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Synergy effect of heat and surface treatment on properties of the Mg-Al-Zn cast alloys

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ABSTRACT

Purpose: The aim of this paper is to present the results of the author's own investigations concerning heat and surface treatment of Mg-Al-Zn magnesium alloys.

Design/methodology/approach: The test results presented concern the characteristics of synergic heat and surface treatment impact on the structure and properties of Mg-Al-Zn cast magnesium alloys. The surface treatment of the magnesium alloys was carried out with the use of chemical and physical deposition methods from PA CVD and CAE PVD gas phase and laser surface treatment, including in particular laser feeding of hard ceramic particles into the surface of materials produced, enabling the production of a quasi-composite MMCs (Metal Matrix Composites) structure. The tests of the surface and internal structure of materials with the use of macro- and microscopic methods were made with the use of light, transmission and scanning electron microscopy as well Raman spectrometry and X-ray phase analysis. The physical and mechanical properties of magnesium alloys after the standard heat and surface treatment operations were tested by methods appropriate for the properties.

Findings: The results of mechanical and functional properties measurements of heat treated samples confirms, that the performed heat treatment, consisting of solution heat treatment with cooling in water, as well aging with cooling in air, causes strengthening of the MCMgAl12Zn1, MCMgAl9Zn1 and MCMgAl6Zn1 cast magnesium alloys according to the precipitation strengthening mechanism, induced by inhibition of dislocation movement due to the influence of strain fields of the homogeny distributed γ -phase Mg17Al12 precipitates. The combination of properly chosen heat treatment with the possibilities of structure- and phase composition modeling of the magnesium alloys matrix using laser feeding provides an additive increase of mechanical and functional properties by significant grain refinement and production of micro-composite layers with homogeny distributed dispersion phases particle and characteristic zone structure. Increase of mechanical and functional properties by creating coatings on the surface from the gas phase.

Practical implications: Achieving of new operational and functional characteristics and properties of commonly used materials, including the Mg-Al-Zn alloys is often obtained by heat treatment, ie, precipitation hardening and/or surface treatment due to application or manufacturing of machined surface layer coatings of materials in a given group of materials used for different surface engineering processes.

Originality/value: The originality of this paper consists in the presentation of a very extensive knowledge related to the methods of structure and properties forming of the surface of Mg-Al-Zn alloys, supported by the results of wide author's research.

Keywords: Thin & thick coatings; PVD and CVD coatings; Laser treatment; Structure; Properties

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1. Introduction

The purpose of this monograph is to present the synergistic effect of heat treatment and surface treatment on properties of the cast Mg-Al-Zn allovs, based on the investigation results published over the last few years [1-22]. In these works there are presented in detail the research methodology, as well as technical details related to the realised technological processes of heat and surface treatment, as well as chemical composition data of the applied engineering materials. The presented work makes it purposeful to carried out research concerning laser treatment as well coatings technology with appliance of the physical vapour deposition PVD and chemical vapour deposition CVD on cast magnesium alloys, as one of the fastest growing areas of surface engineering of light metal alloys. To meet the new requirements set by present users and in line with the current tendencies to eliminate technologies that contaminate natural environment, some universal solutions have been searched for, ones that combine inexpensive, light metal alloys and the best possible properties with appropriately selected technology of its surface processing. As the recycling costs calculated as the sum of material, workmanship, energy and overhead costs represent several up to a few dozen percent of the new chemical composition value, we may draw a conclusion that the economic effects gained upon considering of the profit on application of a layer or coating with better usable properties compared to those of the uncoated material, may appear more feasible. The appropriate interpretation of the mutual correlations between the properties and structure of the top coating and the base and its environment, enables a more extensive analysis and precise identification of the failure mechanisms that occur both on the surface and inside the material core. The gain of simultaneous development of both production technologies and processing of light materials, including in particular magnesium alloys and technologies of formation and protection of their surfaces, also seem to be the key issue here, which in consequence shall enable the maintenance of balance between the modern base material and new generation coating.

The generally available reference studies concerning magnesium and its alloys, cited herein [1-65], as well as the annual conferences and symposiums on the production and processing of light materials indicate that magnesium alloys find a more and more extensive circle of followers, both among the manufacturers and users. This trend is also confirmed by data collected by the United States Geological Survey (USGS) Mineral Resources, according to which the annual global production of prime magnesium, its basic source being dolomite ores, as at 31st December, 2010 was 757 thousand metric tons, increasing by more than 12% within 5 years, while still in 2002 it was just 448 thousand metric tons [23]. Like in case of steel, China is the global leader, with 654 thousand metric tons as at the end of 2010 with almost 85% share in the global production. According to China Non-Ferrous Metals Industry Association in mid-November, 2011, in the first 3 quarters of 2011 the production of prime magnesium grew by further 3% to more than 503.7 thousand metric tons during the period from 1st January to 30th September, 2011 [23].

Magnesium alloys that have been used in various branches of industry for a long time are characterised with combination of low

density and high strength. The above characteristics largely contributed to the application of magnesium alloys to fast moving parts, in places where rapid velocity changes occur and in products where the reduction of the final mass of the product is required. The highest demand for magnesium allovs was shown and still is by automotive industry [2-22, 27-30]. In the mass production of cars the weight of elements made with magnesium alloys ranges from 7 to 21 kg. The tendency of contemporary designers to create possibly the lightest vehicles and, in consequence, with possibly the lowest fuel consumption, contributed to the use of magnesium alloys as the structural material for car wheels, engine pistons, housing of transmission gear and clutch, sunroofs and structures of doors, pedals, suction conduits, collectors, housings of drive shafts, differential gears, cantilevers, radiators and other [1-65]. The cast elements made with magnesium alloys find common applications in electronics as well (including without limitation housings of laptops, PDA, mobile phones, GPS, thermal imaging cameras, industrial modems, LCD screen covers, digital photo frames), in aviation, electrical engineering and for structural elements, as well as in armament, optical, sports and other industries.

In spite of numerous undeniable advantages, characteristic for magnesium alloys, they also have some weak points, such as: low hardness and wear and corrosion resistance compared to alternative engineering materials, which eventually significantly restricts the scope of their applications [24-30]. The progress that has been made lately in the scope of production and surface engineering of light materials allows for the effective improvement of both the matrix and top layer of the magnesium alloys [10-22, 25-27, 29, 30, 33, 41-47, 49-58, 61,65].

Currently, the global development tendencies of production of top layers of light materials mainly focus on learning and improvement of the knowledge of the scope of obtaining and depositing coatings with the use of laser beam and physical and chemical vapour deposition techniques [10-22, 27-31, 33, 42-47, 49-52, 55-57, 61-65]. The trends using multiplex techniques combining the characteristics of several methods, are also noticeable. The laser treatment characteristics, such as touchlessness, selectivity and full automation option, enable the precise processing of selected substrate fragments, with depth and laser bundle action range precisely adjusted. Similarly, deposition of coatings using PVD and CVD methods is one of the most efficient methods of coating production providing the option of forming the aesthetic values, in addition to the usable features required, with the undeniable ecological aspect - non-waste technology meeting clean production requirements.

Nevertheless, despite the fact that interaction of laser radiation with the matter and knowledge of the phenomena occurring during deposited coatings with the PVD and CVD methods have been intensively tested and developed topics for years, the development of state-of-the-art, specialised technologies in this scope, enabling launching new generation materials on the market still requires a lot of effort and extensive laboratory tests. This situation is mainly related to the richness of physical and chemical phenomena accompanying the said surface treatment. Taking up this issue in Poland is related to the continuous tendency to develop and apply state-of-the art methods of structural materials production, particularly the formation of surface layers, frequently responsible for the final properties of the element considered.

2. Structure of cast Mg-Al-Zn alloys in as cast state as well after heat treatment

Own investigations results concerning the structure of the cast Mg-Al-Zn alloys in as cast state as well after heat treatment are presented in references [2-11].

Both the performed investigations as well literature study confirm, that the structure of the investigated alloys, and the mechanical properties obtained, resistance to wear and resistance to the corrosion factor impact are diversified, depending on the alloy component concentration, particularly aluminium changing within the range from 3 to 12%, and on the applied heat and surface treatment of the material (Fig. 1-24). The heat treatment carried out, composed of supersaturation with cooling in water and ageing with cooling in air causes reinforcement of the MCMgAl12Zn1, MCMgAl9Zn1, MCMgAl6Zn1 magnesium alloys, according to the mechanism of precipitation hardening reinforcement caused by stopping dislocation slip due to interaction of the stress fields of evenly located precipitations of γ - Mg₁₇Al₁₂ phase, which, according to the expectations [2-11, 27-32, 34-40, 48, 53, 54], causes additional growth of strength properties, wear resistance and resistance to the corrosion factor impact (Fig. 1, 2).

The γ -Mg₁₇Al₁₂ phase precipitations can also be identified as pseudo-eutectic areas (γ phase precipitation from the solid solution during aging, showing morphology similar to the eutectic forming from liquid phase).



Fig. 1. Structure of the MCMgAl9Zn1 alloy after aging at the temperature of 190°C for 15 hours

Dispersion precipitations present in the solid solution in aged magnesium alloys are in most cases of privileged crystallographic orientation. Some of them (Fig. 3) present the relationships:

$$(1 \overline{1} 01)\alpha - Mg \| (10 \overline{1})Mg_{17}Al_{12} \\ [11\overline{2}0]\alpha - Mg \| [111]Mg_{17}Al_{12}$$

compliant with those provide by S. Guldberg and N. Ryum [48] for Mg alloys occurring without limitation in the eutectic structure of Mg alloys, containing 33% Al. The precipitations of γ -Mg₁₇Al₁₂ phase most frequently assume the form of needles and plates, while the dominant direction of their growth are directions of the family $\langle 110 \rangle \alpha$ -Mg (Fig. 4).

In the solid solution as the matrix of cast magnesium alloys after aging there are present also clusters of dislocations in form of dislocation networks with a density much higher compared to the supersaturated state of the material. Formation of these dislocations is associated with stain generated in the matrix by precipitation of the γ phase particles.



Fig. 2. Structure of the MCMgAl9Zn1 alloy after aging at the temperature of 190°C for 15 hours

3. Influence of laser feeding with carbides and oxides on surface layer structure of the Mg-Al-Zn alloys

In the works [11-16, 21] there are presented investigation result concerning structure of surface layers of the Mg-Al-Zn alloys after laser treatment.

An additional improvement of the mechanical and functional properties may also be obtained as a result of reinforcement of the solid solution with dispersion phase particles of controlled amount of the analysed alloys introduced in the surface layer in the process of laser feeding and through refinement of the grains of the surface area of the material processed [11-16, 27, 29, 30, 33, 47, 49-52, 55, 56, 65]. Obtaining the effect of significant refinement of the grains is possible only thanks to fast heat transport from the remelting lake through magnesium substrate of high thermal capacity and very good thermal conductivity, which, in turn, results with the increase of grain boundaries amount representing a solid obstacle for the dislocations movement and therefore reinforcement of the material.

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Fig. 3. a) bright field, b) dark field (with spot $(\overline{314})$ image of the MCMgAl9Zn1 alloy after aging treatment at the temperature of 190°C for 15 hours with solid solution α - Mg (matrix) and an intermetallic secondary phase γ - Mg₁₇Al₁₂ in the form of needle precipitations, c) diffraction pattern of area shown in a), d) part of solution for diffraction pattern shown in c



Fig. 4. TEM image examples of the intermetallic secondary phase γ - Mg₁₇Al₁₂ in the form of needle precipitations from the MCMgAl9Zn1 alloy after aging at the temperature of 190°C for 15 hours

The structure of the solidified material after laser treatment is characterised with a zone construction with diversified morphology related to the crystallisation of magnesium alloys (Fig. 5, 6). Multiple change of crystal growth direction has been observed for these areas. In the area located on the boundary between the solid and liquid phase, minor dendrites occur the main axes thereof oriented along with the heat disposal directions (Fig. 5).



Fig. 5. Central zone of the MCMgAl3Zn1 alloy surface layer after laser treatment with TiC particles, scan rate: 0.75 m/min, laser power: 1.2 kW



Fig. 6. Structure of the interface between the laser-melted zone, heat affected zone and the substrate of the MCMgAl12Zn1 alloy after laser treatment with WC particles, scan rate: 0.75 m/min, laser power: 2.0 kW

As a result of the metallographic observations, it was confirmed that the structure of the composite layers produced is free of defects, with distinct grain refinement containing mainly evenly distributed dispersion particles of the TiC, WC, SiC carbide or Al_2O_3 oxide applied, which was also confirmed by X-ray or electron graphic tests (Fig. 7).



Fig. 7. X ray diffraction pattern of the MCMgAl12Zn1magnesium cast alloy after laser treatment by fed powders particles: A - TiC; B - WC; C - VC; D - SiC; $E - Al_2O_3$ [11]

The alloys with laser fed particles of vanadium carbide, their share in the remelting zone being slight, are the exception from the rule. During laser feeding, a strong circulation of the liquid metal takes place and after the laser bundle remelting - its rapid solidification. The thickness of the laser formed surface layer is of vital importance in determination of the properties, period of use and final application of the material obtained.

Three zones occur in the surface layer of the cast magnesium alloys: a zone rich with unsolved particles fed in the surface layers on the surface of magnesium alloys, remelting zone (RZ) and heat affected zone (HAZ). Both RZ and HAZ zones, depending on the concentration of aluminium in magnesium matrix, laser power applied and ceramic powder, are of different thickness and shape (Fig. 8).

It was proven that along with the growth of the power applied, the area of occurrence of both remelting zone and heat affected zone increases (Fig. 8), and the face of weld changes, which is also confirmed by the reference studies. The MCMgA112Znl alloys are characterised with the largest thickness of the surface layer, 3.59 mm, processed with laser power of 2.0 kW, with silicon carbide fed into their surface.

The power of the laser within the range 1.2-2.0 kW provides the possibility to obtain flat regular remelting welds with highly smooth surface (Fig. 9, 10).



Fig. 8. Influence of laser power on thickness of the remelted zone RZ, heat affected zone HAZ and the surface layer of cast magnesium alloys after laser feeding



Fig. 9. View of the MCMgAl9Zn1 cast magnesium alloy face of weld after laser treatment with WC powder, scan rate: 0.5 m/min, laser power: 2.0 kW



Fig. 10. View of the MCMgAl9Zn1 cast magnesium alloy face of weld after laser treatment with SiC powder, scan rate: 0.5 m/min, laser power: 2.2 kW

The uneven areas and hollows in the surface layer of the Mg-Al-Zn alloys with laser fed carbide particles are produced as a result of intensive heating of the surface. Depending on the type of substrate, laser power, feeding rate and the powder applied, the surface on which high gradient of surface tension is produced, is unevenly heated, which has a direct influence on the formation of the melted material in the remelting lake. Some of the alloy and ceramic parts embedded in the remelting zone is evaporated under high temperature occurring during laser treatment, therefore the characteristic hollows appear on the remelting surface. It was also found that, disregarding the ceramic powder used, in the laser bundle power range from 1.2 to 2.0 kW the porosity of the composite layers obtained increases, in comparison to that of the raw cast surfaces of magnesium alloys.

4. Structure of the PVD and CVD coatings on the substrate of cast Mg-Al-Zn alloys

The subject of works [17-20, 22] are structure investigations of the PVD and CVD coatings on the substrate of the cast Mg-Al-Zn alloys.

The increase of the exploitation time and hardness enhancement of elements made with Mg-Al-Zn alloys is only possible with the use of their surface layer purification in the vapour deposition, which was also proven upon extensive tests made by the authors, contrary to the

common opinion that coating magnesium alloys with PVD and CVD coats is pointless, due to their low hardness [17-20, 22]. The coatings obtained in selected variants, reinforced by solution, produced as a result of synthesis of non-balance (metastable) phases of the following configuration Ti/Ti(C,N)-gradient/CrN; Ti/Ti(C,N)gradient/(Ti,Al)N; Ti/(Ti,Si)N-gradient/(Ti,Si)N and coatings Cr/CrN-gradient/CrN; Cr/CrN-gradient/TiN and Ti/DLCgradient/DLC are characterised with distinct heterogeneity of the surface, related to the occurrence of numerous micro-particles in the structure, their shapes resembling congealed drops fallen out of the shield during coating deposition process and hollows produced as result of some drops falling out during the solidification process (Fig. 11, 12). The above effect is undoubtedly related to the differences in thermal conductivity coefficients and tension difference between the coating and the set drops of metal produced during the cooling of the substrate surface, upon completion of the coating deposited [68].



Fig. 11. Surface morphology of the Ti/Ti(C,N)/CrN layer coated on the MCMgAl6Zn1 cast magnesium substrate



Fig. 12. Surface morphology of the Cr/CrN/CrN layer coated on the MCMgAl9Zn1cast magnesium substrate

As a result of fracture investigations carried out in electron scanning microscope on the PVD and CVD coatings analysed, it

was found that the deposition coatings are characterised with one-, two- or multi-layered structure, depending on the layer system applied, and the particular layers are applied evenly and tightly adhere to the substrate and one another (Fig. 13, 14). The structure of the layers depends in particular on the type and conditions of the process and the type of the deposition coating.



Fig. 13. Fracture of the Ti/(Ti,Si)N/(Ti,Si)N coating deposited on the MCMgAl9Zn1 cast magnesium alloy



Fig. 14. Fracture of the Ti/Ti(C,N)/CrN coating deposited on the MCMgAl9Zn1 cast magnesium alloy

Based on the structure obtained with the use of the X-ray transmission microscope and dark field imaging technique, it was established that the coatings are characterised with compact structure of high grain homogeneity and low dispersion of their sizes ranging between 10 and 20 nm (Fig. 15). The TiN phase in the Cr/CrN/TiN coating is the only exception, the grain size thereof measured on the level of ~200 nm. As for DLC coatings, it was confirmed that the carbon coating contains slight graphite domains (areas, where graphite layers are arranged almost parallel, at a distance near to 0.335 nm) and may be classified as a partly graphitised carbon material.

(Ti,Al)N



c)

a)

Fig. 15. Structure of the thin foil from Ti/Ti(C,N)/(Ti,Al)N surface layer fracture deposited on the MCMgAl6Zn1 cast magnesium alloy: a) bright field, b) dark field, c) diffraction pattern of the surface layer presented on fig. a and b, solution of the diffraction pattern presented on fig. c), TEM

Slight elements diffusion in the transition zone, being the result of implantation of high energy ions falling on negatively polarised substrate and profile concentration change of chemical elements producing the coatings indicate that the coatings obtained are characterised with a gradient structure, which in case



Fig. 16. Changes in the chemical composition of the Cr/CrN/CrN coating deposited on the substrate of the MCMgAl9Zn1 cast magnesium alloy

of PVD coatings is caused by variable glow of reactive gases and change of current intensity on the arc source of metal couple in the process of cathode arc deposition (Fig. 16, 17), which was also confirmed in the papers [66-68].

10 nm



Fig. 17. Changes in the chemical composition of the Ti/Ti(C,N)/CrN coating deposited on the substrate of the MCMgAl9Zn1 cast magnesium alloy

5. Influence of the surface treatment on mechanical and functional properties of the cast Mg-Al-Zn alloys

In the works [10-20] there are presented the investigation results concerning mechanical properties of surface-layers coated using laser technology or PVD and CVD methods on the cast Mg-Al-Zn alloys substrate. Designing the substrate coating system is founded on appropriate coating material selection, so as to restrict or totally eliminate the dominating wear mechanisms that, in case of magnesium alloys, are particularly visible in the scope of weak corrosion and tribological resistance. Therefore, the reasonable and purposeful use of appropriate Mg-Al-Zn alloy surface layer formation is so important, such layer being predisposed for a given type of application that should effectively increase the durability of the elements. The correlation between the demand, i.e. practically determined need, base material and its properties and the layer application technique, seems to be the key issue here.

The measurement results of mechanical properties of samples subjected to heat and surface treatment confirm that both diversified concentration of aluminium in the alloy matrix and the processing applied impact the change of mechanical properties of the cast magnesium alloys tested. The reason for such condition is suggested in the mechanisms of reinforcing the materials tested, enabling generation of obstacles in crystalline materials against dislocations freely moving therein. The specific types of reinforcement are identified in the range of appropriate heat or surface treatment of the alloys analysed, among which the following reinforcements are distinguished: solution reinforcement through atoms of aluminium, the supersaturating element reinforcement and precipitation reinforcement taking place in alloys after heat treatment characteristic with precipitation of high dispersion (γ -Mg₁₇Al₁₂) hard phases in the alloy matrix, occurring in the range of laser feeding technologies and in case of PVD and CVD coated alloys, solution reinforcements of the depositing coatings.

All the changes of properties of the processed magnesium alloys surface are closely related to the changes of their structure, chemical and phase composition in the areas adjacent to the surface [10-20, 27-31, 33, 43-47, 49, 52, 55, 57, 63, 65]. The mechanical test results obtained after laser treatment presented significant differences, depending on the wide range of its conditions applied, powders and substrate used, confirming that the highest increase of hardness and micro-hardness occurred in case of the MCMgAl3Znl and MCMgAl6Znl alloys reinforced with ceramic particles by laser (Fig. 18-20). Moreover, the analyses carried out and tests results on coatings produced in the PVD and CVD process on the surface of cast magnesium alloys, presented herein, show a distinct, exceeding 100%, growth of micro-hardness, compared to that of the substrate (Fig. 19).

6. Changes of corrosion and wear resistance due to surface treatment of cast Mg-Al-Zn alloys

In the works [21, 22] there are presented the investigation results of corrosion and wear resistance of cast Mg-Al-Zn alloys after appliance of different surface treatment methods.



Fig. 18. Hardness measurements results of cast Mg-Al-Zn magnesium alloys samples, after aging and laser feeding



Fig. 19. Micro-hardness measurements results of cast Mg-Al-Zn magnesium alloys samples, after aging, laser feeding and PVD\CVD treatment



Fig. 20. Measurements results of average mass loss cast Mg-Al-Zn magnesium alloys samples, depending on applied heat- and surface treatment

The growth of surface micro-hardness of the magnesium alloys, as a result of vapour deposition coating often correlates with the growth of wear resistance of the substrate tested, particularly the Ti/Ti(C,N)/CrN and Ti/Ti(C,N)/(Ti,Al)N coatings. Nevertheless, the tendency to increase the surface hardness, in order to increase the wear resistance of the elements tested is not always justified, a good example thereof being diamond-like DLC type of layers, often called selflubricating coatings. The good tribological properties of the DLC coating are mainly related to slip, taking place in the transition layer, produced in the friction touch zone, in consequence of graphitisation and oxidation processes, which is also confirmed by reference [57]. According to the 5 N load applied, the friction path results for DLC coats were on the level exceeding the friction path results, e.g. for a Cr/CrN/CrN coating, even 70 times, their hardness comparable to that of diamond-like coatings (Fig. 20, 21).

All the dependencies presented indicate that the corrosion resistance of magnesium alloys, both after heat and surface treatment is in as much higher in so fare the values of corrosion current density are lower. This is the result of the growing polarisation resistance of the material tested, i.e. lower anode solution of the surface. As the corrosion tests determining the resistance of the Mg-Al-Zn alloys to pitting corrosion for the particular heat and surface treatment variants were made under various conditions, the results need to be considered separately. However, the general noticeable trend resulting from the tests carried out confirms that the cast magnesium alloys with hard fine powders fed into their surface are characterised with lower pitting corrosion resistance in comparison to alloys after normal heat treatment (Fig. 22). The application of PVD and CVD coatings on the surface of cast magnesium alloys may provide higher corrosion resistance of the elements, compared to the corrosion resistance of elements after ordinary heat treatment, in selected processing variants, i.e. upon application of a Ti/DLC/DLC and Cr/CrN/CrN coatings, for all the substrates tested and coating type Cr/CrN/TiN on MCMgA112Zn1 and MCMgA19Zn1 substrates (Fig. 23).

In order to determine the correlations between the assumed processing conditions, substrate and measurement results obtained, designed computational models were used, applying artificial neural networks being an effective tool supporting the process of assessment of the mechanical and usable values of the test objects (Fig. 24). The changes of properties considered in the computational model confirmed the accuracy of the model upon simulation against the experiment results, thus providing additional material to assess the structural causes and mechanisms of their development. The practical aspect created by the models developed requires to be emphasised in particular, as such models may well replace the mentioned technological trials of process conditions and chemical compositions covered by modelling.



Type of substrate material

Fig. 21. Listing of wear path distance until the break of the surface layer as well the minimum and maximum friction coefficient during the wear resistance test (ball-on-disk) for the investigated PVD and CVD coatings deposited on cast magnesium alloys



Fig. 22. Measurements results of corrosion current density icor; polarization resistance Rp, corrosion potential Ecor of the surface of magnesium cast alloys after aging and laser feeding



Fig. 23. Measurements results of corrosion current density icor; polarization resistance Rp, corrosion potential Ecor of the surface of magnesium cast alloys after aging and PVD\ CVD process



Fig. 24. Diagram of the influence of the applied coating and variable aluminium concentration on wear resistance of the produced coatings, described by the wear path distance - the results were obtained by computer simulation using neural networks

7. Summary

Structure and properties of the investigated cast Mg-Al-Zn alloys, are varied depending on the feeding elements concentration in the material, especially aluminium ranging from 3 to 12% mass, as well as the treatment, for example in as cast state before heat treatment, after aging or surface treatment. The aging process, which was confirmed on the basis of thin foils investigations, causes clear change in the structure resulting from the uniform precipitation process of dispersed γ phase particles in a needle form, forming large agglomerates inside the grains, which are also present in the form of pseudoeutectic areas. The results of mechanical- and functional properties measurements of heat-treated samples confirms, that the heat performed treatment, consisting of solution treatment with cooling in water, as well aging with cooling in air, causes strengthening of the MCMgAl12Zn1, MCMgAl9Zn1 and MCMgAl6Zn1 cast magnesium alloys according to the precipitation strengthening mechanism, induced by inhibition of dislocation movement due to the influence of strain fields of the homogeny distributed γ -phase Mg₁₇Al₁₂ precipitates. Whereas the alloys with a lower aluminium content in the matrix of > 6% (MCMgAl3Zn1), where hardness measurements were also performed, are characterised by a lack of occurrence of precipitation strengthening after aging. In such a case, due to the low content of the solution compound in the matrix - in this case aluminium - causes a softening effect by precipitation of the Mg₁₇Al₁₂ phase in the MCMgAl3Zn1 alloy matrix after aging, what in consequence results with decrease of the aluminium atoms amount in the alloy, responsible for additional solutions strengthening.

The combination of properly chosen heat treatment with the possibilities of structure- and phase composition modelling of the metal matrix magnesium alloys using laser feeding, provides an additive increase of mechanical and functional properties by significant grain refinement and production of micro-composite layers with homogeny distributed dispersion phases particle and characteristic zone structure. Beginning from the top of the surface layer there occurs a zone rich in non-dissolved particles located on the surface of magnesium alloys, the next zone is the remelting zone (RZ), with thickness and shape closely depend on the applied laser power as well the heat affected zone (HAZ). These zones, depending on the applied laser power and the used ceramic powder have different thickness and shape.

Increase of mechanical and functional properties of the investigated alloys is also possible by creating coatings on the surface from the gas phase, partially solution hardened, coated in the system of soft substrate - gradient transition layer, with a continuous change of one or more of components from the substrate to the outer surface - and an outer layer, as a result of cathodic arc evaporation as well in the process of plasma assisted chemical vapour deposition, characterized by a compact structure, without visible delamination and defects, evenly coated and tightly adherent to each other and to the substrate.

References

- T. Tański, Synergy effect of heat and surface treatment on properties of the Mg-Al-Zn cast alloys, Habilitation thesis not published, Žilinska Univerzita v Žiline, Žilina 2012.
- [2] L.A. Dobrzański, T. Tański, J. Domagała, Microstructure analysis of MCMgAl16Zn1 MCMgAl8Zn1 MCMgAl4Zn1 magnesium cast alloy, Archives of Foundry Engineering 7/4 (2007) 33-38.
- [3] L.A. Dobrzański, T. Tański, L. Čížek, J. Domagała, Mechanical properties and wear resistance of magnesium casting alloys, Journal of Achievements in Materials and Manufacturing Engineering 31/1 (2008) 83-90.
- [4] L.A. Dobrzański, T. Tański, L. Čížek, Z. Brytan, Structure and properties of the magnesium casting alloys, Journal of Materials Processing Technology 192-193 (2007) 567-574.
- [5] L. Čížek, M. Greger, L. Pawlica, L.A. Dobrzański, T. Tański, Study of selected properties of magnesium alloy AZ91 after heat treatment and forming, Journal of Materials Processing Technology 157-158 (2004) 466-471.
- [6] L.A. Dobrzański, T. Tański, L. Čížek: Microstructure of MCMgAl12Zn1 magnesium alloy, Archives of Foundry Engineering 7/1 (2007) 179-182.
- [7] L.A. Dobrzański, T. Tański, Influence of aluminium content on behaviour of magnesium cast alloys in bentonite sand mould, Solid State Phenomena 147-149 (2009) 764-769.
- [8] L.A. Dobrzański, T. Tański, J. Trzaska, Optimization of heat treatment conditions of magnesium cast alloys, Materials Science Forum 638-642 (2010) 1488-1493.
- [9] M. Krupiński, T. Tański, Prediction of mechanical properties of cast Mg-Al-Zn alloys, Archives of Materials Science and Engineering 56/1 (2012) 30-36.
- [10] L. A. Dobrzański, T. Tański, Sz. Malara, M. Król, Structure and properties investigation of an magnesium alloys processed by heat treatment and laser surface treatment, Materials Science Forum 674 (2011) 11-18.
- [11] L.A. Dobrzański, T. Tański, Sz. Malara, M. Król, J. Domagała-Dubiel, Contemporary forming methods of the

structure and properties of cast magnesium alloys, Magnesium alloys - design, processing and properties, Frank Czerwinski (Ed.), InTech, 2011, 321-350.

- [12] L.A. Dobrzański, T. Tański, J. Domagała, Sz. Malara, M. Król, Effect of high power diode laser surface melting and cooling rate on microstructure and properties of magnesium alloys, Journal of Achievements in Materials and Manufacturing Engineering 37/2 (2009) 238-257.
- [13] A.D. Dobrzańska-Danikiewicz, T. Tański, S. Malara, J. Domagała-Dubiel, Assessment of strategic development perspectives of laser treatment of casting magnesium alloys, Archives of Materials Science Engineering 45/1 (2010) 5-39.
- [14] L.A. Dobrzański, T. Tański, J. Domagała, Sz. Malara, A. Klimpel, Laser surface treatment of Mg-Al-Zn alloys, Journal for Theory and Application in Mechanical Engineering 53/1 (2011) 5-10.
- [15] A.D. Dobrzańska-Danikiewicz, T. Tański, J. Domagała-Dubiel, Unique properties, development perspectives and expected applications of laser treated casting magnesium alloys, Archives of Civil and Mechanical Engineering 12 (in print).
- [16] A.D. Dobrzańska-Danikiewicz, T. Tański, J. Domagała-Dubiel, S. Malara, Technology Foresight results concerning laser surface treatment of casting magnesium alloys, Magnesium alloys, W.A. Monteiro (Ed.), InTech, 53-78.
- [17] T. Tański, Characteristics of hard coatings on AZ61 magnesium alloys, Journal of Mechanical Engineering 2012 (in print).
- [18] T. Tański, Surface layers on the Mg-Al-Zn alloys coated using the CVD and PVD physical and chemical evaporation methods, Journal of Achievements in Materials and Manufacturing Engineering 53/2 (2012) 89-96.
- [19] T. Tański, Investigation of the structure and properties of PVD and PACVD-coated magnesium die cast alloys, Magnesium alloys, W.A. Monteiro (Ed.), InTech, 29-52.
- [20] T. Tański, K. Labisz, K. Lukaszkowicz, Structure and properties of diamond-like carbon coatings deposited on non-ferrous alloys substrate, Solid State Phenomena (in print).
- [21] L.A. Dobrzański, T. Tański, Sz. Malara, Effect of the heat and surface laser treatment on the corrosion degradation of the Mg-Al alloys, Materials Engineering - Materiálové Inžinierstvo 18 (2011) 85-92.
- [22] T. Tański, Structural, mechanical and corrosion resistance properties of gradient/monolithic coatings deposited by PVD and PACVD methods onto the magnesium alloys, Thin Solid Films 2012 (in print).
- [23] http://minerals.usgs.gov/minerals/pubs/commodity/magnesi um/mcs-2012-mgmet.pdf.
- [24] M. Campo, M. Carboneras, M.D. López, B. Torres, P. Rodrigo, E. Otero, J. Rams, Corrosion resistance of thermally sprayed Al and Al/SiC coatings on Mg, Surface and Coatings Technology 203/20-21 (2009) 3224-3230.
- [25] M.C Turhan, R.P. Lynch, H. Jha, P. Schmuki, S. Virtanen, Anodic growth of self-ordered magnesium oxy-fluoride nanoporous/tubular layers on Mg alloy (WE43), Electrochemistry Communications 12/6 (2010) 796-799.
- [26] X. Fan, Y. Liu, Z. Xu, Y. Wang, B. Zou, L. Gu, Ch. Wang, X. Chen, Z.S Khan; D.W Yang; X.Q Cao, Preparation and

Characterization of 8YSZ Thermal Barrier Coatings on Rare Earth-Magnesium Alloy, Journal of Thermal Spray Technology 20/4 (2011) 948-957.

- [27] M. Avedesian, H. Baker (Eds.), ASM Specialty Handbook, Magnesium and magnesium alloys, ASM International, The Materials Information Society, USA, 1999.
- [28] A. Fajkiel, P. Dudek, G. Sęk-Sas, Foundry engineering XXI c, Directions of metallurgy development and light alloys casting, Publishers Institute of Foundry Engineering, Cracow, 2002.
- [29] K.U. Kainem, Magnesium alloys and technology, Willey-VH, Weinheim, 2003.
- [30] E.F. Horst, B.L. Mordike, Magnesium technology, Metallurgy, design data, application, Springer-Verlag, Berlin Heidelberg, 2006.
- [31] K.N. Braszczyńska-Malik, Precipitates of γ-Mg₁₇Al₁₂ phase in AZ91 alloy, Contemporary forming methods of the structure and properties of cast magnesium alloys, Magnesium alloys - design, processing and properties, F. Czerwinski (Ed.), InTech, 2011, 95-112.
- [32] M. Marya, L.G. Hector, R. Verma, W. Tong, Microstructural effects of AZ31 magnesium alloy on its tensile deformation and failure behaviors, Materials Science and Engineering A 418 (2006) 341-356.
- [33] J. Hirmke, M.X. Zhang, D.H. S. John, Surface alloying of AZ91E alloy by Al-Zn packed powder diffusion coating, Surface and Coatings Technology 206/2-3 (2011) 425-433.
- [34] Y. Guangyin, L. Manping, D. Wenjiang, A. Inoue, Microstructure and mechanical properties of Mg-Zn-Si based alloys, Materials Science and Engineering A 357 (2003) 314-320.
- [35] C. Jaschic, H. Haferkamp, M. Niemeyer, New magnesium wrought alloys, Magnesium alloys and their applications, K.U. Kainem (Ed.), Willey-VH, Weinheim, 2000, 41-45.
- [36] J.S. Knut, Magnesium motorcycle wheels for racing applications, in: Magnesium Alloys and their Applications, K.U. Kainem (Ed.), Willey-VH, Weinheim, 2000, 391-395.
- [37] C.D. Yima, K.S. Shinb, Changes in microstructure and hardness of rheocast AZ91HP magnesium alloy with stirring conditions, Materials Science and Engineering A 395 (2005) 226-232.
- [38] P. Venkateswarana, S.G. Sundara Ramana, S.D. Pathaka, Y. Miyashitab, Y. Mutoh, Fatigue crack growth behaviour of a die-cast magnesium alloy AZ91D, Materials Letters 58 (2004) 2525-2529.
- [39] T. Murai, S. Matsuoka, S. Miyamoto, Y. Oki, Effects of extrusion conditions on microstructure and mechanical properties of AZ31B magnesium alloy extrusions, Journal of Materials Processing Technology 141 (2003) 207-212.
- [40] Z. Zhang, X. Zeng, W. Ding, The influence of heat treatment on damping response of AZ91D magnesium alloy, Materials Science and Engineering A 392 (2005) 150-155.
- [41] J.E. Gray, B. Luan, Protective coatings on magnesium and its alloys-a critical review, Journal of Alloys and Compounds 336 (2002) 88-113.
- [42] H. Altun, S. Sen, The effect of DC magnetron sputtering AlN coatings on the corrosion behavior of magnesium alloys, Surface and Coatings Technology 197 (2005) 193-200.

- [43] G. Wu, W. Dai, H. Zheng, A. Wang, Improving wear resistance and corrosion resistance of AZ31 magnesium alloy by DLC/AIN/Al coating, Surface and Coatings Technology 205 (2010) 2067-2073.
- [44] Y.J. Shi, S.Y. Long, S.C. Yang, F.S. Pan, Deposition of nano-scaled CrTiAlN multilayer coatings with different negative bias voltage on Mg alloy by unbalanced magnetron sputtering, Vacuum 84 (2010) 962-968.
- [45] H. Zhao, X.H. Wang, Q.L. Liu, L.J. Chen, Z. Liu, Structure and wear resistance of TiN and TiAlN coatings on AZ91 alloy deposited by multi-arc ion plating, Transactions of Nonferrous Metals Society of China 20 (2010) 679-682.
- [46] Z.M. Liu, W. Gao, Electroless nickel plating on AZ91 Mg alloy substrate, Surface and Coatings Technology 200 (2006) 5087-5093.
- [47] M.X. Zhang, P.M. Kelly, Surface alloying of AZ91D alloy by diffusion coating, Journal of Materials Research 17 (2002) 2477-2479.
- [48] S. Guldberg, N. Ryum, Microstructure and crystallographic orientation relationship in directionally solidified Mg-Mg₁₇Al₁₂-eutectic, Materials Science and Engineering A 289 (2000) 143-150.
- [49] G. Abbas, L. Li, U. Ghazanfar, Z. Liu, Effect of high power diode laser surface melting on wear resistance of magnesium alloys, Wear 260 (2006) 175-180.
- [50] G. Abbas, L. Li, Z. Liu, Effect of high power diode laser surface melting on corrosion resistance of magnesium alloys, Proceedings of the 34th MATADOR International Conference, Manchester, 2004, 225-234.
- [51] G. Abbas, Z. Liu, P. Skeldon, Corrosion behaviour of lasermelted magnesium alloys, Applied Surface Science 247 (2005) 347-353.
- [52] D. Dube, M. Fiset, A. Couture, I. Nakatsugawa, Characterization and performance of laser melted AZ91D and AM60B, Materials Science and Engineering A 299 (2001) 38-45.
- [53] S.F. Hassan, M. Gupta, Development of ductile magnesium composite materials using titanium as reinforcement, Journal of Alloys and Compounds 345 (2002) 246-251.
- [54] S.F. Hassan, M. Gupta, Effect of submicron size Al₂O₃ particulates on microstructural and tensile properties of elemental Mg, Journal of Alloys and Compounds 457 (2008) 244-250.
- [55] Y. Jun, G.P. Sunb, S.S. Jia, Characterization and wear resistance of laser surface melting AZ91D alloy, Journal of Alloys and Compounds 455 (2008) 142-147.
- [56] J.D. Majumdar, R. Galun, B.L. Mordike, I. Manna, Effect of laser surface melting on corrosion and wear resistance of a commercial magnesium alloy, Materials Science Engineering A 361 (2003) 119-129.

- [57] Y.S. Zou, Y.F. Wu, H. Yang, K. Cang, G.H. Song, Z.X. Li, K. Zhou, The microstructure, mechanical and friction properties of protective diamond like carbon films on magnesium alloy, Applied Surface Science 258 (2011) 1624-1629.
- [58] H. Altun, S. Sen, Studies on the influence of chloride ion concentration and pH on the corrosion and electrochemical behaviour of AZ63 magnesium alloy, Materials and Design 25 (2004) 637-643.
- [59] G. Ballerini, U. Bardi, R. Bignucolo, G. Ceraolo, About some corrosion mechanisms of AZ91D magnesium alloy, Corrosion Science 47 (2005) 2173-2184.
- [60] E.M. Gutman, A. Eliezer, Ya. Unigovski, E. Abramov, Mechanoelectrochemical behavior and creep corrosion of magnesium alloys, Materials Science and Engineering A 302 (2001) 63-67.
- [61] Y.F. Jiang, X.W. Guo, Y.H. Wei, C.Q. Zhai, W.J. Ding, Corrosion protection of polypyrrole electrodeposited on AZ91 magnesium alloys in alkaline solutions, Synthetic Metals 139 (2003) 335-339.
- [62] H. Altun, S. Sen, The effect of PVD coatings on the corrosion behavior of AZ91 magnesium alloy, Materials and Design 27 (2006) 1174-1179.
- [63] H. Altun, S. Sen, The effect of PVD coatings on the wear behavior of magnesium alloys, Materials Characterization 58 (2007) 917-921.
- [64] J. Chen, J. Wang, E. Han, J. Dong, W. Ke, States and transport of hydrogen in the corrosion process of an AZ91 magnesium alloy in aqueous solution, Corrosion Science 50 (2008) 1292-1305.
- [65] Y. Gao, C. Wang, H. Pang, H. Liu, M. Yao, The resistance to wear and corrosion of laser-cladding Al₂O₃ ceramic coating on Mg alloy, Applied Surface Science 253 (2007) 5306-5311.
- [66] L.A. Dobrzański, Design and manufacturing of functional gradient tool materials - relationship between properties, technology and thickness of the surface layers with a gradient of chemical or phase composition produced on tools for various applications, Design and manufacturing of functional gradient materials, Polish Academy of Sciences, Cracow, 2007.
- [67] A. Michalski, Physicochemical basics of coatings achievment from the gas phase, Publishing House of Warsaw University, Warsaw, 2000.
- [68] L.A. Dobrzański, M. Staszuk, PVD and CVD gradient coatings on sintered carbides and sialon tool ceramics, Journal of Achievements in Materials and Manufacturing Engineering 43/2 (2010) 552-576.