www.czasopisma.pan.pl PAN www.journals.pan.pl

ARCHIVES of FOUNDRY ENGINEERING

ISSN (2299-2944)
Volume 19
Issue 3/2019

119 – 124

10.24425/afe.2019.129621

20/3

Published quarterly as the organ of the Foundry Commission of the Polish Academy of Sciences

Microscopic Analysis of Layers Containing Mg_2Si and $Mg_{17}Al_{12}$ Phases Fabricated on AZ91 Through Thermochemical Treatment

R. Mola *, M. Cieślik
Kielce University of Technology
al. Tysiąclecia Państwa Polskiego 7, 25-314 Kielce, Poland
* Corresponding author. E-mail address: rmola@tu.kielce.pl

Received 11.06.2019; accepted in revised form 06.09.2019

Abstract

The thermochemical treatment applied to improve the surface properties of AZ91 consisted in heating the material in contact with AlSi10Mg powder at 445 ^oC for 30 min. During heat treatment process the powder was held under pressure to facilitate the diffusion of the alloying elements to the substrate and, accordingly, the formation of a modified layer. Two pressures, 1 MPa and 5 MPa, were tested. The resultant layers, containing hard Mg_2Si and $Mg_{17}Al_{12}$ phases, were examined using an optical microscope and a scanning electron microscope equipped with an energy-dispersive X-ray spectrometer (EDS). The experimental data show that the layer microstructure was dependent on the pressure applied. A thicker, three-zone layer (about 200 µm) was obtained at 1 MPa. At the top, there were Mg_2Si phase particles distributed over the $Mg_{17}Al_{12}$ intermetallic phase matrix. The next zone was a eutectic ($Mg_{17}Al_{12}$ and a solid solution of Al in Mg) with Mg_2Si phase particles embedded in it. Finally, the area closest to the AZ91 substrate was a eutectic not including the Mg_2Si phase particles. By contrast, the layer produced at a pressure of 5 MPa had lower thickness of approx. 150 µm and a two-zone structure. Mg_2Si phase particles were present in both zones. In the upper zone, Mg_2Si phase particles were regularly distributed over the $Mg_{17}Al_{12}$ intermetallic phase matrix. The lower zone, adjacent to the AZ91, was characterized by a higher volume fraction of Mg_2Si phase particles distributed over the matrix composed mainly of $Mg_{17}Al_{12}$. The alloyed layers enriched with Al and Si had much higher hardness than the AZ91 substrate.

Keywords: Surface treatment, Magnesium alloy, Modified surface layer, Microstructure

1. Introduction

Magnesium alloys are characterized by low density, which implies that they are attractive as structural materials for applications where weight reduction is critical. They are widely used in the automotive and aerospace industries; however, in high performance applications, their use is limited due to low hardness and poor wear resistance. Various methods are employed to improve the surface properties of magnesium alloys [1]. One approach is to introduce alloying elements to fabricate a modified surface layer with properties superior to those of the substrate. Such layers are mainly formed on Mg-based materials by laser alloying/cladding [2-8] them with Al or Al+Si. The literature data show that thermochemical treatment can also be applied to modify the surface layer of Mg or Mg alloys. The process involves heating the substrate material in a solid medium, which acts as the source of alloying elements. The solid medium, e.g., Al [9-12], Al+Zn [12-16], Zn+Al [17], Sb+Zn [18] or Zn+Y [19], is in the form of metal powder. Layers fabricated on Mg-based substrates using Al powder contain Mg-Al intermetallic phases. The use of an Al+Zn or Zn+Al powder mixture leads to the enrichment of the surface layer with both elements; in such a case, the modified layer is composed of Mg-Al-Zn intermetallic phases. The heat treatment of AZ91D alloy in a Zn+Y powder mixture results in the formation of a surface layer containing the $Mg_5Al_2Zn_2$ intermetallic phase. As indicated in Refs. [12,16,17], the key factor affecting the formation of alloyed layers on Mg in thermochemical treatment is good contact between the substrate and the solid medium.

This article discusses the fabrication of Al- and Si-enriched surface layers on AZ91 using thermochemical treatment. In their previous paper [20], the authors reveal that the heat treatment of Mg in contact with an 80% Al + 20% Si powder mixture results in the modification of the surface layer involving the formation of Mg_2Si and $Mg_{17}Al_{12}$ phases. Further studies on the fabrication of Al and Si-enriched layers on Mg-based substrates, described here, were conducted using commercially available AlSi10Mg powder to act as the source of diffusion elements. The substrate was AZ91 magnesium alloy since pure Mg is rarely used as structural material. The resultant surface layers were analyzed via optical microscopy and scanning electron microscopy. The chemical composition of the layers was determined using the EDS method.

2. Experimental procedures

AZ91 magnesium alloy composed by weight (wt%) of 9.14% Al, 0.64% Zn, 0.23% Mn, and Mg bal. was used as the substrate material. The fabrication of an Al/Si-enriched layer involved heating an AZ91 specimen in contact with commercially available AlSi10Mg powder (Fig. 1). The powder particles were spherical in shape with a diameter ranging from 5 µm to 60 µm.

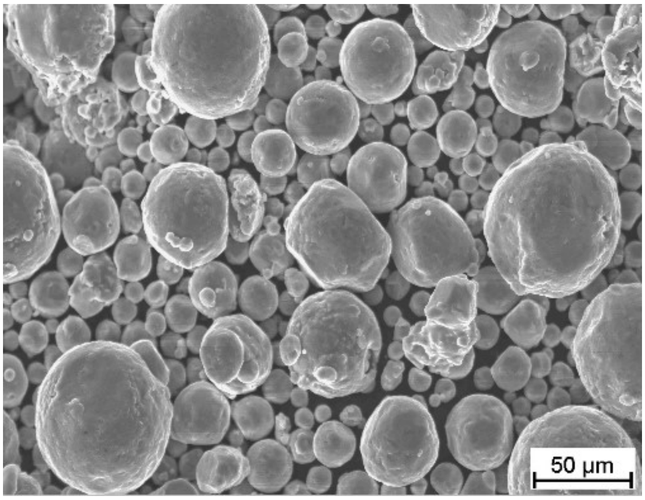

Fig. 1. SEM image of AlSi10Mg powder

The way in which the thermochemical treatment was performed is illustrated in Fig. 2. Each AZ91 specimen (60x20x15mm) had a rectangular 5 mm deep pocket milled at the top surface, where the powder was placed. During the heat treatment process, the powder was kept under pressure using two pressure pads. The specimens were heated in a vacuum furnace from room temperature to 445 °C for 30 min, held at that temperature for another 30 min, and cooled back to room temperature. Two pressures, 1 MPa and 5 MPa, were tested.

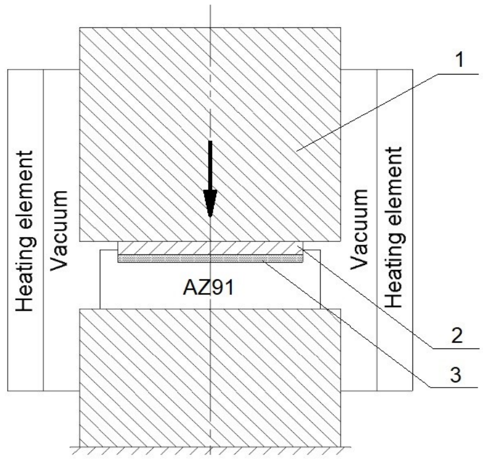

Fig. 2. Experimental setup: 1 – main pressure pad, 2 – auxiliary pressure pad, 3 – pocket filled with AlSi10Mg powder

After the thermochemical treatment process, the specimens were sectioned and prepared for microscopic observations following standard metallographic techniques. However, no etching was performed. The microstructural investigations were carried out using a Nikon ECLIPSE MA 200 optical microscope and a JEOL JSM-5400 scanning electron microscope. The chemical composition of the layers was determined by means of an X-ray energy dispersive spectrometer (EDS) attached to the SEM. The phases were identified from the EDS results on the basis of the Al-Mg [21], Mg-Si [22] and Al-Mg-Si [23] phase diagrams. The microhardness measurements were carried out with a MATSUZAWA MMT Vickers microhardness tester at a load of 100 g.

3. Experimental results and discussion

The OM image in Fig. 3 shows a modified surface layer of AZ91 fabricated by heating the material at 445 °C for 30 min in contact with AlSi10Mg powder. The powder was kept under a pressure of 1 MPa to facilitate the diffusion of the alloying elements from the outside source (AlSi10Mg powder) to the substrate material. The modified layer had a thickness about 200 µm. It was characterized by a nonuniform microstructure. Figure 3 (b) shows details of the layer observed at higher magnification. Three characteristic zones can be distinguished in the microstructure: zone A at the top, zone B in the middle, and zone C closest to the substrate. As can be seen from Fig. 3, pores occurred in zones A and B of the layer; with the porosity being higher in zone B.

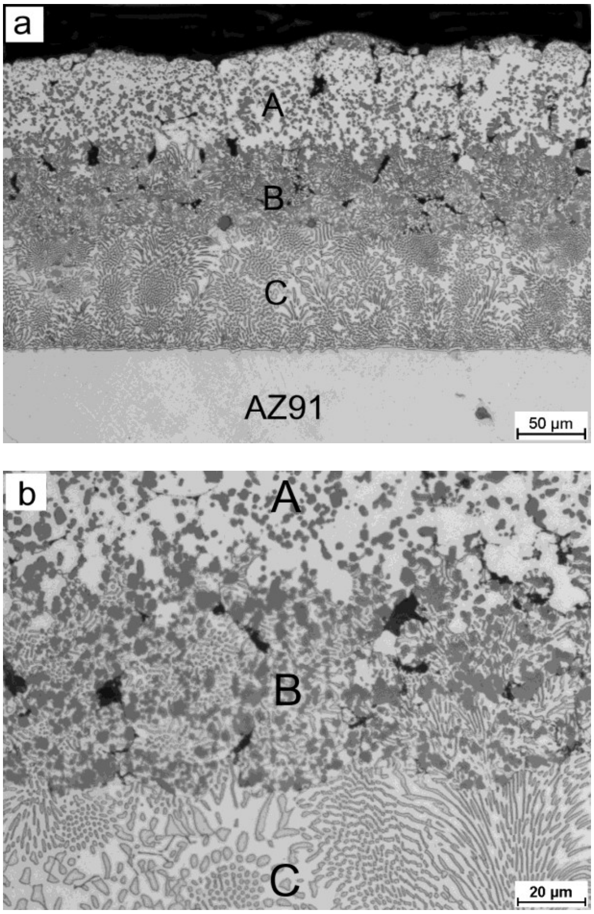

Fig. 3. OM images of an alloyed layer formed on AZ91 thermochemically treated in the presence of AlSi10Mg powder at 1 MPa: (a) low magnification, (b) high magnification

Figure 4 shows the microstructures of the three zones observed via SEM with points at which the EDS analysis was performed. The results of the quantitative analysis are provided in Table 1. Zone A of the layer (Fig. 4(a)) has a two-phase structure: a light matrix (point 1) and grey particles (point 2). The chemical composition of the light matrix suggests the $Mg_{17}Al_{12}$ intermetallic phase. The grey particles contain Mg and Si, with the atomic ratio being almost 2:1, which indicates the Mg_2Si phase [22,23]. Zone B (Fig. 4(b)) has a more complex structure. The grey particles of the Mg_2Si phase (point 3) are distributed in the two-phase matrix composed of light (point 4) and dark (point 5) phases. From the chemical composition, it is evident that the light phase is the $Mg_{17}Al_{12}$ intermetallic phase while the dark phase is a solid solution of Al in Mg. According to the Al-Mg phase diagram [21], the two-phase matrix is a eutectic composed of $Mg_{17}Al_{12}$ and a solid solution of Al in Mg. Zone C (Fig. 4(c)) has a eutectic structure composed of the $Mg_{17}Al_{12}$ phase (point 6) and a solid solution of Al in Mg (point 7). In the eutectic zone (zone C), there is no porosity. Pores are only observed in areas where Mg_2Si phase particles are detected (zones A and B). As the reactions at the substrate/powder interface proceeded with partial melting, the pores probably formed due to solidification shrinkage. Another reason for the occurrence of pores is volume reduction caused by the formation of the Mg_2Si phase. The Mg_2Si phase formed as a result of the reaction of Mg with Si during the thermochemical treatment. The density of the Mg_2Si phase (1.99 Mg/m^3) is lower than that of Si (2.32 Mg/m^3).

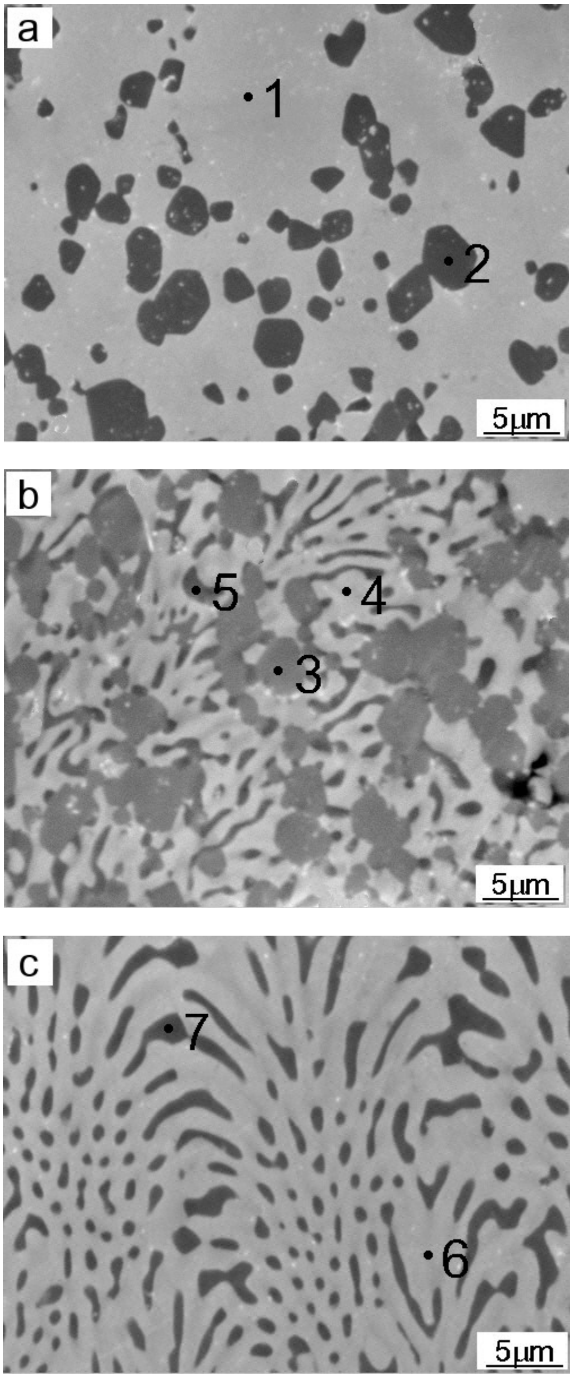

Fig. 4. SEM images showing the microstructures of zones A (a), B (b), and C (c) in the layer fabricated at 1 MPa

Table 1.
Results of the EDS quantitative analysis for points marked in Fig. 4.

Point	Mg at%	Al at%	Si at%
1	60.59	39.41	-
2	67.06	1.91	31.03
3	66.73	1.95	31.32
4	63.51	36.49	-
5	81.65	18.35	-
6	63.79	36.21	-
7	82.94	17.06	-

The OM analysis of the alloyed layer formed at 5 MPa indicates that it is about 150 µm in thickness and has a two-zone structure. A thinner, lighter zone is observed at the top (zone A), while a thicker, darker zone is found close to the substrate (zone B). Figure 5 (b) shows the layer microstructure at higher magnification. This alloyed layer has much lower porosity than that fabricated at lower pressure. Moreover, the pores are very fine.

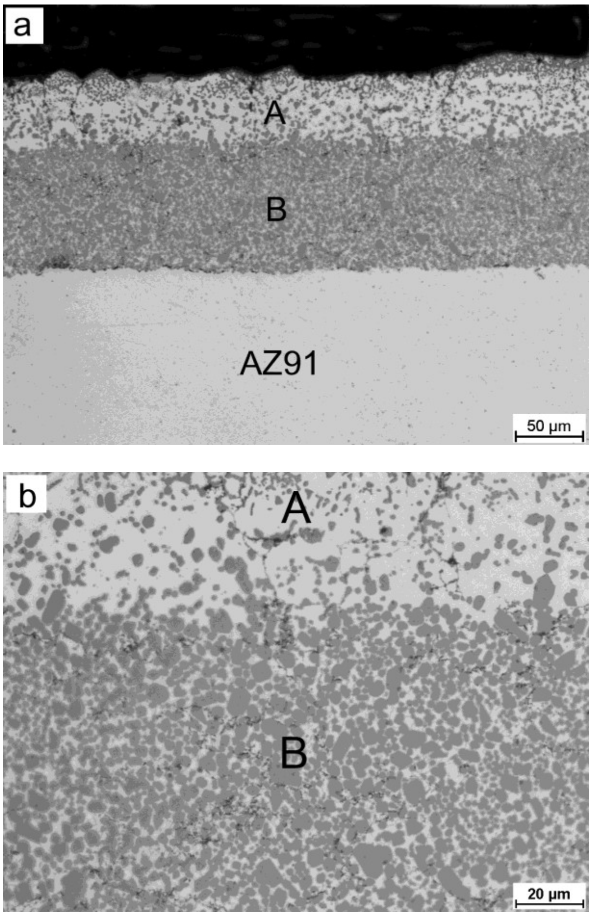

Fig. 5. OM images of the alloyed layer formed via thermochemical treatment on the AZ91 substrate in contact with AlSi10Mg powder kept at a pressure of 5 MPa: (a) low magnification, (b) high magnification

Details of the microstructures of zones A and B are shown in the SEM images in Figs. 6(a) and 6(b), respectively. The EDS quantitative results for the points marked in these figures are given in Table 2. The microstructure of zone A at the top is similar to that observed in the layer fabricated at low pressure, i.e., at 1 MPa. There are particles of the Mg_2Si phase (point 1) embedded in the $Mg_{17}Al_{12}$ intermetallic phase matrix (point 2). In zone B, Mg_2Si phase particles (point 3) are also present in the matrix composed mainly of the $Mg_{17}Al_{12}$ intermetallic phase (point 4). A solid solution of Al in Mg visible as the darkest areas occurs only locally (Fig. 6(b)). The volume fraction of the Mg_2Si phase is found to be much higher than in zone A.

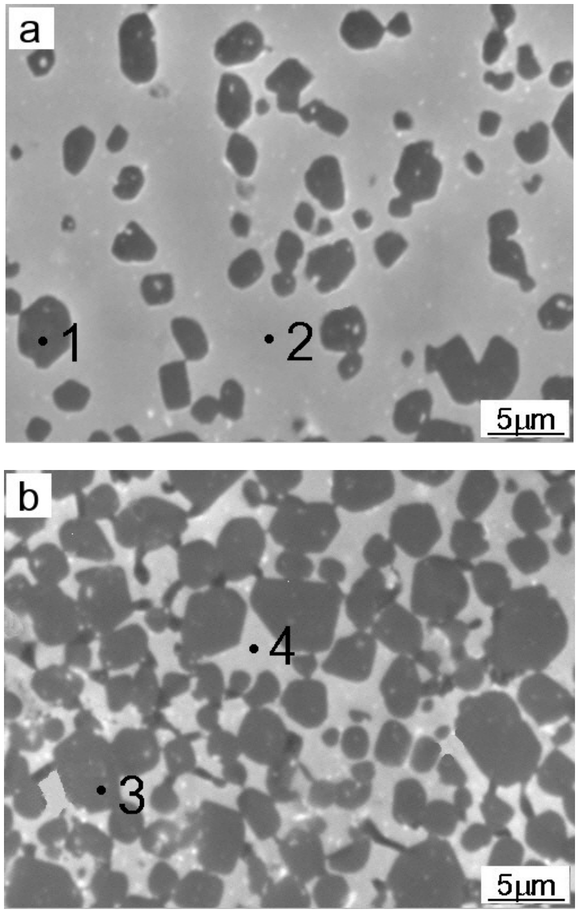

Fig. 6. SEM images showing the microstructures of (a) zone A and (b) zone B in the layer fabricated by applying a pressure of 5 MPa

Table 2.
Results of the EDS quantitative analysis at the points marked in Fig. 6.

Point	Mg at%	Al at%	Si at%
1	66.84	1.83	31.33
2	58.46	41.54	-
3	67.35	1	31.65
4	60.36	39.64	-

To summarize, the use of higher pressure (5 MPa), with the other parameters of the heat treatment unchanged, resulted in a different microstructure of the surface layer. The main difference was observed in the area adjacent to the AZ91 substrate. No eutectic zone was present close to substrate. Detailed cross-sectional analysis of the specimens revealed a thick eutectic layer along each wall of the milled pocket. The eutectic must have been pushed out from the reactive zone (AZ91/AlSi10Mg) located at the bottom of the pocket. This phenomenon is shown in Figure 7. Higher pressure was also responsible for a less porous, more compact structure of the alloyed layer.

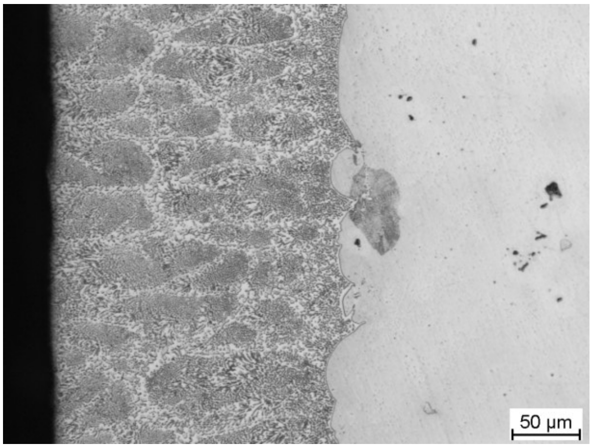

Fig. 7. Eutectic pushed out from the reactive zone (AZ91/AlSi10Mg)

The measurements of the material microhardness were performed using polished cross-sections. The AZ91 substrate was reported to have a microhardness of 53-59 HV. The values obtained for the layers fabricated at 1 MPa ranged from 187 HV to 248 HV. The microhardness was measured in three characteristic zones A, B, and C and the respective values were 210-248 HV, 192-235 HV and 187-203 HV. For the layers fabricated at a pressure of 5 MPa, the microhardness in zones A and B was 230-283 HV and 335-358 HV, respectively. The values were higher than those reported for the material produced at 1 MPa because of a more compact structure and a higher volume fraction of the hard Mg_2Si phase (450 HV [24]). The results of the microhardness tests indicate that the layers had much higher hardness than the substrate material. This method can thus be used to improve the surface properties of Mg-based elements operating under severe friction conditions.

4. Conclusions

The heating of the AZ91 substrate in contact with AlSi10Mg powder at 445 ^{o}C led to the formation of a modified surface layer enriched with Al and Si. During the heat treatment process, the powder was kept under pressure to facilitate the diffusion of the alloying elements from the AlSi10Mg powder to the substrate material. The microstructure of the modified layer was dependent on the pressure.

The layer fabricated at 1 MPa was thicker (about 200 µm) but with higher porosity. 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 three-zone structure. At the top, there were Mg_2Si particles distributed over the $Mg_{17}Al_{12}$ matrix. Next, there was a eutectic ($Mg_{17}Al_{12}$ + a solid solution of Al in Mg) with Mg_2Si phase particles embedded in it. The third zone, adjacent to the substrate, was a eutectic ($Mg_{17}Al_{12}$ + a solid solution of Al in Mg).

When higher pressure (5 MPa) was applied, the layer was thinner (about 150 µm); it was characterized by lower porosity. The layer had a two-zone structure. The zone at the top was composed of Mg_2Si particles distributed over the $Mg_{17}Al_{12}$ matrix. The zone close to the substrate had a high volume fraction of Mg_2Si phase particles embedded in the matrix composed mainly of the $Mg_{17}Al_{12}$ phase.

The microhardness of the surface layers enriched with Al and Si containing the Mg_2Si and $Mg_{17}Al_{12}$ phases was much higher than that of the AZ91 substrate.

Acknowledgements

The research reported herein was supported by Poland's National Science Centre (Grant No. DEC-2017/01/X/ST08/00791).

References

[1] Gray, J.E. & Luan, B. (2002). Protective coatings on magnesium and its alloys – a critical review. *Journal of Alloys and Compounds.* 336, 88-113.

[2] Galun, R., Weisheit, A. & Mordike, B.L. (1998). Improving the surface properties of magnesium by laser alloying. *Corrosion Reviews.* 16, 53-74.

[3] Ignat, S., Sallamand, P., Grevey, D. & Lambertin, M. (2004). Magnesium alloys laser (Nd:YAG) cladding and alloying with side injection of aluminium powder. *Applied Surface Science.* 225, 124-134.

[4] Paital, S.R., Bhattacharya, A., Moncayo, M., Ho, Y.H, Mahdak, K., Nag, S., Banerjee, R. & Dahotre, N.B. (2012). Improved corrosion and wear resistance of Mg alloys via laser surface modification of Al on AZ31B. *Surface and Coatings Technology.* 206, 2308-2315.

[5] Yang, Y. & Wu, H. (2009). Improving the wear resistance of AZ91D magnesium alloys by laser cladding with Al-Si powders. *Materials Letters.* 63, 19-21.

[6] Carcel, B., Sampedro, J., Ruescas, A. & Toneu, X. (2011). Corrosion and wear resistance improvement of magnesium alloys by laser cladding with Al-Si. *Physics Procedia.* 12, 353-363.

[7] Singh, A. & Harimkar, S.P. (2012) Laser surface engineering of magnesium alloys: a review. *JOM.* 64(6), 716-733.

[8] Mola, R., Dziadoń, A. & Jagielska-Wiaderek, K. (2016). Properties of Mg laser alloyed with Al or AlSi20. *Surface Engineering.* 32(12), 908-915.

[9] Shigematsu, M., Nakamura, M., Saitou, K. & Shimojima, K. (2000). Surface treatment of AZ91D magnesium alloy by

aluminum diffusion coating. *Journal of Materials Science Letters.* 19, 473-475.
[10] Zhu, L. & Song, G. (2006). Improved corrosion resistance of AZ91D magnesium alloy by an aluminum-alloyed coating. *Surface and Coatings Technology.* 200, 2834-2840.
[11] Liu, F., Li, X., Liang, W., Zhao, X. & Zhang, Y. (2009). Effect of temperature on microstructures and properties of aluminized coating on pure magnesium. *Journal of Alloys and Compounds.* 478, 579-585.
[12] Mola, R. (2015). The properties of Mg protected by Al- and Al/Zn-enriched layers containing intermetallic phases. *Journal of Materials Research.* 30(23), 3682-3691.
[13] Zhang, M.X. & Kelly, P.M. (2002). Surface alloying of AZ91 alloy by diffusion coating. *Journal of Materials Research.* 17(10), 2477-2479.
[14] Ma, Y., Xu, K., Wen, W., He, X. & Liu, P. (2005). The effect of solid diffusion surface alloying on properties of ZM5 magnesium alloy. *Surface and Coatings Technology.* 190, 165-170.
[15] Hirmke, J., Zhang, M.X. & StJohn, D.H. (2011). Surface alloying of AZ91E alloy by Al-Zn packed powder diffusion coating. *Surface and Coatings Technology.* 206, 425-433.
[16] Mola, R. (2014).The properties of Al/Zn-enriched surface layer on Mg. *Archives of Foundry Engineering.* 14(3), 45-48.
[17] Mola, R. (2016). The microstructure of alloyed layers formed on Mg by the powder-pack method. METAL 2016: 25th Anniversary International Conference on Metallurgy and Materials, 1492-1497.
[18] Chen, Y., Liu, T.M. Lu, L.W. & Wang, Z.C. (2012). Thermally diffused antimony and zinc coatings on magnesium alloys AZ31. *Surface Engineering.* 28(5), 382-386.
[19] Wang, H., Yu, B., Wang, W., Ren, G., Liang, W. & Zhang, J. (2014). Improved corrosion resistance of AZ91D magnesium alloy by zinc-yttrium coating. *Journal of Alloys and Compounds*. 582, 457-460.
[20] Mola, R., Stępień, E & Cieślik, M. (2017). Characterization of the surface layer of Mg enriched with Al and Si by thermochemical treatment. *Archives of Foundry Engineering.* 17(4), 195-199.
[21] Okamoto, H. (1998). Al-Mg (Aluminium-Magnesium). *Journal of Phase Equilibria* 19(6), 598
[22] Phase Equilibria, Crystallographic and Thermodynamic Data of Binary Alloys, Landolt-Börstein /New series IV/ Springer-Verlag Berlin 1998.
[23] Raghavan, V. (2007). Al-Mg-Si (Aluminium-Magnesium-Silicon). *Journal of Phase Equilibria and Diffusion*, 28(2), 189-191.
[24] Westbrook, J.H. & Fleischer, R.L. (2000). Structural applications of intermetallic compounds, John Willey& Sons.