Effects of magnetic fields on the phosphate conversion coating of AZ91D magnesium alloy

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Abstract

An external high parallel magnetic fields (MF) was imposed on the barium phosphate process of AZ91D magnesium alloy. The influences of the permanent MF on the morphology, the phase composition and the corrosion resistance of the barium phosphate coatings were studied using scanning electron microscope, X-ray diffraction, salt spay test. The results show that the coatings with MF are more compact, uniform, and smooth, and have better the corrosion resistance than without MF.

Key words: magnesium alloy; magnetic fields (MF); phosphate conversion coating; corrosion resistance

1. Introduction

Magnesium alloys have many attractive properties, including high strength-to-weight ratio, high thermal and electrical conductivities, and easy recyclables [1, 2]. Unfortunately, the important reason preventing the use of magnesium alloys is their poor corrosion resistance, especially in acidic environments and in salt-water conditions [3]. So magnesium alloys must be surface treated to increase their corrosion resistance when they are used as structural materials, which has the vital practical significance to develop their attractive properties [4].

Techniques for solving the problem included chemical conversion coatings [5], anodizing, micro-arc oxidation [6], vapor-phase processes, laser surface alloy [7], electroless plating and electrical plating [8, 9] and so on. Chemical conversion treatment is paid more attention because the conversion coatings are easy to apply, cost-effective and can increase the following coating’s adhesion [10]. But the traditional chromate chemical conversion coatings are widely used, these coatings provide corrosion protection by presenting a non-reactive barrier to the environment, through their self-healing properties and by the inhibiting effect of Cr. Due to environmental hazards of chromate compounds, environmentally acceptable alternative chemical conversion coatings have been explored [11].

The aim of this paper was to develop a phosphate conversion treatment on the AZ91D magnesium alloy under magnetic fields (MF) and to study the composition and morphology of the conversion coating with MF and its corrosion resistance.

2. Experimental

2.1 Experimental materials

The AZ91D magnesium alloy specimens (100×50×3mm and 15×10×5mm) with the composition (wt %) of 9.21 Al, 1.287 Zn, 0.2 Mn, ≤0.08 Si, ≤0.004 Fe, ≤0.025 Cu, ≤0.001 Ni, and balance Mg were studied. Specimens were mechanically polished with SiC papers of 240, 400, 800 and 1200 grit, and then were cleaned with industrial alcohol under ultrasonic.

2.2 Experimental methods

all specimens were degreased for about 20 minutes in 5 ~10 wt. % NaOH solution, and then pickled in a mixture of 40 ~ 80 g / L HF and 30 ~ 70g / L C₂H₂O₂ pickling bath at room temperature for about 20
seconds, and then alkaline activation processed for about 20 minutes in about 30 wt. % NaOH at room temperature. And finally the conversion coatings were formed by immersing specimens in a bath containing phosphate acid, sodium fluoride.

The sketch map of the phosphate conversion treatment with MF device was shown in Fig.1. The No.1 in the figure is the source of the magnetic field, which is a permanent magnet.

The morphologies of the chemical conversion coatings with and without MF were observer by Environmental Scanning Electron Microscope (ESEM) (Model Quanta-200). The phase composition of the conversion coatings with and without MF was analyzed by Multifunctional X-ray Diffraction. The corrosion resistance of coatings with and without MF were studied by salt immersion corrosion (3.5% NaCl solution, pH = 7).

![Fig.1 Sketch map of the phosphate conversion treatment with MF device](image)

1 magnetic field; 2 container; 3 solution; 4 AZ91D magnesium alloy specimen; 5 thermocouple; 6 heater; 7 temperature controller and power supply)

3. Results and discussions

3.1 The surface morphology of the phosphate conversion coating on AZ91D alloy

The surface morphology of phosphate conversion coatings are shown in Fig.2.

![Fig.2 Surface morphology of the phosphate conversion coating on the AZ91D alloy](image)

(a) Without MF; (b) with MF

It can be seen from Fig.2 (a) that some micro-cracks exist on the surface of the phosphate conversion coating without MF, and the coating with MF is flatter, more compact and smooth.

3.2 The phase composition analysis of the phosphate conversion coating on AZ91D alloy

Figs.3 (a) and (b) show the XRD patterns of the phosphate conversion coating on the AZ91D alloys without and with MF. It can be found that the phase composition of the coating without MF is mainly
some amorphous phases, Mg and Al\textsubscript{12}Mg\textsubscript{17} phases, and the phase composition of the coating with MF is mainly amorphous phases, and some Mg phase, the crystal phase is much less than without MF. The phase composition of the phosphate conversion coating is mainly amorphous phases and the Mg and Al\textsubscript{12}Mg\textsubscript{17} phases is the magnesium alloys matrix phase\textsuperscript{[12]}. The coating with MF has much less matrix phase than without MF, which shows that the coating with MF is flatter, more compact and smooth, much less cracks, because of the more compact coating, the chance of the X radial shooting the magnesium matrix is less.

![Fig.3 XRD patterns of the phosphate conversion coating on the AZ91D alloy: (a) Without MF; (b) with MF](image)

Fig.4 shows the EDS pattern and analysis of the phosphate conversion coating with MF. It can be found that the coating mainly comprises P, O, Al, Ba, F, Mg, and it can be concluded that the composition of the coating mainly is Ba\textsubscript{3}(PO\textsubscript{4})\textsubscript{2}, Mg\textsubscript{3}(PO\textsubscript{4})\textsubscript{2}, AlF\textsubscript{3}, MgF\textsubscript{2}.

![Fig.4 EDS pattern and analysis of the phosphate conversion coating with MF on the AZ91D alloy](image)

| Element | Weight\% | Atomic\% |
|---------|----------|----------|
| C       | 0.10     | 0.27     |
| O       | 22.37    | 44.22    |
| F       | 14.79    | 24.63    |
| Mg      | 2.31     | 3.01     |
| Al      | 4.94     | 5.79     |
| P       | 11.76    | 12.01    |
| Ba      | 43.72    | 10.07    |

3.3 Salt immersion corrosion test of the phosphate coating on AZ91D alloy

In order to study salt immersion corrosion of the phosphate coating, lots of experiment were done, and one of them was shown in Fig.5, it shows the contrast photos between the coating with and without MF after immersion in 3.5\% NaCl solution for 1448h.

It can be found that the specimen without MF has mass corrosion on the edge and has some corrosion spots in the center, but the specimen with MF does not appear corrosion spot in the center and has a little corrosion on the edge. The results demonstrate that the phosphate conversion coating with MF can provide better protect than without MF.

From the sharp capability result contrast between the coatings with MF and without MF, we can conclude that the magnetic flux density in electrolyte volume must be possible.

According to the formula: 

$$ F = q v \times B $$

The magnet power can act on the solution ion and cause them accelerated directional movement along
the magnetic line, thus which accelerate the chemical reaction during the phosphate conversion coating, and the time of forming compact layer shortens and the work efficiency rise, because of lorentz force. Thus the coating with MF is flatter, more compact and smooth, further more the corrosion resistance of the coating is better.

4 Conclusions

1) The surface of the phosphate conversion coating under MF is flatter, more compact and smooth, and there are much less cracks than without MF. The composition of the coating mainly is Ba$_3$(PO$_4$)$_2$, Mg$_3$(PO$_4$)$_2$, AlF$_3$, MgF$_2$.

2) The phosphate conversion coating under magnetic field can provide better protect for magnesium alloy matrix than without MF. Moreover the time of forming compact layer shortens and the work efficiency raise.

3) The magnet power can act on the solution ion and cause them directional movement, thus which accelerate the chemical reaction during the phosphate conversion coating.

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