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# Interface microstructure and mechanical properties of zinc–aluminum thermal diffusion coating on AZ31 magnesium alloy

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# ABSTRACT

The zinc–aluminum (Zn–Al) alloy coating with excellent wear and corrosion resistance was fabricated on the surface of magnesium substrate (AZ31) using thermal diffusion technique. The microstructure, phase constitution and chemical composition were investigated. The experimental observation exhibited that the interfacial microstructures were composed of network eutectic structures and lamellar eutectoid structures at heating temperature of 350 °C for holding time of 30 min under 0.1 MPa in a vacuum of  $10^{-3}$  Pa. X-ray diffraction (XRD) pattern analysis identified that  $\alpha$ -Mg, Mg<sub>7</sub>Zn<sub>3</sub> and MgZn phases were formed in the diffusion layer. The interdiffusion of Mg and Al atoms were restricted by Mg–Zn intermetallic compounds (IMCs). The value of microhardness at the diffusion layer increased due to the formation of Mg–Zn eutectic phases. This technique is beneficial to improving poor wear and corrosion resistance of magnesium alloy.

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#### 1. Introduction

Magnesium alloys are considered as good candidates for many structural components of automobile, aerospace and military industries to satisfy the demand for weight reduction, improving fuel efficiency and reducing greenhouse gas emissions [1]. In addition, magnesium alloys (AZ31) are attractive increasingly for their combination of outstanding properties such as low density, high specific strength and stiffness and high mechanical damping capability [2,3]. Magnesium has good castability, machinability and easy recycling ability. Furthermore, it can also be used in the communication and electronics industry for good electromagnetic shielding characteristics [4]. More recently the usage of magnesium alloy has increased gradually as magnesium alloy has the potential to replace aluminum and some plastics in a variety of applications in the automotive and aerospace industries. However, the application of magnesium alloy has been restricted because of poor surface property. In order to further expand the application of magnesium alloys, surface modification processes such as chemical conversion coatings [5], plasma electrolytic oxidation (PEO) [6,7], thermal spray technology [8], physical vapor deposition (PVD) [9] and laser surface treatment [10,11] have been applied to improve surface properties of Mg alloy.

characteristics, excellent mechanical properties, wear and corrosion resistance [12–14]. Consequently, it is necessary to coat the Zn–Al alloy on the surface of Mg alloy, which can protect the magnesium substrate. For the different physicochemical properties between Mg and Al, the formation of Mg–Al intermetallic compounds (IMCs) with high brittleness at the bonding interfaces leads to low bonding strength [15–17]. To overcome these disadvantages, the investigations of the diffusion bonding of Al and Mg alloys have been studied using a silver foil interlayers, which obtain a good bonding [18,19]. It is well known that silver as precious metals can increase the cost. Moreover, brazing of Zn-base filler metal is referred to as a feasible method to joint dissimilar materials [20]. In the present work, the Zn–Al alloy was successfully coated on A721.

Zinc-aluminum (Zn-Al) alloys combine good physical

AZ31 magnesium alloy through vacuum thermal diffusion technique. The interfacial microstructure was observed, and phase constitution and chemical composition were confirmed. In addition, the microhardness of cross-section was examined. The diffusion coating is an economic and efficient method to overcome the limitation of poor surface properties of magnesium alloy.

# 2. Experimental procedure

The Zn–Al alloy sheet was used as coating material with dimensions of 10 mm  $\times$  10 mm  $\times$  0.5 mm. The chemical compositions of the zinc-27 wt.% aluminum (Zn27Al) alloys were 73 wt.% Zn and





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27 wt.% Al. The base materials employed in the experiment were commercially pure Mg (99.85%), Al (99.90%) and Zn (99.90%) to prepare for the raw materials of magnesium alloy substrate in proportion. The AZ31 magnesium alloy, finally measured compositions presented in Table 1, was performed in a crucible electrical resistance furnace at 750 °C under protection of a mixed gas of  $SF_6$  (1 vol.%) and  $CO_2$  (balance). The molten alloy was manually stirred for 5 min using a graphite impeller and stabilized for 30 min. Then the alloy liquid was cast into stainless steel mold to ingot under protective gas. The base metal samples were machined to 10 mm  $\times$  10 mm  $\times$  10 mm by wire-cutting. Both the AZ31 samples and Zn27Al coating sheet were ground using 2000 grade emery paper to remove oxide films, and ultrasonically cleaned in acetone to degrease. The Zn27Al sheet was fixed on the base metal specimen in the specimen jig with the pressure of 0.1 MPa. The thermal diffusion bonding was carried out in the vacuum furnace in a vacuum of  $10^{-3}$  Pa. According to the Mg–Zn binary phase diagram [20] and the analysis result of reference, the heating temperatures were 350 °C for holding 30 min. After the diffusion bonding, the samples cooled to room temperature in the vacuum furnace chamber.

Coated samples were polished perpendicular to the crosssection, and prepared according to standard metallographic procedures. Samples for microscope observations were prepared by etching in the solution containing 1 g oxalic, 1 ml nitric acid, 1 ml acetic acid and 100 ml distilled water. Microstructures were characterized by an optical microscope (OM; Carl Zeiss-Axio Imager A2m, Germany), a scanning electron microscope (SEM; ZEISS EVO18, Germany). The chemical compositions of microstructures were determined by an energy dispersive X-ray spectrometer (EDS) analyzer (INCA-X-Max, England). Phase analysis of the samples was identified by X-ray diffraction (XRD; D/Max 2500PC, Rigaku, Japan) with Cu Kα radiation. The scanning range was 15–  $80^{\circ}$  with a continuous scanning speed of  $2^{\circ}$  min<sup>-1</sup>, and the working voltage and current were 40 kV and 250 mA, respectively. Vickers microhardness testing was carried out using the 1600-5122VD microhardness tester in order to evaluate the mechanical property changes across the transition laver. The hardness values were adopted from an average of five measurements using a 50 g indentation load for holding 15 s.

### 3. Results and discussion

#### 3.1. Microstructures of AZ31 magnesium and Zn27Al alloy

Fig. 1 displays the features in optical morphology of AZ31 magnesium substrate and Zn27Al alloy. As can be seen from Fig. 1a, the Mg alloy exhibits typical as-cast microstructure and coarse grain, the average size of which is approximately 150  $\mu$ m. The as-cast alloy microstructure of Mg matrix is mainly composed of the light gray  $\alpha$ -Mg solid solution and the dark secondary phase precipitated along the grain boundaries. This structure is similar to the microstructure reported in the Ref. [19]. The Mg–Al binary alloy phase diagram indicates that the secondary phase in the Mg–Al alloy is  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> phase [15]. The optical micrographs of

Table 1			
Chemical composition	of the	materials	(wt %)

Material	Element	Element					
	Al	Zn	Mn	Si	Mg		
Al	Bal.	0.01	0.02	0.05	0.02		
Zn	-	Bal.	-	0.01	-		
Mg	0.05	0.03	0.02	0.05	Bal.		
AZ31Mg alloy	3.05	0.91	0.29	0.10	Bal.		



Fig. 1. Optical micrographs of (a) AZ31 magnesium substrate and (b) Zn27Al alloy.

Zn27Al coating are presented in Fig. 1b. It can be seen that the Zn27Al alloy reveals obvious fine dendritic structures. On the basis of the XRD patterns (PDF No.: 65-2869, 65-3358 and 65-3365) as shown in Fig. 2, it indicates that the light dendritic structures are related to the aluminum-rich solid solution and the dark interdendritic structures are associated with the zinc-rich solid solution. It has been reported that the fine dendritic structure with more homogeneous distribution of eutectic mixture in the interdendritic regions can improve the mechanical properties and corrosion resistance [12–14,21].



Fig. 2. XRD pattern of AZ31 magnesium substrate and Zn27Al alloy (PDF No.: 65-2869, 65-3358 and 65-3365).

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