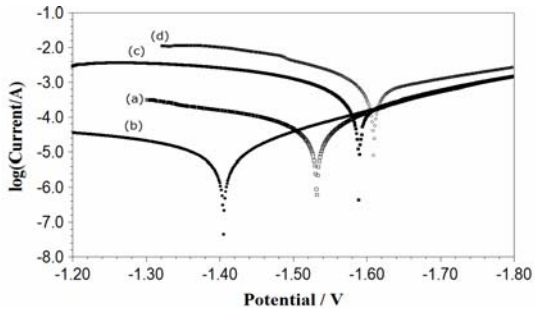

Figure 5. Potentiodynamic polarization curves of AZ31B magnesium alloy samples before and in a 3.5 wt.% sodium chloride aqueous solution: (a) pH=1; (b) pH=2; (c) pH=6; (d) AZ31B magnesium alloy.

Table 1. E_{corr} and i_{corr} obtained from the electrochemical potentiodynamic polarization curves.

samples	E_{corr} (V_{SCE})	i_{corr} (A/cm^2)
(a) treatment in phytic acid solution with pH=1	-1.532	2.325×10-5
(b) treatment in phytic acid solution with pH=2	-1.405	0.376×10-5
(c) treatment in phytic acid solution with pH=6	-1.589	1.712×10-4
(d) AZ31B magnesium alloy	-1.609	5.534×10-4

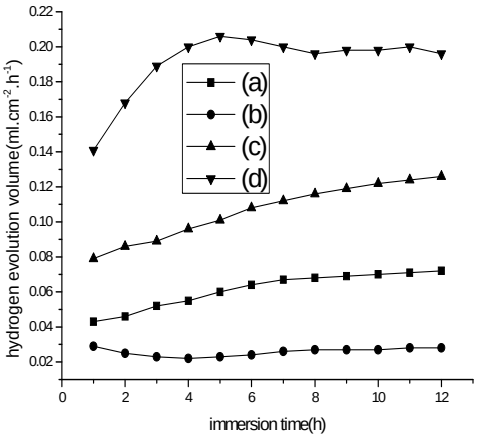

Figure 6. Curves of hydrogen evolution rate of AZ31B magnesium alloy samples before and in a 3.5 wt.% sodium chloride aqueous solution: (a) pH=1; (b) pH=2; (c) pH=6; (d) AZ31B magnesium alloy.

formed under pH=2 had better corrosion resistance than that of the conversion coatings formed under pH=1 and 6. Furthermore, the hydrogen evolution rate of the untreated sample was about 0.20 ml/(h·cm^2). That is to say, the treated samples with phytic acid have also better corrosion resistance than untreated sample.

4. Conclusions

(1) The reaction rate of magnesium alloy with phytic acid was fastest under pH=1, followed by pH=2 and pH=6 during the formation process of the conversion coatings.

(2) The surface of the coatings formed under pH=1 was fragmentized with some big cracks. Some cracks were also on the surface of the coating formed under pH=2 and the cracks were small and uniform. The sample was entirely covered under pH=6 and the conversion coating was thin.

(3) The conversion coating mainly consisted of the compounds of magnesium, aluminum, zinc, oxygen and phosphorus.

(4) The conversion coating formed under pH=2 had higher corrosion resistance than that of the conversion coatings formed under pH=1 and 6 and the treated samples with phytic acid has better corrosion resistance than untreated sample.

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