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Characterization of the Surface Layer of Mg Enriched with Al and Si by Thermochemical Treatment

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Abstract

The modified surface layers of Mg enriched with Al and Si were fabricated by thermochemical treatment. The substrate material in contact with an Al + 20 wt.% Si powder mixture was heated to 445°C for 40 or 60 min. The microstructure of the layers was examined by OM and SEM. The chemical composition of the layer and the distribution of elements were determined by energy dispersive X-ray spectroscopy (EDS). The experimental results show that the thickness of the layer is dependent on the heating time. A much thicker layer (1 mm) was obtained when the heating time was 60 min than when it was 40 min (600 μm). Both layers had a non-homogeneous structure. In the area closest to the Mg substrate, a thin zone of a solid solution of Al in Mg was detected. It was followed by a eutectic with $Mg_{17}Al_{12}$ and a solid solution of Al in Mg. The next zone was a eutectic with agglomerates of Mg_2Si phase particles; this three-phase structure was the thickest. Finally, the area closest to the surface was characterized by dendrites of the $Mg_{17}Al_{12}$ phase. The microhardness of the modified layer increased to 121-236 HV as compared with 33-35 HV reported for the Mg substrate.

Keywords: Magnesium, Surface modification, Thermochemical treatment, Microstructure, Microhardness

1. Introduction

Thermochemical treatment is commonly used to improve the surface properties of a variety of metals and alloys [1,2]. This technique can be employed to modify the surface layer of Mg and Mg alloys. The literature data show that, in the thermochemical treatment process of an Mg-based substrate, a solid or liquid medium acts as a source of diffusion elements. The solid medium is generally in the form of the metal powder, e.g. Al [3-7], Al+Zn [7-11], Zn+Al [12], Sb+Zn [13] or Zn+Y [14]. Layers fabricated on Mg or an Mg alloy using pure Al powder contained Mg-Al intermetallic phases. The heat treatment of an Mg-based substrate in contact with an Al+Zn or Zn+Al powder mixture led to the enrichment of the surface layer with both elements; in such a case, Mg-Al-Zn intermetallic phases were detected in the modified layer. The heat treatment of an AZ91D alloy substrate in contact with Zn+Y powder resulted in the formation of a surface layer containing a large amount of an $Mg_5Al_2Zn_2$ intermetallic phase. The experimental results presented in [6,7,11,12] show that the key factor affecting the formation of alloyed layers on Mg through thermochemical treatment was good contact between the source of diffusion elements and the substrate material. Adequate contact facilitated the diffusion of alloying elements from the outside source to the Mg-based substrate. The heat treatment process required applying pressure to ensure good contact between the powder material acting as the source of diffusion elements and the Mg substrate. Molten salts are also applied as a liquid medium. As indicated in [15-17], the heat treatment of an AZ91D substrate with molten salts containing $AlCl_3$ led to the formation of a surface layer composed of Mg-Al intermetallic phases. Modified layers containing intermetallic phases fabricated by thermochemical treatment exhibit high hardness, high wear resistance and good corrosion resistance.

This article discusses surface layers of Mg enriched with Al and Si fabricated by thermochemical treatment, which involved heating the Mg substrate in contact with the Al+Si powder mixture acting as a source of diffusion elements. The modified surface layer was characterized by performing OM and SEM/EDS microstructural analyses and microhardness measurements.

2. Experimental details

Commercially pure magnesium was selected as the substrate. The samples (40x20x10 mm) were cut from an ingot. Their surfaces were ground with SiC paper progressively up to 800 grit and cleaned using ethanol. The Mg samples were placed in a steel container and embedded in a dry Al+20 wt.% Si powder mixture. The container was placed in a vacuum furnace equipped with a pressure pad, which pressed down the lid of the container to keep the powder under pressure during the heat treatment process. A schematic diagram of the container used in this process is provided in Fig. 1. A pressure of 1 MPa was used to ensure good contact between the source of diffusion elements (the Al+Si powder mixture) and the Mg substrate. The process procedure was as follows: the samples were heated up from room temperature to 445 °C for 30 min, kept at that temperature for 40 or 60 min, and cooled down with the furnace to room temperature.

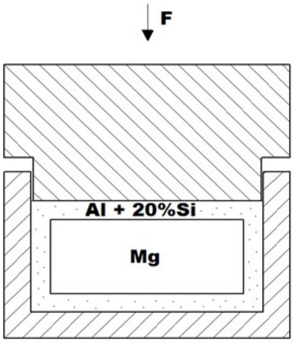

Fig. 1. Schematic diagram of the container used in the thermochemical treatment process

Polished sections were examined to determine the layer microstructure. The analysis was performed using a Nikon ECLIPSE MA 200 optical microscope and a JEOL JSM-5400 scanning electron microscope. The chemical composition of the modified layers was identified with an Oxford Instruments ISIS 300 X-ray energy dispersive spectrometer (EDS) attached to the SEM. The composition of the modified layers was determined by comparing the results of the EDS quantitative analysis with the data from the binary Al-Mg [18] and ternary Al-Mg-Si [19-20] phase diagrams. The microhardness of the surface layer was measured at a load of 0.1 kg using a MATSUZAWA MMT Vickers hardness tester.

3. Results

Figure 2 shows optical micrographs of the Mg specimens thermochemically treated at 445 °C for 40 min and 60 min. As can be seen, the heating of the Mg in contact with the Al + 20 wt.% Si powder mixture led to the formation of a modified surface layer. Its thickness depends on the heating time. A much thicker layer (about 1 mm) was produced at a heating time of 60 min, when compared with that obtained after 40 min (about 600 μm).

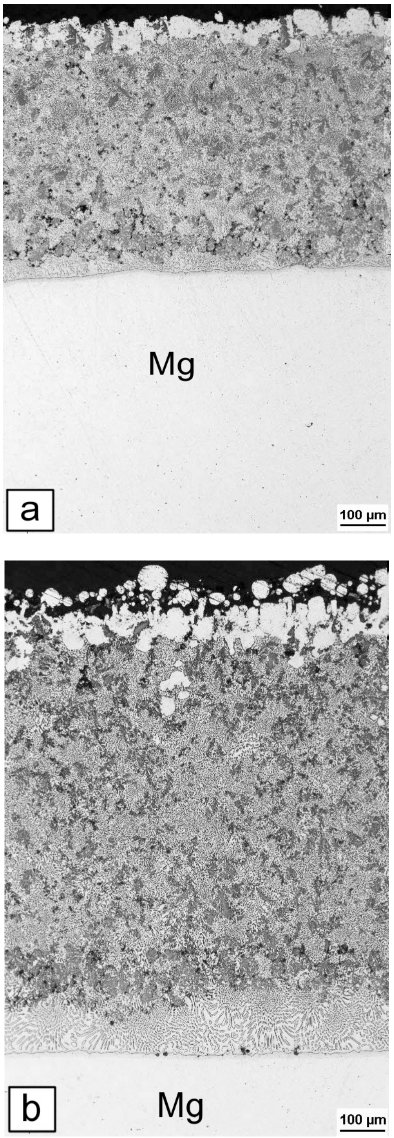

Fig. 2. Cross-sectional views of the Mg specimens after thermochemical treatment at 445 °C for (a) 40 min. and (b) 60 min

No matter which heating time was used, the layers had a similar microstructure. For this reason, an SEM image of only one layer is presented. Figure 3 shows the SEM microstructure of the layer fabricated in 60 min. The concentration of elements along the indexed line clearly suggests that except for Mg, Al and Si are present in the modified layer. As can be seen from Fig. 3, there is a thin zone (about 20 µm in thickness), marked A, adjacent to Mg. From the linear distribution of elements it is evident that Al is present in this zone. Its chemical composition identified with the EDS method (91.58 at.% Mg and 8.42 at.% Al) indicates a solid solution of Al in Mg. Then, there is a two-phase area above the solid solution zone, where the lighter phase is rich in Al and the darker phase is rich in Mg. At a certain distance from the Mg substrate, next to the two-phase structure, areas rich in Si occur in the modified layer. Figure 4 shows a high magnification SEM image of the microstructure of this region. The stoichiometry of elements in the lighter phase (EDS analysis at point 1 with 62.47 at.% Mg and 37.53 at.% Al) suggests the presence of an $Mg_{17}Al_{12}$ intermetallic phase. The results of the quantitative EDS analysis obtained for the darker phase (marked 2) with 91.41 at.% Mg and 8.59 at.% Al indicate that the phase is a solid solution of Al in Mg. The results were analysed using the Mg-Al phase equilibrium. It is clear that the two-phase structure is a eutectic composed of an $Mg_{17}Al_{12}$ intermetallic phase and a solid solution of Al in Mg. Next to the two-phase eutectic, agglomerates of grey particles can be observed (upper part of Fig. 4). From the chemical composition analysis, i.e. EDS analysis, at point 3 (68.90 at.% Mg, 1.40 at.% Al, 29.7 at.% Si) it is evident that the grey particles are an Mg_2Si phase. In terms of thickness, this three-phase structure is the predominant zone in the resulting layer. The heating temperature (445 ^{o}C) was higher than the eutectic temperature of the Mg-Al system (437 ^{o}C); the reactions at the Mg-substrate/mixed-powder interface during the thermochemical treatment occurred in the presence of a liquid phase. During cooling, a continuous layer enriched with Al and Si formed on the Mg substrate as a result of solidification; it was characterized mainly by a ternary eutectic structure (a solid solution of Al in Mg + $Mg_{17}Al_{12}$ + Mg_2Si). The results are in agreement with the literature data [19,20]; the analysis of the Mg-Al-Si ternary system revealed that at a temperature of 435-438 °C magnesium-rich alloys form a ternary eutectic containing a solid solution of Al in Mg, an $Mg_{17}Al_{12}$ intermetallic phase and an Mg_2Si phase. As can be seen from Figs. 3 and 4, some porosity is visible near the agglomerates of the Mg_2Si phase.

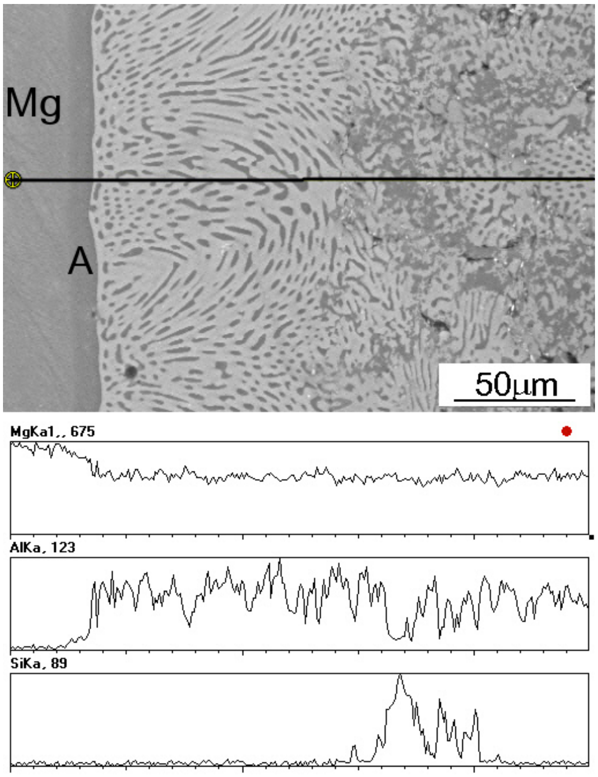

Fig. 3. Microstructure of the layer adjacent to the Mg substrate with the corresponding EDS line spectra

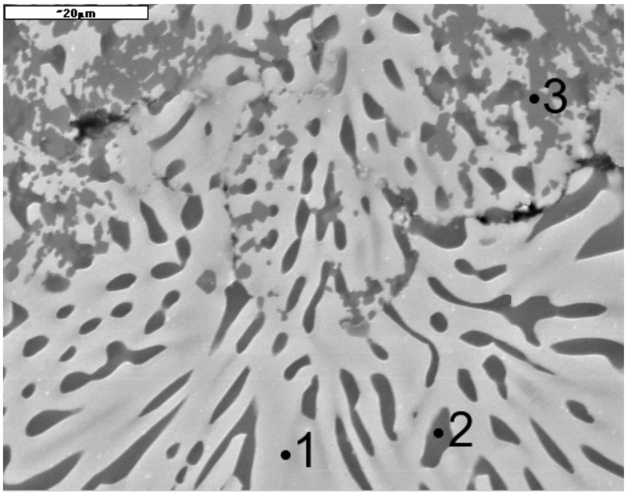

Fig. 4. SEM image of the microstructure of the modified layer close to the Mg substrate

As can be seen from Fig. 2, there is a light area in the surface layers. Figure 5 shows an SEM image of the microstructure of the modified layer close to the surface, where a ternary eutectic and the large light dendrites are visible. The results of an EDS analysis in the area marked 1 (with 61.80 at.% Mg and 38.20 at.% Al) indicate an $Mg_{17}Al_{12}$ intermetallic phase.

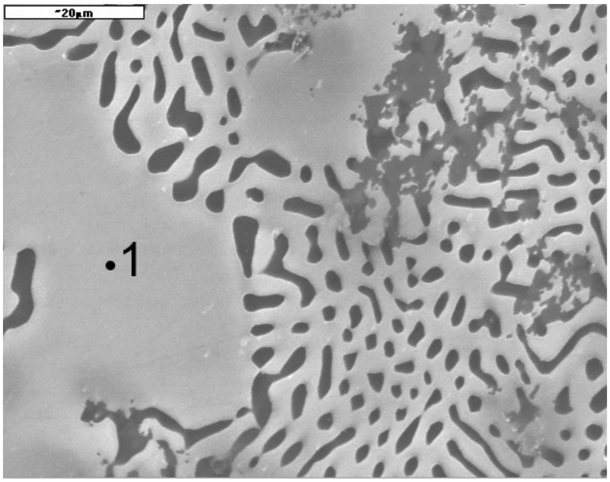

Fig. 5. SEM image of the microstructure of the modified layer adjacent to the surface

Figure 6 shows indentations left by the Vickers penetrator in the modified layer and the Mg substrate. The microhardness of the Mg substrate varied from 33 to 35 HV. The microhardness of the surface layer was in the range 172-186 HV for the eutectic in the area adjacent to the Mg, 201-236 HV for the areas where the eutectic co-occurred with agglomerates of the Mg_2Si phase. In the three-phase area of the modified layer where some porosity was observed, the values of the microhardness were lower, i.e. in the range between 121 and 138 HV. The microhardness reported for the area containing dendrites of the $Mg_{17}Al_{12}$ intermetallic phase varied from 204 to 210 HV.

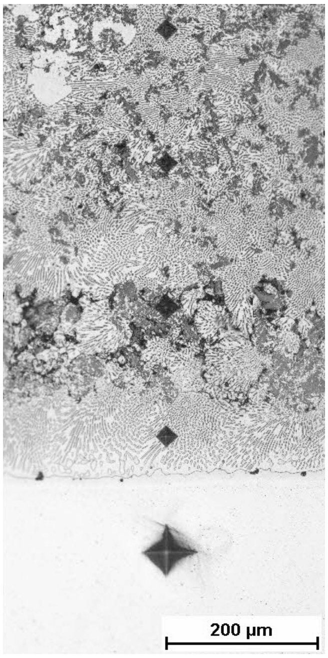

Fig. 6. Indentations in the modified surface layer and the Mg substrate after the Vickers microhardness tests

The experimental results presented in this paper show that the surface layer enriched with Al and Si could be formed on the Mg substrate by thermochemical treatment using an Al+20% Si as a solid medium. This layer is characterized by high microhardness due to the presence hard phases ($Mg_{17}Al_{12}$ and Mg_2Si) in microstructure.This method can also be employed for magnesium alloys. The literature data show that the surface layer containing Mg-Al intermetallic phases and the Mg_2Si phase can be formed on the Mg-based substrate by laser alloying or laser cladding with Al-Si powder [21-26]. It is worth mentioning that thermochemical treatment method presented in this paper is easier and less expensive than the surface modification by laser technology.

4. Conclusions

1. The heat treatment of the Mg substrate in contact with the Al+20% Si powder mixture at 445 °C led to the formation of a modified surface layer enriched with Al and Si.
2. A much thicker layer was produced when the heating time was longer. The layer fabricated in 40 min had a thickness of about 600 µm, while that obtained after 60 min was approximately 1 mm in thickness.
3. The structural constituents identified in the modified layer were: an $Mg_{17}Al_{12}$ intermetallic phase, a solid solution of Al in Mg and an Mg_2Si phase. The layer had a non homogeneous structure. Closest to the Mg substrate, there was a thin zone of a solid solution of Al in Mg. The area immediately adjacent to it was a eutectic (a solid solution of Al in Mg + $Mg_{17}Al_{12}$). Next, there was a thick zone of a ternary eutectic (a solid solution of Al in Mg + $Mg_{17}Al_{12}$ + Mg_2Si) and, finally, the surface layer with dendrites of the $Mg_{17}Al_{12}$ intermetallic phase.
4. The microhardness of the modified layer was several times higher than that of the Mg substrate.

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