Mechanics and Mechanical Engineering
Vol. 12, No. 2 (2008) 157–164

Investigation of Corrosion Resistance of Carbon Coatings Deposited on Magnesium Alloys by PACVD Method

Marcin Gołąbczak
Technical University of Łódź,
Department of Production Engineering
Stefanowskiego 1/15, 90-924 Łódź, Poland

Received (15 October 2008)
Revised (20 October 2008)
Accepted (15 December 2008)

Magnesium alloys are increasingly used in aeronautic, astronautic, automobile, electronic and sporting goods industries etc. However, these alloys display some disadvantageous attributes, like first of all, the susceptibility to corrosion, particularly the electrochemical one, which results in both mass losses and the reduced mechanical durability. To protect magnesium alloys from corrosion the Plasma Activated Chemical Vapour Deposition (PACVD) method of manufacturing of protective carbon coatings on AZ31 magnesium alloys has been used. This report shows results of the study on corrosion resistance of AZ31 magnesium alloy either bearing the carbon coating or not. The corrosion resistance was determined by the electrochemical laboratory method and by the corrosion test in a salt spray chamber.

Keywords: Magnesium alloys, carbon coatings, PACVD method, electrochemical corrosion, salt spray chamber

1. Introduction

Currently, magnesium alloys have been widely used in numerous branches of industry in which the loss of their mass is of great importance. These alloys have been used in aeronautic, astronautic, automobile, electronic and sporting goods industries etc. [1, 2]. The most captivating advantages of magnesium alloys include: the high ratio of mechanical durability to their mass, an excellent conductivity of heat, the low heat expansion, good casting properties, high functional integrity enabling manufacturing of goods with the near–net–shape and good cuttability [1–3]. Magnesium alloys have also some disadvantages, like first of all, the high susceptibility to corrosion that leads to mass losses and decreased mechanical durability. Their other disadvantages comprise the low wear resistance, reduced durability at high temperature and interference of electromagnetic field [2, 3]. These disadvantages considerably limit applications of magnesium alloys in technology.

Presented work demonstrates that deposition of special carbon coatings on the surface of AZ31 magnesium alloys eliminates these disadvantages. Besides, such coatings play both the protective and decorative roles [3]. They were deposited by Plasma Activated Chemical Vapour Deposition method (PACVD) in the Institute of Material Engineering at the Technical University of Lodz [3, 4]. Their corrosion resistance was tested in the Laboratory of Material Sciences ECAM in France by using devices accessible in this laboratory [3, 4, 5,]. PACVD process conditions were optimized and corrosion resistance of carbon coatings deposited on magnesium alloy AZ31 was determined. The reference samples of AZ31magnesium alloy used in studies on corrosion resistance were not coated by protective carbon layers [3, 4]. The corrosion resistance was determined by the relatively fast electrochemical laboratory method and by the corrosion test in a salt spray chamber of type SIGMA DIESEL (BOSCH) [3].

2. Electrochemical method

The accelerated electrochemical method consisted in repeated potentiostatic measurements carried out by using Volta Master 1 set comprising a potentiostat Radiometr-Copenhagen PGP 201. The examined samples were immersed in Tyrod's electrolyte (its chemical composition is shown in Tab. 1) at the temperature of 20 ^{o}C.

Table 1 Chemical composition of Tyrod's electrolyte

$NaCl$ [g/dm^3]	$CaCl_2$ [g/dm^3]	KCl [g/dm^3]	NaH_2PO_4 [g/dm^3]	$MgCl_26H_2O$ [g/dm^3]	$NaHCO$ [g/dm^3]	pH
8.00	0.20	0.20	0.05	0.10	1.00	6.9

Modeling of phenomena occurring at the contact interface between the conductor (metal) and the electrolyte was based on the standard Butler–Volmer equation [6, 7, 8]. It is a half–empirical equation and characterizes the rate of electric charge transfer through the interface of phases: metal–electrolyte. This rate depends, first of all, on the difference of potentials and its sign (positive or negative) at this interface. The analysis of current flow through the medium which is far from the state of equilibrium cannot be done without the model of Butler–Volmer [8]. The model based on an electric nonlinear circuit was proposed to determine the flow of current in the wide range of potential values. This circuit contains some elements responsible for individual physical phenomena that take place during potentiostatic measurements [7, 8]. The scheme of this substitute circuit is shown in Fig. 1.

The proposed model consists of two branches characterizing anodic and cathodic currents. Relationships between the elements of the model shown in Fig. 1 and phenomena occurring at the interface conductor–electrolyte are as follows:

- diodes D_1 and D_2 that are fundamental elements of the proposed model correspond to the exponential components of Butler–Volmer equation that are responsible for diffusion [7, 8],

- resistors R_{S1} and R_{S2} are responsible for the transfer of electric charge carriers and are particularly important at higher values of voltage U,
- voltage generators Ψ_{01} and Ψ_{02} are responsible for the difference in potentials at the contact interface for anodic and cathodic parts of the characteristics.

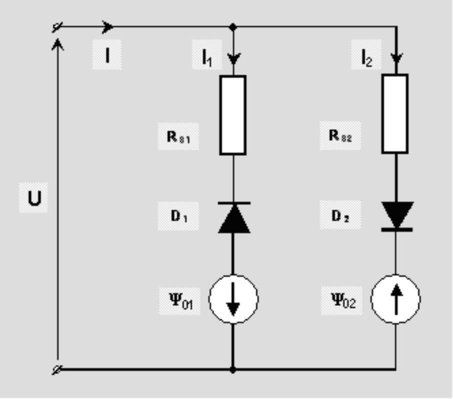

Figure 1 The structure of proposed model in the form of the nonlinear electric circuit with lumped constants

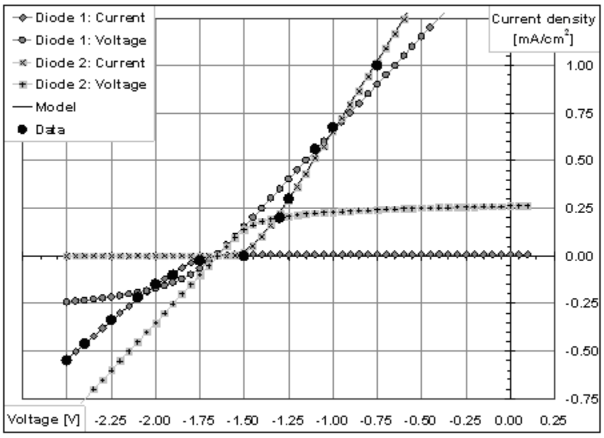

Figure 2 Potentiostatic curve of electrochemical corrosion for AZ31 magnesium alloy free of carbon coating

Equations describing the substitute electric circuit (Fig. 1) are as follows:

- for the anodic branch (left parts of descending curves in Fig. 2 and 3):

$$j_1 = -j_{01}\left(e^{-\frac{qtm_1}{kT}U_{D1}} - 1\right) \tag{1}$$

$$R_{S1}\, j_1 + U_{D1} + \Psi_{01} = U \tag{2}$$

- for the cathodic branch (right parts in ascending curves in Fig. 2 and 3):

$$j_2 = j_{02}\left(e^{\frac{qm_2}{kT}\,U_{D2}} - 1\right) \tag{3}$$

$$R_{S2}\, j_2 + U_{D2} + \Psi_{02} = U \tag{4}$$

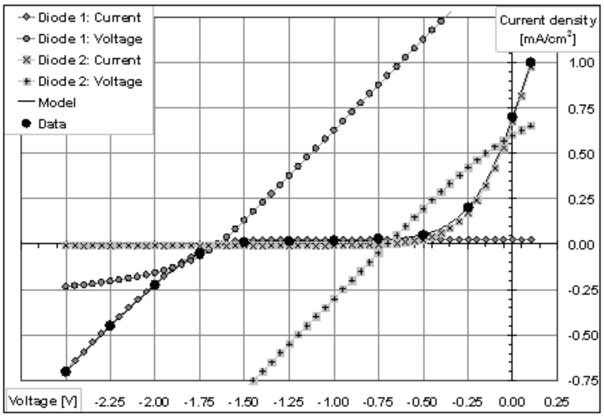

Figure 3 Potentiostatic curve of electrochemical corrosion for AZ31 magnesium alloy protected by carbon coating

The total current flowing through the interface is the sum of anodic current and cathodic current:

$$j = j_1 + j_2 \tag{5}$$

where:

q	–	the elementary charge of an electron, expressed in [C] [A· s], $q = 1.6022 \cdot 10^{-19}$ C
k	–	Boltzman constant, expressed in [J/K] [kg·s^2/m^2·K], $k = 1.3807 \cdot 10^{-23}$ J/K
T	–	the temperature of the contact interface [K]
j_{01}, j_{02}	–	the density of saturation currents, expressed in [mA/cm^2]
R_{S1}, R_{S2}	–	resistances representing the phenomenon of electron transfer, expressed in [Ω]
m_1, m_2	–	coefficients dependent on division of currents and valences of ions in the electrolyte, dimensionless quantities.

Electric parameters of this model for individual potentiostatic curves (Tafel curves) were identified by means of the least square method and by resolving the system of nonlinear equations by the gradient method [9]. The obtained parameters are effective estimators of the true model parameters.

Results of potentiostatic measurements were plotted in Fig. 2 and 3. Intercepts of curves presenting the voltage on diodes with OX axis correspond to potentials on the interface metal–solution. The values of electric parameters that were calculated for the assumed models are presented in Tabs 2. and 3.

Table 2 Electric parameters of the potentiostatic curve of electrochemical corrosion for sample made of AZ31 magnesium alloy free of carbon coating

Model parameters	J_0 [mA/cm^2]	Ψ_0 [V]	m	R_S [Ω]
Diode I	0.009145	-1.6622	0.4276	1092.46
Diode II	0.000100	-1.6482	0.9607	643.96
Fitting error	4.027E-03			
Deviatation 3σ	5.280E-02	[mA/cm^2]		

Table 3 Electric parameters of the potentiostatic curve of electrochemical corrosion for sample made of AZ31 magnesium alloy bearing the carbon coating obtained under conditions for sample-5

Model parameters	J_0 [mA/cm^2]	Ψ_0 [V]	m	R_S [Ω]
Diode I	0.026058	-1.6501	0.3588	892.26
Diode II	0.008067	-0.7000	0.1867	152.36
Fitting error	7.947E-05			
Deviatation 3σ	7.720E-02	[mA/cm^2]		

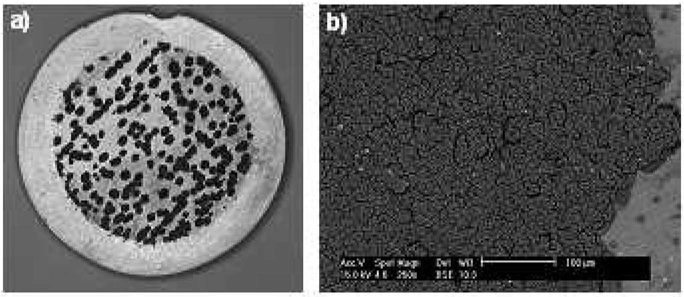

Figure 4 SEM image of AZ31 magnesium alloy surface on completion of the potentiostatic corrosion test; test duration-1h: a) magnification 3x, b) magnification 250x

On completion of potentiostatic measurements the surface of the examined samples was subjected to SEM analysis. Examples of the recorded images are shown in Fig. 4 and 5.

Analysis of results of electrochemical studies revealed that deposition of the carbon coating on the surface of AZ31 magnesium alloy significantly dislocated and increased the difference in potentials (corrosion potential increased) at the interface between the metal and solution (Fig. 3) as compared to the reference sample without the coating (Fig. 2). It provides evidence of the beneficial effect of carbon coating deposited on this alloy because the barrier protecting the latter from electrochemical corrosion was increased.

Also SEM analysis of the surface of the examined samples confirmed this desirable impact (Figs 4 - 5). Only single dark spots (probably very small corrosion pits) were visible at the surface of the samples bearing carbon coating (Fig. 5) whereas harmful results of electrochemical corrosion were visible on the whole surface of unprotected AZ31 magnesium alloy (Fig. 4).

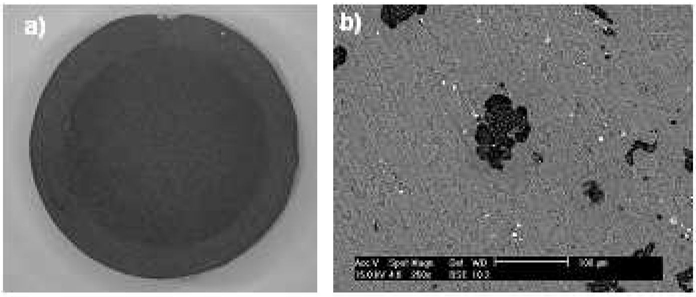

Figure 5 SEM image of the surface of AZ31 magnesium alloy protected by carbon coating on completion of the potentiostatic corrosion test; test duration 1h: a) magnification 3x, b) magnification 250x

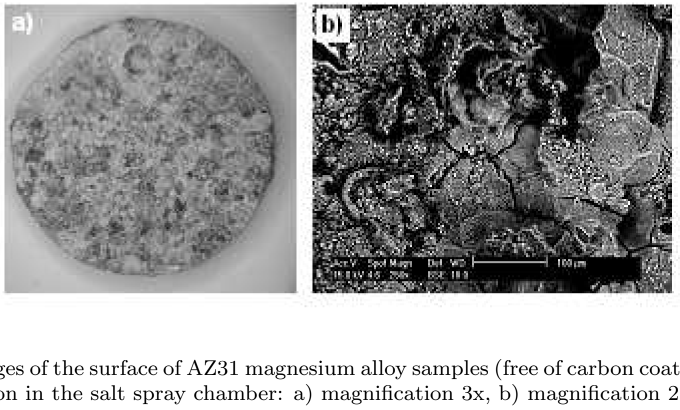

Figure 6 Images of the surface of AZ31 magnesium alloy samples (free of carbon coating) subjected to 5h exposition in the salt spray chamber: a) magnification 3x, b) magnification 250x

3. Determination of corrosion resistance in the salt spray chamber

Determination of corrosion resistance of AZ31 magnesium alloy samples, either bearing carbon coating or not, were carried out in the salt spray chamber of type SIGMA DIESEL (BOSCH) [1]. Conditions of this test are shown in table 4. Samples free of carbon coating were exposed for 5h and samples protected by carbon coatings were sprayed for 200h.

Table 4 Parameters of corrosion test carried out in the salt spray chamber

Test parameters	**Value**
Test duration (Renault Standard Test)	5h and 200 h
Temperature inside the chamber	35 °C ± 1 °C
Humidity inside the chamber	85% - 90%
Spraying intensity (sprayed over 80 cm^2 surface)	2ml ± 0.1ml / h
Air pressure	1.0 bar ± 0.2 bar
NaCl concentration in the solution	5% w/v

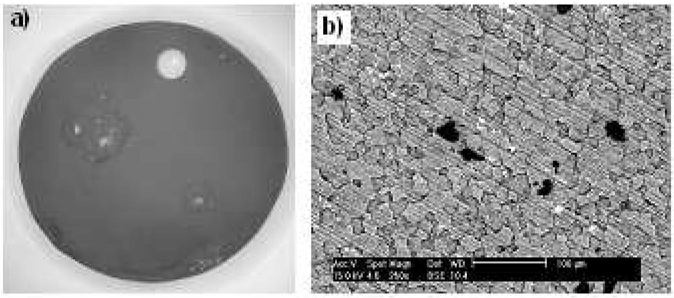

Figure 7 Images of the surface of AZ31 magnesium alloy specimens protected by carbon coating and subjected to 200h exposition in the salt spray chamber: a) magnification 3x, b) magnification 250x

On completion of this test, the surface of both types of samples was observed under metallographic microscope and subjected to SEM analysis. Examples of recorded images are shown in Figs 6 and 7.

Comparison of these images revealed that the surface of naked AZ31 magnesium alloy samples subjected to treatment in the salt spray chamber was corroded after relatively short time of exposition (5h). By contrast, only minimal corrosion pits were visible at the surface of samples bearing the carbon coatings and sprayed for 200h in the salt chamber. Thus the carbon coatings efficiently protected the alloy from corrosion.

4. Conclusions

Technology of carbon coating deposition on magnesium alloys by PACVD method was developed and experimentally tested. Carbon coatings deposited on AZ31 magnesium alloy were characterized by excellent utilitarian properties, in particular by very high corrosion resistance that was corroborated by results of both laboratory investigations and salt spray chamber test. Presented results indicate that the studies should be continued in order to improve PACVD method and produce carbon coatings on specimens with more complex shapes and on internal surfaces of specimens made of magnesium alloys.

References

[1] **Gray, J.E. and Luan, B.**: Protective coatings on magnesium and its alloys – a critical review, *Journal of Alloys and Compounds*, vol.336, 2002, pp.88-113, **2002**.

[2] **Mordike, B.L. and Ebert T.**: Magnesium properties–application–potential, *Material Science and Engineering*, vol.302, pp.37-45, **2001**.

[3] **Gołąbczak, M.**: Deposition of carbon coatings on magnesium alloys by PACVD method. PhD thesis (in Polish), Technical University of Łodz, **2005**.

[4] **Gołąbczak, M. and Mitura, S.**: Studies on utilitarian attributes of carbon coatings deposited by PACVD method on magnesium alloys, Collective publication edited by M. Styp–Rekowski: Constructional and technological aspects of non–conventional manufacturing methods, Bydgoszcz, **2006**, pp.277-284, **2006**, .

[5] **Mitura, S.**: Deposition of thin carbon coatings through hydrocarbon decomposition in electric field. PhD thesis, Technical University of Łodz, **1985**.

[6] **Koryta, J., Dworak, J. and Bochackowa, V.**: Electrochemistry (in Polish), PWN, Warsaw, **1980**.

[7] Collective publication, Electrochemical protection from corrosion (in Polish). WNT, Warsaw, **1991**.

[8] **Galus, Z.**: Theoretical fundamentals of electrochemistry (in Polish). WNT, Warsaw, **1987**.

[9] **Rao, C.**: Fundamentals of linear statistics (in Polish). PWN, Warsaw, **1984**.