INFLUENCE OF PHOSPHATIZED SURFACE LAYER ON CORROSION RESISTANCE OF Mg-Al-RE ALLOY

Katarína Miková[1], Filip Pastorek[1], Libor Trško[1,*], Sylvia Dundeková[1]

[1] Research Centre of the University of Žilina, University of Žilina, Univerzitná 8215/1, 010 26 Žilina, Slovak Republic

*corresponding author: e-mail: libor.trsko@rc.uniza.sk

Resume

This contribution deals with evaluation of the corrosion resistance of extruded Mg-2Al-1RE (AE21) magnesium alloy in the state before and after treatment of ground surface by selected phosphatizing procedure. Specimens were exposed to 0.1M NaCl solution for several time periods starting from 5 minutes up-to 168 hours at room temperature of 22 ± 1 °C. Afterwards electrochemical impedance spectroscopy was carried out on the exposed specimens. Based on the results obtained from the electrochemical tests and visual observation of corrosion attack progress, positive or negative impact of selected phosphating process on the corrosion resistance of Mg-2Al-1RE magnesium alloy under given conditions was assessed.

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1. Introduction

With aim to reduce of manufacturing costs and increasing the operation safety and reliability in various industrial fields, mainly in electrical engineering and communication technology, automotive and aeronautic industry, developers are forced to search for new materials with sufficient mechanical properties, but lower specific weight. Magnesium and its alloys which belong to the group of lightest structural materials and due to their excellent weight/strength ratio are very attractive to use for structural parts in automotive and aeronautic industry. Mainly the ecological aspects of Mg alloys are the reason why significant research is focused on their application in industry. However, besides low plastic deformation abilities, the main reason why application of Mg alloys is strongly limited is their low corrosion resistance. One of the reasons of the low corrosion resistance of Mg is its low value of standard potential (-2.36 V) which makes it very reactive with surrounding environment. Nowadays, enormous effort is made with aim to develop new magnesium alloys with higher corrosion resistance and for optimization of the manufacturing process to make these alloys an equal structural material to other commercially used alloys [1 - 6].

Creation of special surface layers on magnesium alloys is considered as the easiest, cheapest and in many cases as the most effective method to prevent their corrosion [7]. Many methods were developed with aim to create the special layer for corrosion protection and one of them, which is considered in this study, is to create a special conversion layer and consequently grow a phosphate layer (phosphatization), which covers the conversion layer and increases the corrosion resistance.

2. Experimental material and methods

As experimental material was used AE21 magnesium alloy which belongs into

Mg-Al-RE group (alloyed by aluminium and rare earth elements). The chemical composition according to ASTM standard is given in Table 1. The material was manufactured at the Technical University Clausthal in Germany [8]. Casted semi-product in shape of a bar with 70 mm in diameter was consequently extruded at temperature of 350 °C to the shape of bars with 12 mm in diameter [9]. Material after extrusion was marked as AE21 EX.

After standard preparation of metallographic specimens, the microstructure was revealed by etching in solution consisting of 2.5 ml of acetic acid + 2.1 g of picric acid + 5 ml of H_2O + 35 ml of ethanol. The microstructure of the AE21 EX was studied with use of optical metallography microscope Zeiss AXIO Imager (the research was supported by European regional development fund and Slovak state budget by the project ITMS 26220220121). According to Fig. 1a, the microstructure is created by polyhedral grains of solid solution of Al, Mn and RE in magnesium. Quite rarely are in the microstructure present Al_4RE intermetallic

phases (Fig. 1b) [11, 12].

Before the phosphatization process, specimens were ground, rinsed with demineralised water and dried by a stream of hot air. The second step was creation of conversion layer by pickling for 30 seconds in 75 % H_3PO_4 and rinsing by demineralised water. Afterwards was carried out the phosphatizing process in solution with pH = 3 ± 0.2 consisting of: Na_2HPO_4 (20 $g \cdot l^{-1}$) + H_3PO_4 (7.4 ml) + $NaNO_2$ (3 $g \cdot l^{-1}$) + $NaNO_3$ (1.84 $g \cdot l^1$) + $Zn(NO_3)_2$ (5 $g \cdot l^1$) + NaF (1 $g \cdot l^{-1}$). The process lasted for 10 min at temperature of 45 ± 2 °C [13, 14]. During the phosphatizing process, the specimen was rotating at frequency of 350 min^{-1}.

To evaluate the corrosion resistance of AE21 EX before and after phosphatization electrochemical impedance spectroscopy (EIS) was used. The specimen was submerged in electrolyte (0.1M solution of NaCl) at laboratory temperature and after defined exposure time the EIS measurement was carried out.

Table 1

Chemical composition of AE21 according to ASTM standard.

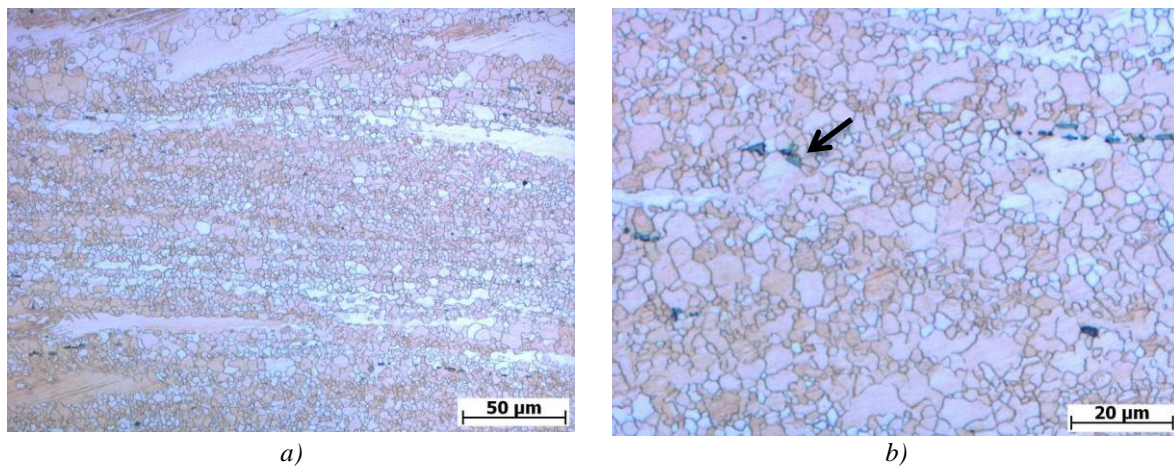| Element	Mg	Al	Mn	Fe	La	Ce	Pr	Nd
Content (weight %)	95.0	2.5	0.3	0.1	0.5	0.9	0.3	0.4

a)   *b)*

Fig. 1. Microstructure of AE 21 EX magnesium alloy, etch. picric acid + acetic acid + ethanol + water: a) Polyhedral grains of solid solution and b) Detail of intermetallic phase Al_4RE. (full colour version available online)

After finishing of the measurement, the specimen was left in the electrolyte and after reaching another defined exposure time, the measurement was carried out again. This was repeated until the last defined exposure time was reached. Due to expectation that the corrosion process will have an exponential behavior, the times of the exposition were defined as 5 min; 1, 4, 8, 16, 24, 48, 96 and 168 hours. The main purpose of this test was to evaluate the changes on the interface of alloy and 0.1M NaCl electrolyte. For the EIS analysis was used Bio-Logic device manufactured by Radiometer Analytical SAS, France (the research was supported by European regional development fund and Slovak state budget by the project ITMS 26220220048). The measurements were carried out in the frequency range from 100 kHz to 50 mHz and the frequency was changing 20 times in a decade. The amplitude of alternate current was 20 mV. More detail description of the used measurement process can be found in [15, 16].

Results of EIS measurements are plotted as the frequency dependence of overall impedance (impedance Bode plot) and frequency dependence of phase shift (Phase Bode plot). Impedance Bode plots for ground specimens of AE21 EX are in Fig. 2 and of phosphatized specimens in Fig. 3. Phase Bode plots for ground AE21 EX specimens are given in Fig. 4 and for phosphatized specimens in Fig. 5. From the impedance Bode plots were consequently evaluated values of polarization resistance with use of software analysis with EC-Lab software (Bio-Logic SAS France). From the analysis of impedance Bode plots were also evaluated values of equivalent circuit elements. Values of polarization resistance R_p, which are the basic characteristics representing the corrosion resistance of material surface layer are given in Table 2.

For the analysis were used equivalent circuits according to Fig. 6 and Fig. 7, which were defined according to shape of phase Bode plots. Equivalent circuit according to Fig. 6 is characterizing a surface on which is present only one layer of corrosion products (one minimum on the phase shift vs. frequency plot). Equivalent circuit in Fig. 7 simulates situation, when on the surface are present areas with different electrochemical properties e. g. there exist two areas with different properties e. g. two different layers or structure with pores (two minimums on the phase shift vs. frequency plot) [17].
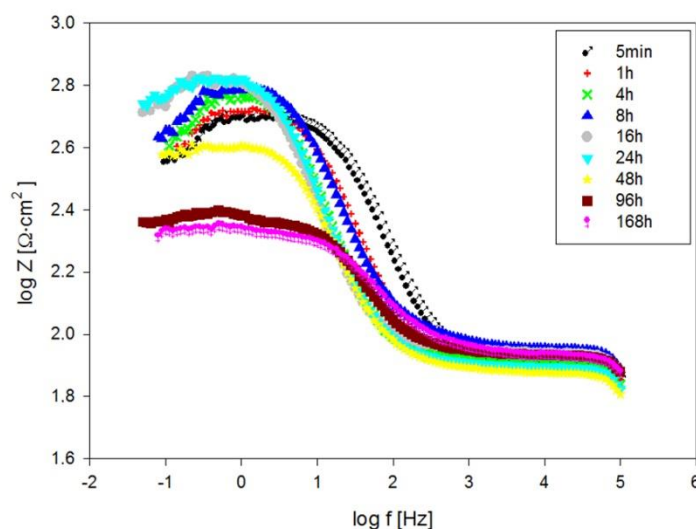

Fig. 2. Impedance Bode plots of ground AE21 EX specimens.
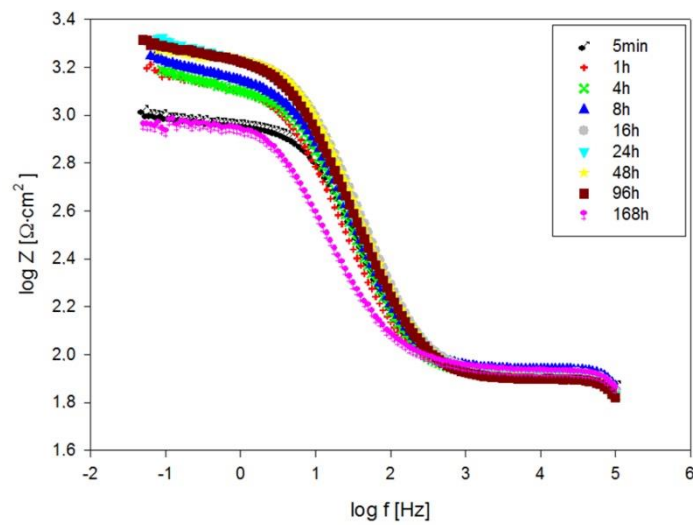(full colour version available online)

Fig. 3. Impedance Bode plots of phosphatized AE21 EX specimens.
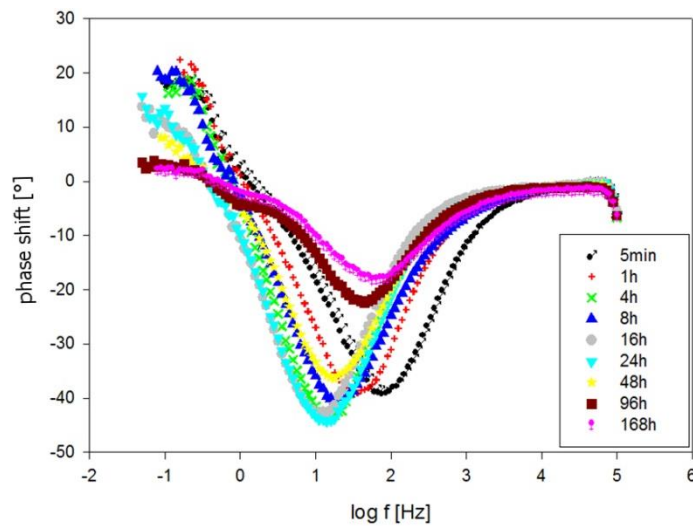*(full colour version available online)*

Fig. 4. Phase Bode plots of ground AE21 EX specimens.
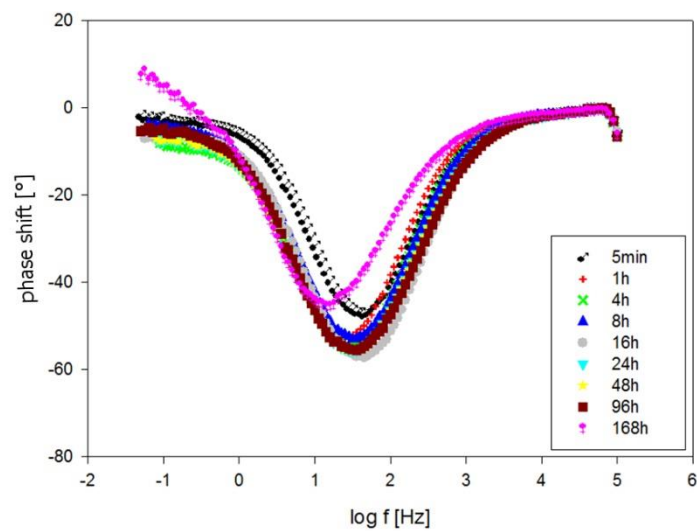*(full colour version available online)*

Fig. 5. Phase Bode plots of phosphatized AE21 EX specimens.
(full colour version available online)

Values of polarization resistance of AE21 EX specimens after exposition in 0.1M NaCl solution for different times.

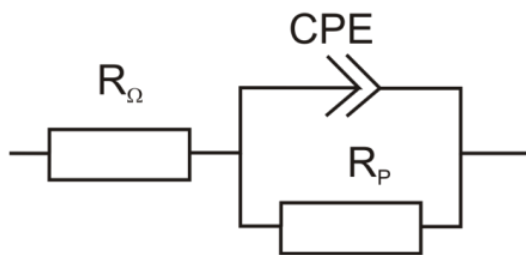| Time of exposition	5 min	1 h	4 h	8 h	16 h	24 h	48 h	96 h	168 h
R_p ($\Omega \cdot cm^2$) Ground	430.2	447.6	515.4	571.8	570.6	611.9	339.1	151.7	111.7
R_p ($\Omega \cdot cm^2$) Phosphatized	832.1	1259.0	1270.0	1372.0	1691.0	1719.0	1707.0	1728.0	866.2

Fig. 6. Equivalent circuit for Bode plot with one minimum in Phase Bode plots.
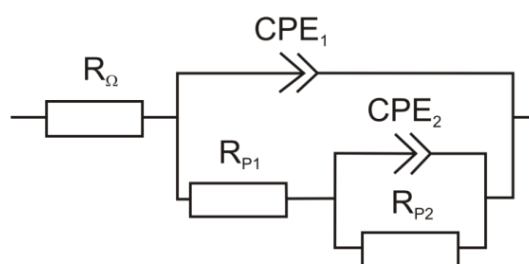

Fig. 7. Equivalent circuit for Bode plot with two minimums in Phase Bode plots.

3. Discussion

After immersion of ground specimens to corrosion environment, on the surface is created a layer consisting of corrosion products based on $Mg(OH)_2$. The integrity and thickness increases with increasing of the exposure time, what also increases the value of polarization resistance R_p. This increase is stopped after reaching 24 hours of exposure when the surface of the specimen has the highest value of polarization resistance (612 $\Omega \cdot cm^2$). In contrary, the value of polarization resistance measured after 5 min exposure was 430 $\Omega \cdot cm^2$ what represents increase for almost half of this value. However, after 24 hour exposure the values of polarization resistance of ground surfaces start to decrease and after the longest exposure time (168 h) is reached the minimum R_p value (111.7 $\Omega \cdot cm^2$), what represents just about quarter of the value reached after 5 min of exposure. This significant decrease of R_p is caused by continuous degradation of the surface as a consequence of dropping off parts of the corrosion products from the surface. This again reveals original surface of the specimen what results in further active development of the corrosion process. After 96 h of exposure, the shape of the measured Phase Bode plots have two minima and the resulted

polarization resistance R_p is in this case equal to summary of the resistance to transport of electric charge and resistance to transport of active components through pores created in the layer of corrosion products. The corrosion attack starts to be localized on few places of the surface, and there are being created two areas on the surface which have significantly different corrosion properties.

On specimens of AE21 EX magnesium alloy with phosphatized surface was measured a double value of R_p (832.1 $\Omega \cdot cm^2$) already after 5 min of exposure, when compared to specimen with ground surface after an equal exposure time. Maximal value of polarization resistance was reached after 96 h of exposure (1728 $\Omega \cdot cm^2$), what is triple of the maximal value of R_p which was reached on a ground surface (for ground specimens the maximal value was reached after 24 h exposure). The mechanism of corrosion process of phosphatized specimens was significantly different when compared to the ground ones. After 5 min of exposure the corrosion products start to appear on the surface of the phosphatized specimen. The reason why corrosion products were created so fast is that small pores are present in the conversion layer and the electrolyte was able to get in contact with the original surface of the specimen.

These corrosion products seal these pores and prevent the electrolyte to reach the original surface what increases the corrosion protection ability of the conversion layer. This is why after an exposure lasting one hour the polarization resistance significantly increases and reaches a value of R_p = 1259 $\Omega \cdot cm^2$, what is double of the value which was measured after exposure lasting for 5 min. After exposure for 8 h the values of polarization resistance were more or less the same as after 1 h. After exposure lasting for 16 h the polarization resistance increased to R_p = 1691 $\Omega \cdot cm^2$, what is an increase for 319 $\Omega \cdot cm^2$ when compared to specimen after 8 h exposure. This increase is probably related with change of the corrosion products, which started to appear locally on the surface of the specimens. Even when the corrosion attack was increasing with increasing of exposure time, the values of polarization resistance were still close to value of 1700 $\Omega \cdot cm^2$ until the exposure time reached 96 h. This means, that the phosphatized surface layer was sufficiently thick and compact to provide corrosion protection. Last change occurred after 168 h of exposure, when the R_p decreased to value of 866.2 $\Omega \cdot cm^2$ what is approximately half of the maximal value reached after 96 h of exposure. This decrease was caused by intensive local infringement of the surface layer by intensive local corrosion.

Conclusions

AE21 extruded magnesium alloy was analyzed to determine the influence of phosphatized surface layer on its corrosion resistance. Electro-impedance spectroscopy tests in 0.1M NaCl solution carried out after defined times of exposure were used for this purpose. Results were compared to material with ground surface to obtain information about the difference in polarization resistance values between these two surface treatments. Based on experimental results can be stated:

- Microstructure of the AE21 EX magnesium alloy consists of polyedric grains of solid solution of Al, RE and Mn in magnesium and by Al_4RE intermetallic phases.

- The value of polarization resistance R_p of phosphatized specimens was higher after all exposure times when compared to the ground surface. This confirmed the positive effect of creation of a conversion layer on the corrosion resistance of the studied Mg alloy.

- Maximal value of polarization resistance R_p of phosphatized specimen, which was obtained after 96 h of exposure (1728 $\Omega \cdot cm^2$) is almost three times higher than the maximal R_p value of ground specimens (611.9 $\Omega \cdot cm^2$), which was obtained after 24 h of exposure.

- Conversion phosphatized layer on the surface of specimens is stable until 96 hof exposure in 0.1M NaCl solution. After this time, the layer is damaged by the corrosion attack and the corrosion process starts to accelerate. In comparison with ground surface, the safe exposure time is about four times higher.

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