CORRODION BEHAVIOUR OF $Mg_3Ta_2O_8$ PSEUDO-BINARY OXIDE DEPOSITION BY PULSED LASER DEPOSITION ON CARBON STEEL DISKS

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Abstract

Hydrothermally obtained $Mg_3Ta_2O_8$ pseudo-binary nanomaterial from MgO and Ta_2O_5 (3:1) precursors was deposited using the pulsed laser deposition (PLD) technique on carbon steel disks. The PLD main processes parameters, i.e. the pulse energy and the deposition time were varied in order to determine the combination that ensures the best corrosion inhibition. Morphological investigations were carried out (scanning electron microscopy and atomic force microscopy). The anticorrosive properties of the deposited layers were studied in 0.3 M NaCl saline solution. The best anticorrosive protection was observed in the case of the deposited layers on carbon steel disk using the lower energy, i.e. 10mJ for a deposition time of 60s, i.e. 61.94 % inhibition efficiency.

Keywords: Mg oxide, hydrothermal, AFM, corrosion, PLD

1. INTRODUCTION

Steel is one of the most used material in constructions and in a lot of other industries, e.g. power plants, petroleum industry, etc. due to its good structural and mechanical properties compared with its price, although is affected by corrosion. Corrosion is a natural process which affects the integrity of steel at its interaction with environment and this affects the integrity of the equipment and constructions that make use of it [1-3]. To prevent control and reduce this process, a lot of researches were focused on understanding the process and on offering solutions for these. Recent advances were noticed in using corrosion inhibitors alongside other anticorrosive methods (electroplating, anodizing, chrome-ting, etc.) [1, 4].

Corrosion inhibitors can be different types of materials with specific properties and can applied onto a surface as a protective layer. Pseudo-binary oxides as: $Zn(Ta_{1-x}Nb_x)_2O_6$, $Zn_3Ta_2O_8$ and $Zn_3Nb_2O_8$ were already reported in literature as acting like corrosion inhibitors with excellent results [5-7].

Beside new materials development, novel techniques for depositing of the corrosion inhibitors were used / developed. Pulse laser deposition (PLD) represent such a technique which implies the irradiation of a target with a laser with the purpose to transport its solid components onto a substrate and thus obtaining a thin films [8-12]. The PLD technique have been successfully applied to a wide range of materials [13].

Also, studying the environments in which an inhibitor acts better in combination with a certain type of steel - dependent onto the future function of the steel component - are necessary to identify the appropriate corrosion inhibitor. The anticorrosion tests for the corrosion inhibitors are performed in various environments like: NaCl, HCl, H_2SO_4, Na_2SO_4 [1-3, 5-7].

The present study was focused on obtaining of $Mg_3Ta_2O_8$ pseudo-binary nanomaterial and on its morphological and topographical characterization. Another purpose of this study was to evaluate the anticorrosive properties of PLD depositions of $Mg_3Ta_2O_8$ on carbon steel disk electrodes in 0.3 mole / L NaCl saline solution.

2. EXPERIMENTAL

2.1. Synthesis

Powder sample of $Mg_3Ta_2O_8$ pseudo-binary oxide nanomaterials were obtained using the hydrothermal method. The precursors used during the synthesis were MgO (99%, Sigma) and Ta_2O_5 (99.99%, Sigma) while keeping the molar ratio 3:1. The pH values for the synthesis were fixed at 12. The obtained mixture were placed into an oven for 12 hours at 250 °C and after the synthesis reaction the precipitate was filtrated, washed with distilled water, then dried.

2.2. Apparatus

The surface morphologies of the PLD realized depositions and the dimensions of particles from the surface were investigated using scanning electron microscopy (SEM - Model Inspect S) and atomic force microscopy (AFM - Model Nanosurf EasyScan 2 Advanced Research). For AFM measurements was used the noncontact mode cantilever (scan size 2.29 µm x 2.29 µm).

The deposited structures of $Mg_3Ta_2O_8$ nanomaterials were obtained by PLD technique on carbon steel disks electrodes (OL) (2 mm thick, 10 mm diameter) with the chemical composition (wt.%): Fe: 98; Si: 0.339; Al: 0.0309; Mo: 0.0309; Nb; 0.0023; Ti: < 0.005; Mn: 0.619; Co: 0.0138; V: < 0.005; Cr: 0.18; Cu: 0.311; Zr: < 0.005; Ni: 0.179; W: < 0.05; P: , 0.005; C: 0.165; Pb:< 0.05 and S: < 0.005.

Before the realizations of the depositions, the carbon steel disks surfaces were mechanically polished using emery paper (different grades), rinsed with double distilled water and degreased in ethanol. Then, using a vacuum chamber ($2.9x10^{-4}$mbar) in combination with an Ekspla SL212P / SH / FH Nd: YAG laser equipment, the deposited structures were realized. The pulse energy (E_{p1} = 10 mJ, E_{p2} = 30 mJ, E_{p3} = 50 mJ) and the deposition time (t_1 = 30 s, t_2 = 60 s) were varied in order to determine the combination that ensures the best corrosion inhibition.

The modified disk electrodes were characterized from an electrochemical point of view using a potentiostat (Voltalab Model PGZ 402) coupled with a three electrode electrochemical cell, comprised of: a platinum wire as counter electrode, a satured calomel electrode as reference electrode and bare or PLD modified carbon steel disk as working electrode. To ensure a controlled active surface, the working electrodes were mounted into a Teflon body. The potentiodynamic polarization measurements were recorded at room temperature (23 °C). The potential was swept in the -1.3 V ÷ -0.6 V at a scan rate of 1 mV /s. The open circuit potential (OCP) of the modified electrodes was monitored for 30 minutes before polarization. The electrolyte solution used for the corrosion tests was 0.3 mole /L Nalco.

The parameters used for the PLD depositions are given in **Table 1**.

Table 1 PLD thin films deposition characteristics

Sample	Deposited material	Pulse energy	Deposition time
a	$Mg_3Ta_2O_8$	E_{p1} = 10 mJ	t_1 = 30 s
b		E_{p2} = 30 mJ	
c		E_{p3} = 50 mJ	
d		E_{p1} = 10 mJ	t_2 = 60 s
e		E_{p2} = 30 mJ	
f		E_{p3} = 50 mJ	
g	OL electrode		

3. RESULTS AND DISSCUSION

In **Figure 1** are presented the SEM micrographs for the realized depositions of $Mg_3Ta_2O_8$ using PLD technique. The micrographs reveal a uniform deposition of the nanomaterial for all electrodes and that the density of the particle's agglomeration increase with time deposition (**Figures 1 d), e)** and **f)**).

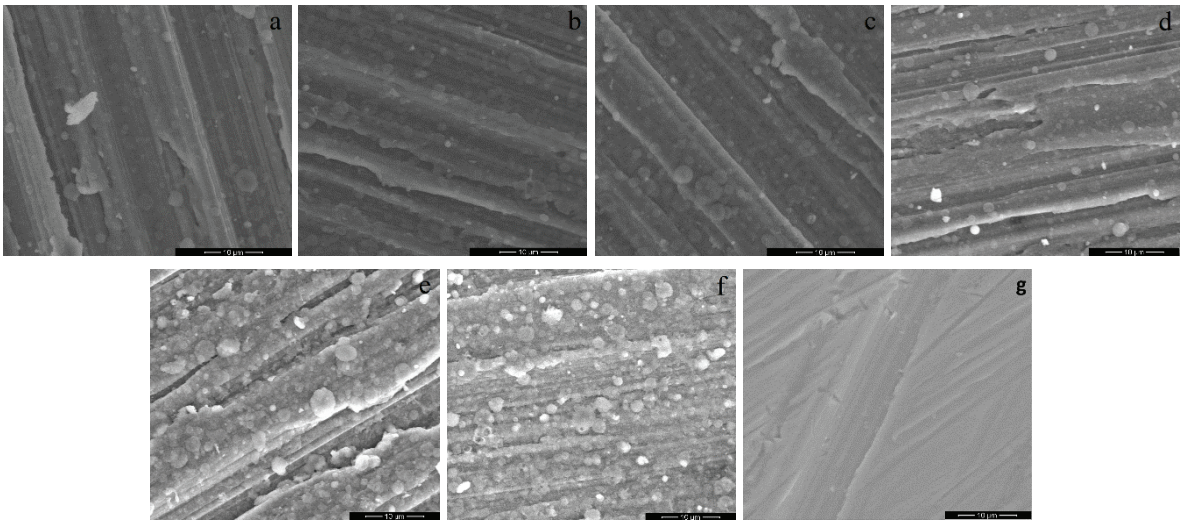

Figure 1 SEM micrographs of $Mg_3Ta_2O_8$ pseudo-binary oxide nanomaterial deposited using PLD technique on carbon steel disks varying the pulse energy and the deposition time: a) $Mg_3Ta_2O_8$ (E_{p1}, t_1); b) $Mg_3Ta_2O_8$ (E_{p2}, t_1); c) $Mg_3Ta_2O_8$ (E_{p3}, t_1); d) $Mg_3Ta_2O_8$ (E_{p1}, t_2); e) $Mg_3Ta_2O_8$ (E_{p2}, t_2); f) $Mg_3Ta_2O_8$ (E_{p3}, t_2); g) OL electrode

Figure 2 shows 2D AFM surface images of the PLD deposited structures using $Mg_3Ta_2O_8$ nanomaterials and varying the deposition parameters E_p and t. As it can be seen from these images, the morphologies of the thin films deposited in 60 s preserve the morphology of their corresponding thin films deposited in 30 s with the same E_p.

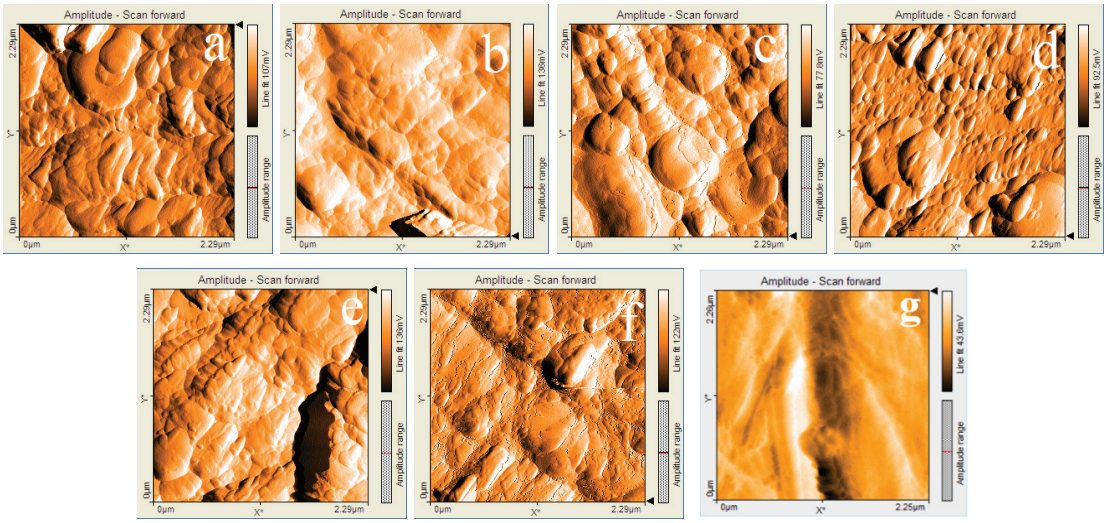

Figure 2 2D AFM surface images of: a) $Mg_3Ta_2O_8$ (E_{p1}, t_1); b) $Mg_3Ta_2O_8$ (E_{p2}, t_1); c) $Mg_3Ta_2O_8$ (E_{p3}, t_1); d) $Mg_3Ta_2O_8$ (E_{p1}, t_2); e) $Mg_3Ta_2O_8$ (E_{p2}, t_2); f) $Mg_3Ta_2O_8$ (E_{p3}, t_2); g) OL electrode

From the AFM data, according to [14], were calculated the surface roughness: S_a - the average roughness and S_q - the mean square root roughness, as is given in **Table 2**. The smallest values for S_a and S_q were

obtained for the carbon steel electrode modified with $Mg_3Ta_2O_8$ (E_{p1}, t_2). These values indicated that the PLD deposition was uniform and continuous, which means that the material has the property of protecting a surface.

Also, the dimension of the particles that are present on the surface of the PLD deposited thin films and their layer thickness (S_y) were calculated and presented in **Table 2**.

Table 2 Surface particle dimensions and the nano-roughness

Sample	Area (pm^2)	S_a (nm)	S_q (nm)	S_y (µm)	Particle dimension (nm)
a	5.305	23	28	0.24	121
b	5.305	40	49	0.40	133
c	5.305	22	27	0.16	38
d	5.305	17	22	0.17	90
e	5.305	39	50	0.34	177
f	5.305	27	35	0.22	90

The open circuit potential versus time for bare and modified carbon steel disk electrodes in 0.3 mole / L NaCl saline solution for 30 minutes is shown in **Figure 3 (a).** It can be observed that the PLD deposited layers determinate the shifting of the OCP of the electrodes toward more positive values compared to the bare OL.

Tafel plots of the carbon steel disk electrodes modified with PLD deposited layers of $Mg_3Ta_2O_8$ recorded in 0.3 mole / L NaCl saline solution are presented in **Figure 3 (b).** The Tafel parameters obtained from Tafel plots are shown in **Table 3**.

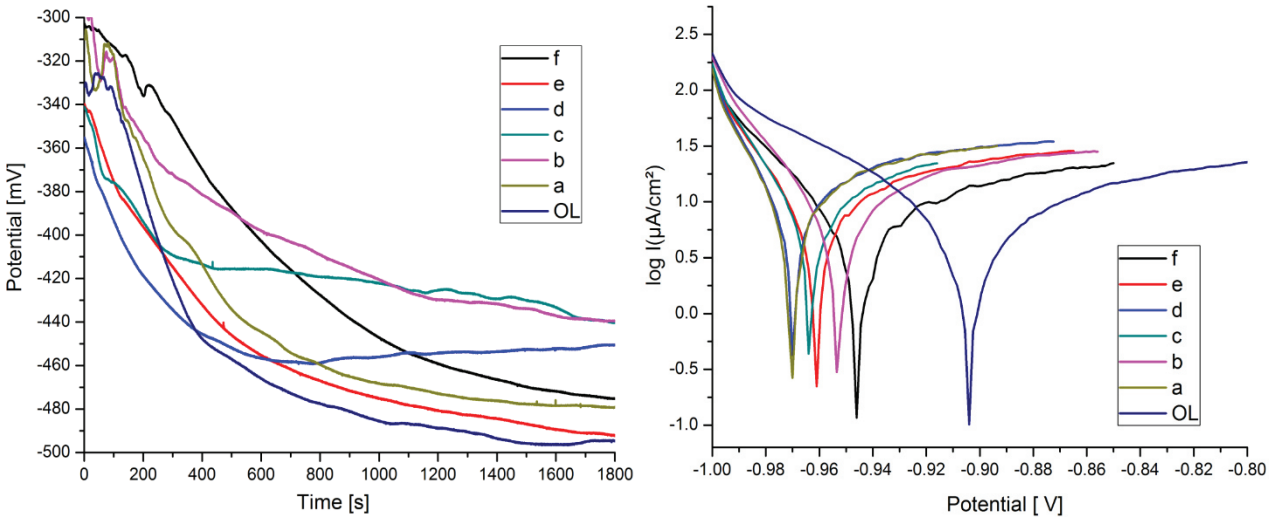

Figure 3 a) Evolution of open circuit potential with time for investigated electrodes, in 0.3 mole / L NaCl saline solution; b) Tafel representation of polarization curves recorded in 0.3 mole / L NaCl saline solution

As it can be seen in **Table 3**, for the bare OL electrode was measured a corrosion potential (E_{corr}) of -905.6 mV and the corresponding current density (i_{corr}) is 11.7579 µA/cm^2. For all modified electrodes, due to the process of deposition of the nanomaterial, the polarization curves were shifted towards lower corrosion current densities which suggest a better stability of the covering nanomaterial. For the bare OL electrode was also recorded the larger polarization resistance (R_p) 2.79 kohm·cm^2 decreasing slightly for the other modified electrodes.

The inhibition efficiency (*IE*) was calculated for each one of the PLD deposited layers of $Mg_3Ta_2O_8$ on the carbon steel disk electrodes using the equation from [15]. The highest *IE* of 61.94 % was obtained for the PLD deposition of $Mg_3Ta_2O_8$ on carbon steel electrode disk using a pulse energy of 10 mJ for a deposition time of 60 s.

Table 3 The Tafel parameters calculated for the investigated electrodes after 30 minutes immersion in 0.3 mole / L NaCl solution

Sample	E (i=0) (mV)	R_p (kohm·cm^2)	I_{corr} (µA/cm^2)	V_{corr} (µm/y)	IE (%)
OL	-905.6	2.79	11.7579	137.5	-
a	-970.5	1.07	5.0089	58.58	57.39
b	-951.5	1.42	5.3826	62.95	54.22
c	-963.1	1.25	4.8175	56.34	59.02
d	**-970.0**	**1.02**	**4.4742**	**52.33**	**61.94**
e	-961.3	1.53	4.7347	55.37	59.73
f	-945.9	2.52	4.63	54.23	60.62

4. CONCLUSION

$Mg_3Ta_2O_8$ pseudo-binary oxide nanomaterial was obtained by hydrothermal method and successfully deposited on carbon steel disk electrodes using the PLD technique. AFM analysis revealed that a longer deposition times will not influence the morphology of the surfaces.

The corrosion tests revealed that increasing the deposition time, in the same conditions of pulse energy, the *IE* increases too. It seems like a longer deposition time offers the condition for an uniform and continuous deposition. The best anticorrosive protection was observed in the case of the deposited layers on carbon steel disk using the lower energy, i.e. 10mJ for a deposition time of 60s, i.e. 61.94 % inhibition efficiency.

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