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RESISTANCE TO CORROSION OF MAGNESIUM ALLOY AZ31 AFTER PLASTIC WORKING

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The study presents results of electrochemical and chemical corrosion resistance tests of magnesium alloy AZ31 after plastic working. Electrochemical measurements were carried out in 1,35 % solution of NaCl. On the ground of registered polarisation curves, typical features characterising resistance to electrochemical corrosion, were determined. Resistance to chemical corrosion was tested by means of immersion in 3,5 % solution of NaCl for the period of 1 ÷ 5 days. By means of scanning electron microscope with field emission FE SEM S-4 200 Hitachi, qualitative and quantitative analysis of chemical composition in microareas was made. Results of surface layer morphology tests were presented. In order to compare corrosion properties, analogical tests were carried out for the alloy AZ31 obtained by means of pressure die casting.

Key words: magnesium alloy AZ31, rolling, pressure die casting, electrochemical and chemical corrosion, potentiodynamic tests

Otpornost na koroziju magnezijeve legure AZ31 nakon plastične obrade. Istraživanje pokazuje rezultate ispitivanja elektrokemijske i kemijske korozijske otpornosti magnezijeve legure AZ31 nakon plastične obrade. Elektrokemijska mjerenja su provedena u 1,35% otopini NaCl. Na osnovi registriranih polarizacijskih krivulja, određene su tipične karakteristike elektrokemijske korozijske otpornosti. Otpornost na kemijsku koroziju je testirana pomoću uranjanja u 3,5% otopinu NaCl u trajanju od 1 do 5 dana. Pomoću elektronskog skening mikroskopa FE SEM S-4200 Hitachi napravljene sus kvantitativne i kvalitativne analize kemijskog sastava u mikropovršinama. Pored toga su dani i rezultati ispitivanja morfologije površinskih slojeva. Da bi usporedili korozijska svojstva, provedeni su analogni testovi na leguri AZ31 dobivenoj tlačnim lijevanjem.

Ključne riječi: magnezijeva legura AZ31, valjanje, tlačno lijevanje, elektrokemijska i kemijska korozija, potenciodinamički test

INTRODUCTION

The interest of aircraft and automotive industry in magnesium alloys results from many favourable physical properties of those materials, and most of all - from their high relative strength. Design engineers take into consideration substantial decrease in vehicles weight and decrease in fuel consumption, that will contribute to the reduction of pollution and decrease in greenhouse effect. Advantages of magnesium are at present used intensively in cast products. In the last couple of years a substantial technological progress took place, regarding the technology of magnesium alloys casting. Magnesium alloys after plastic forming have been scarcely used so far. The main reason was low availability of semi-products made of plastic-formed alloys, as well as their high price. A crucial disadvantage connected with the development of magnesium alloys processing techniques by means of plastic forming is their limited plasticity. Tests of manufacturing processes of semi-products made of plastic-formed magnesium alloys are currently in the phase of intensive development. Application of non-conventional methods of strain enables to obtain grain size reduction up to submicrometric or nano-metric dimensions and those methods of strain facilitate the techniques of conventional strain [1].

Application of magnesium alloys is limited to a great extent by insufficient corrosion resistance. Lately, chemical and electrochemical corrosion resistance tests of casting alloys have been carried out in various countries [2-6]. Together with the increase of applications of alloys manufactured by means of plastic forming in the industry, it is necessary to evaluate their corrosion characteristics.

This study presents the results of electro-chemical and chemical corrosion resistance tests of plastic-formed magnesium alloy AZ31. Electrochemical measurements were carried out in 1,35 % solution of NaCl. Typical elements describing resistance of alloy to electrochemical corrosion resistance were determined on the ground of registered polarisation curves. Chemical corrosion resistance was tested by means of immersion method in 3,5 % solution of NaCl during 1¸5 days.

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By means of scanning electron microscope with field emission FE SEM S-4 200 Hitachi, qualitative and quanti-tative analysis of chemical composition in micro-areas. It also presents the results of measurements of geometrical characteristics of the surface of alloy AZ31 after corrosion tests. In order to compare corrosion properties, analogical tests were carried out for the alloy AZ31 obtained by means of pressure die casting.

MATERIALS AND TESTING METHODO-LOGY

Electrochemical corrosion resistance was evaluated on the ground of registered anodic polarisation curves. In potentiodynamic tests measurement system VoltaLab®PGP201 made by Radiometer was used. Saturated calomel electrode (NEK) of KP-113 type served as reference electrode, whereas platinum electrode of PtP-201 type was used as auxiliary electrode. The tests started with determination of opening potential E_{OCP}. Later, anodic polarisation curves were registered, beginning with the measurement of potential with the value of $E_{initial} = E_{OCP}$-100 mV. Potential changed in the anodic direction at the rate of 1 mV/s. When anodic current reached density of 10 mA/cm^2, polarisation direction was changed. Thus, return curve was registered. Opening potential E_{OCP} of tested samples steadied after 30 minutes. The tests were realised in 1,35 % solution of NaCl. Solution temperature during the test was 21 ± 1^{0}C.

On the ground of registered curves, typical elements describing resistance to electrochemical corrosion were determined, i.e.: corrosion potential, polarisation resistance, corrosion current density and corrosion rate.

Chemical corrosion resistance was tested in ambient temperature by means of immersion method in 3,5 % solution of NaCl for 1,5 days. By means of electron scanning microscope with field emission FE SEM S-4 200 Hitachi in cooperation with spectrometer EDS Voyager 3 500 Noran Instruments, qualitative and quantitative analysis of chemical composition in micro-areas.

The study also presents the results of measurements of geometrical features of AZ31 alloy surface after corrosion tests. The tests were carried out by means of optical profile measurement gauge Micro'prof. (CWL 3 000) made by FRT. Parameters of carried out surface geometry measurement were as follows: measurement field 4×2 mm, resolution 2 000× ×1 000 pixels.

Samples made of magnesium alloy AZ31 after pressure die casting and after hot rolling were used as initial testing material. Chemical composition of the alloy is presented in Table 1. After casting, AZ31 alloy went through homogenising annealing in the temperature of 450 °C for 24 h. After hot rolling, the alloy was annealed in 350 °C for 1 h, and then cooled with air.

Table 1 **Chemical composition of magnesium alloy AZ31 type/% of weight**

Al	Zn	Mn	Cu	Mg
2,83	0,80	0,37	0,002	rest

TEST RESULTS

Electrochemical tests carried out in 1,35 % solution of NaCl showed resistance to pitting corrosion for samples made of magnesium alloy AZ31, which varied depending on the condition of the delivery. Opening potential E_{OCP} for all tested samples steadied after 30 minutes. Average value of corrosion potential for rolled samples equalled E_{corr} = -1 367 mV, whereas for cast samples was smaller by 100 mV and equalled E_{corr} = = -1 467 mV. Anodic polarisation curves for both forms of AZ31 alloy are shown in Figure 1 and Figure 2.

For all analysed samples no passivation current was determined and it proves that no passive layer has been created on the surface of the alloy during polarisation. The determined average corrosion current density i_{corr} and polarisation resistance R_p for rolled samples were: i_{corr} = 80,5 μA/cm^2 and R_p = 330,3 Ωcm^2, whereas average values of corrosion current density i_{corr} and polarisation resistance R_p for cast samples were respectively: i_{corr} = = 15,2 μA/cm^2 and R_p = 2 915,3 Ωcm^2.

The results of corrosion tests of the alloys are shown in Table 2.

By means of scanning microscope, the structure of AZ31 alloy that underwent chemical corrosion in 3,5 % solution of NaCl was tested. Immersion test for rolled

Table 2 **Test results of electrochemical corrosion resistance of magnesium alloy AZ31 type**

Sample No	E_{corr}/ /mV	i_{corr}/ /μA/cm^2	R_p/ /Ωcm^2	Corr./ /mm/year
Magnesium alloy AZ31 after rolling				
1	-1 350	97,4	267	0,90
2	-1 384	63,9	407	0,59
3	-1 377	80,2	324	0,75
Magnesium alloy AZ31 after pressure casting				
1	-1 521	11,6	2 248	0,17
2	-1 430	29,5	881	0,28
3	-1 463	4,6	5 617	0,05

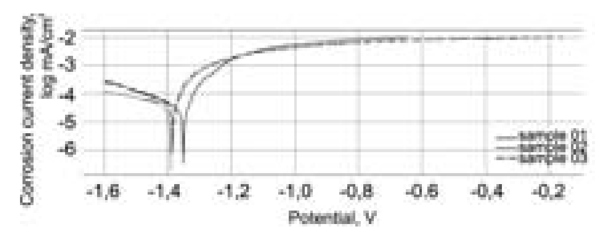

Figure 1 Anodic polarisation curves recorded for rolled samples

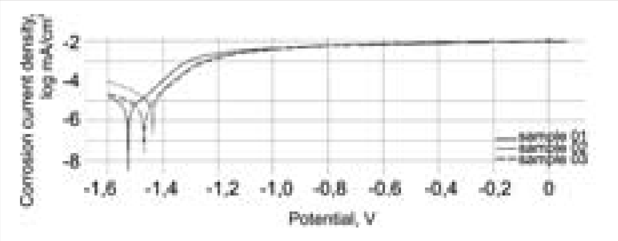

Figure 2 Anodic polarisation curves recorded for cast samples

samples showed that after the first day of the test a specific band-shaped system with areas affected by corrosion of various degrees appeared on the surface. Non-corroded and corroded areas are places next to one another (Figure 3). There is also visible presence of pits (Figure 4). Pictures were taken on the surface cleaned of corrosion products.

Before cleaning the alloy surface it was found that mainly crystals of NaCl are the product of corrosion (Figure 5).

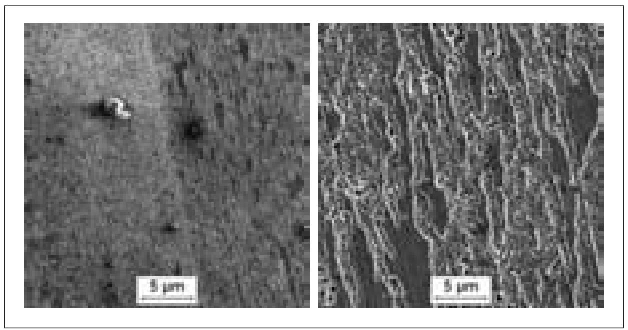

Figure 3 Surface of rolled alloy after 1-day of immersion in 3,5 % NaCl

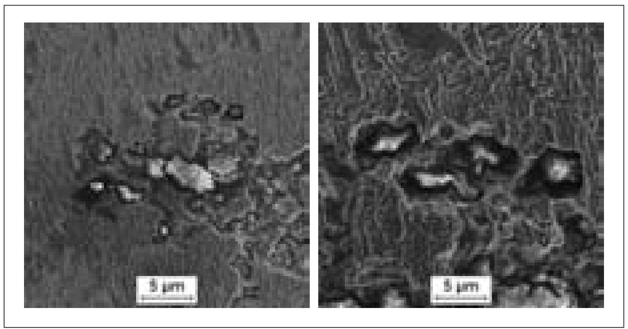

Figure 4 Pits on the surface of rolled alloy

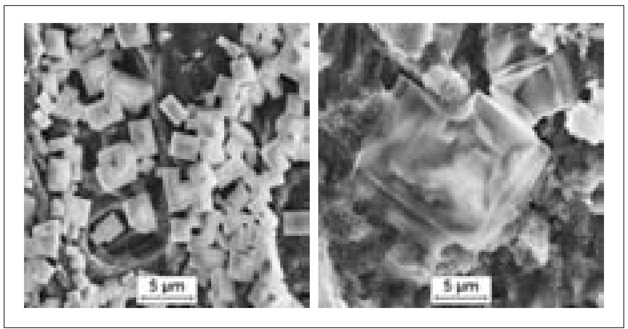

Figure 5 NaCl crystals created on the surface of the alloy after 1-day immersion test

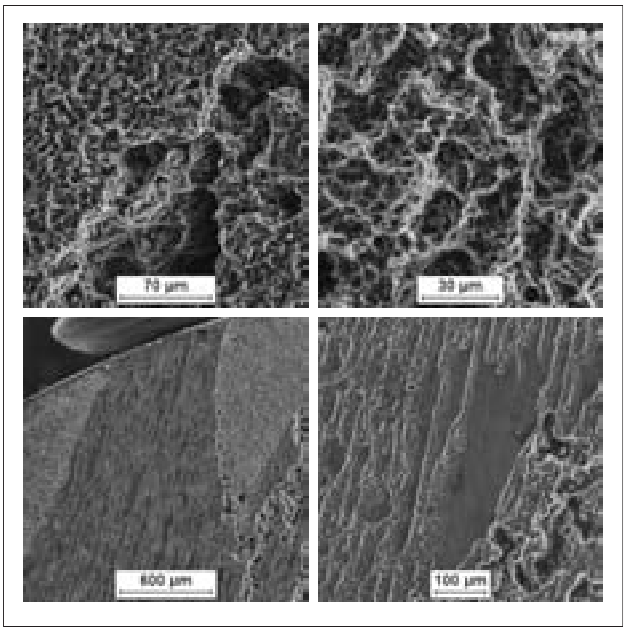

Figure 6 Pits and the surface of rolled alloy AZ31 after 3-day immersion test

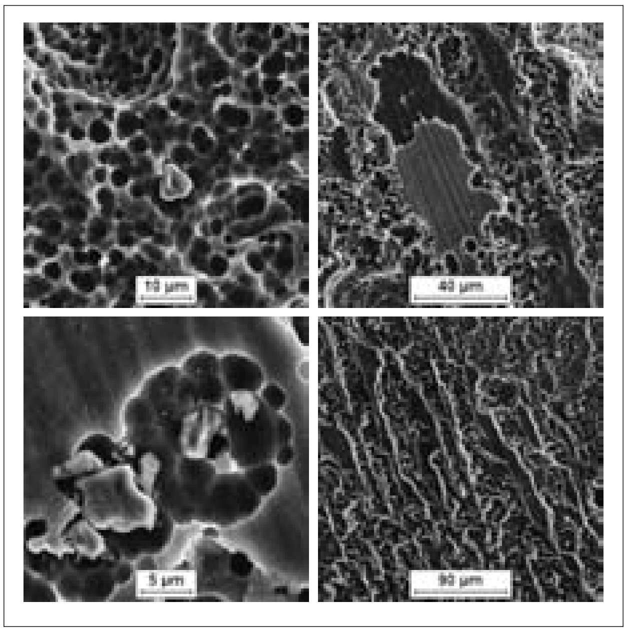

Figure 7 Pits and the surface of rolled alloy AZ31 after 5-day immersion test

After 3-days immersion test on the surface of the rolled alloy small but deep pits were observed. The course of the corrosion is in accordance with the direction of rolling (Figure 6). Further tests showed that after 5 days of immersion in 3,5 % solution of NaCl, very deep pits appeared on the surface of the alloy (Figure 7).

After 1-day immersion test of samples made of cast AZ31 alloy it was found that their surface is extremely oxidised. There are also visible non-corroded, random-shaped areas. These areas are distributed evenly on the whole surface of the material. It proves that the corrosion of the material is uniform (Figure 8). Corroded areas are visible as unevenly solved areas. On the surface of the material there are also dendritic releases of

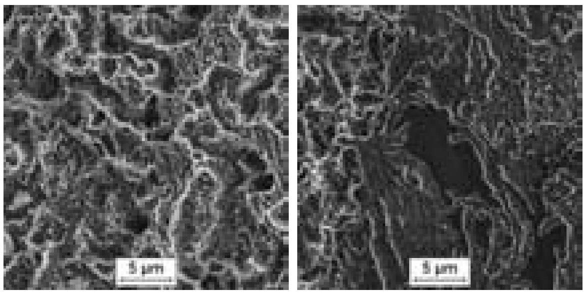

Figure 8 Surface of cast alloy AZ31 after 1-day immersion test

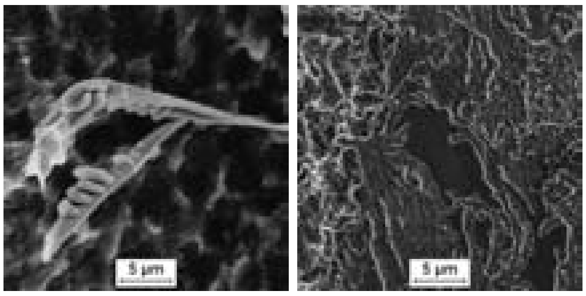

Figure 9 Dendritic release of phase Mg-Si and phase Mg-Si running along the grain boundary

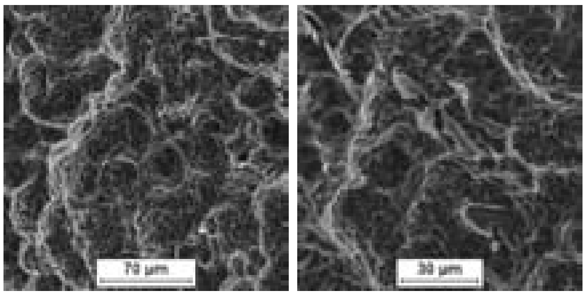

Figure 10 Surface of cast alloy AZ31 after 3-day immersion test

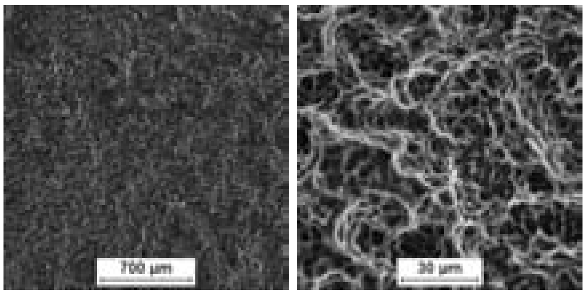

Figure 11 Surface of cast alloy AZ31 after 5-day immersion test

phases Mg-Si (Figure 9). These phases are permanently isola-ted and feature higher resistance to corrosion. This Figure also presents more complex phase running along the grain boundary.

After 3 days of tests it could be seen that there very few areas remained non-corroded (Figure 10). After 5

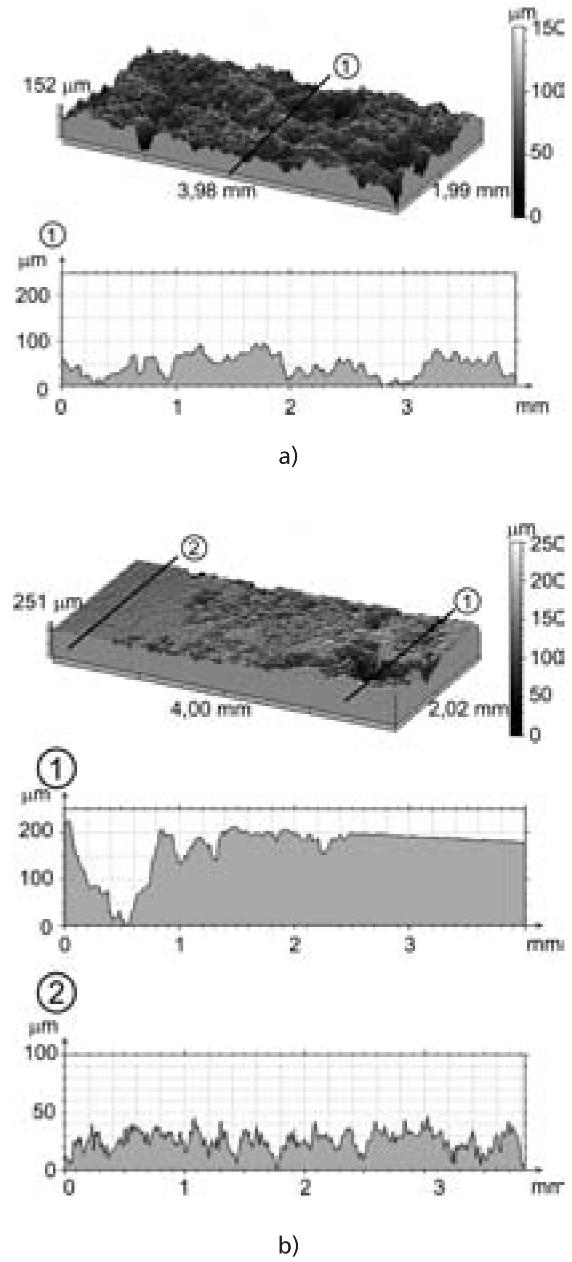

Figure 12 Surface topography 3D and roughness of cast (a) and rolled (b) AZ31 alloy

days of tests it was found that corrosion of cast alloy AZ31 still proceeded at a uniform rate (Figure 11).

Figure 12 presents topography of the surface of alloys and distribution of roughness. The results of geometrical features measurements of the surface of alloys (after immersion test and removal of corrosion products) have been shown in Table 3).

SUMMARY

Potentiodynamic tests carried out in 1,35 % solution of NaCl enabled to obtain information concerning development of resistance to pitting corrosion of AZ31 alloy in relation to the condition of its delivery. Compara-

Table 3 **Parameters representative to AZ31 alloy roughness**

Parameter / μm	Rolled alloy	Cast alloy
R_a	3,14	3,07
R_q	5,53	5,44
R_p	13,1	14,9

tive analysis of anodic polarisation curves showed that cast alloy features higher corrosion resistance in the temperature of 21^0C. Even though its corrosion potential was slightly smaller, the other determined parameters were much more favourable (higher polarisation resistance, lower current density and corrosion rate). However, substantial discrepancy between its corrosion parameters (for example, polarisation resistance falls in the range R_p = 881,5 617 Ωcm^2). It is considered that the reason for such a huge discrepancy in corrosion properties of cast alloy are rattails (previous structural tests showed the presence of micro-caverns [7]).

Corrosion test results after immersion test show that cast alloy is subject to uniform corrosion. Depth of pits does not exceed 100 μm. On the surface of rolled alloy there are visible corroded as well as non-corroded areas. Due to the fact that in rolled alloy the pits can be really deep (up to ~230 μm), it may result in fast and complete destruction of the material. In non-corroded areas roughness does not exceed 5 μm.

Test results prove the necessity of application of protective layers on elements made of magnesium alloy AZ31, irrespective of the condition of its delivery.

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Note: The responsible translator for English language is Agata Budziak, Siemianowice, Poland.