Fabrication and Microstructure of Diffusion Alloyed Layers on Pure Magnesium Substrate

Alloyed layers on pure magnesium were created by means of the heating of the magnesium sample covered with Al+Zn powders mixture containing 20 wt.% Zn and 40 wt.% Zn in vacuum furnace. The microstructure and related composition of the alloyed layers were investigated using optical microscopy and scanning electron microscopy equipped with an energy dispersive X-ray system (EDS). The results revealed that the microstructure, thickness and microhardness of the obtained layers depended on the Zn content in the powder mixture. The alloyed layers were composed of the Mg-Al-Zn intermetallic phases and Mg-based solid solution containing Al and Zn. The multi-phase layer was diffusion bonded with magnesium substrate. The thickness of the layer fabricated by the heat treatment in contact with a powder mixture containing 40 wt.% Zn was twice as high as compared to that obtained with the powder mixture containing 20 wt.% Zn. The hardness value of the alloyed layers was much higher than that of the magnesium substrate.

Keywords: magnesium, alloyed coating, Mg-Al-Zn intermetallic phases, hardness

1. Introduction

Magnesium and its alloys are extensively used in many construction designs, in particular, in the automobile, aircraft and aerospace industries. The application of magnesium alloys is also indispensable in the manufacture of products such as electric devices, computer parts, sporting goods, household equipment and mobile phones. Magnesium exhibit a number of advantageous properties: high strength to weight ratio, high dimensional stability, high thermal conductivity, good machinability and recyclability. However, magnesium and its alloys have insufficient corrosion and wear resistance for many applications due to their high reactivity and low hardness. Designing of new alloys is one of the possible routes to achieve better surface properties. The alloying components such as aluminium, zinc, zirconium can improve mechanical properties and reduce the corrosion sensitivity. Improving of the surface properties of magnesium and its alloy products by the surface modification is one of the low-cost methods [1]. There are various surface treatment technologies available, including laser processing, CVD, PVD methods as well as electroplating, anodizing, thermal spraying, cold spraying, ion implantation, etc. [2-9].

Diffusion coating is a promising method of surface treatment for improving of the corrosion and wear resistance of magnesium and its alloys. This technique has many advantages. First of all, the diffusion coating result in high adhesion strength as there is a strong metallurgical bonding between the coating layer and the substrate. The alloyed layer usually consists of intermetallic phases, which can improve corrosion and wear resistance. Moreover, the process does not need any expensive equipment. Many studies have reported the possibility of magnesium and magnesium alloy products protection using aluminium or aluminium-zinc diffusion alloyed coatings. The coatings can be produced by heating the material in contact with a powdered coating components, or by dipping samples in a molten salts mixture [10-15].

In the present study a simple process was selected to fabricate diffusion alloyed layers on pure magnesium substrate. The layer was obtained by heating the magnesium specimen,
which was formerly painted with paste consisting of Al and Zn powders and glycerol, in vacuum. Recently, Zhu and Song [16] reported that the paste-like glue obtained after mixing Al powder with ethylene glycol, acting as the diffusion Al-source during the heat treatment, has better contact with AZ91D substrate than dry Al powder. The purpose of this research was to determine the effect of the composition of the powder mixture on the microstructure, thickness and microhardness of the fabricated layers.

2. Experimental procedure

A high-purity magnesium ingot was cut into rectangular specimens (40 mm×20 mm×10 mm). The surface of the specimens were grinded using up to 800 grit SiC paper, cleaned with ethanol and then dried in air. Aluminium and zinc powders with particles size 50-120 µm were used to produce alloyed coatings.

The two powder mixtures containing 80 wt.% Al+20 wt.% Zn and 60 wt.% Al+40 wt.% Zn were selected for this study and were denoted afterwards Al20Zn and Al40Zn, respectively. A part of the Al20Zn mixture was mixed with glicerol to obtain a dense paste. The specimens were painted with this paste and embedded in a dry Al20Zn mixture stored in a steel container. Then, the container was closed and placed in a vacuum furnace. The specimens were heated up from room temperature to 450°C for 30 min and hold at constant temperature for 30 min. The samples were successively cooled down with the furnace to 150°C for 2 h. The same procedure was applied to fabricate a diffusion coating using both Al20Zn and Al40Zn mixture. After the heat treatment the specimens were prepared for metallographic observations using a STRUERS automatic polishing machine. Polishing was performed using colloidal silica. The structure of the alloyed layers was observed using a Nikon ECLIPSE MA 200 optical microscope and a JEOL JSM-5400 scanning electron microscope. A chemical composition analysis was carried out by means of X-ray energy dispersive spectrometer (EDS). Microhardness of the sample was determined using a MATSUZAWA MMT Vickers hardness tester at an indenter load of 0.9 N.

3. Results and discussion

The experimental results show that the microstructure of the alloyed layers evidently depends on the Zn content in the powder mixture. SEM image of a cross-sectioned specimen heat treated in Al20Zn in shown in Fig. 1. The profiles of the Mg, Al and Zn concentrations are also shown at the bottom of the figure. The thickness of the diffusion-transformed layer ranged within 60÷80 µm. It is evident that the layer comprises of two phases.

The EDS results of the alloyed layer composition, corresponding to particular points marked in Fig. 1, are summarized in Table 1. The content of both Al and Zn observed for a dark phase (area 1 in Fig. 1) are much lower than those for the grey phase (area 2 in Fig. 1). According to the ternary Mg-Al-Zn phase diagram, the composition of the dark phase suggests the presence of Mg-based solid solution containing Al and Zn additions. The composition of the grey phase is similar to that of the β phase Mg17Al12 in which aluminum is partly replaced by zinc atoms, and can be defined as Mg17(Al, Zn)12 [17]. A narrow zone of the solid solution of Al and Zn in Mg, having a thickness of 20÷30 µm, was formed between the two-phase alloyed layer and the magnesium substrate (area 3 in Fig. 1). The linear distribution of elements along the index line revealed decreased Al concentration in the direction of the magnesium substrate.

<table>
<thead>
<tr>
<th>Location</th>
<th>Mg (at.%)</th>
<th>Al (at.%)</th>
<th>Zn (at.%)</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>90.65</td>
<td>7.47</td>
<td>1.88</td>
</tr>
<tr>
<td>2</td>
<td>62.48</td>
<td>31.03</td>
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</tr>
<tr>
<td>3</td>
<td>91.86</td>
<td>7.11</td>
<td>1.03</td>
</tr>
<tr>
<td>4</td>
<td>99.07</td>
<td>0.73</td>
<td>0.19</td>
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Increasing zinc content in the powder mixture from 20%Zn to 40%Zn leads to an increase in the thickness of the alloyed layer and noticeable change of the microstructure. SEM image of the layer structure is shown in Fig. 2. The alloyed layer has a thickness of about 180 µm.

EDS analysis results, corresponding to particular points marked in Fig. 2, are shown in the Table 2. It can be seen that the microstructure of the alloyed layer consists of two phases: light grains (area 1 in Fig. 2) and dark grains (area 2 in Fig. 2). Moreover, a near-surface fine-grained eutectic area consisting of these two phases can also be distinguished.
(area 3 in Fig. 2). Remaining alloyed layer also contains a grey phase (area 4 in Fig. 2). Zn content in the light gray phase is much higher than that in dark-grayed grains. The composition of the light phase is similar to that of the ternary ϕ phase. Donnadieu et al. [18] reports that the ϕ phase has a nominal formula Mg$_{5}$Al$_{2}$Zn$_{2}$ or Mg$_{6}$Al$_{2}$Zn$_{2}$ with the composition varied within 53-55 at.% Mg, 18-29 at.% Al and 17-28 at.% Zn. The chemical composition of the dark phase point to the development of Mg-based solid solution containing Al and Zn additions. The EDS analysis revealed similar chemical composition of the light phase to the stoichiometry of β phase Mg$_{17}$(Al, Zn)$_{12}$. Area 5 is presumably the zone of the solid solution of Al and Zn in Mg that contains more Al and Zn than the distanced magnesium substrate (area 6).

The results show that Al-Zn powder mixture reacts with the Mg substrate during the heat treatment and Al and Zn atoms diffuse into magnesium substrate. The vacuum heat treatment temperature of 450°C was higher than the eutectic temperature of Mg/Mg$_{17}$Al$_{12}$ (437°C). This indicates that the alloyed layers form during the solidification of the liquid layer, which appears at the interface between magnesium substrate and the Al-Zn powder mixture. In previous work [19] author and co-workers examined the layer growth, which was formed in elevated temperatures at the Mg-Al interface and reported that the rate of the layer growth substantially increases with the appearance of the liquid phase at the interface. Under experiment condition applied in a present work, addition of Zn into the diffusion powder mixture results in the formation of intermetallic phases that exhibit a low melting temperature below 437°C. The formation of the liquid layer accelerates the inter-diffusion of elements between the magnesium substrate and Al-Zn powder mixture. The liquid layer covers the whole surface of the magnesium sample. After the liquid layer solidification, an alloyed coating containing of Mg-Al-Zn intermetallic phases is formed. The microstructure and thickness of those layers depend on Zn content in the diffusion powder mixture. It was found that the increasing Zn content leads to the formation of thicker alloyed layer. The layers were integrated with the magnesium substrate by the layer of Mg-based solid solution containing Al and Zn which have a thickness of 20-40µm., Spencer et al. [1] have reported that mentioned solid solution layer greatly improve the adhesion strength of the coating.

Indentations after a Vickers hardness tests in the alloyed layer fabricated in Al20Zn mixture are shown in Figure 3. The microhardness of two-phase layer was 130-140 HV. Within the alloyed layer, some cracks were observed near the edges of the indentations. As shown in Fig. 3, those cracks were propagated only in the Mg$_{17}$(Al, Zn)$_{12}$ phase. The hardness of the magnesium substrate was also measured and received hardness data ranged within 35-37 HV.

![Fig. 2. SEM image of the magnesium specimen after heat treatment in contact with Al40Zn mixture and corresponding element distribution along the line marked in the figure](image)

![Fig. 3. Indentations in the alloyed layer after diffusion treatment in Al20Zn mixture and comparative indentation in the Mg-substrate](image)

![Table 2](image)

<table>
<thead>
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<th>Mg (at.%)</th>
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<tr>
<td>6</td>
<td>99.02</td>
<td>0.78</td>
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The hardness of the alloyed layers fabricated in both types powder mixtures greatly rose compared to magnesium substrate. It could be estimated that the microhardness of the alloyed layers is more than four times higher than that of the magnesium substrate. This is obviously an important result to expect the improvement of the material wear resistance.

4. Conclusion

Heating of magnesium specimens in contact with an Al-Zn powder mixture containing 20 wt. % and 40 wt. % Zn in vacuum resulted in the formation of a continuous and dense alloyed layer on the magnesium substrate. It was found that the microstructure, thickness and microhardness of received layers depended on the Zn content in the powder mixture. The alloyed layers were composed of the Mg-Al-Zn intermetallic phases and the solid solution of Al and Zn in Mg and were well diffusion bonded with magnesium substrate. When the Zn content in the diffusion powder mixture was 20 wt.%, the received alloyed layer contained Mg$_{17}$(Al,Zn)$_{12}$ intermetallic phase. At high Zn content (40 wt.%) two intermetallic phases were identified in the layer i.e. Mg$_5$Al$_2$Zn$_3$ and Mg$_{817}$(Al,Zn)$_{12}$. The thickness of the alloyed layer fabricated by the heat treatment in a contact with the powder mixture containing 40 wt.% Zn was twice as high as compared to that obtained in powder mixture containing 20 wt.% Zn. The hardness values of the alloyed layers obtained under the same heat treatment conditions by applying both powder mixtures were much higher than that of the magnesium substrate.

REFERENCES