

# Improvement of corrosion resistance of pure magnesium via vacuum pack treatment

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Received 17 May 2007; received in revised form 26 June 2007; accepted 30 June 2007

Available online 7 July 2007

## Abstract

An aluminized coating on pure magnesium was conducted by vacuum pack aluminizing in order to improve its corrosion resistance. XRD and SEM/EDS analysis show that the alloying coating could be divided into two layers: the inner layer is mainly composed of  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> phase and the outer layer is mainly composed of  $\alpha$ -Al. This coating is different from that obtained by diffusion alloying under protective atmosphere in its structure and phase constituents. A visible transition layer of aluminum in magnesium was found between the alloying layer and the magnesium substrate. The electrochemical testing results showed that the corrosion resistance of Mg was significantly improved due to the formation of the Al-rich layer and the large quantity of  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> on the surface. The bonding between the alloying layer and the substrate is metallurgical, and the micro-hardness of this layer is increased significantly.

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**Keywords:** Magnesium; Aluminized coating; Corrosion resistance; Vacuum pack treatment

## 1. Introduction

Magnesium alloy is being increasingly used in automotive industry, electronic industry, aerospace industry, etc., for its low density, high strength-to-weight ratio and good electromagnetic shielding characteristics [1]. However, its poor corrosion resistance has limited its further application [2]. Nowadays, many surface treatments have been applied in magnesium and its alloys to improve their corrosion resistance, such as chemical conversion, anodic oxidation, organic coating and metal coating, etc. [3–8]. However, thin films produced by these processes are insufficient in machine parts used under harsh conditions [9,10]. Recently, Ma et al. [9] has achieved a diffusion alloying layer on the surface of ZM5 magnesium alloy to improve the corrosion and wear resistance by solid diffusion Zn/Al, but the processing time is too long (about 12 h). Zhu and Song [10] has achieved an aluminum-alloyed coating on the surface of magnesium alloy AZ91D. However, a protective gas was needed by both Ma and Zhu in the experiments in order to avoid the oxidation of the Al powder and the Mg matrix. In the present paper, we try to

aluminize the surface of pure magnesium by vacuum pack treatment and give a preliminary investigate on the microstructures, hardness and corrosion property.

## 2. Experimental procedures

An as-received pure magnesium ingot was cut into 15 mm × 15 mm × 4 mm plates and polished up to 1000# SiC paper. The specimens were cleaned ultrasonically in an acetone bath for 10 min and then dried in air. The specimens were embedded in aluminum powder in an iron container. And the aluminum powder, whose purity was 99.5 wt% and whose particle diameter was 200 meshes, was used for the source of diffusion element. A vacuum heat-treatment furnace was used to achieve the aluminized process. The heat treatment for diffusion coating was carried out at 693 K (±1 K) for 90 min with a vacuum level superior to 10<sup>-2</sup> Pa, and the heating rate is 14 K/min approximately. The specimens were cooled down to room temperature in the furnace, then taken out to the air.

After the aluminized processing, the microstructure and the chemical components of the aluminized coating were analyzed by an optical microscope (OM) and a JSM-6700F scanning electronic microscope (SEM) equipped with OXFORD INCA X-ray energy disperse spectrometer (EDS). Before the microstructure observation, the specimens were etched with 5 vol% nital solution lightly. The micro-hardness distributions along depth direction were measured by the HX-1 micro Vickers hardness tester ( $f=50$  g,  $t=10$  s). The phase constitution of the aluminized layer was identified by X-ray diffraction (XRD) with Cu K $\alpha$  radiation on KY-2000 diffract meter. The corrosion property of the aluminized specimen was tested with PS-168A electrochemical testing system. The potentiodynamic polarization measurement was carried out in 5 wt% NaCl solution comparing with the pure Mg and AZ91D magnesium alloy to inves-

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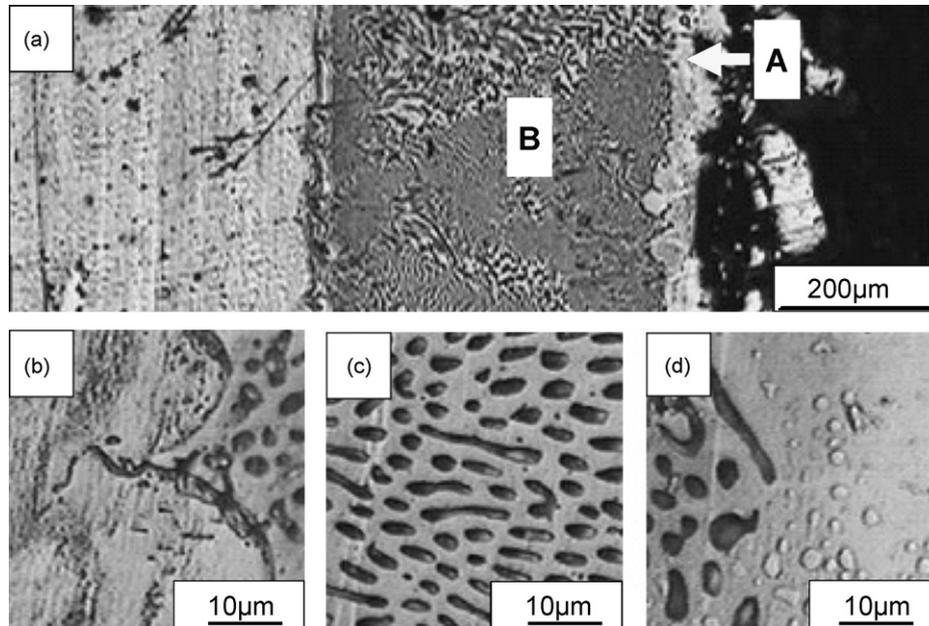


Fig. 1. OM photographs of microstructure of aluminized specimen in cross-section (a) and the magnification of aluminized coating: (b)–(d) (the specimens were etched with 5 vol% natal solution).

investigate the corrosion behavior of the aluminized coating. A saturated calomel electrode (SCE) was used as reference. The counter electrode was made with platinum and the potentiodynamic scan was recorded. The scanning rate was 2 mV/s.

### 3. Experimental results

#### 3.1. Microstructure

Fig. 1 shows the OM photographs of the aluminized specimen in the cross-section. It can be seen from Fig. 1(a) that an alloying coating, which is homogeneous, dense, no cracks and pores, was formed on the surface of the substrate. The whole coating can be divided into two layers: the outer layer is bright with a thickness about 50  $\mu\text{m}$  (marked as A); the inner layer is much thicker than the outer layer with a thickness about 500  $\mu\text{m}$  (marked as B). Fig. 1(b)–(d) were the local magnification graphs of the transition layer, the inner layer and the outer layer of the aluminized coating corresponding to Fig. 1(a), respectively. The inner layer of the aluminized coating contains mainly two different phases, and the discontinuous phase was heavily etched as shown. The outer layer also contained some precipitated phase as presented in Fig. 1(d). The visible transition layer's thickness was about 20  $\mu\text{m}$ . It can also be seen that the transition layer penetrated deeply into the substrate along the grain boundaries [10].

The cross-sectional SEM images of aluminized specimen were presented in Fig. 2(a). It was shown that a large quantity of precipitated phases existed and dispersed in this coating. Fig. 2(b) was the SEM images of the intermetallic compounds layer. Corresponding with the OM graphs shown in Fig. 1, the same conclusion which the alloying layer is homogeneous, dense and no cracks could be got. The white line and the marked numbers show the positions of line scanning and point scanning of chemical composition analysis by EDS, respectively. The results were shown in Fig. 3 and Table 1. The results could indicate that: (1) much more Al than Mg is contained in the outer layer, that is to say that the outer layer makes Al as its matrix; (2) the ratio of Mg-to-Al is not uniform even in the intermetallic compounds layer; (3) the change of Al concentration is apparent in both sides of the diffusion layer, and almost no Al is found in the Mg substrate as shown in Fig. 3.

To further analyze the structure of the intermetallic compounds layer, the SEM images after etched with 5 vol% natal was shown in Fig. 2(b). Some precipitated phase and the gray matrix were found in this layer. The precipitated phase was poor to corrosion and could easily be etched off as shown. Quantitative analysis of the chemical composition of these two phases by EDS was shown in

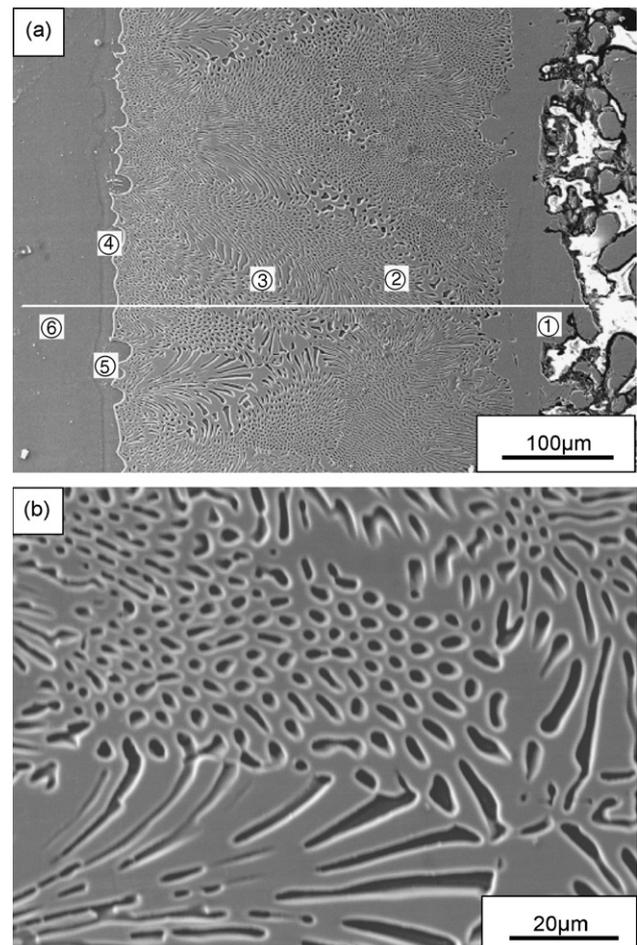


Fig. 2. Cross-sectional SEM images of the aluminized specimen (a) and the Mg–Al intermetallic compounds layer (b) (the specimens were etched with 5 vol% natal solution).

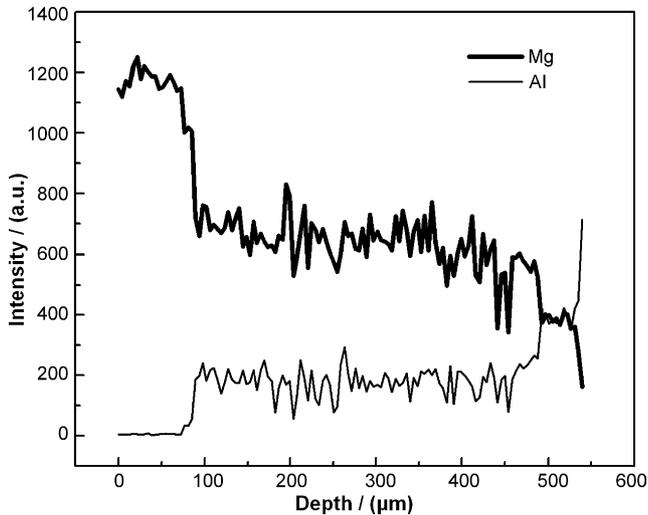


Fig. 3. Line scanning spectrum corresponding to Fig. 2(a).

Table 1  
Concentration analysis results of the aluminized layer corresponding to Fig. 2(a)

Element	Mg		Al	
	wt%	at%	wt%	at%
1	41.21898	43.78	58.78102	56.22
2	69.96587	72.11856	30.03413	27.88144
3	69.53125	71.70259	30.46875	28.29741
4	93.56996	94.16837	6.430041	5.831631
5	93.28012	93.90803	6.719876	6.091968
6	100	100	0	0

Table 2. It indicated that the precipitated phase and the gray matrix apparently had different chemical compositions, i.e., the precipitated phase had little Al than that of the matrix. It could further be deduced by the Mg-to-Al atom ratio that the precipitated phase and the gray matrix in Fig. 2(b) were the magnesium solid solution and the intermetallic compound  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub>, respectively.

### 3.2. Phase constitution

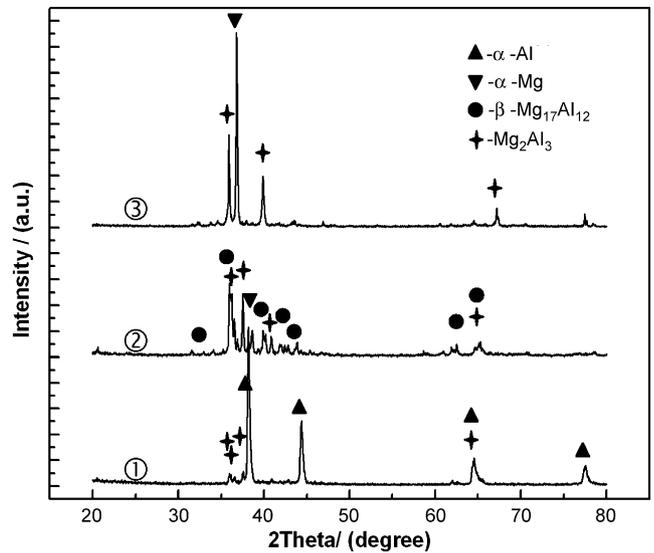
The results of XRD analysis was shown in Fig. 4. Three layers of the coating were tested after polished with SiC waterproof abrasive paper, i.e., 50  $\mu$ m, 150  $\mu$ m and 300  $\mu$ m far from the surface, and were marked as (1), (2) and (3) in Fig. 4, respectively. The results showed that: (1) the outer layer of the aluminized coating was mainly consisted of  $\alpha$ -Al and small amount of Mg<sub>2</sub>Al<sub>3</sub>; (2) the inner layer of the aluminized coating contained large quantities of  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub>. Other phases such as Mg<sub>2</sub>Al<sub>3</sub> and  $\alpha$ -Mg were also found in this area; (3) the third layer analyzed mainly contained  $\alpha$ -Mg and Mg<sub>2</sub>Al<sub>3</sub>, and no  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> was found.

### 3.3. Micro-hardness

The micro-hardness distribution along the depth direction was shown in Fig. 5. The magnesium substrate and the aluminized coating had been repre-

Table 2  
Concentration analysis results of the Al–Mg intermetallic compounds layer

Element	Mg		Al	
	wt%	at%	wt%	at%
Gray zone	57.9926	60.5154	42.0074	39.4846
Precipitated phase	87.1573	88.3037	12.8437	11.6963

Fig. 4. XRD patterns of the aluminized layer after polished different thickness (50  $\mu$ m, 150  $\mu$ m and 300  $\mu$ m).

sented. The testing results showed that the micro-hardness of the specimen was greatly increased by the vacuum solid diffusion treatment. It can be estimated that the micro-hardness of the aluminized coating varied from 65 HV to 120 HV, and it was three times more than that of the substrate, which only had a maximum micro-hardness of 35 HV. And the transition layer also had a much higher micro-hardness than the substrate as shown.

### 3.4. Electrochemical corrosion property

Polarisation curves of aluminized Mg, pure Mg and AZ91 alloy in 5 wt% NaCl solution were presented in Fig. 6. The open circuit potential of Mg is  $-1.250$  V (versus SCE). After aluminized treatment, the open circuit potential increased to  $-0.866$  V (versus SCE), which is much higher than the value of AZ91 magnesium alloy the same experimental condition (which is  $-1.214$  V (versus SCE)). Moreover, the corrosion current density of aluminized simple decreased by one order of magnitude (from  $1.3 \times 10^{-3}$  mA/cm<sup>2</sup> to  $1.0 \times 10^{-4}$  mA/cm<sup>2</sup>). All the results show that the alloying coating on the surface of pure Mg can improve the corrosion resistance of the Mg substrate effectively.

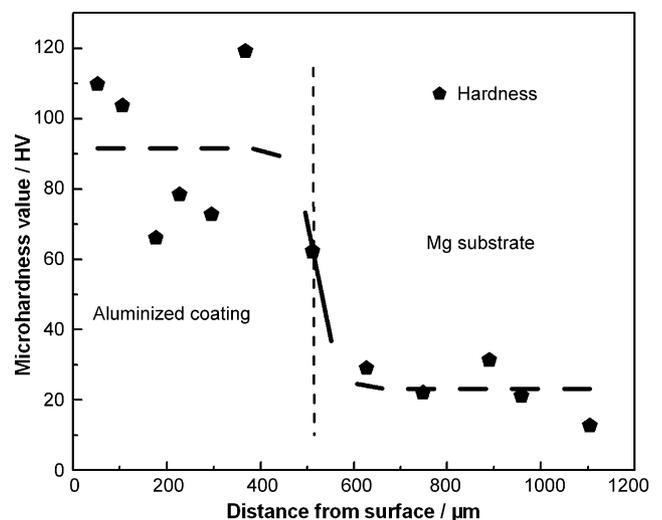


Fig. 5. The micro-hardness distribution in the aluminized layer.

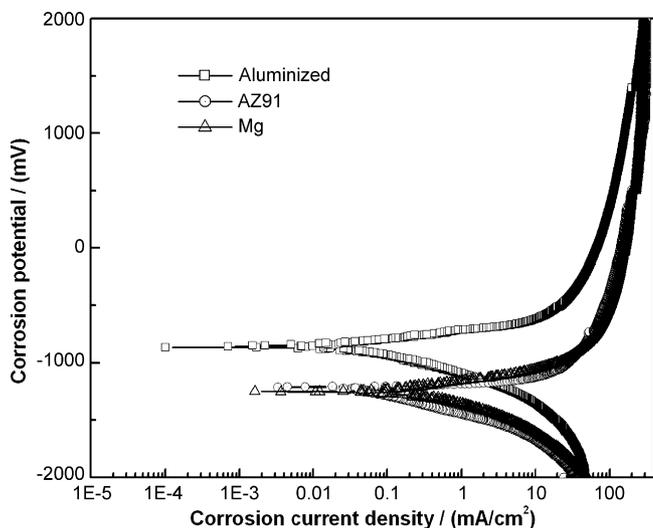


Fig. 6. Polarisation curves of aluminized Mg, pure Mg and AZ91 alloy.

#### 4. Discussion

Mg has a higher chemical activity and can be oxidized in air condition easily, especially when it is heated. For this reason, the methods of protective gas or vacuum condition could be helpful to avoid this problem. In our works, the vacuum furnace was used in diffusion processing.

At the beginning of the aluminizing, the diffusion firstly occurred at the points where Mg surface and Al particles contacting with each other and a solid solution of Al in Mg substrate was formed in these areas firstly. During the diffusion process, Al element would diffusion into the Mg substrate faster along the grain boundaries. For the solid solubility of Al in Mg is limited, reaction diffusion will be occurred and some intermetallic compounds such as  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> will be formed in some areas of the Mg surface along with the diffusion going on. Once these intermetallic compounds connected with each other an intermetallic compounds layer is formed. And for its barrier effect the diffusion speed of Al decreased. Because Al has a lower diffusion speed in intermetallic compounds layer than that in Mg substrate. In addition, it was found that the diffusion of Mg into Al was much easier than that of Al into Mg [11], that is to say interdiffusion would occur during the whole diffusion process. That is to say that the aluminized coating is a new alloying layer produced by the interdiffusion of magnesium and aluminum. This makes the bond between the aluminized coating and the substrate was metallurgical [12].

Furthermore, it is apparent that the microstructure shown in Fig. 1 is different from that of reported by Zhu and Song [10], which is not uniform (from 10  $\mu$ m to 200  $\mu$ m) and mainly contains small equiaxed grains and dendrites. The difference may be caused by the different condition between the protective gas and vacuum and it is interesting to give further research.

It has been well studied that whether or not the  $\beta$ -phase will improve the corrosion resistance of substrate is determined by its volume fraction and distribution. Only a high volume fraction of  $\beta$ -phase would act as a corrosion barrier and significantly reduce the corrosion rate [13–16]. The XRD patterns showed that the

content of  $\beta$ -phase was much higher than other phases. In addition, the aluminized coating's matrix was  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub>, and this contributes a lot to the improvement of the corrosion resistance of substrate. Moreover, the Al-rich layer of the aluminized coating can also works as a protective player for the improvement of the corrosion resistance of the material.

It is apparent that the existence of the intermetallic compounds leads to the increase of the hardness. In another words, the increase of the surface hardness will be good for the improvement of the wear resistant property and will enlarge the serviceable range of magnesium and its alloys.

The aluminized coating can separate the Mg substrate from the NaCl solution effectively; therefore, the corrosion resistance of the Mg substrate is improved. It also should be recognized that if pores or cracks existed in the aluminized coating, the alloying coating would be etched through easily for the formation of the galvanic corrosion. So the corrosion would be accelerated. So the integrity of the coating is very important to the improvement of corrosion resistance. Further research should be carried out to achieve this aim.

#### 5. Summary

- (1) An aluminized coating which is uniform and dense can be formed on the surface of pure magnesium by vacuum pack aluminizing treatment at 693 K for 90 min. The bond between the aluminized coating and the substrate was metallurgical.
- (2) The aluminized coating can be divided into two layers: the outer layer is  $\alpha$ -Al layer and the inner layer is intermetallic compounds layer.
- (3) The micro-hardness of the surface is greatly increased after the vacuum solid diffusion treatment and it is beneficial to the improvement of the wear resistance.
- (4) The alloying layer on the surface can improve the corrosion resistance of the Mg substrate effectively.

#### Acknowledgments

The study was supported by the National Natural Science Foundation of China (NSFC) under Grant no. 50171046, Specialized Research Fund for the Doctoral Program of Higher Education (SRFDP) under Grant no. 20050112001, the Natural Science Foundation of Shanxi Province, China under Grant nos. 20021051, 20021052 and 2006011051 and Specialized Fund for the Innovation of College Student of Taiyuan City under Grant no. 07010727.

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