ELECTROCHEMICAL CORROSION OF MAGNESIUM ALLOY AZ31 IN NaCl SOLUTIONS

J. Przondziono[1], W.Walke[2], E. Hadasik[1], B. Jasiński[1]
[1]Department of Technology Materials, Silesian University of Technology, Krasinskiego 8, 40-019 Katowice, Poland
[2]Institute of Engineering Materials and Biomaterials, Silesian University of Technology, Konarskiego 18a, 44-100 Gliwice, Poland

Received 24.05.2010
Accepted 08.12.2010

Corresponding author: Joanna Przondziono, tel.: +48 32 60344, fax: +48 32 603 4469, Department of Technology Materials, Silesian University of Technology, Krasinskiego 8, 40-019 Katowice, Poland, E-mail: joanna.przondziono@polsl.pl

Abstract
The study presents the results of tests of electrochemical corrosion of AZ31 alloy after casting and metal forming in NaCl solutions. These alloys featured various concentrations of chlorine ions. The tests were carried out in 0.01, 0.2, 0.6, 1.0 and 2.0 M NaCl. System for electrochemical tests VoltaLab®PGP201 was applied. Potentiodynamic tests enabled to register anodic polarisation curves. Stern method was applied to determine parameters typical of corrosion resistance of the alloy. Results showed that corrosion resistance of AZ31 magnesium alloy decrease with increasing of chlorine ions concentration (irrespective of using alloy state). The corrosion resistance of alloy after forming is mildly worse than alloy after die- casting.

Keywords: magnesium alloy AZ31, electrochemical corrosion, potentiodynamic tests, anodic polarisation curves

1 Introduction
Magnesium and its alloys get more and more interest from metallurgical industry. These materials combine density with mechanical and physical properties in a way that makes them perfect to use in light constructions. Therefore, they have a high innovative potential. Advantages of magnesium are already widely used in cast products. A significant progress in magnesium casting technologies has taken place in the last couple of years. Modern solutions in hot chamber technology enable to maintain safety during production process, to keep casting temperature stable, and consequently to ensure process repeatability. Magnesium alloys after plastic forming have been used on a small scale so far. It was mainly caused by poor availability of semi-products made of alloys after plastic forming, as well as their high price. A crucial problem connected with the development of magnesium alloy processing techniques by means of plastic forming is their limited plasticity [1,2]. Low formability in ambient temperature and in higher temperature results from a limited number of crystallographic hexagonal network slip systems [3].
Metal forming of magnesium and its alloys may be effected, depending on the content of alloy components, only in a restricted temperature range. By means of heat-and-plastic working it is possible to obtain grains with diameter up to 10 μm in magnesium alloys. Size reduction below

10 µm is obtained by means of application of huge strain. Application of unconventional methods of strain enables to obtain grain size reduction up to submicrometric or nano-metric and that is why these strain methods support techniques of conventional forming. In magnesium alloys strain processes are carried out in elevated temperatures and therefore it is practically impossible to obtain nano-metric structure by means of development of shear bands. Applied methods that enable to obtain large strain, which leads to grain size reduction of magnesium alloys, usually include equal channel angular pressing (ECAP) or hydrostatic extrusion (HIP) [4-15]. Tests of manufacturing processes of semi-products made of magnesium alloys after metal forming are at present in the phase of intensive development.

Possibilities of application of magnesium alloys after metal forming in aircraft or automotive industry are connected with the need to provide products with proper corrosion resistance. Magnesium is an extremely chemically active element and in the electrochemical series of metals it can be found at one of the first places. As it is extremely electronegative, it is highly prone to passing to electrolytic solutions. High difference of normal potentials between this alloy and other metals gives the ground for creation of local cells, which causes magnesium anodic dissolution. These properties of magnesium contributed to general opinion that magnesium corrodes easily and its total destruction is just a matter of time.

Standard electrochemical potential of magnesium E^o is –2.37 V, whereas in 3% solution of sodium chloride it is –1.63 V (SCE). The main reason for low corrosion resistance of magnesium is low protecting properties of the layer of oxides, that is formed on the surface in the oxidizing atmosphere or of the layer of hydroxides in water solutions.

Magnesium alloys feature good corrosion resistance in weather conditions and when they are put to the reaction of alkaline, chromate and water-fluoric solutions of acids as well as to majority of organic chemical compounds, e.g. hydrocarbons, aldehydes, alcohols (with the exception of methanol), phenols, amines, esters and most of oils [16]. Magnesium is not resistant to the influence of water containing trace elements of heavy metals ions, sea water, inorganic and organic acids and acid salts (e.g. ammonium), anhydrous methanol, gasoline containing lead (and its compounds), freon containing water.

Magnesium is extremely prone to electrochemical corrosion, especially in the environment where chloride ions are present, which limits the area of application of its alloys to a great extent. Electrochemical corrosion is most often displayed by metal defects on the surface (spots and pits) or by deterioration of material strength.

In the last few years, a number of tests related to the evaluation of resistance to corrosion in solutions containing chloride ions have been carried out [17-25]. The tests were related to magnesium alloys produced by means of casting methods, though. As intense research concerning magnesium alloys for metal forming is being carried out, it is necessary to recognize their corrosion behaviour.

The purpose of this study is to evaluate and compare resistance to electrochemical corrosion of magnesium alloy AZ31 as after pressure casting and after hot rolling. Potentiodynamic tests were carried out in NaCl solutions featuring various concentration of chloride ions. Potentiodynamic tests enabled to register anodic polarisation curves. Stern method was applied to determine parameters typical of corrosion resistance of the alloy.

2 Methodology and testing material

Resistance to electrochemical corrosion was determined on the ground of registered anodic polarisation curves. For potentiodynamic tests system VoltaLab®PGP201 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 $E=E_{OCP}-100$ 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 carried out in NaCl with various concentration of chloride ions. Measurements were made in 0.01, 0.2, 0.6, 1.0 and 2.0 M NaCl. Solution temperature during the test was 21±1^{o}C. On the ground of registered anodic polarisation curves, typical elements describing resistance to electrochemical corrosion were determined, i.e.: corrosion potential E_{corr}, corrosion current density i_{corr} and corrosion rate corr. Stern method was applied to determine polarisation resistance R_p.

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^{o}C for 24 h. After hot rolling, the alloy was annealed in 350^{o}C for 1 h, and then cooled with air.

Table 1 Chemical composition of magnesium alloy AZ31, % of mass

Al	Zn	Mn	Cu	Mg
2.83	0.80	0.37	0.002	balance

3 Test results and their review

Potentiodynamic tests carried out in NaCl solutions with various molar concentration enabled to determine corrosion properties of magnesium alloy AZ31 depending on the condition of the delivery. Anodic polarisation curves of the selected samples are shown in **Fig.1** (alloy after casting) and **Fig. 2** (alloy after rolling). Corrosion resistance test results (mean values of measurements) of AZ31 alloy after casting and rolling are compared in **Table 2**.

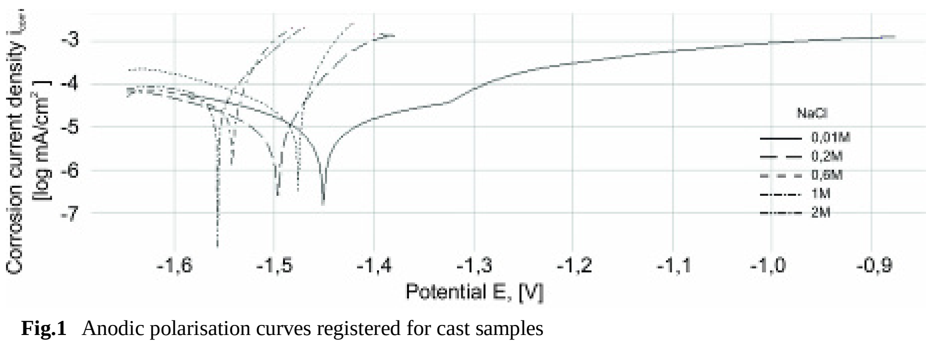

Fig.1 Anodic polarisation curves registered for cast samples

The tests proved that corrosion potential for all tested samples was similar. It was influenced neither by the condition of delivery, nor by molar concentration of NaCl solution. Corrosion potential of samples made of cast alloy can be placed within the range of -1474÷-1544 mV, and for rolled samples: -1490÷-1566 mV.

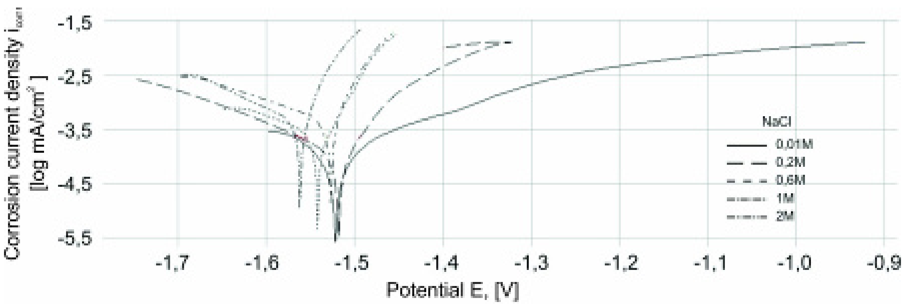

Fig.2 Anodic polarisation curves registered for rolling samples

Table 2 Results of electrochemical corrosion resistance tests of magnesium alloy AZ31 (mean measurement values)

Molar concentration, M	E_{corr}, mV	$I_{corr.}$, A/cm^2	R_p, Ωcm^2	Corr., mm/year
Magnesium alloy AZ31 after pressure casting				
0.01	-1474	0.010	2633	0.220
0.2	-1508	0.010	2067	0.298
0.6	-1473	0.065	582	1.480
1.0	-1523	0.105	237	2.400
2.0	-1544	0.142	196	3.260
Magnesium alloy AZ31 after rolling				
0.01	-1490	0.007	2600	0.260
0.2	-1488	0.023	1100	0.527
0.6	-1538	0.107	281	2.460
1.0	-1537	0.128	210	2.940
2.0	-1566	0.127	208	3.440

Moreover, it was determined that together with the increase in chloride ions concentration, there is the decrease in polarisation resistance as well as the increase in corrosion current density and corrosion rate. With the increase in molar concentration of the solution, polarisation resistance decreased from 2633 Ωcm^2 to 196 Ωcm^2 (cast alloy), and in the case of rolled alloy from 2600 Ωcm^2 to 208 Ωcm^2. Corrosion current density of cast alloys increased from 0.01 A/cm^2 to 0.142 A/cm^2, whereas for alloys after plastic working this parameter increased from 0.007 A/cm^2 to 0.127 A/cm^2. Corrosion rate increased from 0.22 mm/year to 3.26 mm/year (cast alloy) and from 0.26 mm/year to 3.44 mm/year (rolled alloy). The aforementioned corrosion parameters refer to mean measurement values.

These results explicitly show deterioration of corrosion properties of magnesium alloy AZ31 caused by the increase in molar concentration of NaCl solution (irrespective of the condition of alloy delivery).

When comparing the influence of production technology on the resistance of AZ31 alloy to electrochemical corrosion it is clear that the alloy obtained by means of pressure casting features slightly higher corrosion properties. It can be indicated by higher polarisation resistance and higher current density as well as lower corrosion rate for tested molar concentrations of NaCl solution.

On the ground of carried out tests it was also determined that corrosion parameters of samples made of AZ31 alloy, obtained by means of pressure casting method in solutions with the same concentration, were differentiated. For example, polarisation resistance of samples tested in 0.6

M NaCl solution ran within the range of 245÷1100 Ωcm^2, and corrosion current density was from 0.023÷0.106 A/cm^2.
Structural tests proved that after casting and homogeneous annealing in the temperature of 450°C AZ31 alloy featured single-phase heterogenous dendritic structure with numerous twins. Numerous casting defects in the form of micro-voids were observed [26]. It must be expected that the reason for huge differentiation of corrosion properties of cast alloy (with the same concentration of chloride ions) are casting defects. Structural tests of samples that were hot-rolled and annealed in the temperature of 350°C proved that microstructure of AZ31 alloy is single-phase with numerous mechanical twins that were created during the process of rolling. In this case, no macroscopic defects were observed and so corrosion parameters are of a similar range. Pictures of selected structures are shown in **Fig. 3** and **4**. The pictures were taken on an inter-section parallel to the sample axis by means of light microscopy, light field technique.

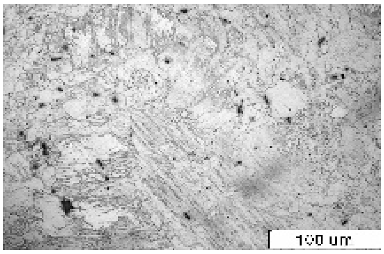

Fig.3 Microstructure of AZ31 alloy after casting and homogenising annealing in the temperature of 450°C in the time of 24 h

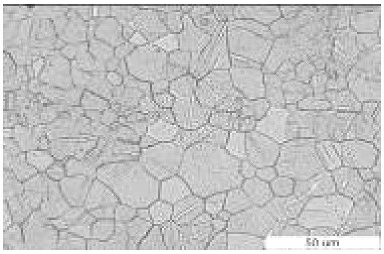

Fig.4 Microstructure of AZ31 alloy after hot rolling and annealing in the temperature of 350°C in the time of 1 h and air cooling

To conclude, it must be highlighted that for both forms of tested alloy pitting corrosion is present. It proves the lack of resistance to this type of corrosion for magnesium alloy AZ31. Tests results show the necessity of protective layers application on elements made of the tested alloy, irrespective of the condition of its delivery.

4 Conclusions

On the ground of carried out tests the following conclusions were formed:

- Together with the increase in chloride ions concentration there is deterioration of corrosion properties of magnesium alloy AZ31 obtained both by means of pressure casting and hot rolling method.
- Corrosion potential of all tested samples was determined at a similar level. It is influenced neither by the condition of delivery, nor molar concentration of NaCl

solution. Together with the increase in chloride ions concentration, decrease in polarisation resistance is observed as well as increase in corrosion current density and corrosion rate of AZ31 alloy, irrespective of its production technology that was applied.
- AZ31 alloy obtained by means of pressure casting features slightly higher corrosion properties. It features higher polarisation resistance and lower corrosion current density and corrosion rate.
- Magnesium alloy AZ31 as cast shows differentiation of corrosion parameters during potentiodynamic tests carried out in solution with the selfame concentration. It must be assumed that it is caused by casting defects and heterogeneity of microstructure. The alloy produced by means of metal forming does not show this defect.

Acknowledgements
Financial support of Structural Funds in the Operational Programme – Innovative Economy (IE OP) financed from the European Regional Development Fund - Project "Modern material technologies in aerospace industry", No POIG.0101.02-00-015/08 is gratefully acknowledged.

References
[1] E. Hadasik, D. Kuc, G. Niewielski, R. Śliwa: Hutnik, Vol. 76, 2009, No. 8, p. 580-584.
[2] D. Kuc, E. Hadasik, G. Niewielski, A. Płachta: Journal of Achievements in Materials and Manufacturing Engineering, Vol. 27, 2008, No. 1, p. 27-30.
[3] E. Hadasik: Badania plastyczności metali. Monografia. first ed., Wyd. Politechniki Śląskiej, Gliwice, 2008, (in polish).
[4] A. Kováčová et al.: Acta Metallurgica Slovaca, Vol. 16, 2010, No. 2, p. 91-96.
[5] J. Bidulská, R. Kočiško, R. Bidulský, M. Actis Grande, T. Donič, M. Martikán: Acta Metallurgica Slovaca, Vol. 16, 2010, No. 1, p. 4-11.
[6] A. Kováčová, T. Kvačkaj, M. Kvačkaj, T. Donič, M. Martikán, M. Besterci: Acta Metallurgica Slovaca, Vol. 15, 2009, No. 2, p. 100-104.
[7] R. Kočiško, T. Kvačkaj, J. Bidulská, M. Molnárová: Acta Metallurgica Slovaca, Vol. 15, 2009, No. 4, p. 228-233.
[8] J. Tiža, T. Kvačkaj, M. Lupták: Acta Metallurgica Slovaca, Vol. 15, 2009, No. 4, p. 241-247.
[9] M. Fujda, T. Kvačkaj, M. Vojtko, O. Milkovič: Acta Metallurgica Slovaca, Vol. 14, 2008, No. 3, p. 331-341.
[10] J. Bidulská, R. Kočiško, T. Kvačkaj, R. Bidulský, M. Actis Grande: Acta Metallurgica Slovaca, Vol. 14, 2008, No. 3, p. 342-348.
[11] M. Besterci, K. Sülleiová, T. Kvačkaj: Acta Metallurgica Slovaca, Vol. 12, 2006, No. 3, p. 257-263.
[12] T. Kvačkaj, A. Kováčová, M. Kvačkaj, I. Pokorný, R. Kočiško, T. Donič: Materials Letters, Vol. 64, 2010, No. 21, p. 2344-2346.
[13] T. Kvačkaj, J. Bidulská, M. Fujda, R. Kočiško, I. Pokorný, O. Milkovic: Materials Science Forum, Vol. 633-634, p. 273-302.
[14] E. Hadasik: Rudy i Metale Nieżelazne, Vol. 53, 2008, No. 12, p. 790-794.
[15] D. Kuc, E. Hadasik, A. Kur: Hutnik, Vol. 77, 2010, No. 8, p. 406-410.
[16] A. Białobrzeski, E. Czekaj, M. Heller: Archiwum Odlewnictwa, Vol. 2, 2002, No. 3, p. 294-313.

[17] G. Song, A. Atrens, X. Wu, B. Zhang: Corrosion Science, Vol. 40, 1998, No. 10, p. 1769-1791.
[18] X.W. Guo, J.W. Chang, S.M. Che, W.J. Ding, X. Wang: Electrochimica Acta, Vol. 52, 2007, p. 2570–2579.
[19] R. Ambat, N.N. Aung, W. Zhou: Corrosion Science, Vol. 42, 2000, No. 8, p. 1433-1455.
[20] H. Altun, S. Sen: Materials and Design, Vol. 25, 2004, No. 7, p. 637-643.
[21] M.Ch. Zhao, M. Liu, G.L. Song, A. Atrens: Corrosion Science, Vol. 50, 2008, No. 7, p. 1939-1953.
[22] F. El-Taib Heakal, A.M. Fekry, M.Z. Fatayerji: Electrochimica Acta, Vol. 54, 2009, p. 1545-1557.
[23] M.Ch Zhao, M. Liu, G.L. Song, A. Atrens: Corrosion Science, Vol. 50, 2008, No. 11, p. 3168-3178.
[24] Z. Shi, G. Song, A. Atrens: Corrosion Science, Vol. 47, 2005, No. 11, p. 2760-2777.
[25] D. Song, A. Ma, J. Jiang, P. Lin, D. Yang, J. Fan: Corrosion Science, Vol. 52, 2010, No. 2, p. 481-490.
[26] E. Hadasik, D. Kuc, A. Szuła: Rudy i Metale Nieżelazne, Vol. 55, 2010, No. 6, p. 313-318.