Effects of the process parameters on the formation of the Zn-enriched surface layer of Mg by thermochemical treatment in a medium containing ZnCl₂

T Bucki¹ and M Konieczny¹

¹Kielce University of Technology, Kielce, Poland, EU
E-mail: tbucki@tu.kielce.pl

Abstract. The fabrication of the Zn-enriched surface layer of Mg involved annealing of the Mg specimens in a contact with the paste containing ZnCl₂. Annealing of the specimen at 440 °C for 120 min resulted in the formation of a surface layer with a complex structure. In the outer zone, dendrites of a solid solution of Zn in Mg were observed at a eutectoid matrix (an MgZn intermetallic phase and a solution of Zn in Mg). The inner, transition zone, which was located at the interface adjacent to Mg substrate, was composed of a solid solution of Zn in Mg. The use of various period of annealing time (30, 60, 90 and 120 min) showed that increasing the annealing time leads to an increase in the thickness of the layer. A similar structure of the layer was observed for each variant of the annealing time. The analysis for the specimen fabricated at 410 °C for 120 min showed that the use of lower temperature resulted in a formation of a thin layer, eutectoid in structure. When higher annealing temperature (470 °C) was used, the thick surface layer with an uneven thickness and containing macroscopic unevenness was produced on the specimen surface.

1 Introduction

The application of magnesium as a structural metal is an effective method to reduce the weight of structures in such industries as automotive, aviation, and electronics. However, the use of magnesium alloys is limited, mainly due to their low resistance to corrosion and abrasion [1,2]. The literature data shows that these properties can be efficiently improved by the surface treatment of magnesium products. Positive results are achieved by enriching the surface with chemical elements that form intermetallic phases with magnesium, i.e. Al, Zn, Cu, Ni, Si and a combination of a few elements, such as Al/Si, Al/Zn, Al/Cu, Al/Mn, Al/Ir, Ni/Cu/Al and Zr/Al/Ni/Cu [3–15]. There are many methods of a heat treatment of magnesium and its alloys. Thermo-chemical treatment is a method which advantages are simple technology and low production cost. It involves annealing of the alloy in contact with a solid or liquid medium. The most common solid media are powders (e.g. aluminum powder [12]), that lead to the formation of a surface layer as a result of diffusion processes. The thermo-chemical treatment with liquid medium can be performed using molten salts, such as AlCl₃ [9]. As a consequence, a surface layer is formed due to the reaction of a liquid substance with an alloy surface and the diffusion between the components. In the literature, there are also studies with the author's contribution [13,14], which show that surface treatment of magnesium or its alloys can also be carried out by annealing of specimens coated with a paste containing ZnCl₂. The results shows that the process led to the formation of a layer containing Zn-rich phases on the surface of a pure Mg and AZ91 alloy. The authors noted also that produced layers were characterized by high microhardness.
The aim of presented work was to analyze how the parameters of the process, i.e. time and temperature of annealing, affect the formation of the Zn-enriched surface layer of Mg, fabricated by thermochemical treatment in a medium containing ZnCl$_2$. The study involved annealing of the specimens covered with a paste containing ZnCl$_2$ in a chamber furnace. Four variants of the annealing time (30, 60, 90 and 120 min) and three different values of the temperature (410, 440 and 470 °C) were applied in the experiment. The microstructure of the surface layers was analyzed with an optical microscope and a scanning electron microscope.

2 Experimental procedure

The specimens with dimensions of 20x15x10 mm were machined from an Mg ingot (99.9 % Mg). Before the application of the paste, the surfaces of the specimens were ground using abrasive papers and then cleaned with ethanol. The upper, largest surface of the specimens (20x15 mm) was coated with a paste containing ZnCl$_2$, and then the specimens were annealed in a chamber furnace. No protective atmosphere was used during the process. The specimens were cooled in the air after they were removed from the furnace. The paste used was a mixture containing ZnCl$_2$, KCl, pine rosin and ethanol. The composition of the mixture was selected on the basis of liquidus and solidus temperatures which are associated with the possibility of a reaction between ZnCl$_2$ and the Mg surface and formation of the surface layer. The results of previous studies [13,14] were also used to develop the proportion of ingredients. However, slight modifications to the paste composition were made to improve the uniformity of the layer thickness. The method of producing a surface layer on magnesium and its alloys using a paste containing ZnCl$_2$ is the subject matter of the patent of Republic of Poland (PL230625-B1).

In order to analyze the effect of the parameters on formation of the layer during the process, four variants of the annealing time and three different values of the temperature were used. The specimens were annealed at the temperature of 440 °C for: 30, 60, 90 and 120 min as well as for 120 min at various temperatures, equal to: of 410, 440 and 470 °C. The specimens for microscopic observations were prepared by using a standard metallographic procedure. The final polishing was carried out with a colloidal silica. The microstructural analysis was conducted using a Nikon ECLIPSE MA200 optical microscope (OM) and a JEOL JSM-7100F scanning electron microscope, which was equipped in a LINK ISIS 300 energy dispersive X-ray spectrometer (SEM/EDS).

3 Results and discussion

Figure 1 presents the microstructure of the surface layers fabricated as a result of annealing of the specimen in contact with a paste containing ZnCl$_2$ in a furnace heated to 440 °C. Specimens were placed in a furnace for 30 min, 60 min, 90 min and 120 min. In the specimen produced when the shortest annealing time was applied (figure 1a), the thickness of the surface layer was about 50 μm. The layer was composed of two zones: outer – lamellar in structure and inner – transition zone. The longer annealing time period of 60 min (see figure 1b) resulted in the formation of a surface layer with a thickness of about 130 μm. In its structure, outer and inner zones can be also distinguished. Gray particles with dendritic shapes were also noticeable in the outer zone on the lamellar matrix background. Further extension of the annealing time period to 90 min (figure 1c) and 120 min (figure 1d) resulted in the increase in thickness of the surface layer to approximately 200 μm and 230 μm, respectively. A complex structure of the layer, similar to the previous variants, was also observed in these cases.
Figure 1. OM micrograph of the surface layer fabricated by annealing of the Mg specimens coated with the paste at 440 °C for: (a) 30 min, (b) 60 min, (c) 90 min, (d) 120 min.

Figure 2 shows the SEM micrograph of the surface layer fabricated by annealing of the Mg specimen coated with a paste containing ZnCl₂ at 440 °C for 120 min. A linear analysis was performed along the line marked in the figure. The distribution of Zn and Mg show that the surface layer of the specimen was enriched in a Zn. In the transition zone marked as 1, a gradually increasing Zn content was observed towards the outside of the specimen. A detailed analysis of the phase composition of the surface layer, which was carried out using the EDS analysis and confirmed by XRD (X-Ray Diffraction) method, was presented in the previous work of authors [14]. According to the results, the transition zone of the surface layer was composed of a solid solution of Zn in Mg. The microstructure of the outer part of the surface layer observed in the SEM at a high magnification is shown in Figure 3. From the results, it is found that dark particles with dendritic shape (marked as 2 in figure 3) are composed of a solid solution of Zn in Mg. The results for the two-phase matrix of the layer (point 3) indicated a eutectoid consisting of an MgZn intermetallic phase and a solid solution of Zn in Mg. Locally distributed bright particles, marked as 4, were also observed in the matrix of the layer. The analysis of the chemical composition showed that they are composed of an Mg₂Zn₃ intermetallic phase.

The analysis of the results and the Mg-Zn system [16] shows that annealing of the specimens in contact with the paste containing ZnCl₂ causes the enrichment of Mg surface in Zn. At the elevated temperature applied during the process, a thin zone composed of a solid solution of Zn in Mg is formed. When the Zn content exceeds the solubility limit, the Zn richer phases are created. Then, during cooling of the specimen, the eutectoid (an MgZn phase and a solid solution of Zn in Mg) as well as the dendrites of a solid solution of Zn in Mg crystallize in the surface layer of specimen.
Figure 2. SEM micrograph and corresponding EDS line scan results for the surface layer fabricated by annealing of the Mg specimen coated with the paste at 440 °C for 120 min.

Figure 3. Details of the microstructure of the surface layer fabricated by annealing of the Mg specimen coated with the paste at 440 °C for 120 min.

Figure 4 presents the OM microstructure observed at high magnification, for the case when the surface layer was produced at a lower temperature, equal to 410 °C, for 120 min. The results show that annealing of the specimen at 410 °C resulted in the formation of the surface layer with a eutectoid structure. The layer was characterized by relatively thin thickness (about 25 μm).

Figure 5 shows the microstructure of the layer fabricated when the higher annealing temperature (470 °C) was applied. In this case, the Zn-enriched surface layer with a microstructure corresponding to that produced in 440 °C was formed. Increasing the annealing temperature of the specimens, however, resulted in the formation of the surface layer which was thick, but uneven in thickness (300-700 μm). The macroscopic unevenness were also clearly visible on the specimen surface.
The analysis of all the variants of annealing temperature show that the temperature of 440 °C was the most appropriate for the production of the Zn-enriched surface layer. This condition led to the formation of the continuous and thick layer, which was uniform in a thickness. It is also evident that the thickness of the layer depends on the annealing time and obviously it is related to the properties of the specimen.

3 Conclusions

The Zn-enriched surface layers of Mg were fabricated by annealing of the Mg specimens coated with the paste containing ZnCl₂.

The experiment showed that when the specimen was annealed at 440 °C for 120 min, a surface layer with a thickness of about 230 μm was formed on the Mg substrate. The microscopic observations indicated that the microstructure of the produced surface layer was complex. Their outer zone contained a eutectoid matrix (an MgZn intermetallic phase and a solid solution of Zn in Mg) with some dendrites of a solid solution of Zn in Mg and fine particles of an Mg₂Zn₃ intermetallic phase. The inner zone of the surface layer was composed of a solid solution of Zn in Mg.
The results also showed that the annealing time affects the thickness of the produced surface layer. The layer formed by annealing of the specimen at 440 °C for 30 min had the lowest thickness (50 μm), but the thickness increased with increasing the annealing time of the specimen (60, 90 and 120 min, respectively). All the layers produced under these process conditions had a similar microstructure.

The application of a lower process temperature (410 °C) resulted in the formation of a layer about 25 μm in thickness that was eutectoidal in structure. The layer observed for the specimen annealed at 470 °C was relatively thick and its microstructure corresponded to that produced in 440 °C. However, in this case, the thickness of the layer was not uniform (300-700 μm) and the macroscopic unevenness was observed on the surface of specimen.

References

[1] Mola R and Bucki T 2018 The microstructure and properties of the bimetallic AZ91/AlSi17 joint produced by compound casting Arch. Foundry Eng. 18 pp 71–6
[2] Mola R, Bucki T and Dziadoń A 2017 Effects of the pouring temperature on the formation of the bonding zone between AZ91 and AlSi17 in the compound casting process IOP Conf. Ser. Mater. Sci. Eng. 179 pp 1–6
[3] Kutschera U and Galun R 2000 Magnesium Alloys and their Applications ed K U Kainer (New Jersey: John Wiley & Sons, Ltd) pp 330–5
[4] Majumdar J D, Maiwald T, Galun R, Mordike B L and Manna I 2002 Laser surface alloying of an Mg alloy with Al + Mn to improve corrosion resistance Laser Eng. 12 pp 147–69
[5] Gao Y, Wang C, Pang H, Liu H and Yao M 2007 Broad-beam laser cladding of Al–Cu alloy coating on AZ91HP magnesium alloy Appl. Surf. Sci. 253 pp 4917–22
[6] Chen C, Wang M, Wang D, Jin R and Liu Y 2007 Laser cladding of Al+Ir powders on ZM magnesium base alloy Rare Met. 26 pp 420–5
[7] Yue T M and Su Y P 2007 Laser multi-layer cladding of Zr65Al7.5Ni10Cu17.5 amorphous alloy on magnesium substrates J. Mater. Sci. 42 pp 6153–60
[8] Yue T M and Li T 2008 Laser cladding of Ni/Cu/Al functionally graded coating on magnesium substrate Surf. Coat. Technol. 202 pp 3043–9
[9] He M, Liu L, Wu Y, Tang Z and Hu W 2009 Improvement of the properties of AZ91D magnesium alloy by treatment with a molten AlCl3–NaCl salt to form an Mg–Al intermetallic surface layer J. Coat. Technol. Res. 6 pp 407–11
[10] Hirmke J, Zhang M-X and StJohn D H 2011 Surface alloying of AZ91E alloy by Al–Zn packed powder diffusion coating Surf. Coat. Technol. 206 pp 425–33
[11] Mola R 2014 Fabrication and microstructure of diffusion alloyed layers on pure magnesium substrate Arch. Metall. Mater. 59 pp 1409–12
[12] Mola R and Jagielska-Wiaderek K 2014 Formation of Al-enriched surface layers through reaction at the Mg-substrate/Al-powder interface Surf. Interface Anal. 46 pp 577–80
[13] Bucki T and Mola R 2016 Metal 2016: 25th Anniversary International Conference on Metallurgy and Materials (Ostrava: Tanger Ltd) pp 1357–61
[14] Mola R, Bucki T and Gwozdzik M 2018 Surface alloying of magnesium and AZ91 by thermochemical treatment in a medium containing zinc chloride and potassium chloride Materialwiss. Werkstofftech. 49 pp 1006–14
[15] Mola R and Cieslik M 2019 Microscopic analysis of layers containing mg2si and mg17al12 phases fabricated on az91 through thermochemical treatment Arch. Foundry Eng. 19 pp 119–24
[16] Agarwal R, Fries S G, Lukas H L, Petzow G, Sommen F, Chart T G and Effenberg G 1992 Assessment of the Mg-Zn system Z. Metallkd. 83 pp 216–23