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Microstructure and corrosion resistance of magnesium alloys with galvanic coatings

Andrzej Kielbus[a*], Grzegorz Moskal[b], Roland Cibis[c]

[a] *Silesian University of Technology, 40-019 Katowice, Poland*
[b] *Silesian University of Technology, 40-019 Katowice, Poland*
[c] *NTP S.A.., 47-225 Kedzierzyn-Kozle, Poland*

Abstract

The article presents the technology of obtaining the galvanic coatings on the ready structural elements made of Mg-Al magnesium alloys. The technology was developed in NTP CIBIS Ltd in cooperation with the Silesian University of Technology. The influence of the mechanical surface preparation and deposition on the basis of sulfamate nickel and copper plating on the layer quality and corrosion resistance were described. The final galvanic layer with a new type of intermediate sulfamate nickel layer is characterized by high uniformity irrespective of an observation location. Corrosion resistance of the elements with the coatings deposited on the surfaces vibro-abrasively machined is much higher than that of the coatings deposited on the surfaces ground and polished.

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Keywords: magnesium alloys; galvanic coatings, corrosion resistance, microstructure;

1. Introduction

Magnesium alloys are presently used in a wide range of structural applications such as automotive, aerospace and other industries. These alloys are characterised by low density and good mechanical properties [1,2], however they also showed some disadvantages. One of the disadvantage of these alloys is their poor corrosion and wear resistance [3,4]. There are many types of coatings used for magnesium alloys, and each of them has advantages and disadvantages [5,6]. Among them there are: conversion, hydride, deposited from gas phase and galvanic coatings. One of the most economical and simple methods is electrochemical deposition of metals on the substrate surface. This process can be divided into two types: galvanic electroplating or electroless plating. In both cases, salts of the deposited metal present in the solution are reduced to metallic form on the treated element surface. In the case of galvanic process, electrons necessary for reduction phenomenon are provided from an external source. In the

* Corresponding author. Tel.: +48-32-603-4407, fax: +48-32-603-4400.
E-mail address: andrzej.kielbus@polsl.pl.

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electroless process, the reduction process is carried out as a result of chemical reactions [7, 8]. The article presents the influence of casting surface preparation and type of intermediate galvanic layer on the quality and corrosion resistance of structural elements made of AZ91D magnesium alloy. The galvanic technology was developed in NTP CIBIS Ltd in cooperation with the Silesian University of Technology. The basic issues of the developed technology were described, especially taking into consideration the mechanical surface preparation and deposition of base layers on the basis of chemical nickel, sulfamate nickel and copper plating.

2. Material and methodology

2.1. Material

Processes of galvanic deposition was carried out on the die-casting structural elements made of AZ91 magnesium alloy. The chemical composition of the alloy is given in Table 1.

Table 1. The chemical composition of the die casting AZ91D magnesium alloy (in wt.%)

Al	Zn	Mn	Si	Cu	Ni	Fe	Mg
8.78	0.71	0.17	0.01	<0.001	<0.001	<0.001	balance

2.2. Methodology

The experiment was carried out on the industrial galvanic line in NTP CIBIS Ltd in Kedzierzyn-Kozle. The process operation details are given in Table 2.

Table 2. The sequence of operation

Stage	Process	Operation/condition
1	surface preparation	grounding or polishing or vibro- abrasive machining
2	chemical degreasing	10 min
3	activation	40°C, preliminary activation 1 min. , final activation 10 min.
4	etching	40°C, preliminary etching 2.5-4 min., final etching 2-3 min.
5	chemical nickel-plating	75°C-80°C
6	copper or sulfamate nickel plating	15 min. / 40A
7	decorative – chemical nickel	40-45 min
8	satin	- chemical nickel 120 min - chemical chromium 125 min.

The macroscopic analysis was carried out by using the Nikon Coolpix 990 digital camera. The analysis of surface geometric features was presented by using the MicroProf optic non-contact profilograph manufactured by FRT. For the microstructure observation, an OLYMPUS GX71 metallographic microscope and a HITACHI S-3400N scanning electron microscope were used. Salt spray exposure of was carried out in 5 wt.% NaCl solution according to ASTMB117 standard.

3. Results

3.1. Surface roughness

The plating process of the elements made of magnesium alloys according to the technological instruction does not always ensure that a coating of satisfactory quality is obtained. The use of mechanical cleaning, grinding, chemical cleaning, etching and activation is insufficient. The similar results could be noticed after manual polishing of the surface. In the technology processed in NTP company, the effectiveness of vibro-abrasive machining as the basic method for preparation of cast surfaces before plating process was used and verified. To verify the obtained results, the tests determining an influence of individual processes on the quality of the obtained coatings were performed. The main variable was the surface preparation method i.e. condition after casting, grinding, polishing and vibro-abrasive machining. The tests showed that the surface condition directly after casting is not suitable for galvanic plating. It is a result of pores and contamination having negative influence on the properties of galvanic coatings connected mainly with adhesion reduction. The tests performed on the polished casts also showed a low suitability of that type of initial machining for plating the magnesium alloys. After process, number of surface defects and contamination on the surface of the polished elements were noticed. The third type of machining involving grinding the cast surfaces, regarding quality of galvanic coatings, was better than previously discussed ones. However, it also showed essential defects. They resulted mainly from the process unrepeatability and possible removal of the skin layer, which uncovered internal porosity of casts.

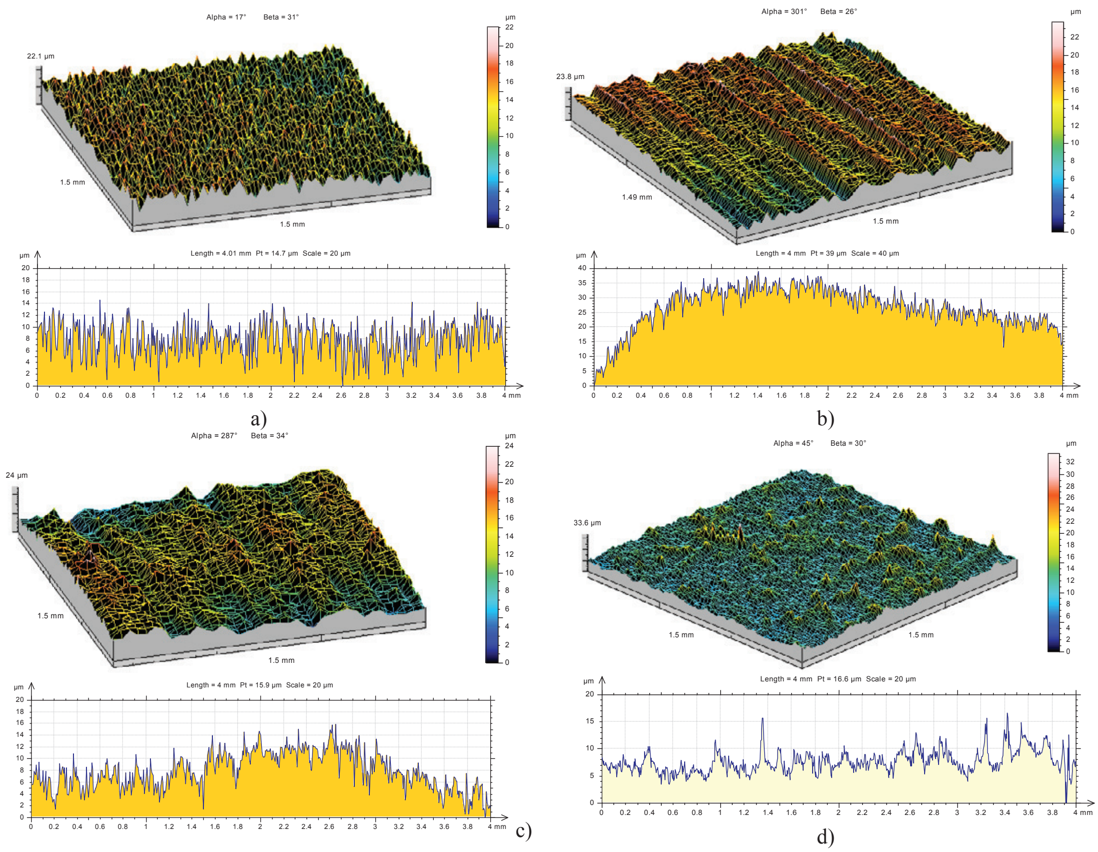


Fig. 1. The 3D surface topography and 2D surface profile of the tested surface after: (a) casting, (b) grinding, (c) polishing, (d) vibro-abrasive machining.

Moreover, lack of adhesion resulting from presence of technological contamination was noticed. The last suggested method of surface preparation is vibro-abrasive machining. The tests of surface quality and quality of the deposited protective coatings showed the significant advantage of this type of initial machining over the previously discussed ones. This advantage involved, among other things, maintaining the skin layer, removal of surface defects and reduction of contamination quantity of technological origin. A type, size of used shaped pieces and time of the used machining are to be optimized. The surface layer test results of the elements made of magnesium alloys after different preparation types are listed in Fig. 1. After vibro-abrasive machining the surface has the smallest roughness in the comparison with remaining tree types of surface preparation (Table 3).

Table 3. The influence of the surface preparation method on surface roughness

Surface preparation	R_a [µm]	R_m [µm]	S_k
after casting	2.01	13.3	0.25
after grinding	1.81	12.74	0.33
after polishing	1.32	10.11	0.04
after vibro-abrasive machining	1.23	9.88	10.41

The analysis of surface preparation condition before chemical nickel plating process showed obvious differences connected with basic quantitative parameters determining the top surface roughness and its topography resulting from the use of different surface preparation types. It was shown that the highest smoothness is obtained by using the polishing. However, those results must also include quality observations of a surface condition and presence of under surface defects. From the above point of view, the most suitable method is the vibro-abrasive machining making it possible to obtain a surface free from contamination and not causing uncontrolled removal of the skin layer. Moreover, this method allows one to mechanically „close" cracks and defects, which facilitates adhesion of the layers deposited in the later stages. It is especially useful in the case of elements with complicated shapes.

3.2. Microstructure of typical layer

The morphology of the cross-section of typical galvanic layer on the AZ91D magnesium alloy, detected by SEM was shown in Fig. 2. This multi-layer has cooper intermediate layer between the nickel base layer and the chromium outer layer.

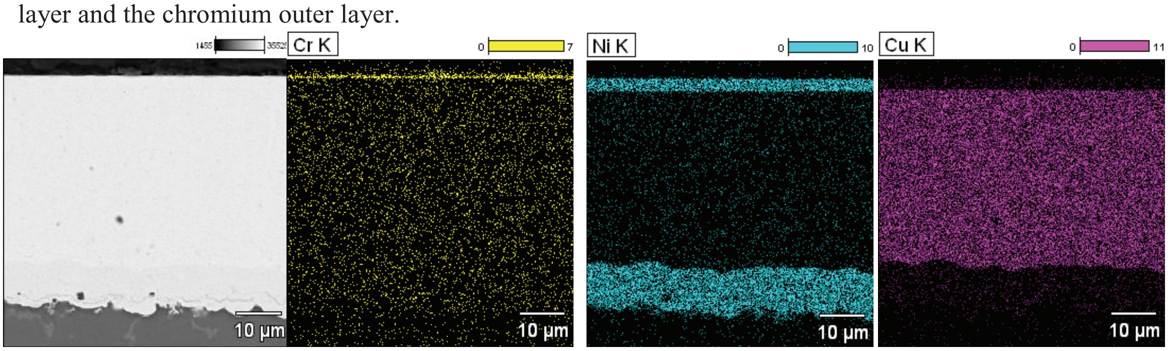
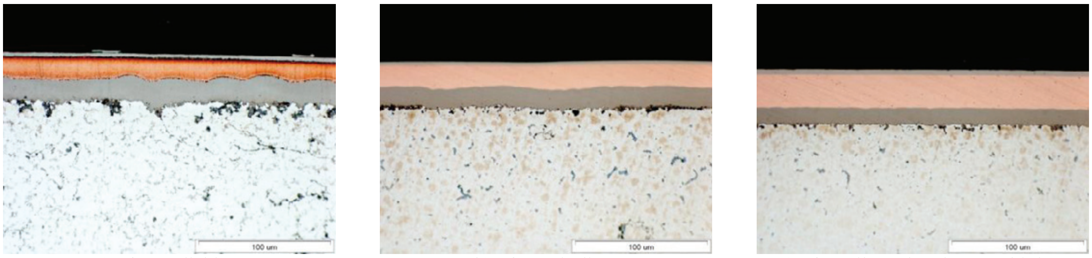


Fig. 2. SEM image and surface distribution of elements within the typical galvanic layer.

3.3. Microstructure of typical layer after different surface preparation

The microstructural analysis showed correct structure and quality of the obtained galvanic coatings in all the tested cases (Fig. 3). However, in the case of the layer deposited on the polished surface, number of cracks and casting defects can be noticed (Fig. 3a). It is result of the mechanical jamming of the chemical nickel layer to the substrate and adhesion improvement. Such results were not noticed in other cases (Fig.3b and c).



a) after polishing b) after grinding c) after vibro-abrasive machining

Fig. 3. Microstructure of typical galvanic layer after different surface preparation.

3.4. Corrosion resistance of typical layer after different surface preparation

The tests in the salt chamber confirmed the results of the previous tests. It was shown that the use of vibro-abrasive machining is the most effective surface preparation method. Corrosion resistance of the elements with the coatings deposited on the surfaces vibro-abrasively machined is much higher than that of the coatings deposited on the surfaces ground and polished. It is a result of minimizing the influence of casting defects and reducing the number of potential penetration areas of salt mist (Fig. 4). In spite of the obviously better results for vibro-abrasive machining, the galvanic coatings on the magnesium alloys have not met acceptance criteria connected with corrosion resistance in the salt mist yet.

a) after polishing b) after grinding c) after vibro-abrasive machining

Fig. 4. View of the elements made of magnesium alloys with galvanic coating after tests in the salt chamber for 48h.

3.5. Microstructure of galvanic layer with sulfamate nickel intermediate layer

In the standard process, copper plating process is used. However, the tests of corrosion resistance in the salt chamber showed that copper plating had negative influence on the lifetime of galvanic layers in those

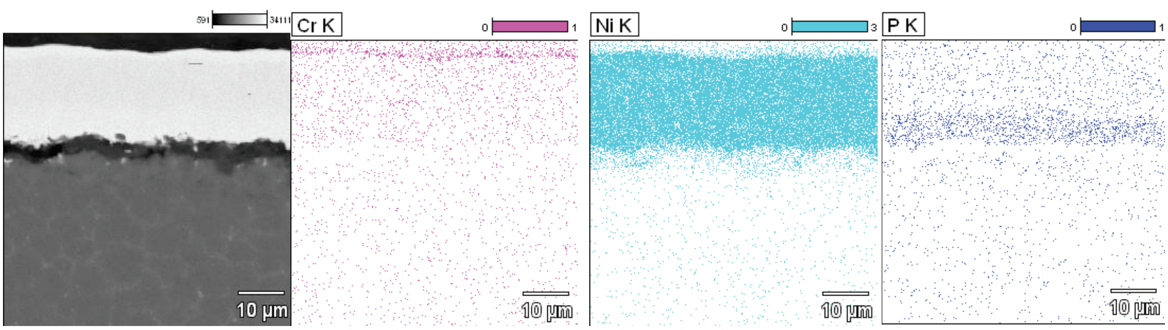


Fig. 5. SEM image and surface distribution of elements within the sulfamate nickel layer.

conditions. Therefore, the use of sulfamate nickel as an intermediate layer was suggested. The coating with the sulfamate nickel layer was uniform with regard to geometric parameters over the whole surface analysed. Analysis of the distribution of elements within the layer area showed also the distinct interface between individual zones of the galvanic layer. The base layer is characterized by presence of phosphorus, while the outer layer by presence of chrome, which was presented in Fig. 5.

4. Conclusions

The tests, carried out at the individual stages of industrial technological process, showed that the essential problem in obtaining the galvanic coatings of satisfactory quality on the elements made of magnesium alloys lies not only in the correct surface preparation, which is a well known phenomenon, but also in the processes of later copper plating. The acid copper plating process, following the chemical nickel plating, is very aggressive, which consequently leads to occurrence of pits in the base layer, in particular in the element hollows such as holes and threads. As a result of loss of the base layer continuity, the sudden deterioration of corrosion resistance occurs in the salt chamber. The modification of galvanic plating technology, in the form of using the vibro-abrasive machining and replacing the copper plating process with sulfamate nickel plating, allowed one to obtain the galvanic plating of chemical nickel/ sulfamate nickel/ decorative nickel type of the required quality and meeting the acceptance criterion connected with corrosion resistance in the salt mist. This type of coatings can be used when it is necessary to meet the requirements connected with the tests in the salt chamber. In the case of the elements which the above requirements are not applied to, the use of only vibro-abrasive machining is sufficient.

Acknowledgements

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