THE MICROSTRUCTURE OF ALLOYED LAYERS FORMED ON Mg BY THE POWDER-PACK METHOD

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Abstract

Alloyed layers enriched with Zn and Al were fabricated on an Mg substrate using the powder-pack method. The Mg specimens were first immersed in Zn+Al powder mixtures serving as the source of diffusion elements and then heated at 440 °C for 60 min. The experimental results revealed that the microstructure of the alloyed layers was dependent on the composition of the powder mixture. The layer produced from a mixture containing 60 % of Zn had a structure composed of an $Mg_{17}(Al,Zn)_{12}$ intermetallic phase, a solid solution of Al and Zn in Mg and a eutectic ($Mg_5Al_2Zn_2$ intermetallic phase + solid solution of Al and Zn in Mg). When a mixture with a higher content of Zn (80 %) was used, the layer had a structure composed of coarser eutectic areas ($Mg_5Al_2Zn_2$ intermetallic phase + solid solution of Al and Zn in Mg) and fine-structured eutectoid areas (MgZn intermetallic phase + solid solution of Al and Zn in Mg). The layers containing intermetallic phases were characterized by high microhardness. The microhardness of the layers was five times higher than that of the Mg substrate.

Keywords: Magnesium, thermochemical treatment, intermetallic phases, microstructure, microhardness

1. INTRODUCTION

Currently, there is a high demand for light materials to be applied in many areas, particularly in the automotive industry. New alloys containing Mg, Al and Ti as well as composites based on them are being intensively studied by researchers all over the world [1-4]. Low density and high strength-to-weight ratio make magnesium and magnesium alloys attractive as structural materials. However, they have undesirable properties such as low hardness and poor wear resistance; they are also prone to corrosion. There exist a large number of surface treatment methods that can be employed to protect magnesium and magnesium alloys. One of the effective ways to improve the surface properties of these materials is by enriching the surface layer with alloying elements that form intermetallic phases with magnesium. Such layers containing intermetallic phases are characterized by high hardness and wear resistance; they also offer effective corrosion protection. As shown in the literature, the surface layer of magnesium can be enriched with the following elements: Al, Si, Ni, Cu, Al+Si, Al+Zn, Al+Cu, Al+Ni, Al+Mn and Zn+Y. The single-step and two-step processes applied to fabricate an alloyed layer include laser surface alloying [5, 6], surface alloying using welding methods [7], thermal and cold spraying combined with heat treatment [8, 9], electrochemical plating with subsequent annealing [10], thermochemical treatment [11-17], casting method [18, 19], PVD combined with heat treatment [20] and ion implantation [21].

The investigations described in this paper involved enriching the surface layer of Mg with Zn and Al. The thermochemical treatment was carried out in a solid medium. Two Zn+Al powder mixtures differing in the content of Zn were used. The composition of the powder mixture affected the microstructure and microhardness of the alloyed layers.

2. EXPERIMENTAL PROCEDURE

The specimens with dimensions of 20 x 20 x 10 mm were cut from pure Mg ingots, ground with up to 800 grit SiC paper, cleaned with ethanol and dried. A thermochemical method, i.e. pack powder cementation, was used to enrich the surface layer of Mg with Zn and Al. Two Zn+Al powder mixtures were employed as a source

of alloying elements: 60 wt.% Zn + 40 wt.% Al and 80 wt.% Zn + 20 wt.% Al. The Mg specimens were embedded in a dry Zn+Al powder mixture in a steel container. The container was closed and placed in a vacuum furnace. During the heat treatment process, the powder in the container was held under a pressure of 1 MPa to ensure good contact between the source of diffusion elements and the Mg substrate. The specimens were heated up from room temperature to 440 °C for 30 min, kept at that temperature for 60 min and cooled down first in the furnace to 150 °C for 2 h and then in air. After the thermochemical treatment, the specimens were prepared for microscopic observation using a standard metallographic technique. The final polishing was performed with a Struers polishing machine using a 0.02 μm colloidal silica suspension. The preparation of the specimens for the microscopic examinations did not include etching. The structure analysis was conducted using a Nikon ECLIPSE MA 200 optical microscope and a JEOL JMS-5400 scanning electron microscope. The chemical composition of the phases was determined by means of an Oxford Instruments ISIS 300 EDS system attached to the scanning electron microscope. Phase identification involved performing a quantitative analysis and plotting Mg-Zn and Mg-Al-Zn phase diagrams [22]. The microhardness of the layers was investigated using a MATSUZAWA MMT Vickers (HV0.1) hardness tester.

3. RESULTS AND DISCUSSION

Figure 1 presents the cross-sectional SEM images of Mg specimens after the thermochemical process. The heat treatment of Mg specimens in contact with Zn+Al powder mixtures at 440 °C for 60 min. led to the enrichment of the surface layer with Zn and Al (see the EDS line scans in **Figures 1a** and **1b**. During the process, Zn and Al atoms diffused and reacted with Mg and, as a result, a layer containing new phases formed on the Mg substrate.

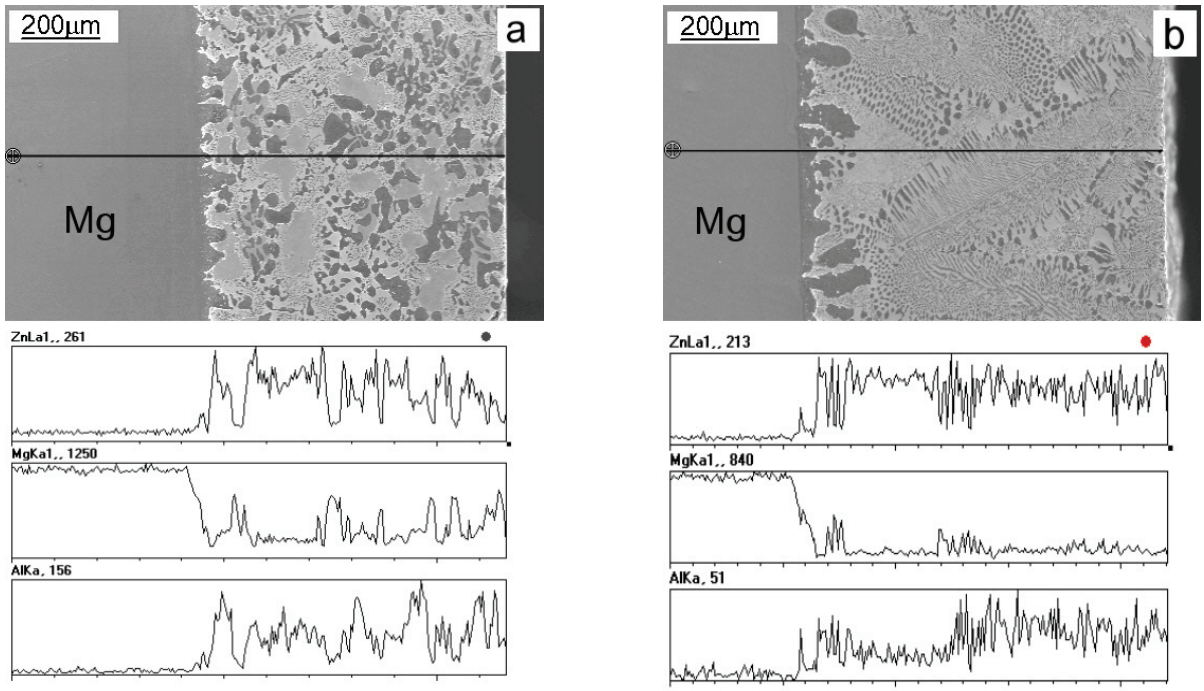

Figure 1 Cross-sectional SEM images of heat treated Mg specimens in contact with Al + Zn powder mixtures with EDS line scans: **(a)** a layer produced from a 60 % Zn + 40 % Al powder mixture, **(b)** a layer produced from an 80 % Zn + 20 % Al powder mixture

The layer obtained from a powder mixture containing 60 % Zn had a thickness of about 600 μm (**Figure 1a**). A thicker layer of about 700 μm (**Figure 1b**) was produced when the powder mixture containing more Zn (80 %) was used. A thin, transition zone was observed between the alloyed layers and the Mg substrate.

The EDS line scans show that the concentration of Mg in this zone drops with a decrease in the distance from the alloyed layer. The contents of Al and Zn at the interface between the layer and the substrate were about 6-8 at.% and 1-3 at.%, respectively, which indicates a solid solution of Al and Zn in Mg. From the chemical composition of the dendrites adjacent to the transition zone (for example, 87.65 at.% Mg, 9.19 at.% Al and 3.16 at.% Zn) it is clear that the dendrites solid solution of Al and Zn in Mg penetrated deeper into the alloyed layer.

Figure 2 shows a high magnification SEM image of the layer enriched with Zn and Al fabricated from a powder mixture containing 60 % Zn. The resulting microstructure consists of large areas of the grey phase (marked 1), areas of the light phase (marked 2), areas of the dark phase (marked 3) and eutectic regions (marked 4). The results of the EDS quantitative analysis for the marked areas are given in **Table 1**. The Mg:Al ratio for the grey phase suggests that it is an $Mg_{17}Al_{12}$ intermetallic phase; as some of the Al atoms were replaced by Zn, the phase is frequently defined as $Mg_{17}(Al,Zn)_{12}$. The chemical composition of the light phase corresponds to a ternary $Mg_5Al_2Zn_2$ intermetallic phase. The results of the point analysis for the dark areas indicate a solid solution of Al and Zn in Mg. The high content of Zn in the eutectic suggests that the $Mg_5Al_2Zn_2$ intermetallic phase and the solid solution of Al in Zn are constituents of this two-phase mixture.

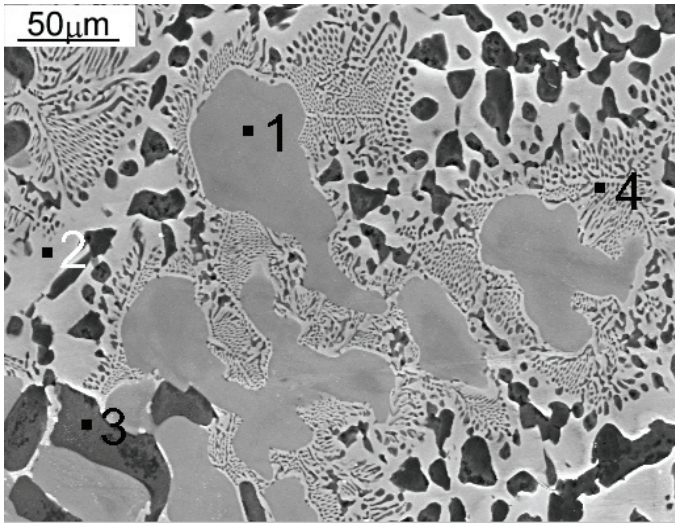

Figure 2 SEM view of the microstructure of the layer produced from a powder mixture containing 60 % Zn

Table 1 Results of the EDS quantitative analysis corresponding to the points marked in **Figure 2**

Point	Mg (at.%)	Zn (at.%)	Al (at.%)
1	60.91	7.27	31.85
2	54.06	23.29	22.64
3	89.27	2.62	8.11
4	69.29	12.36	18.35

When the Mg specimens were heat treated in a powder mixture containing more Zn (80 at.% Zn + 20 at.% Al), with the parameters of heating being the same as above, the alloyed layer that formed on Mg had a different microstructure. As can be seen from **Figure 3a**, the layer consists of two-phase areas with a coarse-grained structure (marked A) and two-phase areas with a fine-grained structure (marked B). Details of the microstructure of the area with a fine grained structure are shown at high magnification in **Figure 3b**. The results of the EDS quantitative analysis for the points marked 1, 2, 3 and 4 in **Figures 3a** and **3b** are presented in **Table 2**. From the EDS analysis we can conclude that the coarse-grained two-phase structure is a eutectic composed of an $Mg_5Al_2Zn_2$ phase (point 1) and a solid solution of Al and Zn in Mg (point 2). The quantitative EDS analysis also reveals that the fine-grained two-phase structure is a eutectoid composed of an MgZn intermetallic phase (point 3) and a solid solution of Al and Zn in Mg (point 4). In the layer fabricated from a powder mixture containing 80 at.% Zn, no single-phase areas of an $Mg_{17}(Al,Zn)_{12}$ phase rich in Al were observed. To summarize, the layers fabricated from a powder mixture rich in Zn contained intermetallic phases rich in this element, i.e. $Mg_5Al_2Zn_2$ and MgZn. The presence of eutectics in the microstructure of both types of layers indicates that the reactions at the interface between the Mg and the Zn+Al powder mixture resulted in the occurrence a liquid phase.

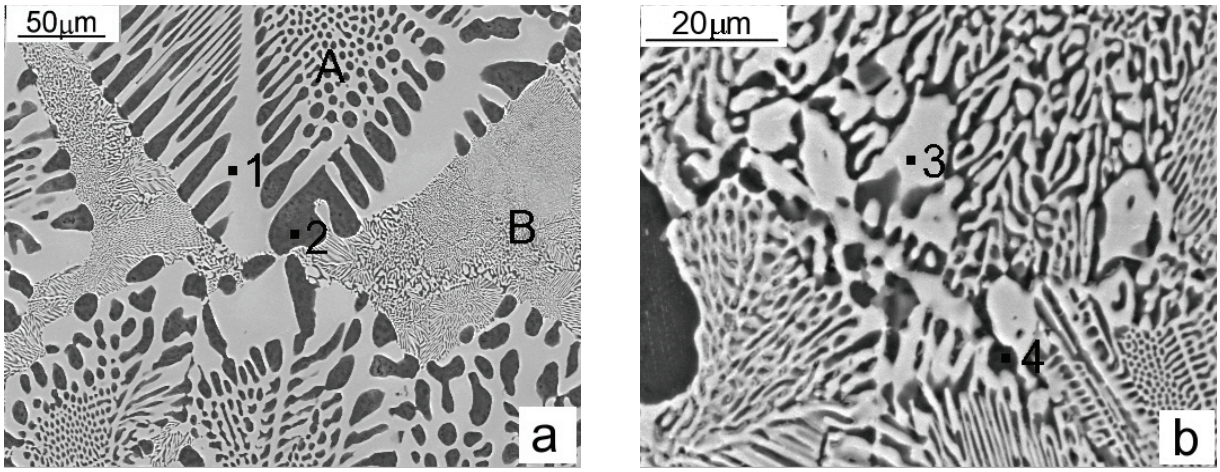

Figure 3 SEM view of the microstructure of the layer produced from a powder mixture containing 80 % Zn with the EDS analysis points: **(a)** microstructure at a lower magnification, **(b)** microstructure of the area marked as B in **Figure 3a** observed at a higher magnification

Table 2 Results of the EDS quantitative analysis corresponding to the points marked in **Figures 3a** and **3b**

Point	Mg (at.%)	Zn (at.%)	Al (at.%)
1	53.40	28.61	17.99
2	90.68	4.01	5.31
3	48.04	43.70	8.26
4	93.05	4.78	2.17

Figure 4 shows the two types of surface layers with indentations after Vickers hardness tests. The microhardness values obtained for the layer produced from the powder mixture containing 60 % Zn (**Figure 4a**) are presented in **Table 3**. **Table 4** provides results from the microhardness tests for the layer produced from the powder mixture containing 80% Zn (**Figure 4b**).

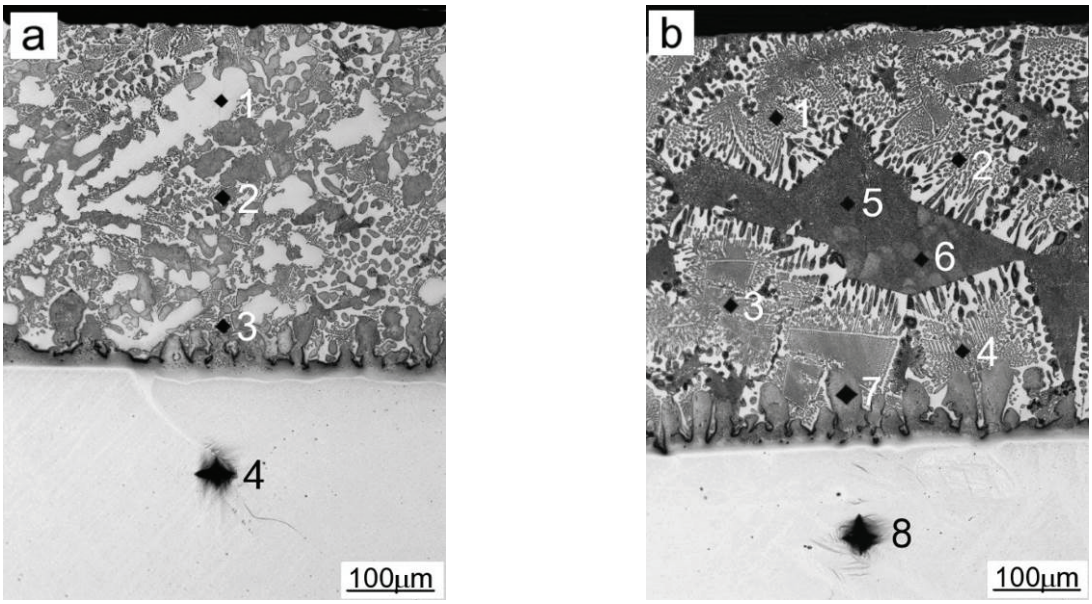

Figure 4 Indentations left in the alloyed layers and the Mg substrate after a Vickers hardness test: **(a)** layer fabricated from the mixture containing 60 % Zn, **(b)** layer fabricated from the mixture containing 80 at.% Zn

Table 3 Microhardness at the indentation points shown in **Figure 4a**

Indentation	Microhardness HV0.1
1	214
2	160
3	169
4	29

Table 4 Microhardness at the indentation points shown in **Figure 4b**

Indentation	Microhardness HV0.1
1	156
2	166
3	170
4	161
5	180
6	175
7	87
8	30

The microhardness of the alloyed layer containing intermetallic phases was more than five times higher than that of the Mg substrate. The highest microhardness values were reported for single-phase areas of $Mg_{17}(Al,Zn)_{12}$ in the layers produced from the powder mixture containing 60 % Zn (indentation marked 1 in **Figure 4a**). In the layers fabricated from the powder mixture containing 80 % Zn, there were areas of a coarser eutectic (indentations 1, 2, 3 and 4 in **Figure 4b**) containing an $Mg_5Al_2Zn_2$ intermetallic phase, the microhardness of which was slightly lower than that of the fine-grained eutectoid (indentations 5 and 6 in **Figure 4b**) containing an MgZn intermetallic phase.

4. CONCLUSIONS

This paper has demonstrated that powder pack cementation is an effective thermochemical method to fabricate protective Zn+Al layers on Mg. The microstructure of the layers was dependent on the composition of the Zn+Al powder mixture used as a source of diffusion elements. The layer produced from the powder mixture containing 60 % Zn had a thickness of about 600 μm and was composed of $Mg_{17}(Al,Zn)_{12}$, $Mg_5Al_2Zn_2$ and a solid solution of Al and Zn in Mg. When the powder mixture contained more Zn (80 %), the layer was thicker (about 700 μm) and it was characterized by a microstructure consisting of areas of a coarser eutectic (an $Mg_5Al_2Zn_2$ phase and a solid solution of Al and Zn in Mg) and areas of a fine-grained eutectoid (an MgZn phase and a solid solution of Al and Zn in Mg). The layers were metallurgically bonded with the Mg substrate by a thin zone of a solid solution of Al and Zn in Mg. The microhardness measurements showed that the Zn/Al-layers were more than five times harder that the Mg substrate.

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