Magnesium alloys have very interesting physical properties which make them ‘materials of the future’ for tools and machine components in many industry areas. However, very low corrosion and tribological resistance of magnesium alloys hampers the implementation of this material in the industry. One of the methods to improve the properties of magnesium alloys is the application of the solutions of surface engineering like hybrid technologies. In this paper, the authors compare the tribological and corrosion properties of two types of "MgAl_intermetallic / PVD coating" composite layers obtained by two different hybrid surface treatment technologies. In the first configuration, the "MgAl_intermetallic / PVD coating" composite layer was obtained by multisource hybrid surface treatment technology combining magnetron sputtering (MS), arc evaporation (AE) and vacuum heating methods. The second type of a composite layer was prepared using a hybrid technology combined with a diffusion treatment process in Al-powder and the electron beam evaporation (EB) method. The authors conclude, that even though the application of "MgAl_intermetallic / PVD coating" composite layers can be an effective solution to increase the abrasive wear resistance of magnesium alloys, it is not a good solution to increase its corrosion resistance.

Keywords: magnesium alloys, composite layers, electron beam evaporation

Stopy magnezu charakteryzują się bardzo interesującymi właściwościami fizycznymi które powodują że, są one określone mianem materiałów przyszłości dla narzędzi oraz elementów maszyn stosowanych w wielu obszarach gospodarki. Ze względu na bardzo niską odporność korozjonalną oraz tribologiczną występują trudności we wdrażaniu stopów magnezu do przemysłu. Jedną z metod poprawy właściwości stopów magnezu jest zastosowanie nowoczesnych rozwiązań inżynierii powierzchni. W artykule autorzy porównali trzbiologiczne oraz korozjonalne właściwości dwóch różnych konfiguracji warstw kompozytowych typu „MgAl_intermetallic / powłoka PVD” otrzymywanych dwoma różnymi metodami hybrydowej obróbki powierzchniowej. W pierwszej konfiguracji warstwa kompozytowa „MgAl_intermetallic / powłoka PVD” została otrzymana z wykorzystaniem wieloźródłowej hybrydowej technologii obróbki powierzchniowej, obejmującej połączenie rozpylania magnetronowego (MS), odparowania (AE) oraz próżniowej obróbki cieplnej. Drugi rodzaj warstwy kompozytowej został otrzymany z wykorzystaniem technologii hybrydowej łączącej proces dyfuzyjny w proszku aluminium z metodą odparowania wąską elektrownami (EB). Wykazano, że wytwarzanie warstw kompozytowych typu „MgAl_intermetallic / powłoka PVD” na stopach magnezu jest efektywim rozwiązaniem w celu zwiększenia odporności na zużycie ścieńne, jednakże nie zapewnia wymaganego zwiększenia odporności korozjonalnej tych stopów.

1. Introduction

Magnesium is the eighth root in point of the abundance on Earth, and constitutes more than 2% of the total mass of the planet. The magnesium alloys have very interesting physical properties, such as: high thermal conductivity, high dimensional stability as a function of temperature, as well as interesting functional properties, like: excellent workability and easy recycling. The listed properties mean that magnesium alloys are identified as materials of the future for many structural components in the automotive, aerospace, electronics, tool, and medical industry. An obstacle to the effective implementation of magnesium and its alloys in the above areas concerns properties negative in terms of practical use of magnesium alloys, the out of which very low corrosion and tribological wear resistance are most important. The actions indicated to be the most effective in increasing corrosion and tribological resistance of magnesium and its alloys is surface engineering [2]. The surface layer with a suitably designed structure and properties can provide an excellent barrier from the environment, significantly limiting the corrosion processes.
and greatly improving the tribological characteristics of magnesium alloys.

The various methods of the surface treatment developed for magnesium alloys have different application efficiency. The surface treatment methods of magnesium alloys, that are most commonly used in industrial conditions, are the methods of chemical and electrochemical deposition of liquid solutions [3-7], including the following:

- Cu-Ni-Cr coatings deposited to increase corrosion resistance; however, the weak resistance of this type of coatings to a highly salty environment limits their use in the automotive, aerospace and marine industry;
- Ni coatings deposited to increase corrosion resistance, wear resistance and to improve the electrical conductivity of elements used in electronics;
- Ni-Au coatings deposited to improve the reflectance and the electrical conductivity of the elements used in the aerospace industry;
- Anodic coatings, based on oxides chromate and phosphate.

Another group of methods used for the magnesium alloy surface treatment are the vapor phase deposition methods realized with the participation of plasma, belonging to CVD and PVD technology. Many different coating materials, including nitrides and carbonitrides of metals [8-10], DLC coatings [11-12], alloy coatings [13] and layers, containing diffusion layers [14] and implanted layers [15] are deposited using these methods. Among this group of materials the deserve particular attention that layers, one Al-Mg intermetallic diffusion layers [16] and the diffusion layers of metal nitrides [17] which in a case of AZ91D significantly increase its hardness and corrosion resistance. The high potential of increasing the efficiency of modification of the properties of surface layer of magnesium alloys create the hybrid surface treatment technologies combining different methods of forming the surface layer properties in one multistage technological process [18]. In papers [19-20] the authors present the treatment of AZ91D magnesium alloy consisting of two stages. In the first step a thin layer was prepared by plasma anodizing, while in the second step a hard coating of Al2O3 using a magnetron sputtering method was prepared. The treated samples were characterized by good anticorrosive properties, and enhanced tribological resistance. To improve the properties of magnesium alloys the method used for the machining of aluminum alloys, combining microarc oxidation (MAO) with the deposition of DLC coatings [21] by filtered cathode arc deposition method was also applied. The MAO/DLC “duplex” coating is characterized by better tribological properties in comparison with the single-layer of DLC or MAO coatings. The use of a MAO coating as an interlayer between the soft substrate of the magnesium alloy and the DLC coating enables the of transfer of higher loads. Moreover the DLC coating also gives a low friction coefficient. The analysis of the state of the art showed that the modern surface treatment methods can significantly improve the functional properties of magnesium alloys. The paper presents the results of research concerning the production of “MgAlintermetallic layer / PVD coating” hybrid layer using two different configurations of hybrid technology, which is a combination of the diffusion and PVD methods of surface engineering [22]. The aim of this work was to obtain the “MgAlintermetallic / PVD coating” hybrid layer that increases tribological and corrosion resistance.

2. Experimental

The AZ91D magnesium alloy (Al 8.7±9.3%, Zn 0.5±0.7%) was used as a substrate material in the form of disc shaped elements with the diameter of 25 mm and the thickness of 15 mm. The substrates were mechanically polished using sandpaper 1000, and chemically cleaned in a trichloroetylen (CHCl) ultrasonic bath. The “MgAlintermetallic / PVD coating” composite layer, was obtained with the use of two different variants of a hybrid surface treatment technology, i.e.: multisource hybrid surface treatment technology employing the diffusion process of Al from thin aluminium coating obtained on the surface for the creation of the MgAlintermetallic layer, and multistage hybrid surface treatment technologies employing the diffusion process of Al from aluminium powder for the creation of the MgAlintermetallic layer.

2.1. Multisource hybrid surface treatment technology

In variant 1 the “MgAlintermetallic / PVD coating” composite layer was obtained by multisource hybrid surface treatment technology including the three steps shown in Fig. 1. In the first step, the 6 µm pure Al coating was obtained using the magnetron sputtering (MS) method. In the second step, the 2.5 µm TiN coating was deposited by means of the arc evaporation (AE) method. In the last step, the Al/TiN complex was heated in vacuum according to the parameters T = 440°C, p = 0.7 mbar, and t = 4 h.

Fig. 1. The scheme of a multisource hybrid surface treatment technology for the deposition of “MgAlintermetallic / TiN” composite layer

The multisource hybrid technology was executed using the special vacuum device, which was designed and manufactured at the Institute for Sustainable Technologies – National Research Institute [23].

2.2. Multistage hybrid surface treatment technology

In variant 2, the “MgAlintermetallic / PVD coating” composite layer was obtained by means of the multistage hybrid surface treatment technology shown in Fig.2, which encompassed the diffusion treatment process in aluminium powder and the deposition of the Al2O3 ceramic coating by means of the electron beam evaporation method (EB).
the wear volume of the tested coatings and the wear index of the coating according to the formula: \( W_z = V / P \cdot S \), where: \( V \) – volume wear, \( P \) – load of friction pair, \( S \) – distance of the friction. The corrosion tests were executed using the potentiodynamic method on the corrosion tester PARSTAT 2263. The test electrode was the AZ91D alloy sample with the area of about 1 cm² covered by the “MgAl\textsubscript{intermetallic} / Al\textsubscript{2}O\textsubscript{3}” composite layer. The reference electrode was the Cl-Ag electrode with the electrode potential of 0.222 mV, and the assisting electrode was a platinum gauze. The research included the determination of the corrosion potential \( E_{corr} \). The investigation was carried out at a constant current in 0.5 NaCl molar solution after 1 hour stabilisation.

3. Results and discussion

3.1. Multisource hybrid surface treatment technology

The “MgAl\textsubscript{intermetallic} / TiN” composite layer obtained by multisource hybrid surface treatment technology according to the diagram shown in Fig. 1 had very many defects. For the whole sample surface characteristic “bubbles” were observed (Fig. 3a). The “MgAl\textsubscript{intermetallic} / TiN” composite layer obtained by multisource hybrid surface treatment technology according to the diagram shown in Fig. 1 had very many defects. For the whole sample surface characteristic "bubbles” were observed (Fig. 3a).

The metallographic analysis carried out in a plane perpendicular to the surface of the sample combined with the analysis of chemical composition by EDS method (Fig. 3b) showed that the cause for the formation of “bubbles” was intense diffusion of Zn in the direction of the surface. The authors showed that the content of Zn in the subsurface zone of AZ91D alloy (point 4) decreased to \(<0.5\%\). As a result of the diffusion of Zn, the delamination between MgAl\textsubscript{intermetallic} layer formed in the substrate by the diffusion of Al into the AZ91D alloy (point 3) and MgAl\textsubscript{intermetallic} layer formed in the substrate by the diffusion of Mg into the Al layer (point 2) occurred. The Zn content in the area of delamination was about \(\approx 12\%\). The replacement of the TiN coating with the CrN coating obtained by arc evaporation method and Al\textsubscript{2}O\textsubscript{3} coating obtained by electron beam evaporation method caused similar effects. As a result, the “MgAl\textsubscript{intermetallic} / TiN” composite layer again turned out to be unsuitable for further research.
3.2. Multistage hybrid surface treatment technology

The multistage hybrid surface treatment technology, whose scheme is shown in Fig. 2, enables the preparation of the cohesive, defect-free “MgAl\textsubscript{intermetallic} / Al\textsubscript{2}O\textsubscript{3}” composite layer. The results of the metallographic investigation, the chemical composition research by EDS method, and the phase structure analysis by X-ray diffraction “MgAl\textsubscript{intermetallic} / Al\textsubscript{2}O\textsubscript{3}” composite layer are shown in Fig. 4.

As a result of the diffusion process in the Al powder, a 1.5 mm thick diffusion layer composed of Mg\textsubscript{17}Al\textsubscript{12} phase dispersed in the AZ91D alloy was prepared. The hardness of the Mg\textsubscript{17}Al\textsubscript{12} phase is about 150 HV and is twice harder than the AZ91D alloy (~65 HV). The analysis employing the EDS method showed that the chemical composition of the Mg\textsubscript{17}Al\textsubscript{12} phase, i.e. ~60% Mg, ~38% Al and about 1 ~2% Zn, is similar to the chemical composition of the MgAl\textsubscript{intermetallic} phase (~56.5% Mg, ~42% Al, ~1.5% Zn) obtained by means of a multisource hybrid surface treatment technology (Fig. 3).

The Al\textsubscript{2}O\textsubscript{3} coating obtained using the electron beam evaporation method is about 25 μm thick, and its surface (Fig. 5b) reflects the surface topography of the MgAl\textsubscript{intermetallic} layer (Fig. 5a).

3.3. The results of wear resistant and corrosion properties

The tribological resistance test employing the ball-cratering method was performed only for the “MgAl\textsubscript{intermetallic} / Al\textsubscript{2}O\textsubscript{3}” composite layer obtained by multistage hybrid surface treatment technology joining the diffusion process in Al-powder and electron beam evaporation method for creation directly Mg\textsubscript{17}Al\textsubscript{12} diffusion layer and Al\textsubscript{2}O\textsubscript{3} coating. The results of tribological resistance and corrosion resistance tests on the “MgAl\textsubscript{intermetallic} / Al\textsubscript{2}O\textsubscript{3} coating” composite layer are shown in Table 1.

|                | Wear resistance Wz \[m^3/N\cdot m\] | Corrosion resistance \(E_{cor}\) [mV] |
|----------------|------------------------------------|---------------------------------------|
| AZ91D          | \(1.0 \times 10^{-12}\)            | -1500                                 |
| AZ91D + MgAl\textsubscript{intermetallic} | \(4.3 \times 10^{-13}\)            | -1320                                 |
| AZ91D + MgAl\textsubscript{intermetallic} + Al\textsubscript{2}O\textsubscript{3} | \(1.2 \times 10^{-16}\)            | -1180                                 |

The result of tribological tests indicate, that the abrasive wear resistance of the AZ91D alloy with the “MgAl\textsubscript{intermetallic} / Al\textsubscript{2}O\textsubscript{3}” composite layer increased compared to pure AZ91D alloy. Wear index Wz was reduced from the value of \(1.0 \times 10^{-12}\) \[m^3/N\cdot m\] for the AZ91D alloy to the value of \(1.2 \times 10^{-16}\) \[m^3/N\cdot m\] for AZ91D alloy with “MgAl\textsubscript{intermetallic} / Al\textsubscript{2}O\textsubscript{3}” composite layer.

At the same time, the corrosion tests carried out using the potentiodynamic method did not show any significant changes between the corrosion resistance of the AZ91D magnesium alloy and the AZ91D magnesium alloy with the “MgAl\textsubscript{intermetallic} / Al\textsubscript{2}O\textsubscript{3}” composite layer. The formation of the “MgAl\textsubscript{intermetallic} / Al\textsubscript{2}O\textsubscript{3}” composite layer on the surface of the AZ91D magnesium alloy using the multistage hybrid surface treatment technology combining the diffusion process in the Al-powder and the electron beam evaporation method increased the corrosion potential \(E_{cor}\) only by about 20%.
4. Conclusions

The authors compared the properties of two types of the “MgAl\textsubscript{intermetallic} / PVD” composite layers obtained by means of two different hybrid surface treatment technologies. The results showed, that while the prepared “MgAl\textsubscript{intermetallic} / PVD coating” composite layers in magnesium alloys can be an effective solution to increase the abrasive wear resistance of magnesium alloys, it does not improve its corrosion resistance. The correct configuration of each stages of the hybrid surface treatment technology is very important. There are many different technological aspects which guarantee good cohesion between intermetallic layer and PVD coating.

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