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FUNCTIONALLY GRADED SUBSTRATE LAYERS OF MAGNESIUM ALLOYS PRODUCED BY ELECTRON BEAM TECHNOLOGY

FUNKCJONALNIE ZMIENNE WARSTWY PODŁOŻA STOPÓW MAGNEZU WYTWARZANYCH TECHNIKĄ WIĄZKI ELEKTRONOWEJ

In this paper some examples of surface modification of magnesium-base alloys produced by means of electron beam in vacuum are presented. In particular, for functionally graded surface layer formation one step process based on electron beam welding technology using cored wire electrodes as well as two-steps process consisting of thermal spraying of composite coatings and subsequent electron beam remelting have been applied. In all cases, including pure remelting of base material, the modified zone of the examined magnesium alloys AM20, AZ31, AE42 and AZ 91 exhibits a very fine microstructure and an increased microhardness. The distribution of the alloying elements and the hard particles in the modified outer zones strongly depends on process parameters. Cracks and pores can be almost fully avoided by suitable processing. Comparative corrosion and wear tests are carried out.

Keywords: magnesium alloys, surface modification, EB treatment, microstructure, wear resistance, corrosion resistance

W pracy przedstawiono przykłady zastosowania techniki elektronowo-promieniowej do obróbki materiałów w próżni, dla modyfikowania warstwy wierzchniej stopów magnezu. W szczególności do wytwarzania powierzchniowych warstw o własnościach gradientowych zastosowano metodę jednostopniową, opartą na technologii spawania wiązką elektronową z wykorzystaniem drutów proszkowych, oraz dwustopniową, która polega na przetopieniu wiązką elektronową powłok kompozytowych natryskiwanych cieplnie na powierzchnie stopów Mg. Modyfikowane warstwy przypowierzchniowe wszystkich badanych stopów (AM20, AZ31, AE42 i AZ 91) jak również i przetopione bez dodatku innych elementów wykazują bardzo drobną mikrostrukturę oraz podwyższoną mikrotwardość. Rozkład pierwiastków w domieszkowanej strefie zależy od parametrów procesu obróbki, których optymalizacja pozwala na otrzymanie modyfikowanych warstw bez porów i pęknięć. Były przeprowadzone również porównywalne badania odporności na korozje i zyżycie otzymanych warstw.

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1. Introduction

Magnesium alloys are the lightest structural materials being extensively used in automotive and aeronautic applications. Magnesium alloys show high specific strength and so engineers in automotive industry are keen on using magnesium in their vehicles. Magnesium offers greater weight saving capacity than aluminium, as its density, 1.7 $g \cdot cm^{-3}$, is two thirds the density of aluminium, 2.7 $g \cdot cm^{-3}$, without significant loss of strength. On the other hand surface properties like wear and corrosion resistance are rather poor.

Electron beams (EB) are mainly used for welding, but also EB surface treatment of metallic parts, e.g. for surface hardening, is known for quite long time and for a number of applications has found its implementation in industry. A lot of research work is dedicated to the development of methods of EB alloying, cladding and reinforcement in order to increase wear or/and corrosion resistance of different materials [1, 2], light metals being among them [3, 4]. The growing interest in magnesium alloys applications [5] increases importance to adapt EB methods for formation of surface layers on these alloys showing improved properties in use.

The aim of this work was to investigate the possibilities to modify magnesium alloys by means of electron beam treatment in vacuum and definition of the optimal added materials and methods for electron beam alloying / reinforcement of the surface layers in magnesium alloys with the purpose of increasing wear resistance of magnesium alloys without decreasing their corrosion resistance.

2. Materials and methods

2.1. Substrate materials

As substrate materials four different magnesium alloys are used. Besides the most commonly in industry applied alloy AZ91 also an alloy with decreased content of aluminium AZ31, a ductile alloy AM20 and an alloy with addition of rare earth elements for improved creep resistance AE42 are investigated. Chemical compositions are shown in Tab. 1.

TABLE

Chemical composition of substrate materials

Alloy	Al [%]	Zn [%]	Mn [%]	Si [%]	Fe [%]	Cu [%]	Ni [%]	Ca [%]	RE [%]
AZ31	2.5-3.5	0.5-1.5	0.05-0.4	0.1	0.03	0.1	0.005	0.04	—
AM20	2.042	0.05	0.388	0.012	0.001	0.001	< 0.001	< 0.001	—
AZ91	8.5-9.5	0.45-0.9	0.17-0.4	max. 0.05	max. 0.004	max. 0.025	max. 0.001	< 0.001	—
AE42	4.29	0.029	0.442	0.012	0.003	0.001	0.001	< 0.001	2.5

2.2. Alloying and reinforcing materials

Alloying / dispersing is carried out in one-step as well as two-steps processes. One step process is realised in the case of directly supplying of additive material in the form of wire or powder mixture into the melt pool formed by the electron beam. For two steps process as the first step an alloying material mixture is deposited on the surface of substrates as pastes or thermal spray coatings. The second step consists of melting of the surfaces in order to form modified layers. Additive materials are applied in the form of mechanically alloyed powders with different content of hard particles and aluminium, mechanically mixed powders and cored wires with aluminium cover and hard particles filler. For High Velocity Oxy-Fuel (HVOF) spraying mechanically alloyed powders with 50 vol.-% content of hard particles (Al_2O_3, Cr_2O_3 and TiO_2) and pure aluminium as matrix material were applied as well as mechanical powder mixture of Al12Si and TiO_2 (50:50 vol.-%) [6]. Mechanical powder mixture Al/SiC (50:50 vol.-%) is also used to obtain coatings by vacuum plasma spraying (VPS) method. Cored wires with aluminium cover and hard particles (Si, TiO_2, SiC, B_4C or WSC) filler are used for direct EB-reinforcing as well as for arc spraying of coatings in two steps process.

2.3. Experimental procedure

Electron beam surface treatment is carried out in vacuum. Electron beam equipment S20 (pro-beam Anlagen GmbH, Neukirchen, Germany) is used. Surface treatment is carried out using the following parameters:

- vacuum chamber volume: $2 m^3$
- accelerating voltage: 60 kV — 80 kV
- chamber pressure: 10^{-4} kPa — 10^{-5}kPa
- beam current: 5 — 25 mA
- traverse velocity: 5 — 30 mm/s
- wire diameters: 1.3 — 1.6 mm

The resulting microstructure of the electron beam modified surfaces is characterized materialographically using optical microscopy, scanning electron microscopy (LEO 1455VP) and energy dispersive X-ray microanalysis (EDISON). Additionally, the local micro hardness (HV0.05) was determined.

Wear resistance of specimens is tested by Miller abrasion test (sample dimensions: 25,4 mm × 12,7 mm; oscillation amplitude S — 200 mm; oscillation rate — 20 m/min; time — 3 × 2 h; pressure *F* — 22,24 N) as well as by adhesion pin-on-disk test (diameter of samples: 6 mm; rotating rate: 120 min^{-1}; relative velocity: 0.5 m/s; pressure: 2 MPa). Electrochemical characteristics are obtained in 0.5M- und 0.15M-NaCl solutions. Polarisation curves are measured after 1 hour immersion with potential sweep 1 mV/s. Additionally immersion test and salt fog test are carried out.

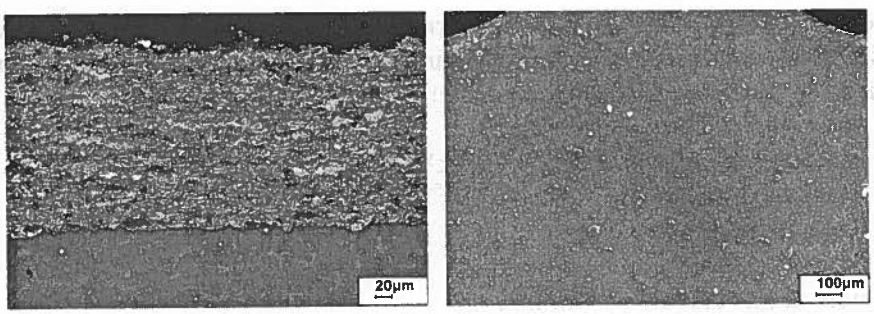
3. Results

3.1. Microstructure

Electron beam treatment of all investigated magnesium alloys under pure remelting conditions without addition of alloying elements results generally in the formation of very fine microstructure without pores and cracks with relatively flat surface. Due to grain refinement microhardness increases for all investigated alloys. Increase depends on content of aluminium in the respective alloy and is largest (50 HV0.05) for AZ91.

Attempts of surface modification using paste layers as a source of alloying / dispersing elements are generally not successful. Modified layers are very rough and element and particles distribution in these layers are not sufficiently homogeneous. It can be explained by low thermal conductivity of paste layers, which is especially important for processing in vacuum. Due to this fact overheating of magnesium alloy surfaces occurs, which leads to its fast melting and evaporation. Further investigations are carried out with thermally sprayed coatings that provide sufficient heat conductivity.

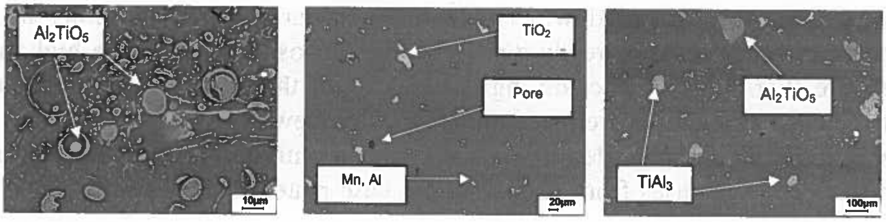
When mechanically alloyed powders are used for thermal spraying, the dimensions of oxide particles are rather small ($<3\ \mu m$). In the case of Al/Al_2O_3 coatings, depending on EB processing parameters, a uniform distribution of these particles or their dissolution in the remelted layer can be observed. For the coatings obtained by HVOF spraying of mechanically alloyed Al/TiO_2 or Al/Cr_2O_3 powders after EB remelting formation of secondary oxides uniformly distributed in modified layers is observed.



a b

Fig. 1. Microstructure of HVOF sprayed coating obtained from mechanically alloyed Al/TiO_2 powder on AZ91 substrate — a; modified layer with secondary oxides obtained after EB remelting in vacuum — b

In Fig. 1 typical microstructure of a modified surface layer that is formed by EB remelting of HVOF sprayed coating obtained from mechanically alloyed Al/TiO_2 powder on AZ91 substrate in vacuum is shown. In the case of Al/TiO_2 powder mainly secondary mixed oxide Al_2TiO_5 is formed (Fig. 2, a). Bonding of these particles to matrix material is very good. Slightly decreasing particle concentration from the surface of the alloyed layer to the base material is observed.



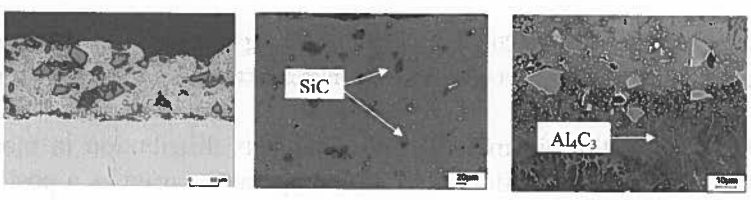
a b c

Fig. 2. Oxide particles in modified layer obtained on AZ91 substrate by EB remelting of sprayed coating; Al_2TiO_5 particles formation for HVOF coating sprayed from mechanically alloyed Al/TiO_2 powder — a; TiO_2 particles distribution for HVOF coating sprayed from mechanically mixed Al12Si/TiO_2 powder — b; $TiAl_3$ and Al_2TiO_5 particles distribution for arc sprayed coatings obtained from Al/TiO_2 cored wires — c

After remelting of HVOF coatings that were sprayed from mechanically mixed powder Al12Si/TiO_2 (50:50 vol.-%) not remelted TiO_2 particles that are uniformly distributed in surface near areas are observed. However, bonding of these particles to the matrix material is comparatively weak and dimensions of oxide particles are smaller than in initial state. Also some pores can be observed (Fig. 2, b).

In modified layers that are formed by remelting of arc sprayed coatings obtained from Al/TiO_2 cored wires (80:20 vol.-%), the formation of secondary particles is also observed (Fig. 2, b). Mainly $TiAl_3$ particles formed during spraying and a small amount of secondary mixed oxides Al.$_2$TiO$_5$ is observed in the coating.

For all investigated modified surface layers formed by EB remelting of thermal sprayed coatings obtained from carbide containing coating systems, namely VPS coatings (mechanically mixed Al/SiC powder) and arc sprayed coatings (cored wires with aluminium cover and SiC, B_4C or FTC filler) generally high roughness and poor bonding of hard particles to the matrix compared to oxide particles is observed. The most uniform distribution of carbide particles is obtained in the case of VPS Al/SiC coatings (Fig. 3). Besides this, in the alloyed areas with rather high concentration of aluminium formation of brittle Al4C3crystals can be observed (Fig. 3, c).



a b c

Fig. 3. Modified layer formed on AZ91 substrate by EB remelting of VPS coating: as-sprayed coating obtained from mechanically mixed powder Al/SiC (50:50 vol.-%) — a; SiC particles distribution — b; Al_4C_3 crystals formation — c

By arc spraying of cored wires with tungsten carbide particles filler a partial melting of carbides occurs already during coating deposition due to the high process temperature (Fig. 4, a). Further during EB melting of the coated substrate dispersion of not remelted carbides as well as formation of the new phase $Al_{12}Mg_{17}$ takes place (Fig. 4, b). Despite the high density of FTC, its concentration in the modified layer is not uniform and decreases from surface to the base material (Fig. 4, c).

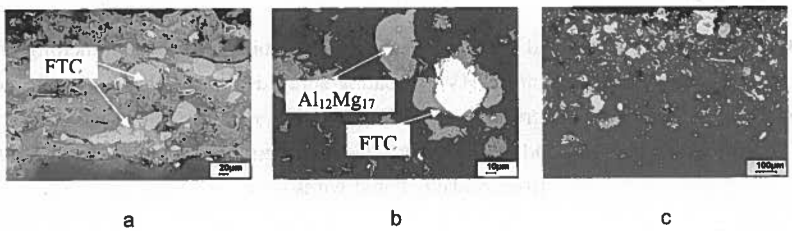


Fig. 4. Modified layer formed in AZ91 substrates by Ebremelting of arc sprayed coating: as-sprayed coating obtained from cored wire Al/FTC — a; types of hard phases — b; particles distribution — c

During alloying and reinforcement of magnesium alloys cored wires with aluminium cover and Si, $Al._2O_3$, TiO_2, SiC or FTC filler as source of additive materials are used. Due to peculiarities of heat conduction conditions the temperature of melting process is higher compared to remelting of sprayed coating. As a result thicker modified layer are obtained, but the amount of dispersed particles is much lower (Fig. 5, a).

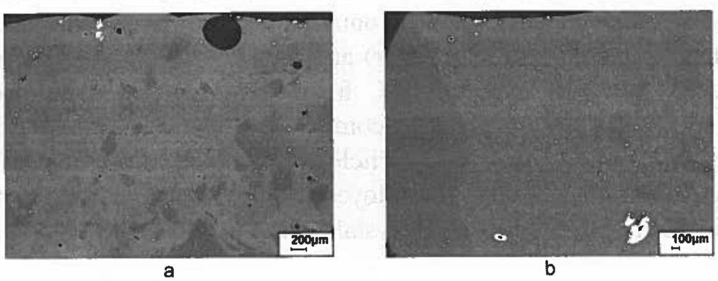


Fig. 5. Modified layer formed in AM20 substrate by EB alloying / reinforcement using cored wires with aluminium cover and TiO_2 filler, after alloying — a; microstructure after additional EB melting – - b

Moreover, due to the big melt pool the elements distribution in modified layers is rather non uniform. An additional EB remelting can be used as a post treatment to make the element distribution more homogeneous, but the amount of distributed hard particles is even more decreased (Fig. 5, b).

The most uniform modified layers in magnesium alloys were obtained during alloying with Al/Si cored wires. Monotonous decrease of microhardness from the surface to the base material can be obtained (Fig. 6).

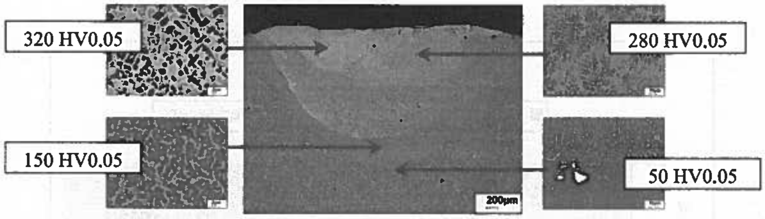


Fig. 6. Microstructure and microhardness distribution in modified layer formed on AM20 substrate by EB alloying / reinforcement using cored wires with aluminium cover and Si filler

In the case of cored wires with carbide filler the attempt to obtain modified layers with satisfactory roughness and particle distribution is not successful.

3.2. Wear resistance

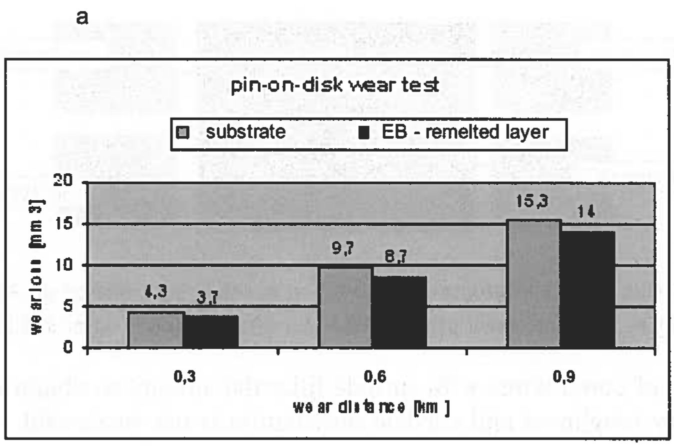
Investigations on the wear resistance by Miller abrasion test as well as by adhesion pin-on-disk test show that surface layers of magnesium alloys modified by means of electron beam alloying / dispersing exhibit higher wear resistance. The value of this increase strongly depends on the microstructure and element distribution of alloyed layers.

Generally more effective improvement of wear resistance is observed in the abrasion wear test. During the adhesion wear investigations hard particles that are dispersed in modified layer are pulled out from the layer and are acting as an additional abrasive medium that can provide an accelerated wear of both bodies. Nevertheless, even in this case increase of wear resistance of modified layers up to 25% is observed (Fig. 7, a). By oscillation wear test the improvement of wear resistance is factor 3 to 7 (Fig. 7, b). In adhesion wear test the strongest improvement of wear resistance is observed in the case of EB melting of arc sprayed coatings obtained from Al/WSC cored wires, i.e. 80% volume loss compared to pure magnesium alloy AM20 and 55% volume loss compared to pure AZ91.

3.3. Corrosion resistance

Corrosion resistance of magnesium samples after pure EB melting was characterized by means of polarisation curves measured in aerated 3% NaCl after stabilisation of the free corrosion potential, i.e. after 24 hours and 120 hours of immersion. The results of electrochemical examinations have shown that for all investigated Mg alloys after surface remelting the open-circuit potential is more positive. However, difference in comparison to as-received samples is not significant [7, 8]. Slight improvement in general corrosion resistance is observed for all alloys. The strongest effect is detected for AZ31 alloy. Pitting potential does not change significantly after remelting.

Corrosion resistance of modified by EB alloying / dispersing layers strongly depends on the chemical composition. Alloying with Al improves corrosion properties



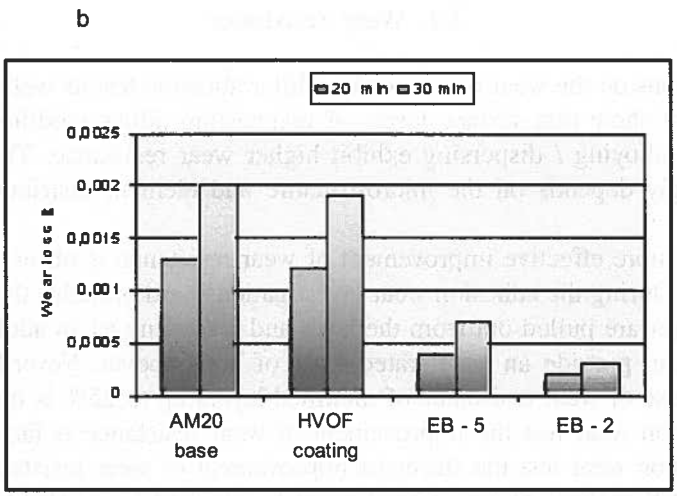


Fig. 7. Wear resistance of surface layer of magnesium alloy AM20 obtained by EB alloying / dispersing with HVOF coating Al12Si — TiO_2 (50:50): adhesion wear pin-on-disk test — a; oscillation wear test (width of electron beam track: 4 mm, overlap: 2.6 mm [EB1] and 1.5 mm [EB2]) — b

of EB modified layers. Reinforcement with oxide and secondary formed mixed oxide particles generally does not have negative influence on corrosion properties. In the case of carbide particles the influence on corrosion resistance of modified layers depends on the sort of dispersed carbides, the homogeneity of the microstructure and the presence of defects in the layer. As it was shown earlier, by reinforcement with carbide particles the morphology of remelted layers is not satisfactory, which can decrease corrosion resistance. Observations that were obtained during the immersion test and salt fog test proved these results.

The surface state has strong influence on corrosion resistance. Polished surfaces of modified layer show better corrosion resistance in the both applied tests in comparison to as processed surfaces. Oxide and mixed oxide particles have practically no influence on the process of corrosion. Worse corrosion resistance is observed for modified layers, which are obtained by EB remelting of arc sprayed coating from cored wire Al/FTC. After immersion in NaCl solution as well as after salt fog test practically the whole alloyed layer is dissolved. In contrast alloying/dispersing with cored wire Al/SiC leads to only slight decrease of corrosion resistance compared to processing with oxide particles.

4. Conclusions

For all investigated substrate materials pure EB remelting leads to formation of homogeneous layers with fine microstructure and moderately increased microhardness (10 — 30HV0.05). Corrosion properties of remelted layers are improved in comparison to base material.

Alloying of surface near layers of magnesium alloys by means of EB treatment permits formation of modified layers with homogeneous distribution or monotonically decreasing concentration of reinforcing hard phases from surface to base material.

Alloying with Al increases corrosion properties of EB modified layers. Oxide and mixed oxide particles have no negative influence on corrosion properties. Carbide particles can decrease corrosion resistance.

Addition of alloying elements, formation of new phases and proper distribution of hard particles during EB alloying / reinforcement from thermal sprayed coatings as well as dispersion from cored wires have positive influence on the wear resistance of modified layers.

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