

## THE MICROSTRUCTURE OF MG MODIFIED BY SURFACE ALLOYING WITH AN ALMG4.5MN WIRE

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### Abstract

A TIG torch was used as the heat source for surface alloying of Mg. The alloying material in the form of an AlMg4.5Mn wire was directly fed into the melt pool. Both the microstructure and thickness of the alloyed layers are strongly dependent on the process parameters. When a higher current was used, the 2 mm thick Al-enriched layer produced on the Mg substrate consisted of dendrites of a solid solution of Al in Mg and a eutectic ( $\text{Mg}_{17}\text{Al}_{12}$  + a solid solution of Al in Mg) distributed in the interdendritic spaces. Surface alloying of Mg at a lower current led to the formation a thinner alloyed layer comprising mainly an  $\text{Al}_3\text{Mg}_2$  intermetallic phase. In the first case the hardness of the surface layer was 70-102 HV<sub>0.1</sub>, in the second 236-245 HV<sub>0.1</sub>.

**Keywords:** Magnesium, surface alloying, TIG method, Mg-Al intermetallic phases, microstructure.

### 1. INTRODUCTION

Magnesium and its alloys have some very attractive properties such as low density, high strength-to-weight ratio, high thermal conductivity, good formability and castability, as well as excellent machinability and recyclability. At the same time, they are characterized by poor surface properties, including low hardness, and wear and corrosion resistance. These disadvantages limit their extensive use in many fields. There are, however, various surface treatment methods that can be used to enhance the surface properties of magnesium and its alloys, and accordingly, extend the range of their applications [1, 2]. As shown in the literature, the wear and corrosion resistance of the Mg-based substrate can be improved by forming an alloyed surface layer containing intermetallic phases. The most common alloying element is Al; its combinations with other elements (Al+Si, Al+Zn, Al+Cu, Al+Ni, Al+Mn) are also applied. The methods employed to fabricate alloyed surface layers include: thermochemical treatment in solid medium (Al [3-6] or Al+Zn powder [7-10]) or liquid medium (molten salts) [11-13], electrodeposition with subsequent heating [14], cold spray coating combined with heat treatment [15, 16], PVD coupled with heat treatment [17, 18] and laser surface alloying/cladding [19-26]. Among these methods, laser surface alloying/cladding is most extensive utilize to fabricate alloyed layers on the Mg substrate. Recent studies show that a TIG torch can also be used as the heat source for surface alloying/cladding of magnesium alloys [27, 28].

The aim of the study was to form an Al-enriched alloyed layer containing Mg-Al intermetallic phases on the Mg surface using a TIG torch as the heat source and an AlMg4.5Mn wire as the alloying material. Alloyed layers with different microstructures were produced using different process parameters. The paper focuses on the characterization of the microstructure and microhardness of the layers.

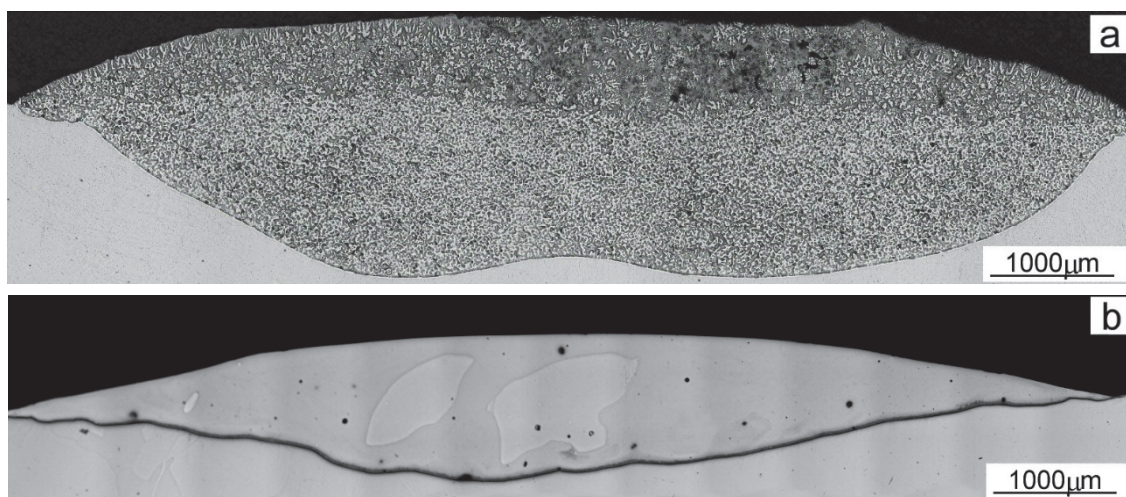
### 2. EXPERIMENTAL PROCEDURE

Pure magnesium (99.9 % Mg) was selected as the substrate material. 60x40x15 mm samples sectioned from an ingot were prepared by grinding with abrasive papers up to 800 grit and cleaning with ethanol. The alloying material used in this study was a 2.5 mm AlMg4.5Mn wire. Surface alloying was carried out by hand using a Lorch T220 AC/DC TIG welder. It involved simultaneously melting the magnesium substrate and feeding the alloyed material. The welding was performed using an alternating current of 25 or 40 A with the AC frequency and the percentage of positive current being 150 Hz and 67 %, respectively. A tungsten electrode with a

diameter of 1.6 mm was used. Argon with a purity of 99.995 % and a flow rate of 10 l/min was used as the shielding gas. The microstructure analysis and the microhardness tests were conducted on samples cut in the direction perpendicular to the TIG torch movement. The surface alloyed samples were prepared following the standard metallographic procedures. The microstructure analysis was performed using a Nikon ECLIPSE MA 200 optical microscope and a JEOL JMS-5400 scanning electron microscope. The chemical composition of the alloyed layers was studied by means of an Oxford Instruments ISIS 300 EDS detector attached to the SEM. The microhardness of the layers was measured with a MATSUZAWA MMT Vickers hardness tester at a load of 100 g.

### 3. RESULTS AND DISCUSSION

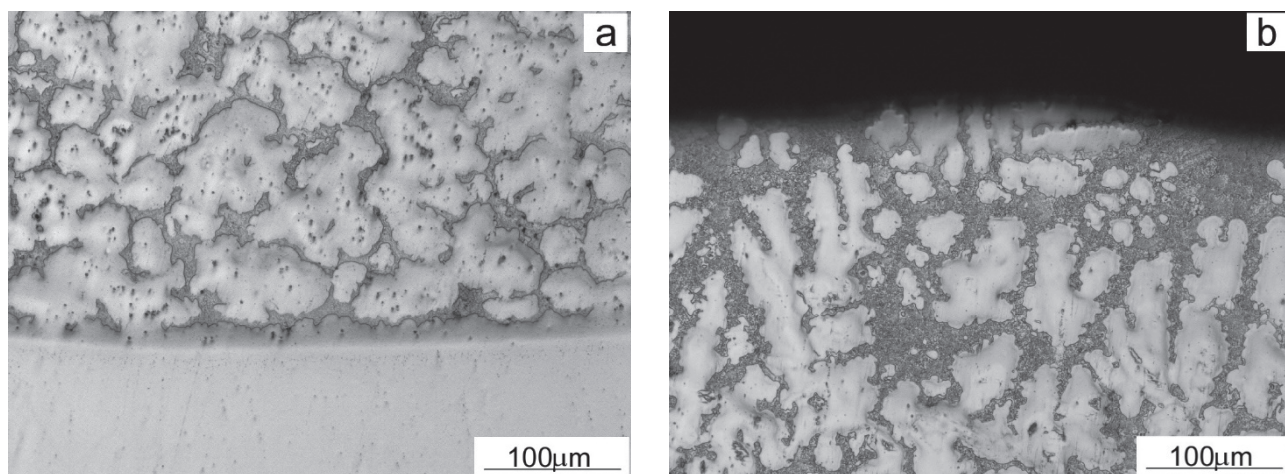
**Fig. 1** shows the microstructure of an Mg specimen after surface alloying with an aluminum wire using the TIG method. It can be seen that the microstructure and thickness of the alloyed layer are dependent on the process parameters. Surface alloying of Mg at a higher current (40 A) led to the formation a thicker layer - **Fig. 1(a)**. Two zones can be distinguished in the layer microstructure: a thick, lighter zone adjacent to the Mg substrate and a thinner, darker outer zone. In the outer zone, local pores are observed. When a lower current was used (25 A), a thinner alloyed layer was produced on the Mg substrate - **Fig. 1(b)**. In this case, the layer microstructure seems to be more homogeneous. However, some large brighter areas with clearly defined interfacial boundary were also observed. Pores in the layer occurred locally.



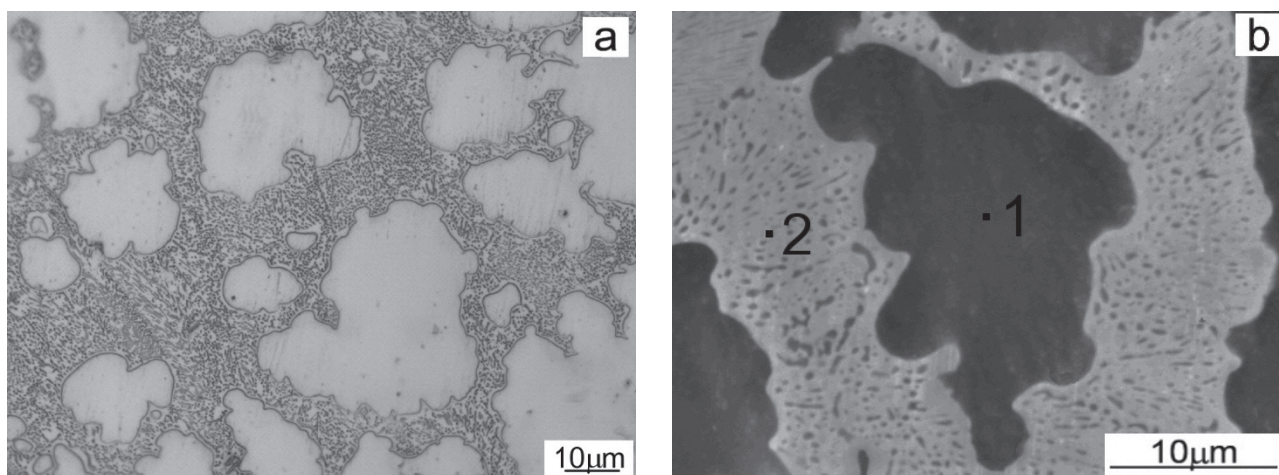
**Fig. 1** Cross-sections of magnesium samples surface-alloyed with aluminum using the TIG method: (a) at a higher current (40 A), (b) at a lower current (25 A)

**Fig. 2** shows OM images of the microstructure of two characteristic zones observed in the alloyed layer produced at a higher current of the process - see **Fig. 1(a)**. In both cases, the liquid phase solidifies initially in the form of dendrites and crystallizes in the interdendritic areas (darker areas in **Fig. 2(a)**). Comparison of **Figs. 2(a)** and **2(b)** show that in the outer zone the darker areas are larger.

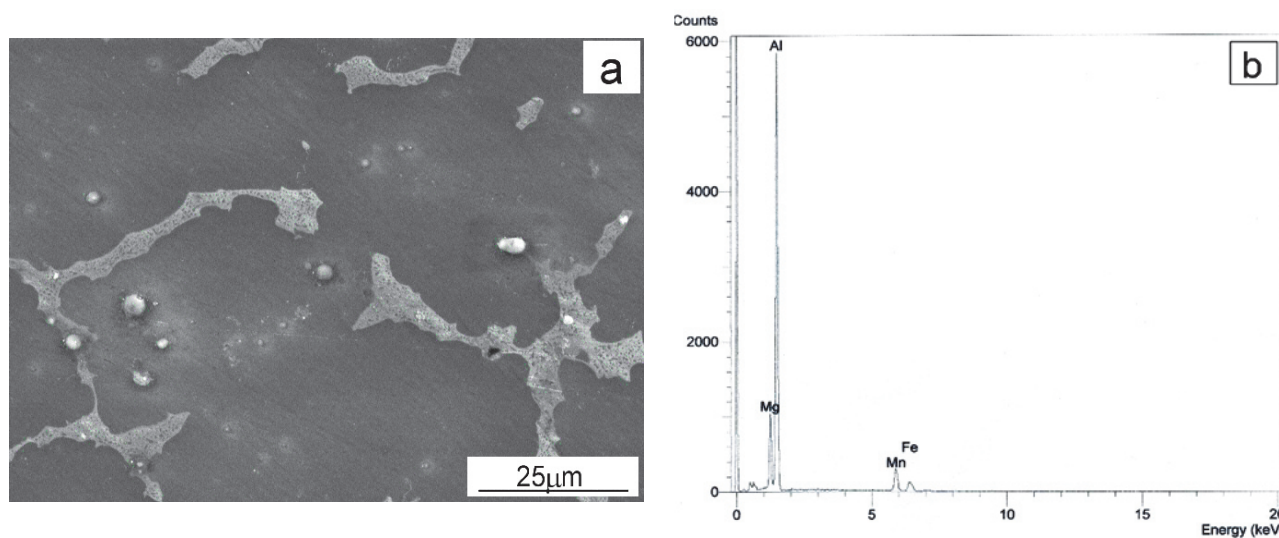
At higher magnifications, the darker areas reveal a eutectic structure - see **Fig. 3(a)**. **Fig. 3(b)** presents its SEM image. An EDS quantitative analysis was performed at points marked in **Fig. 3(b)**. The analysis of the layer microstructure was based on the Mg-Al binary phase diagram [29]. The contents of Mg and Al in the dendrites (area 1 in **Fig. 3(b)**) – 89.88 at.% Mg, 10.12 at.% Al – indicate a solid solution of Al in Mg. The results from the two-phase structure area (area 2 in **Fig. 3(b)**) – 71.01 at.% Mg, 28.99 at.% Al – suggest that the Mg<sub>17</sub>Al<sub>12</sub> phase and the solid solution of Al in Mg are constituents of the eutectic.



**Fig. 2** Microstructure of the inner (a) and outer (b) zones in a layer fabricated on Mg at a higher current



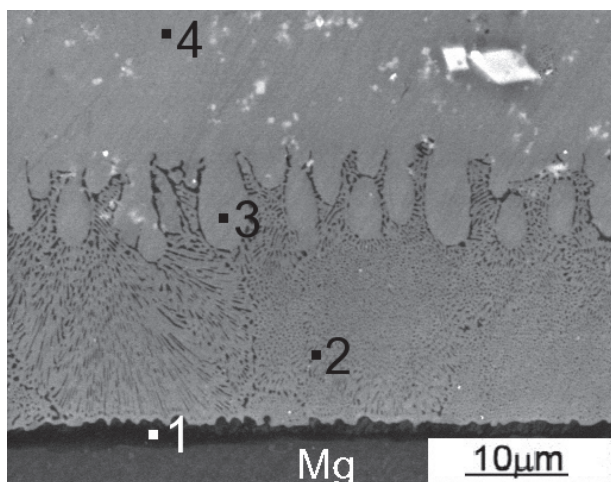
**Fig. 3** Details of the layer microstructure observed at higher magnification: (a) OM image, (b) SEM image with the marked points of the EDS analysis



**Fig. 4** (a) Distribution of white particles in the alloyed layer, (b) X-ray spectrum for a white particle

As can be seen from the SEM image - see **Fig. 4(a)**, there are white particles in the alloyed layer. The EDS spectrum for this phase is presented in **Fig. 4(b)**. Apart from Al and Mg, the phase also contains Mn and a Fe impurity, which originates probably from the AlMg4.5Mn wire used for the surface alloying of magnesium.

In the OM image - **Fig. 1(b)**, we can see large lighter areas in the microstructure of the layer fabricated at a lower current. Example results of the quantitative EDS analysis (94.42 at.% Al, 5.58 at.% Mg) indicate that the areas are a solid solution of Mg in Al. The SEM image in **Fig. 5** shows details of the microstructure of the layer near the Mg substrate. **Table 1** presents results of the EDS analysis for the points marked in **Fig. 5**. Between the alloyed layer and the Mg substrate there is a thin dark, almost black layer. From the chemical composition of this zone (marked 1 in **Fig. 5**) it is clear that it is a solid solution of Al in Mg. Above the solid solution a fine eutectic is observed. The concentration of Al in this two-phase structure (marked 2) is lower than that in the Mg-Al intermetallic phases presented in the Mg-Al phase diagram and higher than that reported for the solid solution of Al in Mg [29]. For the area marked 3 in **Fig. 5**, the Mg:Al ratio is nearing to that of the Mg<sub>17</sub>Al<sub>12</sub> phase. The results suggest according to Mg-Al binary phase diagram [29], that the two-phase structure is a eutectic composed of an Mg<sub>17</sub>Al<sub>12</sub> phase and a solid solution of Al in Mg. It is interesting that the aluminum content between points 3 and 4, over a distance of about 20 µm, gradually increasing. When the analysis was conducted in the area marked 4 Al:Mg ratio corresponds to Al<sub>3</sub>Mg<sub>2</sub> intermetallic phase. The results indicate that Al<sub>3</sub>Mg<sub>2</sub> is the predominant phase in the microstructure of the alloyed layer. White particles – single large particles or agglomerates of fine particles – were observed also in the layer produced at a lower current. The chemical composition of white particle was as follows: 77.15 at.% Al, 13.27 at.% Mg, 6.92 at.% Mn, 2.66 at.% Fe, which indicates that it is an Al-Mg-Mn-Fe phase.



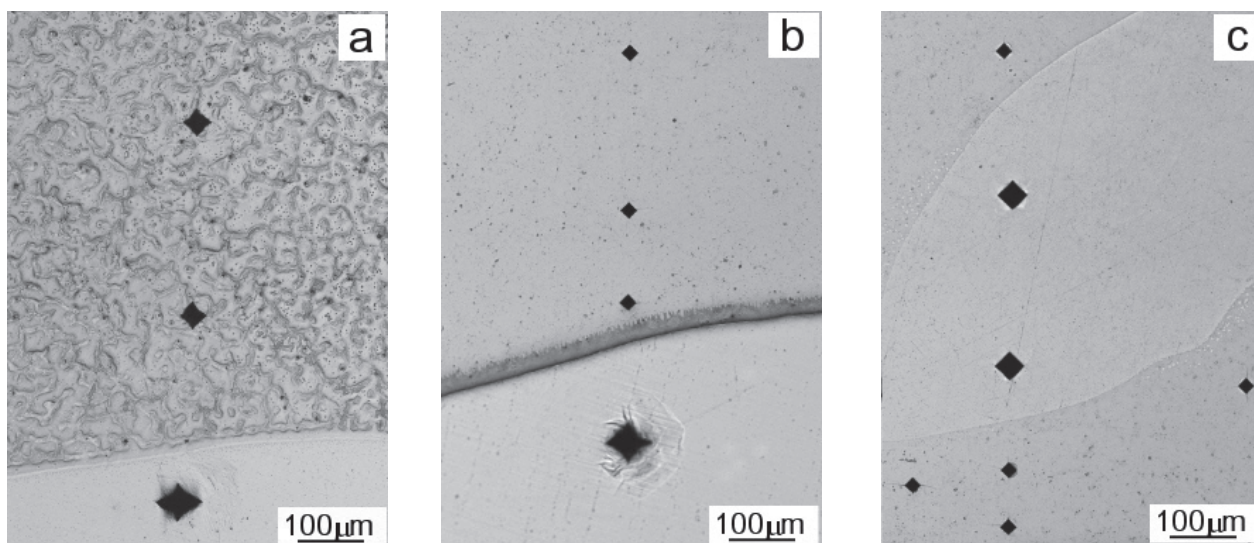
**Fig. 5** SEM image showing details of the microstructure of the alloyed layer fabricated on Mg at a lower current with marked points of the quantitative EDS analysis.

**Table 1** EDS results corresponding to the points marked in **Fig. 5**

Point	Mg (at.%)	Al (at.%)
1	91.87	8.13
2	70.07	29.93
3	63.33	36.67
4	39.79	60.21

The microstructure analysis of the Al-enriched layers fabricated at different process parameters with the same amount of the Al wire fed suggests that when a higher current was applied, the concentration of Al in the alloyed layer was lower and so was the volume fraction of the phase rich in Al in the microstructure. That was due the fact that a thicker layer of Mg was melted during the alloying process. Surface alloying of Mg performed at a lower current led to the melting of only a thin layer of Mg. Thus, the melted zone was more enriched in Al and the resultant layer comprised mainly an Al-rich phase - Al<sub>3</sub>Mg<sub>2</sub>.

Traces of the Vickers indenter in the Al-enriched layers fabricated on Mg using the TIG method are shown in **Fig. 6**. The microhardness of an Al-enriched layer fabricated at a higher current was lower than that obtained at a lower current, with the values being 70-102 HV<sub>0.1</sub> - **Fig. 5(a)** and 236-245 HV<sub>0.1</sub> - **Fig. 6(b)**, respectively. In the solid solution areas, the microhardness was lower, i.e. 82-87 HV<sub>0.1</sub> - **Fig. 6(c)**. The microhardness of the Mg substrate was 35 HV.



**Fig. 6** Microhardness tester indentations in the Al-enriched layer and the Mg substrate: (a) layer fabricated at a higher current, (b) layer fabricated at a lower current, (c) traces of hardness measurements in  $\text{Al}_3\text{Mg}_2$  phase and in area of solid solution Mg in Al

## CONCLUSIONS

- It was demonstrated that using a TIG torch as a heat source the Al-enriched alloyed layer can be fabricated on Mg substrate.
- The depth of molten magnesium surface, and consequently the concentration of aluminum in the liquid phase determinates the microstructure and hardness of the alloyed layer.
- If the alloying process was carried out using a current of higher amperage (40 A) layer composed of dendrites a solid solution of Al in Mg surrounded by eutectic ( $\text{Mg}_{17}\text{Al}_{12}$  and a solid solution of Al in Mg) was produced.
- Layer fabricated at a lower current (25 A) was thinner and comprised mainly an  $\text{Al}_3\text{Mg}_2$  intermetallic phase.
- The microhardness of Al-enriched alloyed layers was much higher than that of the Mg substrate.

## REFERENCES

- [1] GRAY J.E., LUAN B. Protective coatings on magnesium and its alloys - a critical review. J. Alloys Compd., Vol. 336, 2002, pp. 88-113.
- [2] STANKIEWICZ A., LASZCZYŃSKA A., WINIARSKI J., SZCZYGIEŁ B. Possible methods of obtaining of protective coatings on magnesium and its alloys. Ochrona przed korozją, No. 4-5, 2010, pp. 286-292.
- [3] SHIGEMATSU M., NAKAMURA M., SAITOU K., SHIMOJIMA K. Surface treatment of AZ91D magnesium alloy by aluminum diffusion coating. J. Mater. Sci. Lett., Vol. 19, 2000, pp. 473-475.
- [4] ZHU L., SONG G. Improved corrosion resistance of AZ91D magnesium alloy by an aluminum-alloyed coating. Surf. Coat. Technol., Vol. 200, 2006, pp. 2834-2840.
- [5] MOLA R. Fabrication and microstructure of layers containing intermetallic phases on magnesium. Archives of Foundry Engineering, Vol. 13, No. 1, 2013, pp. 99-102.
- [6] MOLA R., JAGIELSKA-WIADEREK K. Formation of Al-enriched surface layers through reaction at the Mg-substrate/Al-powder interface. Surf. Interface Anal., Vol. 46, 2014, pp. 577-580.
- [7] ZHANG M.X., KELLY P.M. Surface alloying of AZ91D alloy by diffusion coating. J. Mater. Res., Vol. 17, 2002, pp. 2477-2479.

- [8] HIRMKE J., ZHANG M.X., STJOHN D.H. Surface alloying of AZ91E alloy by Al-Zn packed powder diffusion coating. *Surf. Coat. Technol.*, Vol. 206, 2011, pp. 425-433.
- [9] MOLA R. Fabrication and microstructural characterization of Al/Zn-enriched layers on pure magnesium. *Mater. Charact.*, Vol. 78, 2013, pp. 121-128.
- [10] MOLA R. The properties of Al/Zn-enriched surface layers on Mg. *Archives of Foundry Engineering*, Vol. 14, No. 3, 2014, pp. 45-48.
- [11] HE M., LIU L., WU Y., TANG Z., HU W. Improvement of the properties of AZ91D magnesium alloy by treatment with a molten  $\text{AlCl}_3$ -NaCl salt to form an Mg-Al intermetallic surface layer. *J. Coat. Technol. Res.*, Vol. 6, No. 3, 2009, pp. 407-411.
- [12] ZHONG C., HE M.F., LIU L., CHEN Y.J., SHEN B., WU Y.T., DENG Y.D., HU W.B. Formation of an aluminum-alloyed coating on AZ91D magnesium alloy in molten salts at lower temperature. *Surf. Coat. Technol.*, Vol. 205, 2010, pp. 2412-2418.
- [13] ZHONG C., HE M., LIU L., WU Y., CHEN Y., DENG Y., SHEN B., HU W. Lower temperature fabrication of continuous intermetallic coatings on AZ91D magnesium alloy in molten salts. *J. Alloys Compd.*, Vol. 504, 2010, pp. 377-381.
- [14] YANG H., GUO X., WU G., DING W., BIRBILIS N. Electrodeposition of chemically and mechanically protective Al-coatings on AZ91D Mg alloy. *Corros. Sci.*, Vol. 53, 2011, pp. 381-387.
- [15] SPENCER K., ZHANG M.X. Heat treatment of cold spray coatings to form protective intermetallic layers. *Scr. Mater.*, Vol. 61, 2009, pp. 44-47.
- [16] BU H., YANDOUZI M., LU C., JODOIN B. Effect of heat treatment on the intermetallic layer of cold sprayed aluminum coating on magnesium alloy. *Surf. Coat. Technol.*, Vol. 205, 2011, pp. 4665-4671.
- [17] HUO H., LI Y., WANG F. Improvement on the corrosion resistance of AZ91D magnesium alloy by aluminum diffusion coating. *J. Mater. Sci. Technol.*, Vol. 23, No. 3, 2007, pp. 379-382.
- [18] ZHU T., GAO W. Formation of intermetallic compound coating on magnesium AZ91 cast alloy. *Mater. Sci. Eng.*, No. 4, 2009, pp. 1-6.
- [19] SINGH A., HARIMKAR S.P. Laser surface engineering of magnesium alloys: a review. *JOM*, Vol. 64, No. 6, 2012, pp. 716-733.
- [20] MAJUMDAR J.D., 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*, Vol. 12, No. 3, 2002, pp. 147-169.
- [21] IGNAT S., SALLAMAND P., GREVEY D., LAMBERTIN M. Magnesium alloys laser (Nd:YAG) cladding and alloying with side injection of aluminum powder. *Appl. Surf. Sci.*, Vol. 225, 2004, pp. 124-134.
- [22] GAO Y., WANG C., PANG H., LIU H., YAO M. Broad-beam laser cladding of Al-Cu alloy coating on AZ91HP magnesium alloy. *Appl. Surf. Sci.*, Vol. 253, 2007, pp. 4917-4922.
- [23] 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. *Surf. Coat. Technol.*, Vol. 202, 2008, pp. 4901-4914.
- [24] YANG Y., WU H. Improving the wear resistance of AZ91D magnesium alloys by laser cladding with Al-Si powders. *Mater Lett*, Vol. 63, 2009, pp. 19-21.
- [25] DZIADOŃ A., MOLA R. Microstructure analysis of magnesium surface layer enriched in aluminum by means of laser alloying procedure. *Rudy i Metale Nieżelazne*, Vol. R56, No. 5, 2011, pp. 272-278.
- [26] DZIADOŃ A., MOLA R. Microstructure characteristic of magnesium surface layer enriched in aluminum and silicon with the aid  $\text{CO}_2$  laser. *Rudy i Metale Nieżelazne*, Vol. R58, No. 10, 2013, pp. 551-556.
- [27] DING W., JIANG H., ZENG X., LI D., YAO S. The properties of gas tungsten arc deposited  $\text{SiC}_p$  and Al surface coating on magnesium alloy AZ31. *Mater. Lett.*, Vol. 61, 2007, pp. 496-501.
- [28] ELAHI M.R., SOHI M.H., SAFAEI A. Liquid phase surface alloying of AZ91D magnesium alloy with Al and Ni powders. *Appl. Surf. Sci.*, Vol. 258, 2012, pp. 5876-5880.
- [29] *Crystallographic and Thermodynamic Data of Binary Alloys*. Landolt-Börnstein New Series, Group IV, Springer-Verlag Berlin, 1998.