Effect of nitrogen incorporated into oxide layer, formed on the magnesium alloys by using r.f. PECVD process, on their corrosion resistance

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Summary

This paper presents the changes in corrosion resistance of SiO_2 coatings generated in the plasma process PECVD (Plasma Enhanced Chemical Vapour Deposition), using RF plasma (13.56 MHz), under the influence of the introduction of nitrogen to their volume. Two magnesium alloys AZ32 and AZ91 were put under the tests. On each of Mg alloys the coating of SiO_2 was made with a thickness of 1000 nm, and the coatings of SiO_xN_y (oxynitride) with a thickness of 60 nm and 500 nm. The obtained results were compiled with the reference samples of these alloys. The corrosion properties of the tested coatings were determined based on the analysis of voltammetric curves. The obtained results show that the introduction of nitrogen to a volume of a thin layer of plasma produced SiO_2, which is the formation of the layer of SiO_xN_y improves the corrosion resistance of both examined magnesium alloys. With a much smaller thickness of SiO_xN_y layer in relation to the thickness of SiO_2 oxide layer the similar corrosion current density decreases were obtained.

Keywords: *corrosion resistance, plasma process, electrochemical methods, magnesium alloys*

Introduction

In a study of new materials for applications in automotive, aviation and aerospace industry the application of light metal alloys, especially magnesium alloys, is still increasing. Among their undeniable advantages are their low specific gravity and yield strength as well as modulus of elasticity, allowing the transfer of great loads. The ratio of strength to weight of castings is also advantageous as well as good machinability. Despite many advantages, magnesium alloys have also drawbacks. The most important of these is the low corrosion resistance and susceptibility to pitting corrosion even in the presence of small concentrations of other metals. In order to increase the corrosion resistance, magnesium and its alloys are subjected to the processes of both physical and chemical surface treatment, which aim is to create a barrier coating between the metal and the surrounding environment. Typical examples of such coatings include chromate coatings. However, due to the high toxicity of their main component, namely Cr (VI), they can no longer be used and are replaced with the conversion coatings generated with using other technologies. Unfortunately, these coatings are much less effective. Therefore, the new technologies for generation and modification of corrosion properties of layers, in order to obtain the best protection against corrosion for light metal alloys, including magnesium, are still researched. In this context, the plasma technologies, ie: thin film deposition (PECVD - Plasma Enhanced Vapor Deposition [1,2] or PACVD Plasma Assisted Chemical Vapour Deposition) [3] and etching (RIE - Reactive Ion Etching), are becoming increasingly popular [4].

The plasma technologies, including the PECVD technologies, are the processes during which the production of a solid layer on any substrate from the reactants takes place, which react each other in the reactor chamber, under vacuum and in a volatile phase. The substrate, in such a process fulfills the role of the mechanical carrier. Working gases containing appropriate reagents are introduced into the reactor where the chemical reaction between them takes place in plasma. The product of this reaction is a solid, which creates a new layer on the surface of mechanical carrier. The advantage of plasma layers is a low temperature of their production (below 350 ^{o}C), high purity of the process (under vacuum) and the ability to control freely the chemical composition and thickness of the generated layers by means of the plasma process parameters, namely: the choice of working gases, the process temperature, time and pressure.

The influence of nitrogen introduced into the volume of SiO_2 coatings produced in the PECVD plasma process, with using RF plasma, on the corrosion properties of magnesium alloys AZ32 and AZ91 is presented in this paper. On each of the two types of alloys the two types of coatings were deposited: SiO_2 coating with a thickness of 1000 nm and SiO_xN_y coatings with a thickness of 60 nm and 500 nm. For comparative purposes, the tests were also performed on the reference samples of each of the Mg alloys. The corrosion properties of the tested coatings were determined based on the analysis of voltammetric curves.

Description of the experiment

For the experiment, four samples were prepared for each of the tested magnesium alloys AZ32 and AZ91. Prior to plasma deposition processes, the surface of each sample was ground and polished, and then cleaned using the standard RCA microelectronic procedure (SC1 + SC2 + buffered HF). On the samples marked with a number 1 the SiO_2 layer with a thickness of 1000 nm was deposited on the plasma stand type Oxford Plasmalab 80 Plus by the PECVD method using RF plasma (13.56 MHz). On the samples marked with the numbers 2 and 3 the layer of SiO_xN_y was deposited by the same method, with the thicknesses of 60 nm and 500 nm. The samples marked with the number 4 were not protected with any of the above mentioned coatings. In this way, we had the reference samples, for each of the examined magnesium alloys. The parameters of the performed plasma deposition processes PECVD are presented in Table 1.

Table 1. The main parameters of PECVD plasma processes carried out under this work.

Sample No	PECVD plasma deposition processs					Coating thickness [nm]
	Temperature [°C]	Plasma power [W]	Pressure in reactor [Pa]	Time of deposition process [min.]	Gas flow [ml/min]	
1	350	15	46,6	55	SiH_4 = 50; N_2O = 50	1000
2	350	10	38,8	2,30	SiH_4 = 150; N_2O = 24; NH_3 = 32	60
3				55		500

Thickness of the deposited layers was measured using single-wavelength ellipsometer (λ = 632.8 nm). Ellipsometry measurements were carried out immediately after the PECVD plasma deposition processes.

The examinations of corrosion properties of magnesium alloys were performed by voltammetric technique [5] [6]. For this purpose, the current density-potential curves (polarization curves) were recorded at the rate of change of the potential of 1mV/sw in the environment of the electrolyte consisting of 0.15M NaCl. Before performing the polarization curves the corrosion potential of the samples was recorded during 1h. The measurements were done in non-thermostated, three-electrode vessel with Ag / AgCl electrode as the reference electrode. The AUTOLAB PGSTAT 302N potentiostat with GPES software was utilized in the tests.

Test results.

Figures 1 and 2 show the polarization curves recorded for the tested coatings and for magnesium alloys without coating. Among the tested coatings the lowest value of corrosion current density was obtained for the SiO_2 layer with a thickness of 1000 nm generated on AZ32. In this case, the value of i_{kor} was 0.08 μA/cm^2. It should be noted that for a 500nm thick layer formed on the same alloy, but containing nitrogen atoms (SiO_xN_y coating) the value of the corrosion current is slightly higher and amounts to 0.10 μA/cm^2. In the case of magnesium alloy AZ91 a similar phenomenon was also observed, ie, the corrosion current density values for the SiO_2 coating with a thickness of 1000 nm are slightly lower than the corrosion current density values obtained for the SiO_xN_y coating, however with a thickness of 500 nm. The i_{kor} values amount to 0.19 μA/cm^2 for SiO_2 coating and 0.27 μA/cm^2 for SiO_xN_y coating.

Table 2. Electrochemical parameters of corrosion processes obtained from voltametric curves.

Material	AZ32			AZ91		
	E_{kor} (V)	i_{kor} (μA/cm^2)	E_{pit} (V)	E_{kor} (V)	i_{kor} (μA/cm^2)	E_{pit} (V)
Pure alloy	-1.504	8.47	-1.375	-1.531	1537	--
1000nm SiO_2	-1.441	0.08	-1.384	-1.485	0.19	-1.391
60nm SiO_xN_y	-1.379	3.72	-1.204	-1.500	2.08	-1.355
500nm SiO_xN_y	-1.469	0.10	-1.374	-1.558	0.27	-1.451

Pitting corrosion was observed only in the case of AZ91 alloy without coating. A lack of pitting corrosion can be associated with high intensity of corrosion processes (high value of corrosion current density, Table 2) on the surface of the tested sample, leading to the formation of the sealed oxide layer. Among the other tested materials the greatest difference of potentials: corrosion potential (E_{kor}) and pitting corrosion potential (E_{pit}) were characteristic for SiO_xN_y coatings for which these differences were 175 mV for the coating with a thickness of 60nm on AZ32 and 145 mV for the coating of 60 nm on AZ91.

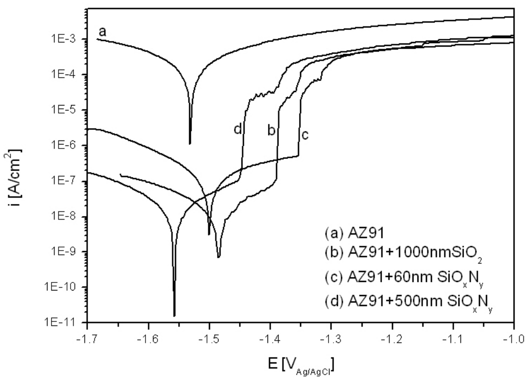

Fig. 1. Voltametric curves for magnesium alloy AZ91: a) as-received, b) with 1000nm SiO_2, c) with SiO_xN_y 60nm, d) with SiO_xN_y 500nm.

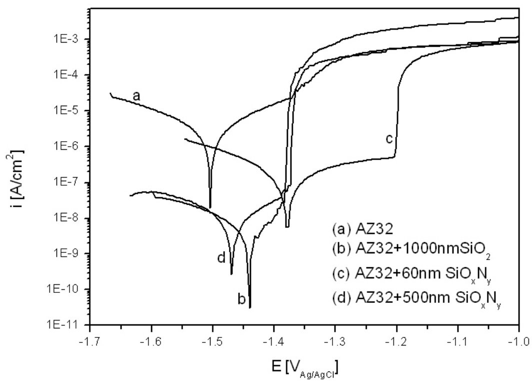

Fig. 1. Voltametric curves for magnesium alloy AZ32: a) as-received, b) with 1000nm SiO_2, c) with SiO_xN_y 60nm, d) with SiO_xN_y 500nm.

Summary

On the basis of experiments carried out in this work, it was found that the process of plasma deposition of SiO_2 and SiO_xN_y layers from RF plasma (PECVD) is suitable for surface modification of Mg alloys to increase their corrosion resistance.

In this paper we examined the protective properties of plasma deposited coatings SiO_2 and SiO_xN_y (using the method of PECVD) on the magnesium alloys AZ32 and AZ91. The lowest corrosion current density values were obtained for the SiO_2 coating with a thickness of 1000 nm (for alloy AZ32 i_{kor} = 0.08 μA/cm^2, for AZ91 i_{kor} = 0.19 μA/cm^2). It should be noted that the corrosion current density value obtained for SiO_xN_y coating with a thickness of 500 nm, for both magnesium alloys is close to the value of this parameter obtained for the SiO_2 layer with a thickness of 1000nm. For the AZ32 alloy the corrosion current density value obtained for the coating SiO_xN_y (500nm) is higher by 0.02 μA/cm^2 compared to the value of this parameter obtained for the coating SiO_2 (1000nm). For the AZ91 alloy, the i_{kor} value for the coating SiO_xN_y (500nm) is higher by 0.08 μA/cm^2 compared to the value of this parameter obtained for the coating of SiO_2 (1000nm).

The results obtained show that the introduction of nitrogen to a volume of a thin plasma deposited layer of SiO_2, ie. generation of SiO_xN_y layer, considerably increases its resistance to the corrosive environment (for both magnesium alloys). For SiO_xN_y coating with a thickness of 500nm the similar decreases of corrosion current density were obtained as for the oxide layer SiO_2 with a thickness of 1000nm.

Bibliography

1 Y.T. Kim et al., „PECVD SiO_2 and SiON films dependant on the rf bias Power for low-loss silica waveguide" Thin Solid Films 475, 271-274 (2005)

2. A. Boogaard, "Plasma-enhanced chemical vapour deposition of silicon dioxide: Optimizimg dielectric films through plasma characterization" Ph.D Thesis, MESA+ Institute for Nanotechnology (2011)

3 J. Olivares Roza et al., "Plasma assisted chemical vapour deposition silicon oxide films grown from SiH4 + NH3 + O2 gas mixtures" Journal of Vacuum Science and Technology A, 16, 2757-2761 (1998)

4 M. Jagadesh Kumar et al., "Selective Reactive Ion Etching of PECVD silicon nitride over amorphous silicon in CF4/H2 and nitrogen containing CF4/H2 plasma gas mixtures" Solid State Electronics 39, 1, 33-37 (1996)

5. X.L. Zhang, Zh.H. Jiang, Zh.P. Yao, Y. Song, Zh.D. Wu, Corrosion Science, 51, 3, (2009) 581

6. S. D. Cramer, S. B., Covino Jr., ASM Handbook: Corrosion : Fundamentals, Testing, and Protection, ASM International, 2003