ELECTROCHEMICAL CHARACTERISTICS OF SHOT-PEENED AND PHOSPHATIZED AE21 MAGNESIUM ALLOY

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Abstract

Paper deals with the evaluation of surface treatment of Mg-2Al-1RE magnesium alloy on its electrochemical behaviour in 0.1M NaCl solution. The surfaces of the magnesium alloy specimens were treated mechanically by grinding and shot-peening using glass-balls blasting tools and electrochemically using zinc-phosphating. The surfaces after grinding, grinding + phosphating and grinding + shot-peening + phosphating were evaluated using electrochemical impedance spectroscopy method in combination with immersion tests up to 168 hours of exposition. The measured impedance spectra (as Nyquist plots) were analysed using various equivalent circuits. It was observed that shot-peening pre-treatment increases the corrosion resistance of phosphate surface in comparison with only grinded and phosphate surface.

1 Introduction

Magnesium alloys exhibit many desirable properties including low density and high strength/weight ratio, high thermal conductivity, very good electromagnetic features and being easily recycled. These properties make it valuable in a number of industrial fields including automobile, aerospace components, mobile phones and sporting goods. However, magnesium and its alloys are characterized by poor corrosion and low wear resistance, which limits their use [1-5]; their very low electrode potential easily leads to even reactivation in the atmosphere. Unfortunately, the natural oxide layer on magnesium surfaces is very loose and does not offer an effective resistance to corrosion. Therefore, it is very important to improve the anti-corrosion performances of magnesium alloys in industrial applications [3].

Shot-peening is one of the most important surface treatment and/or pre-treatment. This technology is mechanical type of a basic material surface treatment. Shot-peening medium causes elastic plastic deformation of surface layer after its impact on a treated material. As a result, domain refinement, and microstrain, etc., are introduced to the deformation layer. Typical application of shot-peening is pre-treatment of the surfaces before deposition of organic or inorganic coatings. Other applications are creation of suitable morphology of the surface, surface hardening, increasing of fatigue strength and stress corrosion resistance, etc. [6, 7]. In shot peening, air is used as the propelling media in air-blast system. As the most efficient air-blast system, direct pressure system produces the highest shot velocity among all the methods. The shot velocity depends on the air pressure and the diameter of the nozzle. The shot peening media

is considered as the tool of shot peening process. Its shape and material have direct impact on the final quality of the process. Most peening is done with cast steel shot. Cut wire conditioned to round balls is used for some very critical applications. Glass beads are used for some peening applications where the sections are thin or where steel shot would leave iron contamination on the part. The fatigue strength is higher after shot peening with glass balls than after electropolishing [8-10].

An effective way to prevent corrosion of magnesium alloys is to coat the substrate materials. Surface treatments, such as the formation of conversion coatings, are commonly applied to magnesium alloys in order to increase the corrosion resistance [11].

Chromate conversion coatings have been extensively used to prevent the magnesium alloys from corrosion, and provide a greater adhesion of organic coating on the magnesium alloy surface. However, chromate coatings including Cr^{+6} ions (hexavalent chromium) produce toxic and carcinogenic materials [12, 13]. Phosphate coatings due to theirs lower toxicity and theirs appropriate properties have been used as one of the suitable alternative instead of chromate coatings. It has been understood that using zinc phosphate coating both the coating resistance against corrosion and the coating adhesion to metal surface can be superiorly improved. Moreover, less toxic materials as well as less bath sludge can be produced using this kind of conversion coating compared to the chromate one. However, due to the high electrochemical activity of the magnesium the control of phosphate coating creation process over the magnesium alloy seems to be complex. The corrosion resistance of the phosphated magnesium increased at high temperatures [12]. Phosphating conversion films of the magnesium alloy were widely used to the base film of paint for ensuring good contact between the paint film and the magnesium alloy substrate [14, 15].

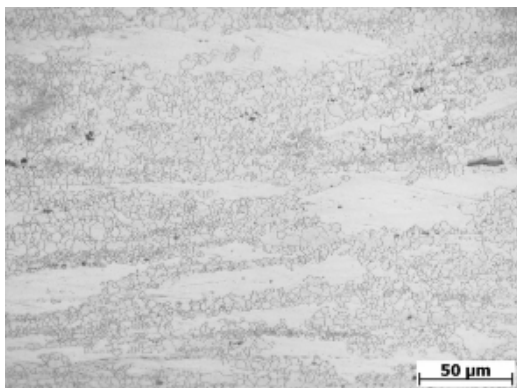## 2   Material and Experimental Methods
2.1   Experimental material

An AE21 magnesium alloy with chemical composition in **Table 1** was used as experimental material. The alloys was gravity casted in Z-F-W GmbH Clausthal-Zellerfeld and then extruded at University of Technology in Clausthal using direct extrusion at 350°C with extrusion ratio of 19. The microstructure of extruded AE21 alloy is in **Fig. 1**. Microstructure is created by polyedric grains of solid solution of alloying elements (mainly aluminium and rare earths) in magnesium and by particles od Al_4RE and/or $Al_{11}RE_3$ [16-18]. The microstructure is bimodal with the areas of fine-grains with average dimension of 14 µm and non-recrystallized areas with grain size of about 120 µm.

Table 1   Chemical composition of tested AE21 magnesium alloy

Chemical element	Al	RE	Mn	Si	Cu	Fe	Mg
Composition [wt.%]	1.83	0.83	0.40	0.02	<0.01	< 0.01	balance

The shot-peening of the materials surfaces was realized at Faculty of Mechanical Engineering Technical University in Košice using air-blasting machine. Glass-balls were used as shot-peening tool, blasting pressure was 6 MPa and the output velocity of balls was 70 m.s^{-1}. Surfaces after shot-peening were phosphatized using the method of zinc-phosphate. The surfaces after grinding and grinding+shot-peening were rinsed in distilled water at 22°C followed by pickling in 75 % H_3PO_4 at 22°C during 30 s. After second water rinsing the phosphating treatments were

carried out at about 45±2°C for 10 min. The phosphating bath was composed of Na_2HPO_4(20g.dm^{-3}) + H_3PO_4(7.4 ml.dm^{-3}) + $NaNO_2$(3 g.dm^{-3}) + $NaNO_3$(1.84 g.dm^{-3}) + $Zn(NO_3)2$(5 g.dm^{-3}) + NaF(1 g.dm^{-3}) [18-20].

Fig.1 Microstructure of AE21 magnesium alloy – longitudinal section, light microscopy, etch.: Picric acid + acetic acid + ethylalcohol + distilled water

2.2 Experimental methods

We used combination of immersion tests and electrochemical impedance spectroscopy (EIS) tests for determination of polarization resistances of the tested surfaces after grinding+phosphatizing and grinding+shot-peening+phosphatizing. The surfaces were evaluated in 0.1M NaCl solution at 22±1°C after various time of immersion (5 min – 168 hours). After each time of immersion, the EIS tests were performed using VSP measuring system (producer Bio-Logic SAS France). The scheme of circuit connection and measuring principle is described in detail elsewhere [21]. Frequency range of measurements was from 100 kHz to 50 mHz with frequency changing of 10 times per decade. Amplitude of AC voltage was 20 mV and measured area was 1 cm^2.

3   Experimental results and discussion

The EIS measurements after various immersion times resulting in Nyquist plots of each evaluated surfaces in tested solution. The Nyquist plots of AE21 alloy with grinded, grinded + phosphatized and grinded + glass-balls shot-peened + phosphatized surfaces are in **Fig. 2**, **Fig. 3** and **Fig. 4**, respectively. The plots measured on non-phosphatized surface after immersion less than 96 minutes are created by one well-defined capacitive loop at high and medium frequencies followed by inductive loop (-Z_i<0) in low frequency range. When the die cast or also extruded specimens are immersed into 0.1 M NaCl solutions, the anodic reactions occur on the surfaces:

$$Mg \rightarrow Mg^+ + e^- \tag{1}$$

and

$$Mg + 2H_2O \rightarrow Mg^{2+} + 2OH^- + H_2 \tag{2}$$

Mg^+ is a metastable ion and is easily oxidized to Mg^{2+} ion. The cathodicreaction occurs

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{3}$$

and finally the corrosion products are formed as a layer with relatively low porosity according to reaction [20, 21]

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2 \tag{4}$$

$Mg(OH)_2$ film on the surface of the alloy particles consumes active material, affects the charge-transfer across the alloy/electrolyte interface and may act as a barrier for hydrogen diffusion in and out of the alloy. These two mechanisms (diffusion of active parts and charge transfer) resulted in one loop in the Nyquist plots. It is too difficult to separate of each mechanism because of relatively low thickness of corrosion product film. The inductive loop may be due to the existence of relaxation processes of adsorbed species on the electrode (Mg alloy) surface [24]. After 96 and 168 hours of immersion, the complex corrosion products on hydroxide and/or oxide and/or chloride of magnesium are created on the surfaces (EDX analyses are presented in [18]). These products have relatively high porosity and two different areas are created on the surface. It resulted in two well-defined capacitive loops. The high-frequency capacitive loop is connected to diffusion processes of active parts through the pores in the layer of corrosion products. The medium-frequency capacitive loop is characterized by charge transfer at the bottom of the pores. On the basic of these facts, we used the equivalent circuits in Fig. 5a and Fig. 5b for analyses of Nyquist plots with one capacitive loop and with two capacitive loops, respectively. The constant phase elements (CPE) were used in the equivalent circuits. Use of this element is described in [25, 26]. The results of the analyses are in Table 2. Total polarization resistance as the sum of partial resistances (R_{p1} and R_{p2}) is increased with the increase of immersion time up to 24 hours. It is due to increasing of the thickness of $Mg(OH)_2$ film and formation rate of this film decreases with increasing of its thickness. Therefore R_p is not increasing uniformly with immersion time (moreover scattering of measured data influences uniformity of R_p increasing). The corrosion products achieved the critical weight after 24 hours and therefore they dropped out and the active surface is uncovered for aggressive media of 0.1M NaCl. Hence the polarization resistance is decreased and the value of total polarization resistance after more than 96 hours of immersion shows that surface is totally degraded.
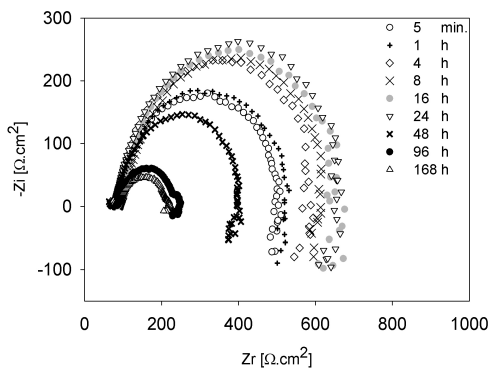
Fig.2 Nyquist plots of grinded surface of AE21 Mg alloy in 0.1M NaCl after various immersion times
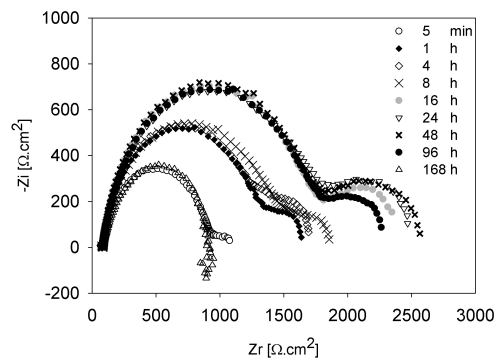
Fig.3 Nyquist plots of grinded and phosphatized surface of AE21 Mg alloy in 0.1M NaCl after various immersion times
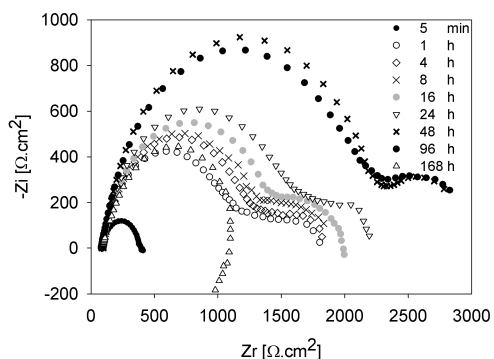
Fig.4 Nyquist plots of grinded, glass-balls shot-peened and phosphatized surface of AE21 Mg alloy in 0.1M NaCl after various immersion times

Different situation is in the case of phosphatized surfaces. The layer of the corrosion products on the surface is more complex. Magnesium ions (Mg^{2+}) are used for formation of hydroxide layer (equation 4) and moreover for formation of phosphate layer according to equation (the full process of magnesium – zinc phosphate layer formation is described elsewhere [27]:

$$3Mg + 3Zn^{2+} + 4H_2PO_4^- + 4\ H_2O \rightarrow Zn_3(PO_4)_2 \cdot 4H_2O + 3H_2 + Mg_3(PO_4)_2 + 2H^+ \qquad (5)$$
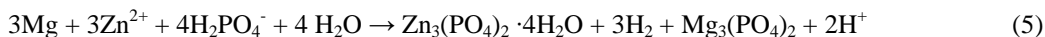
The Nyquist plots are mainly created by two well-defined capacitive loops (except 5 min of phosphatized surface after shot peening and 168 hours in both cases). The phosphatized layer was formed on the surface and the diffusion processes through this layer is characterized by medium-frequency capacitive loop. The high-frequency capacitive loop is due to charge transfer of the corrosion reaction. The corrosion processes during 168 hours of exposition cause the surface damage and it is too difficult to identify the boundary between both processes (diffusion and charge transfer). It resulted in one capacitive loop Nyquist diagram. The equivalent circuit in Fig.5c was used for the analyses of plots with two capacitive loops and equivalent circuit in Fig. 5a was used for one capacitive loop plots. Results of the analyses of phosphatized surfaces are in Tab. 3 and Tab. 4 for grinded and grinded + shot-peened surfaces, respectively. The phosphated surface, immediately after phosphating process, is porous and its porosity depends on the quality of pre-treated surface. The shot-peened surface is rougher and the pores are wider and deeper than in the case of grinded surface [18]. On the other hand the thickness of the phosphate layer on the shot-peened surface (7.6 µm) is about 60% higher than on the grinded surface (4.7 µm). It is due to more reactive shot-peened surface during phosphating process. Because of wider pores the polarization resistance of phosphatized shot-peened surface after 5 minutes is lower. The total polarization resistances of both phosphatized surfaces increase with increasing of immersion time, the clogging of the pores occurred in the layer and total polarization resistance increases up to 48 hours of immersion. In comparison of polarization resistance of only grinded surface after 24 hours, the polarization resistance of grinded + phosphatized and grinded + shot-peened + phosphatized surface is about 4 times and 6 times higher, respectively. The higher polarization resistance value of shot-peened surface is associated with higher thickness of phosphate layer and therefore more complex conditions for corrosion processes (diffusion and charge transfer). The polarization resistances are decreased only slightly after 96 hours of immersion and after this time, the mixed corrosion products (phosphate + oxide + hydroxide +

chloride of magnesium – results of the EDX analyses are presented in [18]) achieved the critical weight and the parts of products dropped out from the surface. Then the degradation of the surface started and polarization resistance decreased to 2.5 times in both phosphatized surfaces.
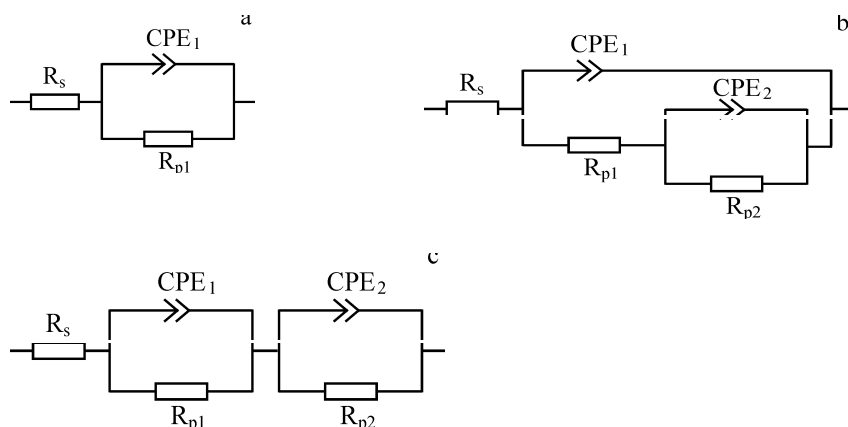
Fig.5 Equivalent circuits for analyses of Nyquist plots

Table 2 Electrochemical characteristics of grinded surface of AE21 Mg alloy

Immersion time	R_s [$\Omega.cm^2$]	CPE_1 [$10^{-6}.Fs^{n-1}$]	n_1	Rp_1 [$\Omega.cm^2$]	CPE_2 [$10^{-3}.Fs^{n-1}$]	n_2	Rp_2 [$\Omega.cm^2$]
5 min	82.4	24.0	0.88	430.2	–	–	–
1 h	84.7	45.6	0.89	447.6	–	–	–
4 h	84.9	70.3	0.91	515.4	–	–	–
8 h	84.9	72.7	0.93	571.8	–	–	–
16 h	90.3	93.6	0.91	570.6	–	–	–
24 h	79.7	95.6	0.88	611.9	–	–	–
48 h	76.5	92.5	0.87	339.1	–	–	–
96 h	86.4	91.3	0.85	151.6	17.3	1	11.9
168 h	92.9	87.0	0.84	113.2	64.6	1	7.1

Table 3 Electrochemical characteristics of grinded and phosphatized surface of AE21 Mg alloy

Immersion time	R_s [$\Omega.cm^2$]	CPE_1 [$10^{-6}.Fs^{n-1}$]	n_1	Rp_1 [$\Omega.cm^2$]	CPE_2 [$10^{-3}.Fs^{n-1}$]	n_2	Rp_2 [$\Omega.cm^2$]
5 min	80.9	24.8	0.92	789	4.6	0.52	183.8
1 h	85.3	38.2	0.88	1228	4.4	0.86	304.7
4 h	80.4	30.2	0.89	1239	2.9	0.90	421.6
8 h	85.3	27.7	0.88	1345	2.7	1	431.9
16 h	81.8	20.1	0.90	1606	3.0	0.66	589.7
24 h	82.8	27.5	0.87	1625	2.3	0.75	739.1
48 h	82.4	20.8	0.89	1737	2.9	0.80	681.3
96 h	83.6	27.4	0.87	1632	3.3	0.62	530.7
168 h	85.6	76.8	0.86	866	-	-	-

Table 4 Electrochemical characteristics of grinded, shot-peened and phosphatized surface of AE21 Mg alloy

Immersion time	R_s [$\Omega.cm^2$]	CPE_1 [$10^{-6}.Fs^{n-1}$]	n_1	Rp_1 [$\Omega.cm^2$]	CPE_2 [$10^{-3}.Fs^{n-1}$]	n_2	Rp_2 [$\Omega.cm^2$]
5 min	86.8	37.6	0.86	298	3.8	1	6.4
1 h	84.1	53.0	0.84	1082	3.7	1	451.4
4 h	88.3	42.6	0.84	1332	4.5	0.91	388.3
8 h	92.2	34.0	0.84	1420	3.6	0.92	449.3
16 h	84.6	32.7	0.86	1523	2.9	0.94	487.4
24 h	82.9	31.6	0.88	1695	1.9	0.94	639.7
48 h	83.2	23.2	0.85	2348	7.3	0.92	597.2
96 h	81.8	34.3	0.84	2293	5.1	0.92	592.4
168 h	91.4	82.9	0.82	1120	-	-	-

4   Conclusions

The electrochemical characteristics of AE21 magnesium alloy in 0.1M NaCl after various surface treating were investigated. The following conclusions can be drawn:

- The surface after zinc-phosphating treatment resists against the corrosion 3 times longer that only grinded surface. The maximum polarization resistance of grinded surface was achieved after 24 hours of immersion while maximum polarization resistances of both phosphatized surfaces were observed up to 96 hours of immersion.
- Polarization resistance increased after zinc phosphating treatment. The value of total polarization resistance of grinded and phosphatized surface (2481 $\Omega.cm^2$) increased 4 times against to maximum polarization resistance of only grinded surface (612 $\Omega.cm^2$).
- Shot-peening treatment followed by phosphatizing treatment causes additional increase of the polarization resistance and the value of shot-peened and phosphatized surface (2945 $\Omega.cm^2$) is 6 times higher in comparison with only grinded surface.

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