

The Properties of Al/Zn-enriched Surface Layers on Mg

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Abstract

The Al/Zn-enriched surface layers were fabricated on Mg substrate by heating the specimens in contact with an Al + 40 wt.% Zn powder mixture at 445°C for 60 min. The microstructure and corrosion and wear resistance of the layers were investigated and discussed. The experimental results show that the layers were composed of $Mg_{17}(Al,Zn)_{12}$ and $Mg_3Al_2Zn_2$ intermetallic phases and a solid solution of Al and Zn in Mg. They were integrated with the substrate through a zone of a solid solution of Al and Zn in Mg. The potentiodynamic polarization measurements indicated that the specimens with Al/Zn-enriched layer had better corrosion resistance than the bare Mg. The microhardness of the layers containing Mg-Al-Zn intermetallic phases was much higher than that of the Mg substrate. The sliding wear tests showed that the wear resistance of the specimens with a surface layer containing intermetallic phases was also superior to that of untreated Mg.

Keywords: Magnesium, Surface modification, Mg-Al-Zn intermetallic phases, Microstructure, Corrosion resistance, Wear resistance

1. Introduction

Currently, there is a growing interest in the application of Mg and its alloys as structural materials. However, their poor surface properties, i.e. low hardness and low wear and corrosion resistance limit the widespread applications in many industrial areas. Surface treatment seems to be a good solution to overcome this drawback. Modification of Mg surface by fabricating an alloyed layer enriched with Al is an effective way to improve both corrosion and wear resistance. Al-enriched and Al/Zn-, Al/Cu-, Al/Si-, Al/Ni-enriched layers can be produced using the following methods: laser surface alloying [1-3], diffusion treatment in molten salts [4-6], diffusion aluminizing treatment [7-14], ion implantation [15,16], PVD combined with annealing [17,18], post-cold spray heat treatment [19,20] and electrodeposition [21].

The purpose of this study was to fabricate an Al/Zn-enriched layer on Mg by heating specimens in contact with an Al+Zn

powder mixture and to evaluate the effect of the surface modification on the corrosion and wear resistance of Mg.

2. Experimental details

Pure magnesium was selected as the substrate material. The samples (20x20x10 mm) were cut from an ingot, ground with SiC paper progressively up to 800 grit and cleaned using ethanol. The surfaces of the Mg samples were painted with a dense paste of Al and Zn powders (80 wt.% Al + 40 wt.% Zn) mixed with glycerol, placed in a steel container and embedded in a dry Al+Zn powder mixture. Then, the powder was pressed down and the container was closed and placed in a vacuum furnace equipped with a pressure pad, which enabled the lid of the container to keep the powder under pressure. During the heat treatment process, a pressure of 1 MPa was used to ensure good contact between the

source of diffusion elements and the Mg substrate. The specimens were heated up from room temperature to 445 °C for 30 min, kept at that temperature for 60 min, and cooled down in the furnace to room temperature.

The layer microstructure was examined with a Nikon ECLIPSE MA 200 optical microscope and a JEOL JSM-5400 scanning electron microscope. The chemical composition analysis was conducted using an Oxford Instruments ISIS 300 X-ray energy dispersive spectrometer (EDS) attached to the SEM. The layer microhardness was determined at a load of 100 G using a MATSUZAWA MMT Vickers hardness tester.

The corrosion properties of the layers were investigated using a CHI 1130A electrochemical analyzer. The potentiodynamic polarization measurements were conducted in 3.5 wt.% NaCl solution using a standard three-electrode configuration, with the AgCl/Ag electrode as the reference electrode, the platinum wire as the counter electrode and the specimen as the working electrode. Before the tests the specimens were immersed in 3.5 wt.% NaCl solution for 1 h to obtain a stable open circuit potential (OCP). The polarization tests were carried out at a scan rate of 1 mV s⁻¹ with the exposed area being 0.25 cm².

The tribological behaviour of the layer was studied under dry sliding conditions using a block-on-ring tribometer. 15.75 mm x 10 mm x 6.35 mm blocks were cut from the treated and untreated Mg. The ring, made of 100Cr6 bearing steel (HRC65) was used as the counter material. Before the tests, the working surface of each block (15.75 mm x 6.35 mm) was ground using SiC paper progressively finer up to 1200 grit. The wear tests were conducted for surfaces in linear concentrated contact, with the block being pressed down to touch the rotating ring. The testing parameters used for the experiment are summarized in Table 1. The losses of mass were calculated from the differences in the weight of the specimens measured before the test and after every sliding distance of 66 m. The tests were continued until a total sliding distance of 660 m was reached. The specimens were weighed using a microbalance with an accuracy of 0.0001 g.

Table 1.

Wear test parameters

Parameter	Block-on-ring test
Ring diameter (mm)	35
Ring width (mm)	9
Block width (mm)	6.35
Sliding velocity (m/s)	0.055
Applied force (N)	3
Test length (m)	660
Replicate	3

3. Results

Figure 1 shows an optical micrograph of the cross-section of the Mg specimen heat treated at 445 °C for 60 min in contact with the Al + 40 wt.% Zn powder mixture. The layer was about 850 µm in thickness. The high-magnification SEM image presented in Fig. 2 illustrates the microstructure of the layer with marked points of chemical composition analysis by EDS. Table 2 lists the results of the quantitative analysis. The following phases can be

distinguished in the layer microstructure: light (marked A in Fig. 2), grey (marked B) and dark (marked C). The grey phase areas are surrounded by a fine eutectic structure composed of the light and dark phases (marked D). The stoichiometry of the elements for the light phase suggests the presence of an Mg₅Al₂Zn₂ phase. The quantitative EDS analysis shows that the grey phase is an Mg₁₇Al₁₂ phase with a small amount of Zn, and this phase can be defined as Mg₁₇(Al,Zn)₁₂ [22]. The dark phase is the phase richest in Mg. The EDS analysis indicates that this phase is a solid solution of Al and Zn in Mg. From the chemical composition analysis it is evident that the eutectic structure is a mixture of an Mg₅Al₂Zn₂ phase and a solid solution of Al and Zn in Mg. The formation process of the Al/Zn-enriched layer proceeded as follows. During the heating process at a temperature of 445 °C, which is higher than the eutectic temperature of the Mg-Al system (437 °C), the interface reactions occurred between the Mg-substrate and powder-mixture, resulting in the formation of a thin liquid layer at the bond interface. During cooling the interfacial liquid solidified into a continuous layer characterized by a eutectic structure.

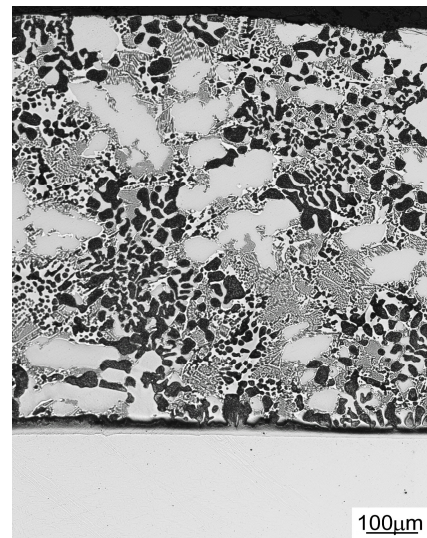


Fig. 1. Cross-section of the Mg specimen after heat treatment at 445 °C for 60 min. in contact with the Al+Zn powder mixture

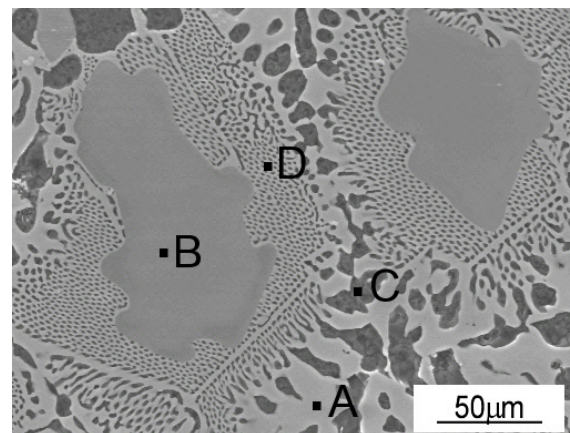


Fig. 2. SEM image of the microstructure of the layer on Mg

Table 2

EDS results of the Al/Zn-enriched layer corresponding to the points marked in Fig. 2

Point	Mg (at.%)	Al (at.%)	Zn (at.%)
A	54.60	22.70	22.70
B	61.11	32.10	6.79
C	91.14	6.51	2.35
D	69.06	17.45	13.49

Figure 3 shows a SEM view of the interface between the Mg substrate and the Al/Zn-enriched layer with the distribution of elements along the marked line. The content of Mg, Al and Zn in the dendrites observed near the Mg substrate (point E: 90.88 at.% Mg, 6.78 at.% Al and 2.34 at.% Zn), was similar to that in the dark phase described above. This suggests the presence of a solid solution of Al and Zn in Mg. The chemical composition of the narrow zone in the neighbourhood of Mg (marked F) is as follows: 96.20 at.% Mg, 3.57 at.% Al and 0.23 at.% Zn. Moreover, the EDS element line scanning spectra show that the concentration of Al and Zn decreases in this zone with a decreasing distance from the Mg substrate. From this analysis it is evident that the Al/Zn-enriched layer is diffusion bonded with the Mg substrate through a zone of a solid solution of Al and Zn in Mg.

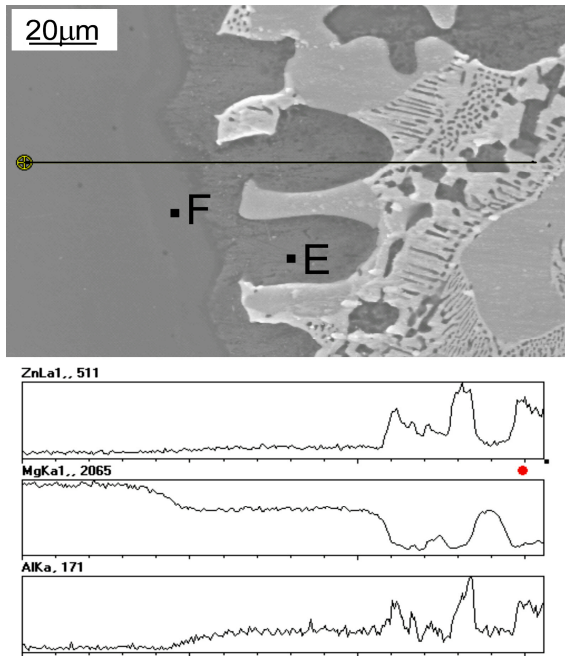


Fig. 3. SEM view of the interface between the Mg substrate and the Al/Zn-enriched layer with the corresponding EDS spectra

The corrosion resistance of the fabricated layers was assessed using potentiodynamic electrochemical measurements in the 3.5 wt.% NaCl solution. The polarization curves for Mg with an Al/Zn-enriched surface layer and untreated Mg are shown in Fig. 4. The corrosion potential of Mg with the modified layer (-1.56 V) is higher than that of bare Mg (-1.73 V). The treated specimens are characterized by lower corrosion current density than the bare

Mg. According to the electrochemical principles, the former have less corrosion tendency than the latter.

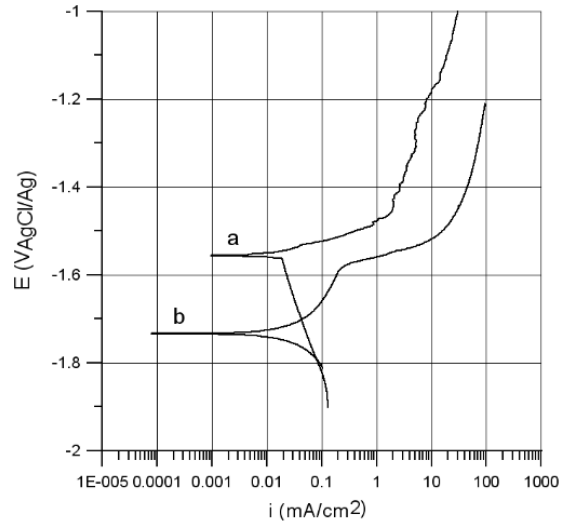


Fig. 4. Polarization curves: a - Mg with the Al/Zn-enriched surface layer, b - bare Mg

The microhardness measured in the characteristic areas of the layer was: about 210 HV for the $Mg_{17}(Al,Zn)_{12}$ phase, 180 HV for the fine eutectic structure and 80 HV for the solid solutions of Al and Zn in Mg. The microhardness of the Mg substrate was 36 HV. The results obtained from the dry sliding block-on-ring wear tests are presented in Fig. 5 as weight loss vs sliding distance. The overall weight loss of the pure Mg specimen after a sliding distance of 660 m was 4.5 mg. By contrast, the weight loss of the Mg specimen with an Al/Zn-enriched layer was 2.9 mg. It can be seen that the surface layer containing hard intermetallic phases caused an increase in the wear resistance of the Mg.

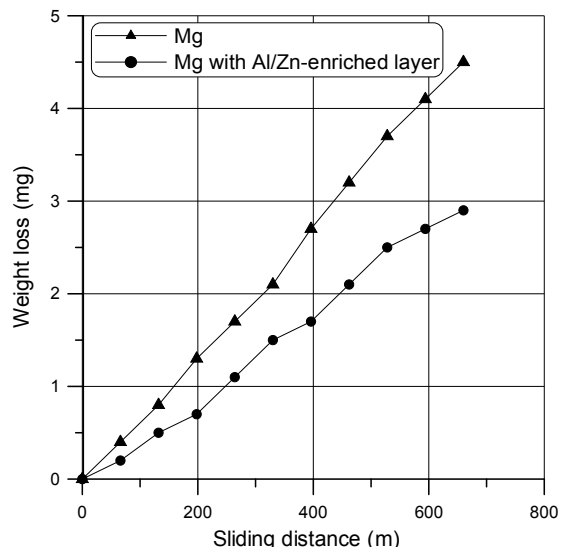


Fig. 5. Variation of weight loss against sliding distance for the bare Mg and Mg with an Al/Zn-enriched surface layer

4. Conclusions

1. The Al/Zn-enriched surface layers were fabricated by heating the Mg specimens in contact with the Al + Zn powder mixture at 445 °C for 60 min.
2. The layers were composed of Mg₁₇(Al,Zn)₁₂ and Mg₅Al₂Zn₂ intermetallic phases and a solid solution of Al and Zn in Mg.
3. The corrosion resistance of the Mg improved after enriching the surface layer with Al and Zn.
4. The microhardness and wear resistance of the modified layers containing Mg-Al-Zn intermetallic phases were higher than those of the Mg substrate.

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