



ARCHIVES
of
FOUNDRY ENGINEERING

DOI: 10.1515/afe-2016-0013

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

ISSN (2299-2944)
Volume 16
Issue 1/2016

112 – 116

Formation of Al-alloyed Layer on Magnesium with Use of Casting Techniques

R. Mola*, T. Bucki, A. Dziadoń

Department of Applied Computer Science and Armament Engineering, Faculty of Mechatronics and Machine Engineering, Kielce University of Technology, Al. Tysiąclecia Państwa Polskiego 7, 25-314 Kielce, Poland

*Corresponding author: E-mail address: rmola@tu.kielce.pl

Received 10.06.2015; accepted in revised form 17.07.2015

Abstract

Al-enriched layer was formed on a magnesium substrate with use of casting. The magnesium melt was cast into a steel mould with an aluminium insert placed inside. Different conditions of the casting process were applied. The reaction between the molten magnesium and the aluminium piece during casting led to the formation of an Al-enriched surface layer on the magnesium substrate. The thickness of the layer was dependent on the casting conditions. In all fabricated layers the following phases were detected: a solid solution of Mg in Al, Al_3Mg_2 , $Mg_{17}Al_{12}$ and a solid solution of Mg in Al. When the temperature of the melt and the mould was lower (variant 1 – 670°C and 310 °; variant 2 – 680°C and 310°C, respectively) the unreacted thin layer of aluminium was observed in the outer zone. Applying higher temperatures of the melt (685°C) and the mould (325°C) resulted in deep penetration of aluminium into the magnesium substrate. Areas enriched in aluminium were locally observed. The Al-enriched layers composed mainly of Mg-Al intermetallic phases have hardness from 187-256 HV0.1.

Keywords: Magnesium, Al-enriched surface layer on Mg, Mg-Al intermetallic phases, Casting process

1. Introduction

The widespread use of magnesium and its alloys as structural materials is attributable to their excellent properties including low density, high specific strength, and formability (castability, workability, machinability). However, their industrial application is sometimes limited because they are not resistant to corrosion or abrasion. This drawback can be eliminated by surface processing, which does not affect the bulk material. As shown in the review papers [1,2], there are many methods used for improving the surface properties of magnesium and its alloys. One of the most effective ways is to fabricate alloyed layers on a magnesium-based substrate. Positive results are obtained when aluminium is used as an alloying element. Al-enriched layers can be produced using various methods, e.g. laser surface alloying/cladding [3-5], diffusion treatment in molten salts [6,7], diffusion aluminizing

treatment [8-15], PVD combined with annealing [16-17], cold spray with subsequent heat treatment [18,19], welding [20], and electrodeposition [21]. The findings reported in the above works suggest that it is the Mg-Al intermetallic phases forming in the microstructure of Al-enriched layers that are responsible for an increase in the hardness as well as corrosion and wear resistance of magnesium and magnesium alloy products.

This study deals with Al-enriched layers containing Mg-Al intermetallic phases fabricated on a magnesium substrate by casting. It analyzes the effect of the casting parameters on the microstructure and thickness of the layers.

2. Experiment

Pure magnesium was selected as the cast material and it was melted under the pure argon atmosphere. The casting process involved pouring 150 grams of molten magnesium into a steel mould. The aluminium insert placed inside the mould had a wall thickness of 0.8 mm, a height of 30 mm, and a diameter of 40 mm. The casting was performed under different conditions. As shown in Table 1, three temperature variants were considered.

Table 1.

Variants of the casting process

Variant	Melt temperature °C	Mold temperature °C
1	670	310
2	680	310
3	685	325

The microstructure and thickness of the alloyed surface layers formed by casting were determined by means of a Nikon ECLIPSE MA 200 optical microscope and a JEOL JSM-5400 scanning electron microscope. Their chemical composition was analyzed using an Oxford Instruments ISIS 300 X-ray energy dispersive spectrometer (EDS) attached to the SEM. The microhardness of the layers was measured with a MATSUZAWA MMT Vickers hardness tester under a load of 100 g.

3. Results and discussion

Figure 1 shows the microstructure of the surface layers formed on the magnesium substrate by the reaction between the molten metal and the aluminium insert placed in the mould cavity. As can be seen, the thickness and microstructure of the layer are dependent on the temperature of the molten magnesium and the temperature of the mould with the aluminium insert. In variant 1

of the casting process, the temperatures of the molten magnesium and the mould were the lowest, 670°C and 310°C, respectively. This led to the formation of a reactive layer with a thickness of about 650 µm at the Mg/Al interface (Fig. 1a). As the aluminium insert was not fully consumed and converted into an alloyed layer, there was a 250 µm thick layer of unreacted aluminium in the outer zone. In variant 2, the temperature of the poured magnesium was higher (680°C), while the temperature of the mould remained the same (310°C). As shown in Fig. 1b, the reactive layer formed at the Mg/Al interface was much thicker (1.2 mm) than that observed for variant 1. The layer of unreacted aluminium in the outer zone had a thickness of about 150 µm. In variant 3, the highest temperatures were applied. The temperature of the molten metal was 685°C, whereas the temperature of the mould was 325°C. It is interesting to note that although all the aluminium was consumed to react with magnesium, the alloyed layer (Fig. 1c) was thinner than that produced in variant 2 of the casting process. In Fig. 1c we can also see that the microstructure of the magnesium substrate is locally modified. As the effect was not observed in variants 1 or 2, we can conclude that in variant 3 the reaction at the Mg/Al interface proceeded much faster resulting in the complete consumption of aluminium.

The microstructural analysis of the alloyed layers produced in all the three variants of the casting process (Fig. 1) showed the following characteristic zones: dendrites adjacent to the outer aluminium layer (for variants 1 and 2), the transition zone, and the eutectic close to the magnesium substrate. In Fig. 2, the zones (marked A, B and C, respectively) are presented in higher magnification. The SEM images in Fig. 3 with marked points of the quantitative EDS analysis show details of each microstructural zone. The microstructural analysis was based on the Mg-Al phase diagram [22]. The chemical composition of the dendrites observed in zone A (marked 1 in Fig. 3a) was as follows: 87.6 at. % Al, and 12.4 at. % Mg. From the contents of the elements it is clear that this is a solid solution of magnesium in aluminium.

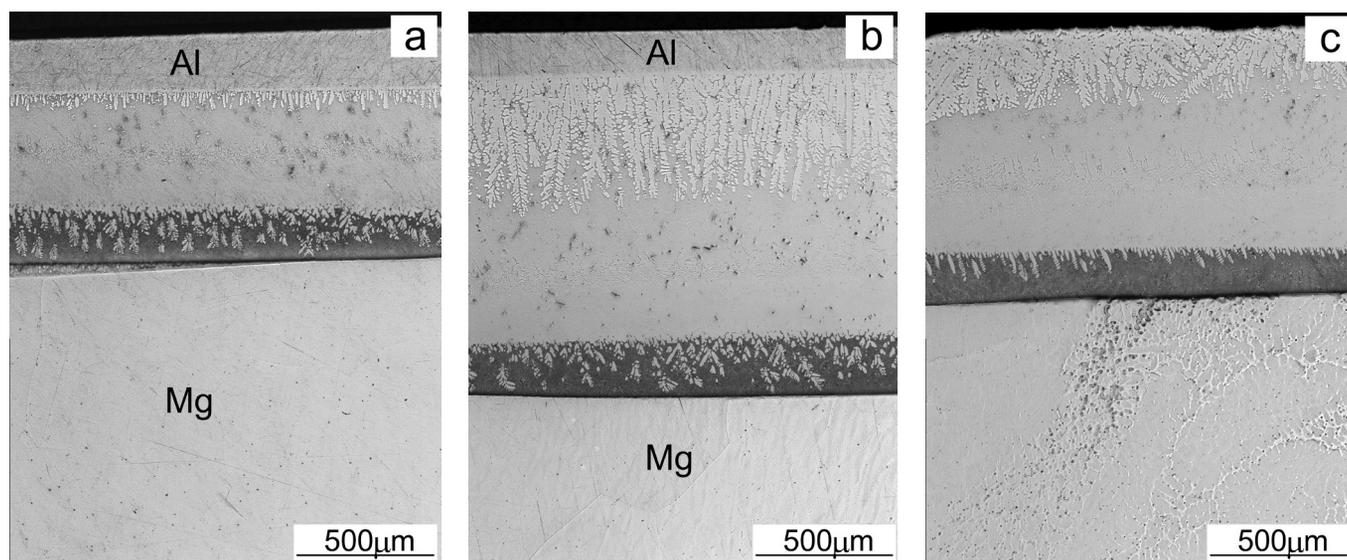


Fig. 1. Microstructures of the surface layer formed by the reaction between the molten magnesium and the aluminium insert: (a) variant 1, (b) variant 2, and (c) variant 3

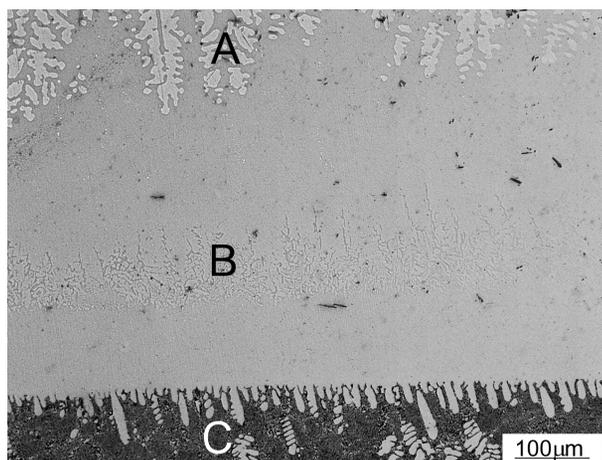


Fig. 2. Enlarged OM image of the layer microstructure

In the single phase area (marked 2) located below the dendrites, the Al:Mg ratio (61.36 at. % Al : 38.37 at. % Mg) suggests that this is the Al_3Mg_2 phase. In the transition zone marked B in Fig. 2 was also found area of single phase (Fig. 3(b), point 3) whose chemical composition was as follows 60.14 at.% Mg, and 39.86 at.% Al. This result indicates the $Mg_{17}Al_{12}$ intermetallic phase. The eutectic (zone C in Fig. 2) formed in the area adjacent to the magnesium substrate is shown at a higher magnification in Fig. 3c. In this zone, we can observe dendrites that penetrate into the eutectic. The chemical composition of the dendrites (marked 3 in Fig. 3c) – 63.53 at.% Mg, and 36.47 at.% Al – suggests that this is the $Mg_{17}Al_{12}$ phase. The content of Mg and Al in the eutectic (analysis at point 4: 71.58 at.% Mg, and 28.42 at.% Al) suggests that the $Mg_{17}Al_{12}$ and the solid solution of aluminium in magnesium are constituents of the eutectic. As shown in Fig. 3 a and b, the Al-enriched layer contains particles of white phase. The quantitative analysis for a white particle with a more compact shape indicates the presence of a phase rich in Al, Fe, Mg, and Mn (e.g. 15.84 at.% Mg, 66.12 at.% Al, 17.63 at.% Fe, and 0.41 at.% Mn). When the white phases are needle-shaped, they contain more Fe (e.g. 2.73 at.% Mg, 71.40 at.% Al, 25.43 at.% Fe, and 0.44 at.% Mn).

The EDS quantitative analysis was also performed to study the modified microstructure of the magnesium substrate, which was observed in specimens produced in variant 3 of the casting process – Fig. 1(c). In the lighter areas, the aluminium content was in the range 4-5 at. %. This result confirms that the aluminium diffused into the magnesium substrate. It also explains why under such conditions a thinner alloyed layer was formed compared with variant 2. In variant 3, the temperatures of the molten magnesium and the mould were the highest so when the magnesium was poured over the aluminium insert, all the aluminium, reacted with the magnesium and was converted into the alloyed layer. Then, the layer was partially consumed by the magnesium and, locally, areas enriched in Al were observed in the substrate.

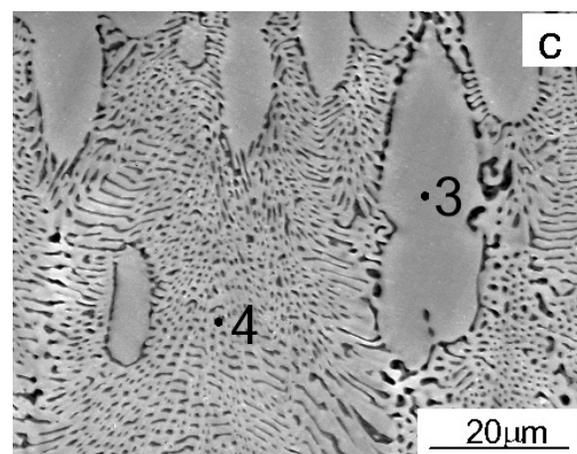
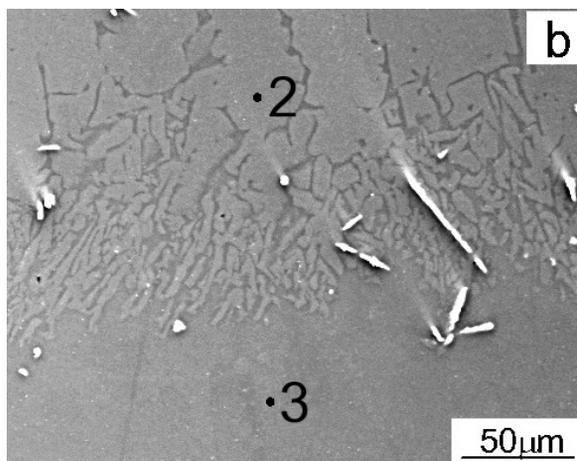
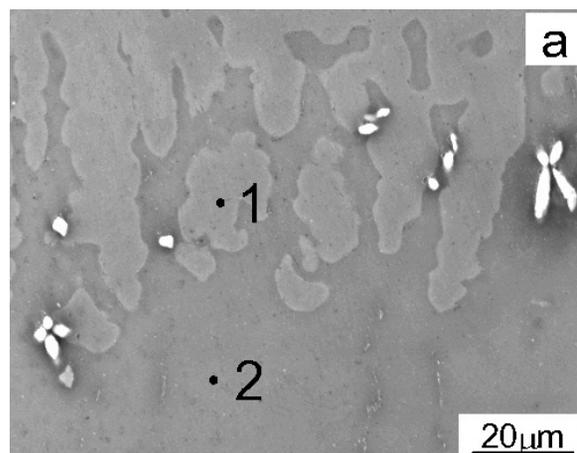


Fig. 3. SEM images showing details of the layer microstructure: (a) zone A, (b) zone B, (c) zone C

Figure 4 presents the indentations left by the Vickers indenter in the Al-enriched layers produced on the Mg substrate by casting. The values of the microhardness measurements were provided next to the indentations in Fig. 4.

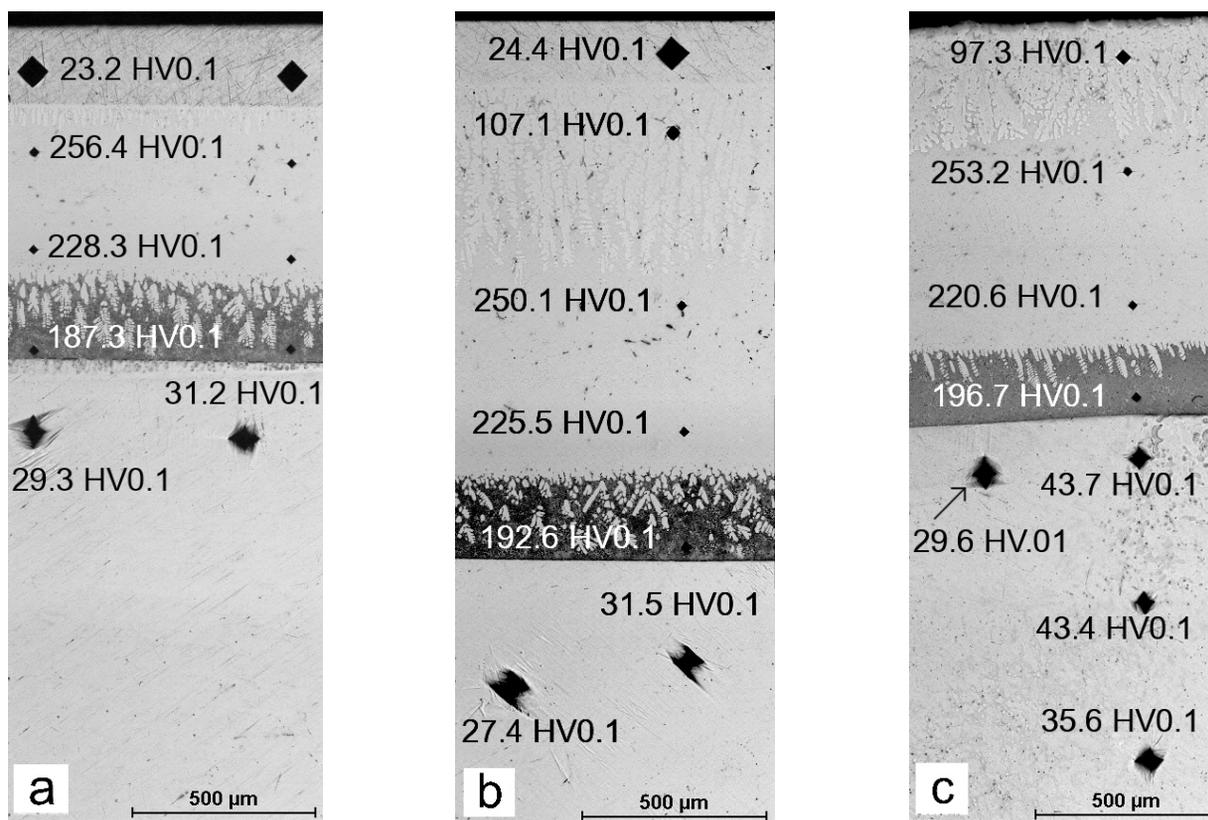


Fig. 4. Indentations in the Al-alloyed layers and the magnesium substrate formed under various casting conditions: (a) variant 1, (b) variant 2, (c) variant 3

These results show that the alloyed layers containing Mg-Al had much higher hardness than the magnesium substrate. The highest hardness was reported in the single phase zone of Al_3Mg_2 (250-256 HV0.1). Slightly lower values of microhardness were observed in the $\text{Mg}_{17}\text{Al}_{12}$ phase zone (221-228 HV0.1). The microhardness of the eutectic, which contained the $\text{Mg}_{17}\text{Al}_{12}$ phase and a solid solution of aluminium in magnesium ranged from 187 to 197 HV0.1. The microhardness measurements conducted for the magnesium substrate also confirmed that in variant C of the casting process, there was a diffusion of aluminium into magnesium. Locally, the microhardness values were higher (36-44 HV0.1) than those of the magnesium substrate (30 HV0.1). It was also found that the indentations in the magnesium were irregular in shape (Fig. 4(a), (b) and (c)) due to plastic anisotropy of this metal but in the areas where the substrate was enriched in aluminium, the indentations were more regular.

4. Conclusions

The Al-enriched layers formed on the magnesium surface by casting contained Mg-Al intermetallic phases. The influence of the casting process conditions on the microstructure, hardness and

thickness of the resultant layers was studied and the following conclusions were drawn:

- In the alloyed layers the following phases were detected: a solid solution of Mg in Al, Al_3Mg_2 , $\text{Mg}_{17}\text{Al}_{12}$ and a solid solution of Mg in Al.
- The Al-enriched layers had much higher hardness (187-256 HV0.1) than the magnesium substrate (30 HV0.1).
- When the temperature of the mould with the aluminium insert was low (310°C) and the temperature of the poured magnesium was the lowest (670°C), a reactive layer with a thickness of about 650 μm formed at the Mg/Al interface. A thin layer of unreacted aluminium was observed in the outer zone.
- Increasing the temperature of the melt (680°C) and maintaining the temperature of the mould (310°C) led to the formation of a much thicker reactive layer (1.2 mm) at the Mg/Al interface and a much thinner unreacted aluminium layer in the outer zone.
- At the highest temperature of the melt (685°C) and the highest temperature of the mould (325°C), a thinner reactive layer (850 μm) formed. All the aluminium was converted into the alloyed layer, and then part of it dissolved in the molten magnesium. As a result, areas enriched in aluminium formed in the substrate.

References

- [1] Gray, J.E. & Luan, B. (2002). Protective coatings on magnesium and its alloys – a critical review, *J. Alloys Compd* 336, 88-113.
- [2] Stankiewicz, A., Laszczyńska, A. Winiarski, J. & Szczygieł, B. (2010). Selected methods for preparing the coating on magnesium and its alloys., *Ochrona przed korozją*, 53, nr 4-5, 286-292. (in Polish)
- [3] Singh, A. & Harimkar, S.P.(2012). Laser surface engineering of magnesium alloys: a review. *JOM*, 64(6), 716-733. DOI: 10.1007/s11837-012-0340-2.
- [4] Ignat, S., Sallamand, P., Grevey, D. & Lambertin, M. (2004). Magnesium alloys laser (Nd:YAG) cladding and alloying with side injection of aluminium powder. *Appl. Surf. Sci.*, 225, 124-134. DOI: 10.1016/j.apsusc.2003.09.043.
- [5] Dziadoń, A. & Mola, R. (2011). Microstructure analysis of magnesium surface layer enriched in aluminium by means of laser alloying procedure. *Rudy i Metale Nieżelazne* R56 5, 272-278.
- [6] Zhong, C., He, M., Liu, L., Wu, Y., Chen, Y., Deng, Y., Shen, B. & Hu, W. (2010). Lower temperature fabrication of continuous intermetallic coatings on AZ91D magnesium alloy in molten salts. *J. Alloys Compd.* 504, 377-381. DOI: 10.1016/j.jallcom.2010.05.120.
- [7] He, M., Liu, L., Wu, Y., Tang, Z. & Hu, W. (2009). Improvement of the properties of AZ91D magnesium alloy by treatment with molten AlCl₃-NaCl salt to form an Mg-Al intermetallic surface layer. *J.Coat. Technol. Res* 6(3), 407-411. DOI: 10.1007/s11998-008-9132-6.
- [8] Shigematsu, M., Nakamura, M., Saitou, K. & Shimojima, K. (2000). Surface treatment of AZ91D magnesium alloy by aluminum diffusion coating. *J. Mater. Sci. Lett.* 19, 473-475.
- [9] Ma, Y., Xu, K., Wen, W., He, X. & Liu, P. (2005). The effect of solid diffusion surface alloying on properties of ZM5 magnesium alloy. *Surf. Coat. Technol.* 190, 165-170. DOI: 10.1016/j.surfcoat.2004.08.214.
- [10] Zhu, L. & Song, G. (2006). Improved corrosion resistance of AZ91D magnesium alloy by an aluminum-alloyed coating. *Surf. Coat. Technol.* 200, 2834-2840. DOI: 10.1016/j.surfcoat.2004.11.042.
- [11] Liu, F., Li, X., Liang, W., Zhao, X. & Zhang, Y. (2009). Effect of temperature on microstructures and properties of aluminumized coating on pure magnesium. *J. Alloys Compd.* 478, 579-585. DOI: 10.1016/j.jallcom.2008.11.093.
- [12] Mola, R. (2013). Fabrication and microstructure of layers containing intermetallic phases on magnesium. *Archives of Foundry Engineering* 13(1), 99-102. DOI: 10.2478/afe-2013-0019.
- [13] Mola, R. (2013). Fabrication and microstructural characterization of Al/Zn-enriched layers on pure magnesium. *Mater. Charact.* 78, 121-128. DOI: 10.1016/j.matchar.2013.02.004.
- [14] Mola, R. & Jagielska-Wiaderek, K (2014). Formation of Al-enriched surface layers through reaction at the Mg-substrate/Al-powder interface. *Surf. Interface Anal.* DOI: 10.1002/sia.5579.
- [15] Mola, R. (2014). The properties of Al/Zn-enriched surface layers on Mg, *Archives of Foundry Engineering, Special Issue 1* 4(3), 45-48.
- [16] Huo, H., Li, Y. & Wang, F. (2007). Improvement on the corrosion resistance of AZ91D magnesium alloy by aluminum diffusion coating. *J. Mater. Sci. Technol.* 23(3), 379-382.
- [17] Zhu, T. & Gao, W. (2009) Formation of intermetallic compound coating on magnesium AZ91 cast alloy, *Mater. Sci. Eng.*, 4, 1-6. DOI: 10.1088/1757-899X/4/1/012024.
- [18] Spencer, K. & Zhang, M.X.(2009). Heat treatment of cold spray coatings to form protective intermetallic layers. *Scr. Mater.* 61, 44-47. DOI: 10.1016/j.scriptamat.2009.03.002
- [19] Bu, H., Yandouzi, M., Lu, Ch. & Jodoin, B. (2011) Effect of heat treatment on the intermetallic layer of cold sprayed aluminum coatings on magnesium alloy. *Surf. Coat. Technol.*, 205, 4665-4671. DOI: 10.1016/j.surfcoat.2011.04.018.
- [20] Mola, R., Bucki, T. & Dziadoń, A. (2015) Surface alloying of magnesium by GTAW using AlMg₄5Mn wire, *Rudy i Metale Nieżelazne*, R60, 3, 110-114
- [21] Yang, H., Guo, X., Wu, G., Ding, W. & Birbilis, N. (2011). Electrodeposition of chemically and mechanically protective Al-coatings on AZ91D Mg alloy. *Corros. Sci.* 53, 381-387. DOI: 10.1016/j.corsci.2010.09.047.
- [22] Crystallographic and Thermodynamic Data of Binary Alloys, Landolt-Börnstein New Series, Group IV, Springer-Verlag Berlin 1998.