MICROSTRUCTURAL ANALYSIS OF THE SURFACE LAYERS OF THE AZ91D ENRICHED WITH AL AND SI BY THERMOCHEMICAL TREATMENT

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Abstract

Surface layers enriched with Al and Si were fabricated on an AZ91D substrate using thermochemical treatment in solid media. The AZ91D specimens were heated in an Al+Si powder mixture acting as a source of diffusion elements. Two temperatures were applied: 430 °C and 445 °C. The microstructural characterization of the layers was performed using an optical microscope and a scanning electron microscope equipped with an energy-dispersive *X-ray* spectrometer (EDS). The layer produced at 430 °C had a thickness of 50 µm; the structure was composed of intermetallic $Mg_{17}Al_{12}$ and Al_3Mg_2 phases and an Mg_2Si phase. When a higher temperature (445 °C) was used, the layer was much thicker (600 µm) and the structure was predominantly a eutectic (an $Mg_{17}Al_{12}$ intermetallic phase + a solid solution of Al in Mg) with agglomerates of Mg_2Si phase particles distributed over the eutectic matrix.

Keywords: Magnesium alloy, thermochemical treatment, diffusion, surface layer, microstructure

1. INTRODUCTION

Low density and high strength-to-weight ratio make Mg alloys attractive as structural materials for applications where weight reduction is critical, so they are widely used in the automotive and aerospace industries. However, low hardness and poor wear resistance, which are undesirable, limit their use in high performance applications. There are several ways to improve the mechanical properties of magnesium alloys. One approach is to introduce alloying elements and fabricate new alloys with superior properties. Another is to fabricate Mg-matrix composites with various types of reinforcement. Research results concerning the fabrication of Mg-matrix composites reinforced with an Mg_2Si phase [1-4] show that Mg_2Si is a promising reinforcement material because of its excellent properties such as low density (1.99 g/dm^3), high melting point (1085 °C), high Young modulus (120 MPa) and high hardness (350-450 HV0.01) [2,5,6]. Some studies have focused on the deposition of Mg_2Si coatings [6] or the fabrication of alloyed surface layers containing Mg_2Si phase on an Mg-based substrate [7-17]. As indicated in [6], the deposition of a thin film of an Mg_2Si phase on an AZ31 substrate by RF sputtering led to better corrosion and wear resistance of the Mg alloy. Layers containing Mg_2Si particles on Mg-based substrates are fabricated mainly by laser alloying/cladding [7-16] and by casting [17]. Modified surface layers provide superior protection against wear [8,11,12,14-17] and corrosion [7,8-10,12,14,15].

This paper discusses the use of thermochemical treatment to enrich AZ91D surface with Al and Si. Previous studies by Mola show [18,19] that this method can also be employed to fabricate Al-, Al/Zn-, Zn/Al-enriched layers on an Mg substrate. An Al-enriched layer produced from pure Al powder had a eutectic structure (a solid solution of Al in Mg + $Mg_{17}Al_{12}$) [18]. Al/Zn-enriched layers produced from Al+20% Zn and Al+40% Zn powder mixtures consisted of $Mg_{17}(Al,Zn)_{12}$, $Mg_5Al_2Zn_2$ and a solid solution of Al and Zn in Mg [18]. A Zn/Al-enriched layer fabricated from Zn+20% Al was characterized by a microstructure consisting of areas of a eutectic ($Mg_5Al_2Zn_2$ and a solid solution of Al and Zn in Mg) and areas of a eutectoid (MgZn and a solid solution of Al and Zn in Mg) [19]. Data from recent research [20] suggest that the heat treatment of Mg in contact with an Al+20 % Si powder mixture results in the formation of an alloyed surface layer containing an $Mg_{17}Al_{12}$ intermetallic phase and an Mg_2Si phase. Since pure Mg is rarely applied as a structural material, this study was conducted for AZ91D alloy used as a substrate material.

2. EXPERIMENTAL PROCEDURE

The specimens with dimensions of 50 x 20 x 10 mm were cut from an AZ91D ingot composed of (in wt%) Al - 9.5, Zn - 0.8, Mn - 0.27 and Mg - balance. The surface preparation involved grinding with up to 800 grit SiC paper, cleaning with ethanol and drying. The thermochemical method was used to fabricate an alloyed surface layer on the AZ91D substrate. The process was conducted in solid media. An Al 80 wt.% + Si 20 wt.% powder mixture was used as a source of alloying elements. The morphologies of the Al and Si powders are shown in **Figure 1.**

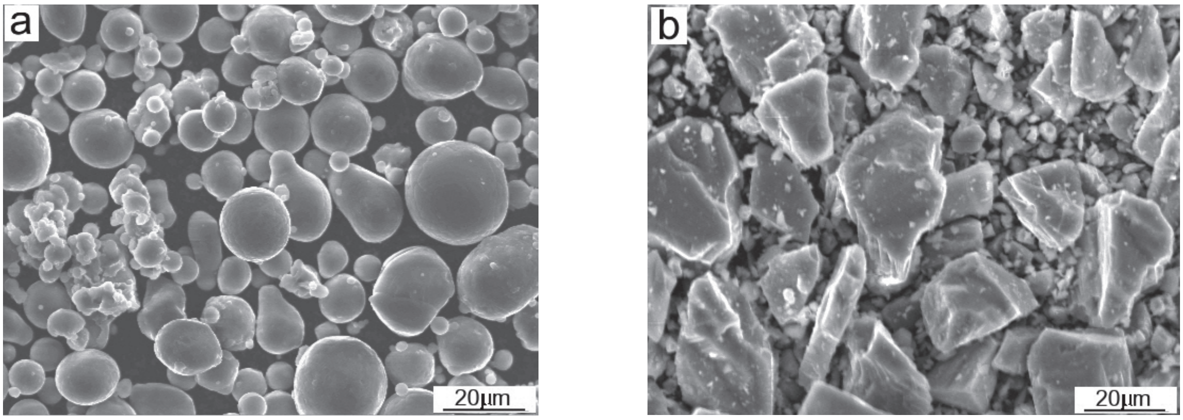

Figure 1 Morphologies of the powders used for the Al+20%Si mixture: **(a)** Al, **(b)** Si

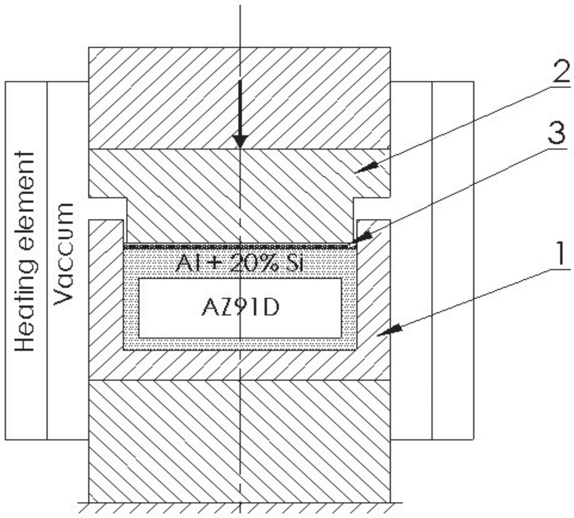

Figure 2 Schematic diagram of the thermochemical treatment process: 1 - steel container, 2 - container lid pressed down, 3 - layers of aluminum foil to seal the container

The AZ91D specimens were placed in a steel container and embedded in the Al+Si powder mixture. 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 AZ91D substrate. A schematic diagram of the process is provided in **Figure 2**. The specimens were heated from room temperature to 430 °C or 445 °C for 30 min, kept at that temperature for 30 min and cooled in the furnace back to room temperature. The specimens removed from the container were cross-sectioned and prepared for microscopic observations using a standard metallographic technique. The structure analysis was conducted with a Nikon ECLIPSE MA 200 optical microscope (OM) and a JEOL JMS-5400 scanning electron microscope (SEM). The chemical composition of the structural constituents of the fabricated layer was determined by means of an Oxford Instruments ISIS 300 EDS system attached to the SEM.

3. RESULTS AND DISCUSSION

Figure 3 shows a cross-section of an AZ91D specimen with a surface layer enriched with Al and Si produced by heat treatment at 430 °C. As can be seen, the surface layer is thin and its structure differs from that of the AZ91D substrate. It has a thickness of about 50 µm. The OM image in **Figure 3 (a)** reveals a light matrix and an irregularly distributed gray phase area. In the SEM image in **Figure 3 (b)** two sublayers can be distinguished in the light matrix. The darker (marked 1) is close to the AZ91D substrate while the lighter (marked 2) is close to the surface. The quantitative EDS analysis indicates that the chemical composition of the darker sublayer (Mg - 59.04 at.% and Al - 40.96 at.% Al) corresponds to an $Mg_{17}Al_{12}$ intermetallic phase, whereas that of the lighter sublayer (Mg - 39.78 at.% and Al - 60.22 at.%) is similar to an Al_3Mg_2 intermetallic phase. The linear distribution of elements shows that the gray area is rich in Si. The results of the EDS analysis obtained for this area (point 3: Mg - 66.34 at.%, Si - 31.4 at.% and Al - 2.26 at.%) indicate the presence of an Mg_2Si phase.

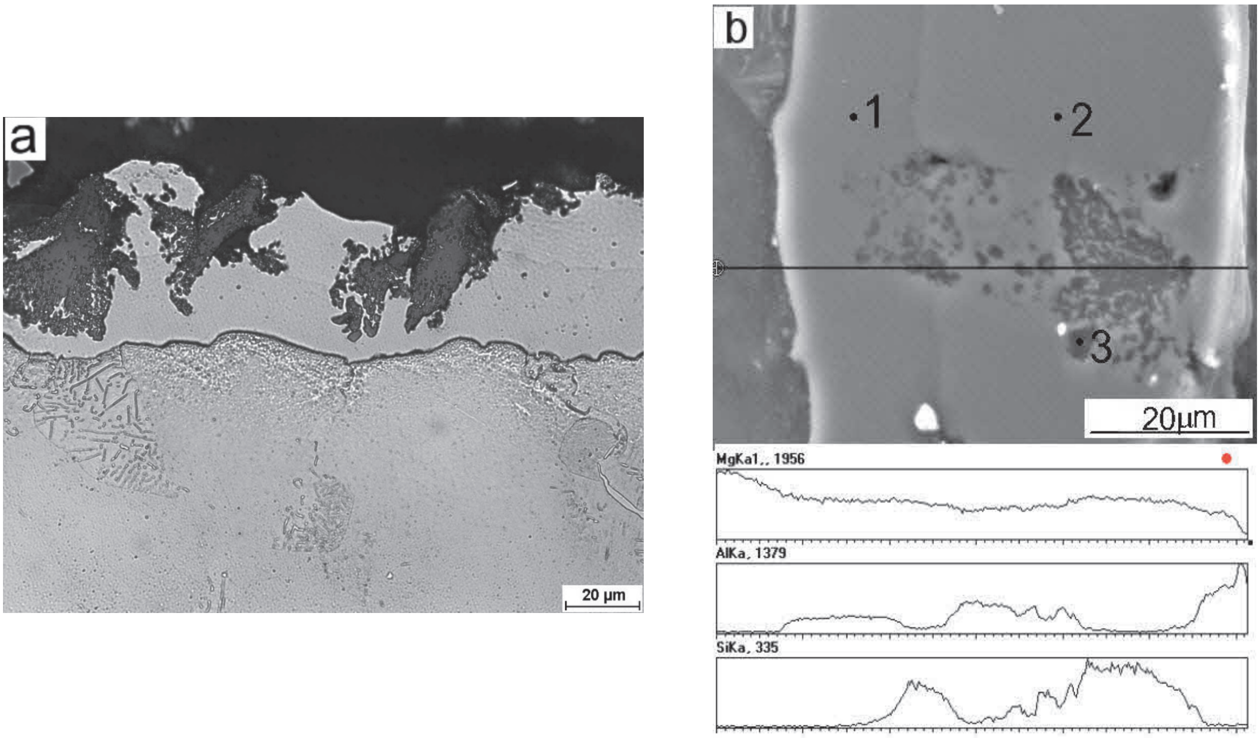

Figure 3 Microstructure of the AZ91D surface layer enriched with Al and Si through thermochemical treatment at 430 °C: (a) OM image, (b) SEM image with EDS line scan results showing the distribution of elements along the index line

As observed from **Figure 4(a)**, the heat treatment of the solid AZ91D in contact with the Al+Si powder mixture at a temperature of 445 °C, with the other parameters remaining unchanged, led to the formation of a much thicker surface layer. The layer had a thickness of about 600 µm. **Figure 4(b)** presents the layer microstructure observed near the AZ91D substrate. The interface is not flat. The microstructure of the AZ91D alloy contains a solid solution of Al in the Mg area and large regions with a lamellar structure of a solid solution and an $Mg_{17}Al_{12}$ intermetallic phase. The high magnification image in **Figure 4(c)** reveals clear plate-shaped precipitates of the $Mg_{17}Al_{12}$ phase in these regions. As can be seen in the upper part of the figure, the alloyed layer very close to the substrate has a two-phase structure. Moving further from the substrate, the layer microstructure contains single gray particles or agglomerates of gray particles co-occurring with the two-phase structure. The high magnification image in **Figure 4(d)** shows the area of the alloyed layer with agglomerates of gray particles.

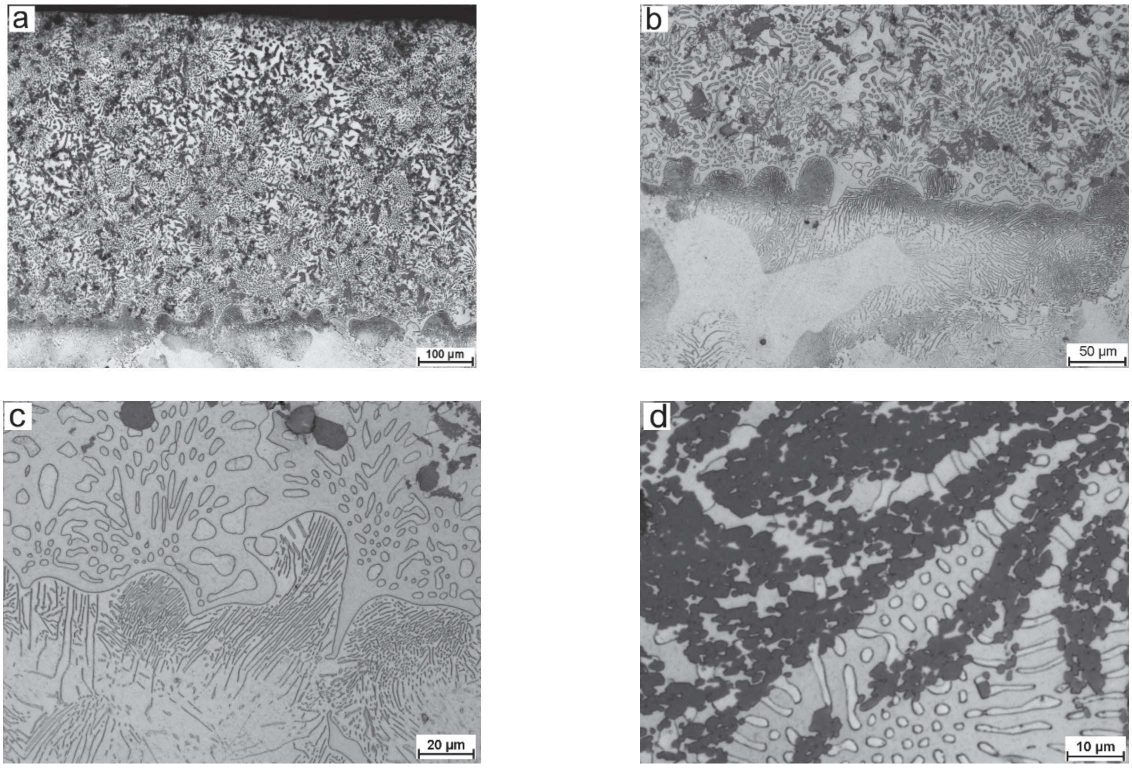

Figure 4 Low and high magnification OM images of the microstructure of the AZ91D surface layer fabricated at 445 °C: **(a)** surface layer, **(b)** and **(c)** area adjacent to the AZ91D substrate, **(d)** area further from the substrate.

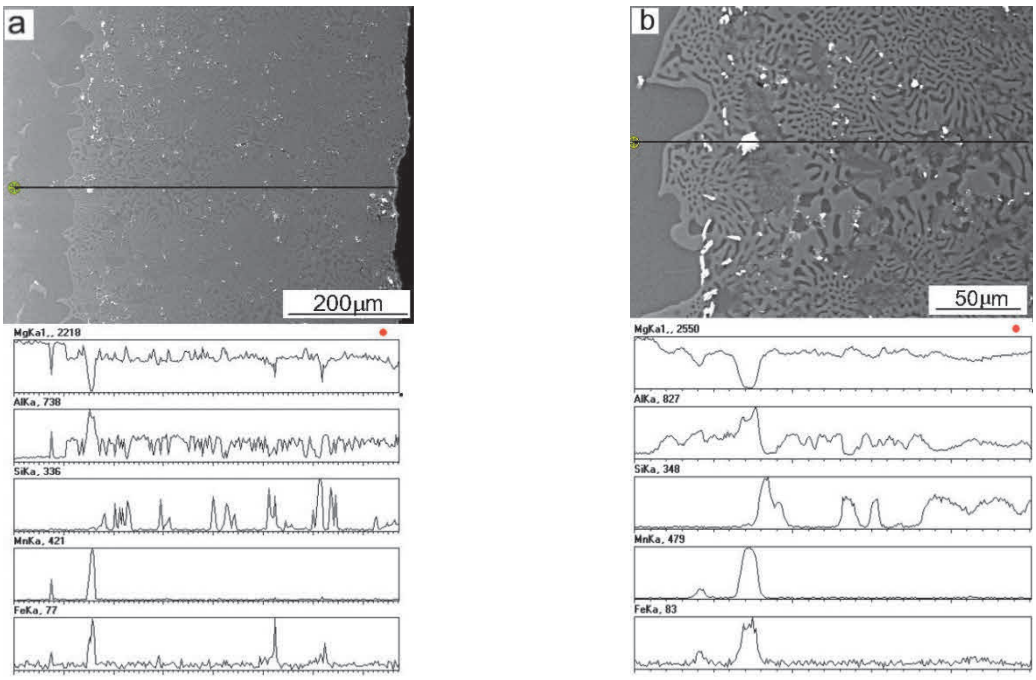

Figure 5 SEM images of AZ91D enriched with Al and Si through thermochemical treatment at 445 °C; EDS line scan results showing the distribution of elements along the index line: (a) lower magnification, (b) higher magnification.

Figure 5(a) shows a low magnification SEM image of the alloyed surface layer fabricated at 445 °C. The EDS line scan results indicate a high concentration of Mg, Al and Si. It can be seen that the distribution of Si is highly irregular and Mn and Fe occur locally. The higher magnification image in **Figure 5(b)** reveals a two-phase structure rich in Mg and Al with grey areas rich in Si and white particles rich in Al, Mn and Fe.

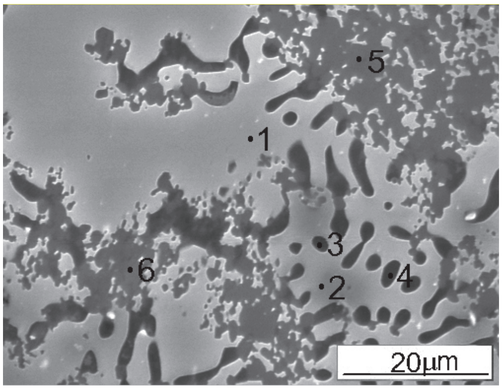

Figure 6 Higher magnification image of the layer microstructure.

Details of the layer microstructure are presented in **Figure 6. Table 1** provides results of the quantitative EDS analysis for the marked points. The two-phase structure is composed of light and dark phases. The chemical composition of the light phase (analysis at points 1 and 2) refers to an $Mg_{17}Al_{12}$ intermetallic phase. A small amount of Zn was detected in the $Mg_{17}Al_{12}$ phase areas. Zn is present in AZ91D as an alloying element. The literature data [21] show that Zn can substitute some of the Al in the $Mg_{17}Al_{12}$ intermetallic phase. The composition of the dark phase (analysis at points 3 and 4) corresponds to a solid solution of Al in Mg. According to the Mg-Al phase diagram [22], the results suggest that the two-phase structure is a eutectic composed of $Mg_{17}Al_{12}$ and a solid solution of Al in Mg. There are agglomerates of gray particles over the eutectic. The results of the EDS analysis for these particles (analysis at points 5 and 6) indicate an Mg_2Si phase. The chemical composition of the white particles observed in the layer close to the AZ91D substrate (e.g., Al - 57.75 at.%, Mn - 39.41 at.%, Mg - 1.46 at.%, Si - 1.07 at.%, Fe - 0.31 at.%) reveals a multicomponent phase rich in Al and Mn. The AZ91D alloy contains 0.2 Mn; hence the presence of the phase in the layer close to the substrate. The white particles observed closer to the surface (e.g., Al - 11.27 at.%, Mn - 0.27 at.%, Mg - 9.20 at.%, Si - 59.47 at.%, and Fe - 19.79 at.%) are also a multicomponent phase but richer in Si and Fe. The occurrence of multicomponent particles rich in Fe in the layer close to the surface is due to the fact that the Si powder contained Fe as an impurity.

Table 1 Results of the EDS quantitative analysis corresponding to the points marked in **Figure 6**

Point	**Mg**	**Al**	**Zn**	**Si**
	(at.%)			
1	62.84	36.80	0.36	-
2	63.68	36.02	0.30	-
3	91.75	8.25	-	-
4	90.44	9.56	-	-
5	67.00	2.69	-	30.31
6	69.79	2.34	-	27.87

The formation of the alloyed layer on the AZ91D substrate was assumed to proceed as follows. Heating the AZ91D in contact with the Al+Si powder mixture resulted in the diffusion of Al and Si atoms into the substrate. During heat treatment, the concentration of Al and Si in the top surface layer increased; new phases formed as a result of the reaction between the alloying elements of the powder mixture and the elements of the substrate material. The application of a lower heating temperature, i.e., 430 °C, led to the formation of a thin modified layer with a microstructure indicating that the reaction at the substrate/powder mixture interface proceeded in the solid state. The presence of the eutectic in the microstructure of the layer fabricated at the higher temperature (445 °C) indicates that the reactions at the interface proceeded with the contribution of the liquid phase. The formation of the liquid phase accelerated the inter-diffusion of the elements; the layer produced under such conditions was much thicker. The large amount of precipitates of the $Mg_{17}Al_{12}$ intermetallic phase in the AZ91D close to the layer indicates that, during the thermochemical treatment process, Al diffused deep into the AZ91D substrate making the area adjacent to the surface layer richer with this element.

4. CONCLUSIONS

This paper has demonstrated that it is possible to fabricate an Al and Si-rich surface layer on an AZ91D substrate by thermochemical treatment in solid media (powder mixture with 80 wt% of Al and 20 wt% of Si). The experimental data show that the microstructure of the layer was dependent on the heating temperature. At both temperatures (430 °C and 445 °C), one of the structural constituents of the surface layer was an Mg_2Si phase. The layer produced at 430 °C had a thickness of about 50 μm and contained $Mg_{17}Al_{12}$ and Al_3Mg_2 intermetallic phases and an Mg_2Si phase. When a higher temperature (445 °C) was applied, the layer was much thicker (about 600 μm) and it had a eutectic structure (an $Mg_{17}Al_{12}$ intermetallic phase and a solid solution of Al in Mg) with agglomerates of Mg_2Si phase particles.

ACKNOWLEDGEMENTS

The research reported herein was supported by a grant from the National Science Centre (No. DEC-2017/01/X/ST08/00791).

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