SURFACE MODIFICATION OF MAGNESIUM BY A THERMOCHEMICAL TREATMENT IN A MEDIUM CONTAINING $ZnCl_2$+KCL

BUCKI Tomasz, MOLA Renata

Kielce University of Technology, Kielce, Poland, EU

Abstract

A surface layer enriched with zinc was formed on magnesium by heating specimens painted with a paste containing $ZnCl_2$+KCl at 440 °C for 120 min using no protective atmosphere. The study focused on the microstructure, phase constitution and microhardness of the alloyed layer. The layer, which was about 200 µm in thickness, had a microstructure composed of a eutectoid mixture (an MgZn intermetallic phase + a solid solution of zinc in magnesium) and some dendrites (a solid solution of zinc in magnesium). At the interface between the alloyed layer and the magnesium substrate, there was a zone of a solid solution of zinc in magnesium. The thermochemical process increased the hardness of the specimens at the surface from 30 HV 0.1 (Mg) to 110-164 HV 0.1 (the layer containing the MgZn intermetallic phase).

Keywords: Magnesium, zinc layer, zinc chloride

1. INTRODUCTION

Poor surface properties of magnesium and magnesium alloys, i.e. low resistance to both wear and corrosion, represent a major obstacle to a wider application of the materials. These properties can be improved using different surface treatment methods. The latest trends include enriching the surface layer of magnesium or magnesium alloys with appropriate alloying elements that tend to form intermetallic phases with magnesium. Protective surface layers on magnesium or its alloys are now frequently produced by laser surface alloying. A review of the literature shows that the most common alloying additions are aluminum, zinc, copper, nickel, silicon, and their combinations, i.e. Al+Si, Al+Zn, Al+Cu, Al+Ni, Al+Mn, Al+Ir and Ni+Cu+Al [1-11]. Layers containing intermetallic phases can also be formed by thermochemical treatment. The major advantages of this method are a low cost and simple technology. A workpiece can be heated in a solid or liquid medium. An example of a solid medium is aluminum powder [11-13] or a mixture of aluminum and zinc powders [14-17]. Layers produced using aluminum powder contained Mg-Al intermetallic phases. When zinc powder is added, the resultant layers contain Mg-Al-Zn intermetallic phases. Thermochemical treatment of magnesium alloys in a liquid medium can be conducted using molten salts (NaCl+$AlCl_3$) [18]. This method is employed to fabricate layers enriched with aluminum, which contain Al-Mg intermetallic phases.

The aim of this study was to produce a surface layer enriched with zinc on a magnesium substrate by thermochemical treatment using a paste containing zinc chloride. The thermochemical treatment involved heating the specimens painted with the paste in a chamber furnace. The paper discusses the microstructure, chemical composition and microhardness of the layer.

2. EXPERIMENTAL DETAILS

High purity magnesium (99.9%) was used as the substrate material. Specimens with dimensions of 30x15x5 mm were cut from an ingot. The surfaces of the specimens were prepared by first grinding them with abrasive papers (up to 800 grit) and then degreasing. Layers enriched with zinc were formed by heating the specimens painted with a paste containing zinc chloride in a chamber furnace. Zinc chloride acted as a source of active zinc atoms. The paste was prepared according to the following procedure. First, zinc chloride (68 wt.%) and potassium chloride (32 wt.%) were mixed. From the phase diagram of KCl-$ZnCl_2$ [19] it is evident that the salts form low melting point eutectics. The salt mixture with 68 wt.% $ZnCl_2$ has a melting temperature of about 230°C. The paste was prepared by blending 10 g of the mixture of salts with 2 ml of a solution of pine rosin in ethanol, with the ratio being 1 g of rosin to 1 ml of ethanol. The magnesium specimens were painted with the paste then placed for 2 h in a chamber furnace preheated to 440 °C and finally air cooled. No protective atmosphere was used during heating.

The microstructural analysis of the surface layer was carried out with a Nikon ECLIPSE MA200 inverted microscope and a JEOL JSM-7100F scanning electron microscope equipped with a LINK ISIS 300 energy dispersive X-ray spectrometer. The layer microhardness was measured at a load of 100 g using a Vickers microhardness tester.

3. RESULTS AND DISCUSSION

Figure 1 shows the microstructure of a Zn-enriched surface layer of magnesium, which was formed by heating the magnesium specimen painted with a paste containing $ZnCl_2$+KCl at 440 °C for 120 min using no protective atmosphere. The overall thickness of the layer was about 200-240 µm. A two-phase area and dark dendrites were observed in the microstructure. **Figure 2** presents SEM images and EDS line scan results obtained for the layer. The concentration of magnesium and zinc along the marked line (**Figure 2a**) suggests that the layer enriched with zinc was formed on the magnesium surface during the heating process. **Figure 2b** shows the microstructure of the interface between the magnesium substrate and the resultant surface layer observed at a higher magnification. A thin transition zone was observed at the interface between the layer and the magnesium substrate. The chemical composition of this area (point 1: 95.77 at.% Mg, 4.23 at.% Zn; point 2: 96.10 at.% Mg, 3.90 at.% Zn) suggests the presence of a solid solution of zinc in magnesium. From the linear distribution of the elements in this zone (**Figure 2b**) it is clear that the closer to the magnesium substrate, the lower the content of zinc and the higher the content of magnesium.

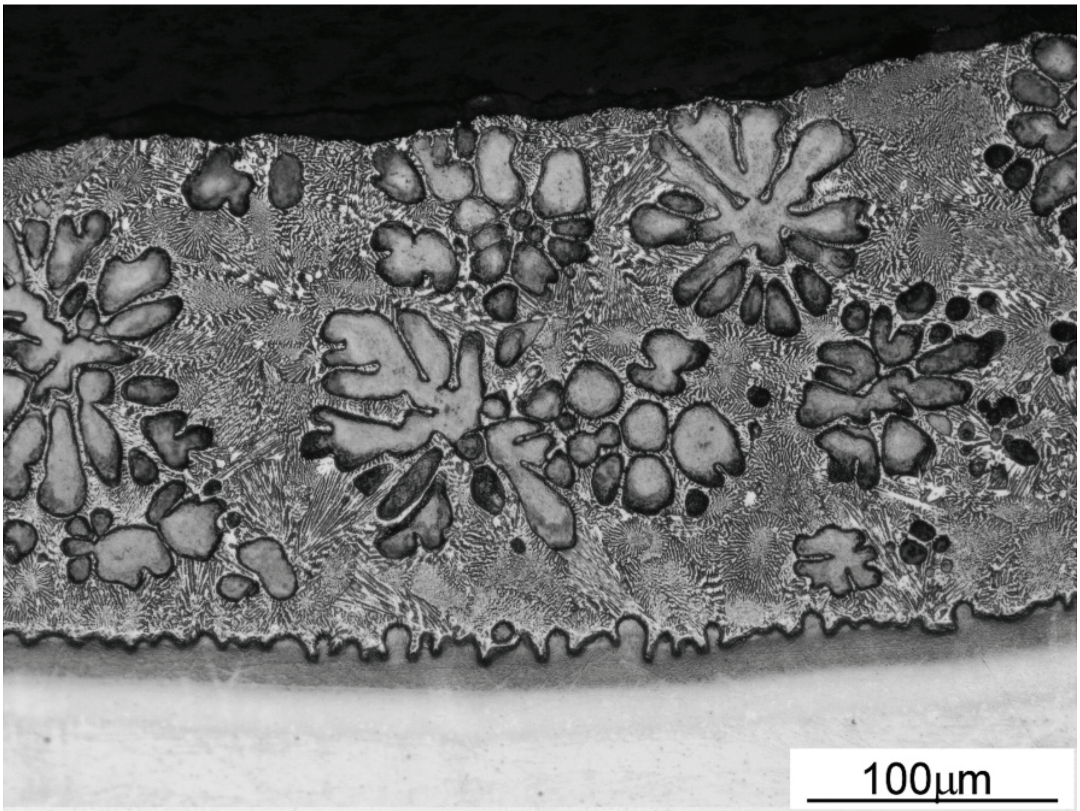

Figure 1 Microstructure of the Zn-enriched surface layer of magnesium formed by thermochemical treatment

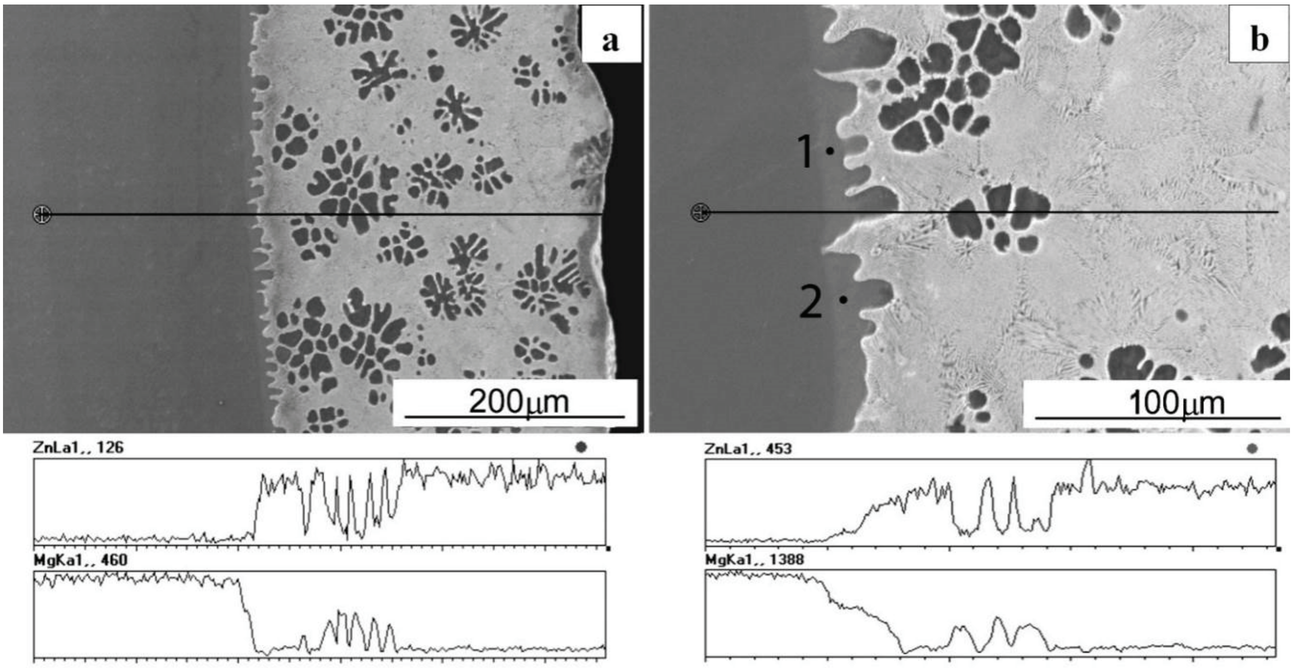

Figure 2 SEM microphotographs of the alloyed surface layer with the corresponding linear distribution of zinc and magnesium along the marked line, a) lower magnification, b) higher magnification

The SEM image in **Figure 3** shows details of the microstructure of the Zn-enriched surface layer of magnesium. The EDS analysis was performed at the points marked in this figure. The results of the quantitative analysis at point 1 (94.93 at.% Mg and 5.07 at.%. Zn) indicate that the dark dendrites observed in the layer microstructure are a solid solution of zinc in magnesium. The chemical composition of the two-phase area (marked as 2 in **Figure 3**) was as follows: 66.18 at.% Mg and 33.82 at.% Zn. According to the Mg-Zn phase diagram [20], this result suggests that the two-phase area is a eutectoid mixture of an MgZn intermetallic phase and a solid solution of zinc in magnesium. In the surface layer, the lighter phases are distributed locally. The Mg:Zn ratio of about 2:3 for this phase (analysis at point 3: 40.11 at.% Mg and 59.89 at.% Zn) suggests an Mg_2Zn_3 intermetallic phase.

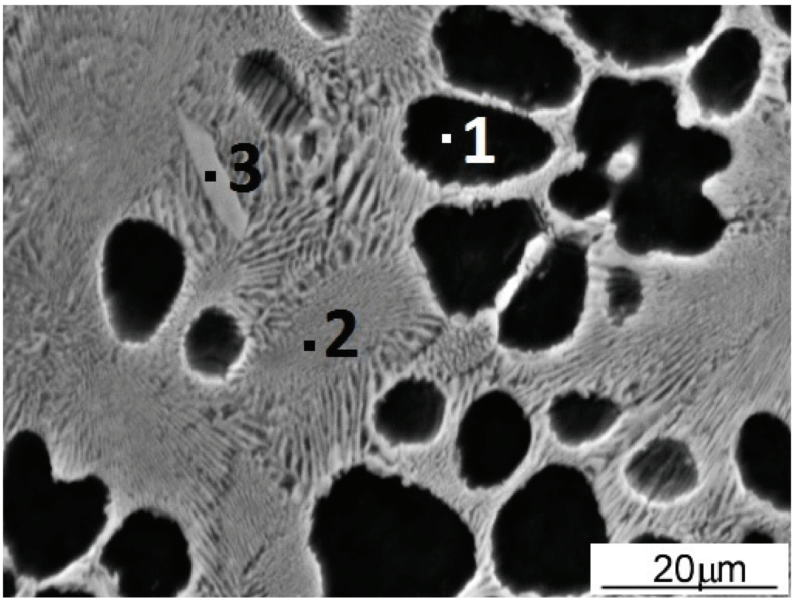

Figure 3 SEM view of the surface layer with the EDS analysis points observed at a higher magnification

The results indicate that the Zn-enriched surface layer of magnesium, which contains Mg-Zn intermetallic phases, can be fabricated by heating the magnesium specimen painted with a paste containing zinc chloride. During the heating process, there was a reduction in zinc chloride when it came into contact with magnesium. The active atoms of zinc diffused into the magnesium substrate. The formation of low melting Mg-Zn intermetallic phases began after the solubility of zinc in solid magnesium exceeded the limit value. The reaction at the paste-surface interface occurred with the contribution of the liquid phase. The thin layer of liquid that solidified during cooling formed the surface layer enriched with zinc.

The surface layer and the substrate were measured for Vickers microhardness. **Figure 4** shows the indentations. The microhardness of the magnesium substrate was about 30 HV 0.1. The values obtained for the surface layer ranged from 152 to 164 HV 0.1 in the eutectoid; in the dendritic areas, they were slightly lower, ranging between 110 and 146 HV 0.1. The data shows that the surface layer enriched with zinc containing Mg-Zn intermetallic phases had higher hardness, which should contribute to higher resistance to wear than the magnesium substrate.

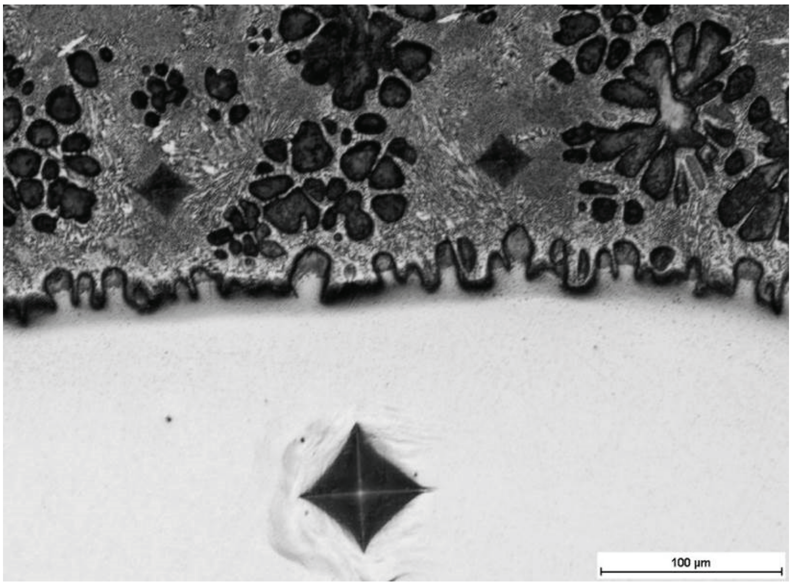

Figure 4 Microhardness test indentations into the Zn-enriched surface layer and the magnesium substrate

4. CONCLUSIONS

- The Zn-enriched surface layer of magnesium, formed through thermochemical treatment in a medium containing zinc chloride, had a thickness of about 200-240 µm.
- The surface layer had a microstructure composed of the eutectoid mixture (MgZn + a solid solution of Zn in Mg), some dendrites (a solid solution of zinc in magnesium) and particles of an Mg_2Zn_3 intermetallic phase sparsely distributed over the eutectoid matrix.
- The thin transition zone at the interface between the surface layer and the magnesium substrate was a solid solution of zinc in magnesium.
- The microhardness of the surface layer ranged between 110 and 164 HV 0.1 and it was about 5 times higher than that of the magnesium substrate.

REFERENCES

[1] IGNAT, S., SALLAMAND, P., GREVEY, D., LAMBERTIN, M. Magnesium alloys laser (Nd:YAg) cladding and alloying with side injection of aluminum powder. *Applied Surface Science*, 2004, vol. 225, pp.124-134.

[2] DZIADOŃ, A., MOLA, R. Analiza mikrostruktury warstwy wierzchniej magnezu w zbogaconej w aluminum w wyniku stopowania laserowego.*Rudy iMetaleNieżelazne,* 2011, vol. 56, no.5, pp. 272-278.

[3] PAITAL, S.R., BHATTACHARYA, A., MONCAYO, M., HO, Y.H., MAHDAK, K., NAG, S., BANERJEE, R., DAHOTRE, N.B. Improved corrosion and wear resistance of Mg alloys via laser surface modification of Al on AZ31B.*Surface and Coatings Technology,* 2012, vol. 206, pp. 2308-2315.

[4] KUTSCHERA, U., GALUN, R. Wear behavior of laser surface treated magnesium alloys.*Magnesium Alloys and Their Application, ed. Kainer K.U., Wiley-VchVerlag*, 2000, pp. 330-335.

[5] DZIADOŃ, A., MOLA, R. Charakterystyka mikrostruktury warstwy wierzchniej magnezu w zbogaconej w aluminumikrzem zapomocą lasera CO_2. *Rudy i Metale Nieżelazne*, 2013, vol. 58, no. 10, pp. 551-556.

[6] VOLOVITCH, V., MASSE, J.E., FABRE, A., BARRALLIER, L., SAIKALY, W. Microstructure and corrosion resistance of magnesium alloy ZE41 with laser surface cladding by Al-Si powder.*Surface and Coatings Technology*, 2008, vol. 202, pp. 4901-4914.

[7] GAO, Y., WANG, C., PANG, H., LIU, H., YAO, M. Broad-beam laser cladding of Al-Cu alloy coating on AZ91HP magnesium alloy.*Applied Surface Science*, 2007, vol. 253, pp. 4917-4922.

[8] MAJUMDAR, J.D., DUTTA, J., MAIWALD, T., GALUN, R., MORDIKE, B.L., MANNA, I. Laser surface alloying of an Mg alloy with Al+Mn to improve corrosion resistance. *Lasers in Engineering*, 2002, vol. 12, no. 3, pp. 147-169.

[9] CHEN, C., WANG, M., WANG, D., JIN, R., LIU, Y. Laser cladding of Al+Ir powders on ZM magnesium base alloy.*Rare Metals*, 2007, vol. 26, no. 5, pp. 420-425.

[10] YUE, T.M., LI, T. Laser cladding of Ni/Cu/Al functionally graded coating on magnesium substrate.*Surface and Coatings Technology*, 2008, vol. 202, pp. 3034-3049.

[11] SHIGEMATSU M., NAKAMURA M., SAITOU K., SHIMOJIMA K. Surface treatment of AZ91D magnesium alloy by aluminum diffusion coating. *Journal of Materials Science Letters*, 2000, vol. 19, pp. 473-475.

[12] ZHU, L., SONG, G. Improved corrosion resistance of AZ91D magnesium alloy by an aluminum-alloyed coating. *Surface and Coatings Technology*, 2006, vol. 200, pp. 2834-2840.

[13] MOLA, R., JAGIELSKA-WIADEREK, K. Formation of Al-enriched surface layers through reaction at the Mg-substrate/Al-powder interface. *Surface and Interface Analysis*, 2014, vol. 46, pp. 577-580.

[14] MOLA, R. The properties of Mg protected by Al- and Al/Zn-enriched layers containing intermetallic phases.*Journal of Materials Research*, 2015,vol. 30, pp. 3682-3691.

[15] ZHANG, M.X., KELLY, P.M. Surface alloying of AZ91 alloy by diffusion coating.*Journal of Materials Research*, 2002, vol. 17, no. 10, pp. 2477-2479.

[16] HIRMKE, J., ZHANG, M.X., STJOHN, D.H. Surface alloying of AZ91E alloy by Al-Zn packed powder diffusion coating.*Surface and Coatings Technology*, 2011, vol. 206, pp. 425-433.

[17] MOLA, R. Fabrication and microstructural characterization of Al/Zn-enriched layers on pure magnesium.*Materials Characterization*, 2013, vol. 78, pp. 121-128.

[18] HE, M., LIU, L., WU, Y., TANG, Z., HU, W. Improvement of the properties of AZ91D magnesium alloy by treatment with a molten $AlCl_3$-NaCl salt to form an Mg-Al intermetallic surface layer.*Journal of Coatings Technology and Research*, 2009, vol. 6, no. 3, pp. 407-411.

[19] ROMERO-SERRANO, A., HERNANDEZ-RAMIREZ, A., CRUZ-RAMIREZ, A. Optimization and calculation of the MCl- $ZnCl_2$ (M = Li, Na, K) phase diagrams.*ThermochimicaActa*, 2010, vol. 510, pp. 88-92.

[20] LANDOLT-BÖRNSTEIN.*Numerical Data and Functional Relationships in Science and Technology, New Series, Group IV: Physical chemistry,PhaseEquilibria, Crystallographic and Thermodynamic data of binary alloys*.Berlin:Springer-Verlag, 1998.