

Novel Nanometer Thin Films On Magnesium Alloy Prepared By Ultra-Shallow Nitrogen Implantation Using PECVD Method

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The low density of magnesium alloys makes them especially attractive especially for the automotive, electronic and aeronautical industries. Unfortunately, magnesium alloys have a strong susceptibility to atmospheric, galvanic and pitting corrosion and need to be protected with anticorrosive coatings. Traditionally magnesium and magnesium alloys have been protected with chromium-based coatings with the consequent problem of pollution by Cr(IV) ions. The development of new corrosion resistant coatings, by using clean and environmentally friendly processes is very important and strategic for the European industry due to environmental, health and economic considerations.

In this context plasma technology, including: Plasma Enhanced Chemical Vapor Deposition (PECVD) are becoming increasingly popular.

In this paper, magnesium alloys AZ91 were treated using nitrogen plasma (N₂ and NH₃) generated in PECVD reactor. Then, some of magnesium alloys samples were oxidized in oxygen plasma, and for some magnesium alloys samples SiO₂ layer was deposited (in PECVD reactor).

The obtained coatings were investigated using various characterization methods. Electrochemical properties were based on analysis of the voltammetric curves and electrochemical impedance spectroscopy, the microscopic examination was performed by using the techniques of SEM / EDS.

Key words: corrosion resistance, plasma process, electrochemical methods, magnesium alloys, PECVD.

Introduction

In the researches on new materials for applications in automotive and aviation industries and aerospace engineering the light metal alloys are widely used, especially magnesium alloys. The advantages of Mg alloys are: low specific gravity and yield strength and modulus of elasticity, allowing the transfer of great loads. The ratio of strength to weight of castings and good machinability are also advantageous. Despite of many strong points, these alloys also have 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 are aimed to create a barrier layer 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 other coatings and layers to increase the corrosion resistance. However, new technologies for improving the corrosion resistance of Mg alloys are not sufficiently effective. Therefore, it is necessary to modify the existing ones or develop new methods to improve the corrosion properties of magnesium alloys. One of the widely developed methods is coating the Mg surface with the layer of SiO₂ in the "sol-gel" process" [1] and anodic oxidation leading to generation of an oxide layer. However, the plasma technologies enable deposition of SiO₂

layers, and also the surface oxidation of Mg alloys. These methods also lead to improved corrosion resistance of magnesium alloys [2-4].

The paper presents the properties of magnesium alloy AZ91 after the process of implantation with nitrogen molecules before the formation of SiO₂ layer in the process of plasma deposition and before plasma oxidation. The SiO₂ layer and plasma oxidation were performed by PECVD (Plasma Enhanced Vapor Deposition) technique. Nitrogen was introduced to the Mg alloy surface by a process of ultra-shallow implantation with radio-frequency plasma (13.56 MHz) in the PECVD reactor. Plasma generated in the gases N₂ or NH₃ was used in the implantation process.

Materials and Methods

PECVD plasma technologies, are the processes during which the solid layer formation takes place on any substrate from the reactants, which react each other in the reactor chamber, under vacuum and in volatile phase. The substrate, in such a process, fulfills the role of a mechanical carrier. Working gases containing appropriate reactants are introduced into the reactor where the chemical reaction proceeds between them in plasma. The product of this reaction is a solid, which forms a new layer on the surface of the mechanical carrier. The advantage of plasma layers is a low temperature (below 350°C) of their generation, high purity of the process (under vacuum) and the ability to free control of the chemical composition and thickness of the produced layer using the process parameters (composition of working gases, temperature, time, power and pressure). Plasma reactors also allow you to conduct multistage processes, such as cleaning the surface of the samples, ultra-shallow ion implantation to the surface of the sample, deposition of the proper layer and annealing, without contacting the sample with the environment.

Before the formation of SiO₂ layers and before the plasma oxidation the surface of samples was cleaned and then subjected to nitrogen implantation process. Implantation was carried out with radio-frequency plasma in the PECVD reactor using N₂ or NH₃ gas. The parameters of the surface treatment processes of AZ91 alloy are shown in Table 1.

All processes were carried out on the plasma stand Oxford Plasmalab 80 Plus, with PECVD method using radio-frequency plasma (13.56 MHz).

Table 1. The main parameters the processes of plasma deposition and plasma oxidation.

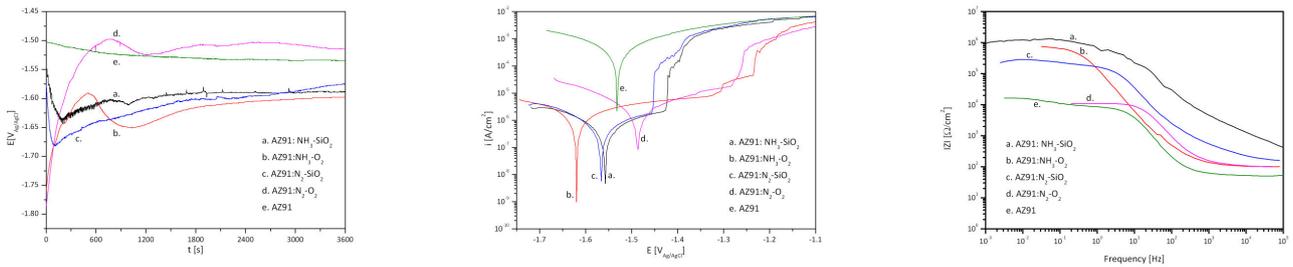
Sample No.	Implantation	Plasma deposition				Plasma oxidation				Thickness [nm]
		Power [W]	Temp. [°C]	Gas flow [ml/min]	Time [min]	Power [W]	Temp. [°C]	Gas flow [ml/min]	Time [min]	
1	NH ₃	80	300	SiH ₄ =150 N ₂ O=100	10	--	--	--	--	30
2	NH ₃	--	--	--	--	100	300	O ₂ =50	10	14
3	N ₂	80	300	SiH ₄ =150 N ₂ O=100	10	--	--	--	--	44
4	N ₂	--	--	--	--	100	300	O ₂ =50	10	20

Voltametric measurements were carried out with a scan rate of 1 mV/s within the range of -150 mV to 1000 mV versus open circuit potentials and polarization curves corresponding to every examined material were recorded. Prior to each polarization experiments, the samples were immersed in the electrolyte solution 0.5M/l NaCl for 1 h while monitoring the open circuit potential to establish steady state conditions. A three-electrode cell arrangement was applied using the Ag/AgCl electrode as reference electrode and a platinum wire as the auxiliary electrode (counter electrode). The measurements were carried out by means of EcoChemie System of AUTOLAB PGSTAT 302N with relevant software. The impedance (electrochemical impedance spectroscopy, EIS) data was obtained

at the open circuit potential with a Princeton Applied Research model VersaStat 3 system. The frequency range analysed, went from 10^6 Hz up to 10^{-3} Hz, with the frequency values spaced logarithmically (ten per decade). The amplitude of sinusoidal voltage signal applied to the system was 10 mV rms (root-mean-square). Prior to the beginning of the measurements, the specimens were maintained for 1.5 h in sodium sulphate (VI) solution Na_2SO_4 of 0.5 M/l (pH=6.0) for stabilisation of an open – circuit potential. The chemical composition of the layers obtained on magnesium alloys was examined using secondary ion mass spectrometer - MiniSIMS.

Results

Electrochemical measurements

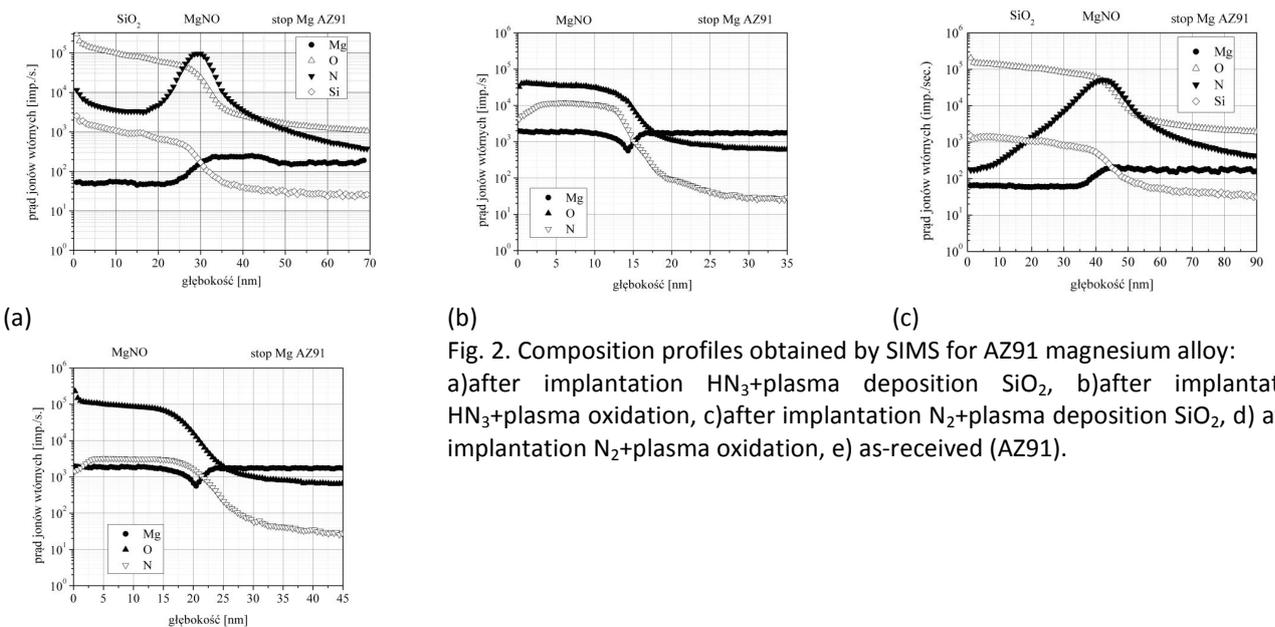


(a) (b) (c)
Fig. 1. Open circuit potentials (a), voltametric curves (b) in 0.15M NaCl and impedance modulus (c) in 0.5 M Na_2SO_4 for magnesium alloy AZ91: a)after implantation HN_3 +plasma deposition SiO_2 , b)after implantation HN_3 +plasma oxidation, c)after implantation N_2 +plasma deposition SiO_2 , d) after implantation N_2 +plasma oxidation, e) as-received (AZ91).

Table 2. Electrochemical corrosion parameters of the samples obtained from polarization curves.

Sample	E_{corr} [V _{Ag/AgCl}]	i_{corr} [$\mu\text{A}/\text{cm}^2$]	E_{pitt} [V _{Ag/AgCl}]	$E_{\text{corr}} - E_{\text{pit}}$ [V _{Ag/AgCl}]
As-received (AZ91)	-1.531	700.0		
implantation HN_3 +plasma deposition SiO_2	-1.558	3.0	-1.426	-0.132
implantation HN_3 +plasma oxidation	-1.620	6.3	-1.323	-0.297
implantation N_2 +plasma deposition SiO_2	-1.566	2.4	-1.456	-0.110
implantation N_2 +plasma oxidation	-1.487	5.0	-1.283	-0.204

Surface composition



(a) (b) (c)
Fig. 2. Composition profiles obtained by SIMS for AZ91 magnesium alloy: a)after implantation HN_3 +plasma deposition SiO_2 , b)after implantation HN_3 +plasma oxidation, c)after implantation N_2 +plasma deposition SiO_2 , d) after implantation N_2 +plasma oxidation, e) as-received (AZ91).

(d)

Conclusions

1. Plasma processes occurring on the surface of magnesium alloy AZ91 influenced its corrosive properties. For the samples with a layer produced in the process of plasma deposition and after plasma oxidation compared to the pure alloy a significant decrease in corrosion currents was observed as well as significant increase of impedance modulus.
2. The smallest values of i_{corr} and greatest values of impedance modulus, and thereby the highest corrosion resistance, were characteristic for the samples with the layer produced in the plasma deposition process.
3. The corrosion resistance of AZ91 magnesium alloy after the process of implementation of nitrogen molecules with radio-frequency plasma in the PECVD reactor using N_2 or NH_3 gas and after formation of the layer in the plasma deposition or plasma oxidation process was similar. However, it should be noted that for the samples after the oxidation process the thickness of the generated layer was 14-20 nm and was smaller than the layer produced in the process of plasma deposition (30-40nm).
4. For the samples with a layer generated in the plasma oxidation process the greatest difference of corrosion potential and pitting corrosion potential was observed. These samples were characterized by the greatest resistance to the occurrence of local corrosion processes (pitting corrosion).

References

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