CORROSION TEST IN 0.1 M HCl OF THE PSEUDO-BINARY OXIDES UNDOPED AND DOPED WITH Er^{3+} IONS

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Abstract
This study presents the realization of new type materials based on $Zn_3Nb_2O_8$ undoped and doped with Er^{3+} ions designed to improve corrosion inhibition of steel in aggressive media. The thin films structures were obtained on carbon steel through the spin-coating technique. Morphological investigations of thin films were carried out by atomic force microscopy (AFM). The inhibition of a steel corrosion process was evaluated in an aggressive environment of 0.1 M HCl by performing electrochemical investigations such as open circuit potential (OCP) and the potentiodynamic polarization technique. The influence of variations in the cathodic Tafel slopes β_c and anodic Tafel slopes β_a over the corrosion rates was discussed. The best corrosion inhibition efficiency of 93.3% was realized by the steel electrode covered with spin coating techniques were obtained when the layer was made for the $Zn_3Nb_2O_8:Er^{3+}$ type structure obtained first by the solid-state method using $Zn(NO_3)_2x4H_2O$, Nb_2O_5 and $Er(NO_3)_3x5H_2O$.

Introduction
Nowadays corrosion is a natural process and also a universal phenomenon of metals and is one of the main problems faced by almost all industries and can lead to safety issues and destroy the integrity of equipment and consumables. Corrosion of metals is a natural and inevitable process that imposes considerable costs on many industries and can also have irreparable consequences. Corrosion is the deterioration of metal in the presence of the environment by chemical or electrochemical means [1–5]. Corrosion of metals leads to a huge economic loss worldwide [6-8]. There are various methods of reducing or preventing corrosion. The use of corrosion inhibitors is one of the ways to protect metal surfaces against corrosion [9-13]. There are several methods, such as: cathodic protection, galvanizing, painting and coatings, to prevent metal corrosion. Choosing the best corrosion prevention method depends on many factors, including cost, effectiveness, metal type, and corrosive environment, but it can be said that coatings are probably the most convenient method of preventing metal corrosion due to their low cost, availability of raw materials, flexibility, and simplicity. In this study, we have developed new knowledge in the field of advanced materials that provide efficient anticorrosion protection, through the design of new nanostructured films based on pseudo-binary oxides of the type $Zn_3Nb_2O_8$ undoped and doped with Er^{3+} ions. The new materials were obtained by solid-state synthesis and were applied to inhibit the corrosion of the carbon steels (OL) by using technologies for the production of thin films by spin-coating in an acidic environment (0.1 M HCl).

Experimental
Nanomaterials of the tyep $Zn_3Nb_2O_8$ undoped and doped with Er^{3+} were obtained by the solid-state method at a temperature of 1100 °C for 4 hours at a heating/cooling rate of 5 °C/min in a

SNOL calcination furnace. The precursors used in the solid-state synthesis are presented in Table 1.

Table 1. Precursors used in solid-state synthesis

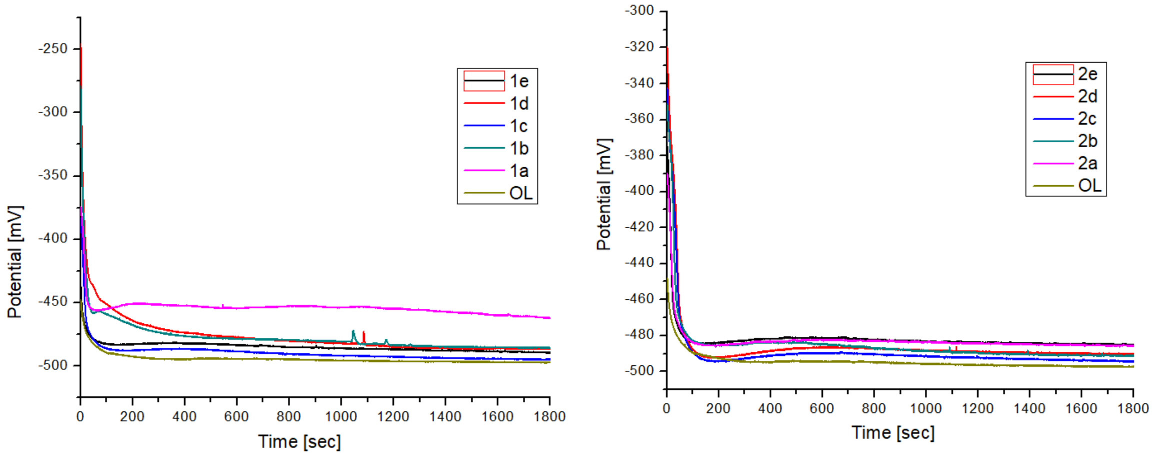
Sample	Precursor 1	Precursor 2	Precursor 3	Molar ratio
1a	Nb_2O_5	$Zn(NO_3)_2x4H_2O$	-	1:3
1b	Nb_2O_5	$Zn(NO_3)_2x4H_2O$	$Er(NO_3)_3x5H_2O$	1:3:0.01
1c	Nb_2O_5	$Zn(NO_3)_2x4H_2O$	$Er(NO_3)_3x5H_2O$	1:3:0.02
1d	Nb_2O_5	$Zn(NO_3)_2x4H_2O$	$Er(NO_3)_3x5H_2O$	1:3:0.1
1e	Nb_2O_5	$Zn(NO_3)_2x4H_2O$	$Er(NO_3)_3x5H_2O$	1:3:0.2
2a	Nb_2O_5	$Zn(CH_3COO)_2x2H_2O$	-	1:3
2b	Nb_2O_5	$Zn(CH_3COO)_2x2H_2O$	$Er(NO_3)_3x5H_2O$	1:3:0.01
2c	Nb_2O_5	$Zn(CH_3COO)_2x2H_2O$	$Er(NO_3)_3x5H_2O$	1:3:0.02
2d	Nb_2O_5	$Zn(CH_3COO)_2x2H_2O$	$Er(NO_3)_3x5H_2O$	1:3:0.1
2e	Nb_2O_5	$Zn(CH_3COO)_2x2H_2O$	$Er(NO_3)_3x5H_2O$	1:3:0.2
3a	Nb_2O_5	ZnO	-	1:3
3b	Nb_2O_5	ZnO	$Er(NO_3)_3x5H_2O$	1:3:0.01
3c	Nb_2O_5	ZnO	$Er(NO_3)_3x5H_2O$	1:3:0.02
3d	Nb_2O_5	ZnO	$Er(NO_3)_3x5H_2O$	1:3:0.1
3e	Nb_2O_5	ZnO	$Er(NO_3)_3x5H_2O$	1:3:0.2

Thin film depositions were performed by spin-coating technique on steel disks with a diameter of 10 mm and a thickness of 2 mm. Before the deposits were made, these discs were polished with sandpaper of various degrees of roughness, washed with double distilled water and then degreased with ethanol.

After the thin films were made, they were subjected to corrosion tests by electrochemical methods in order to validate them as corrosion inhibitors. The open circuit potential (OCP) of the modified electrodes was monitored for 30 minutes before polarization. The corrosive environment in which the corrosion tests were performed consisted of 0.1 M HCl acidic solution.

Results and discussion

The open circuit potential (OCP) measurements in Figure 1 showed that the coated electrodes stabilize at approximately 400-500 s. This result provides preliminary information about the nature of the processes occurring at the interfaces between the metal/thin film and the electrolyte. The OCP is a qualitative indicator of the corrosion state of the steel substrate in an acidic environment and helps to determine the immersion time required to reach the equilibrium state.



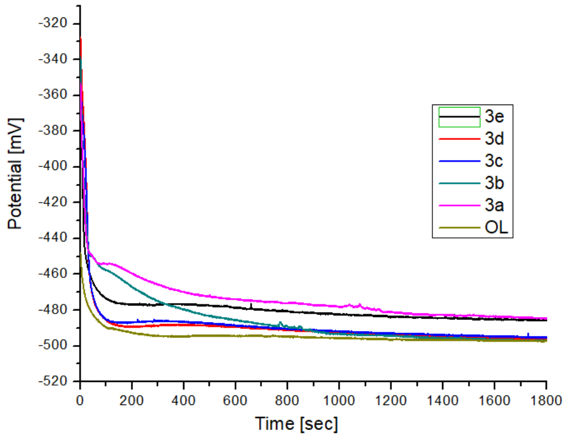


Figure 1. The OCP for electrodes modified by spin coating technique for 30 minutes immersed in 0.1 M HCl: steel electrode, $Zn_3Nb_2O_8$ and $Zn_3Nb_2O_8$: Er^{3+} (notations according to table 1)

The polarization curves were analyzed using VoltaMaster 4 v.7.09 software and the Tafel parameters were determined: corrosion potential (E_{corr}), polarization resistance (R_p), corrosion current density (i_{corr}), anodic (β_a) and cathodic (β_c) Tafel curves as well as corrosion rate (v_{corr}). The degree of corrosion inhibition (*IE*) [7] was calculated for each drop casting deposit.

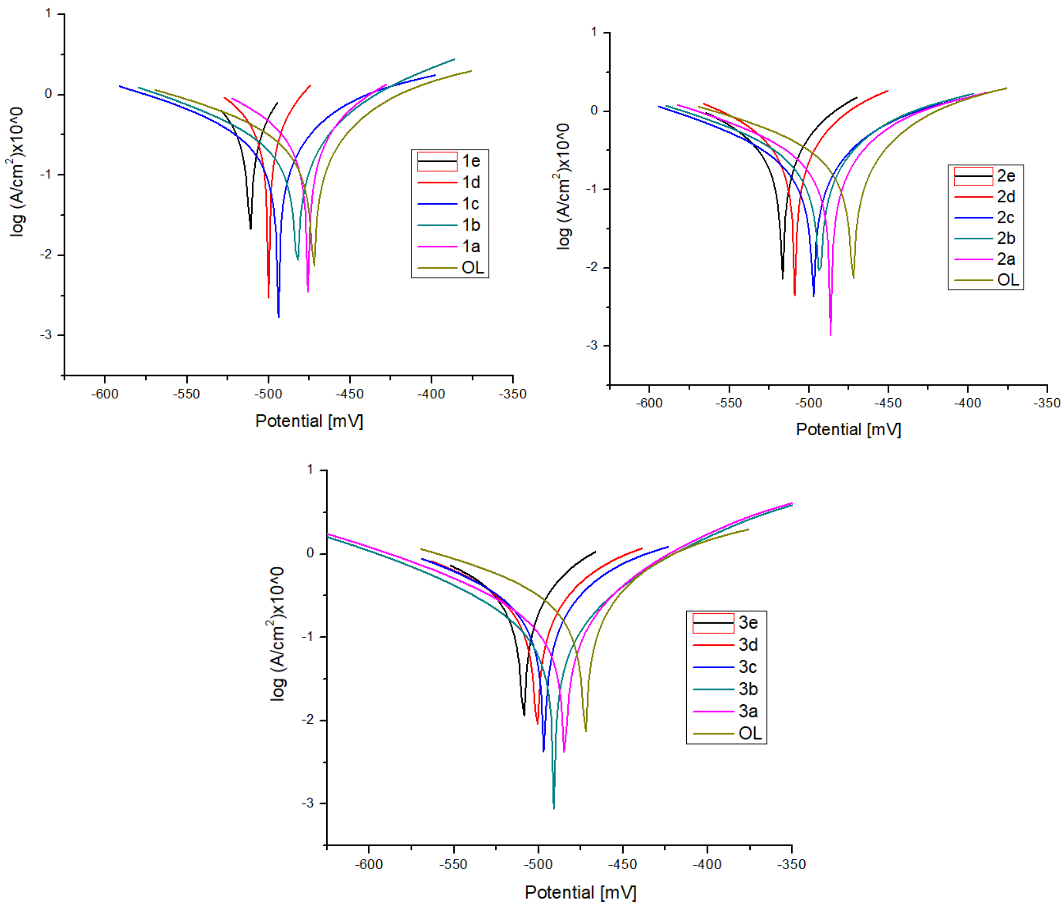


Figure 2. Tafel polarization curves for electrodes modified by spin coating technique after immersion in 0.1 M HCl media of: steel electrode, $Zn_3Nb_2O_8$ and $Zn_3Nb_2O_8$: Er^{3+} (notations according to table 1)

Table 2. Tafel parameters for electrodes deposited by spin coating technique analyzed after 30 minutes immersion in 0.1 M HCl medium.

Electrodes	**E (I = 0) (mV)**	**R_p (Ωxcm^2)**	**i_{corr} (mA/cm^2)**	**β_a (mV)**	**β_c (mV)**	**v_{corr} (mm/Y)**	**IE (%)**
OL	-471.07	96.95	0.9501	207.2	-220.2	5.265	-
1a	-475.9	129.21	0.1314	70.8	-123.3	1.536	86.16
1b	-482.7	183.37	0.1216	86.6	-133.3	1.422	87.20
1c	-485.1	175.14	0.1096	79.1	-122.5	1.282	88.46
1d	-488.5	179.66	0.0864	70.7	-99.6	1.010	90.90
1e	**-494.1**	**164.13**	**0.0639**	**49.7**	**-74.9**	**0.748**	**93.3**
2a	-486.8	112.3	0.2727	111	-178.9	3.190	71.3
2b	-486.4	152.7	0.1977	110.9	-164.1	2.311	79.19
2c	-493.8	146.49	0.1527	91	-149.0	1.785	83.92
2d	-493.8	210.35	0.1350	133	-107.8	1579	85.79
2e	-497.4	188.88	0.0971	76.6	-116.9	1.135	89.78
3a	-484.6	123.69	0.2601	97.44	-169.5	3.042	72.62
3b	-488.8	147.44	0.2421	98.5	-163.9	2.831	74.51
3c	-496.1	177.14	0.2323	89.9	-124.5	2.716	75.54
3d	-496.7	167.47	0.2153	76.4	-106.4	2.518	77.33
3e	-504.8	162.55	0.2046	67.5	-134.7	2.393	78.46

In all cases analyzed of steel electrodes modified by spin coating of thin films made of pseudo-binary oxides, an improvement in their corrosion inhibition was found between 71% and 93%.

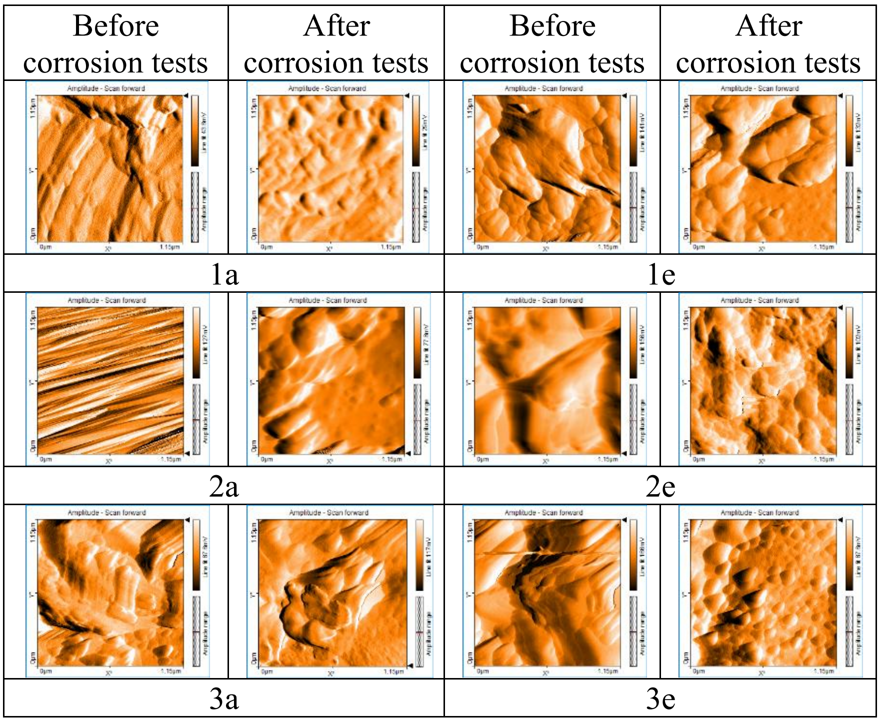


Figure 3. AFM images before and after corrosion tests for samples deposited by spin-coating technique according to table 1

Analyzing the variation of the corrosion potential and corrosion current as the inhibition efficiency increases (Tables 2), it can be observed that the corrosion current decreases proportionally to the corrosion rate, and the corrosion potential moves towards cathodic values. For all deposits with materials obtained by the solid-state method and tested in acidic media, the polarization resistance (*Rp*) of the modified OL steel electrode increases. From the AFM (Figure 3) investigations it can be observed that after contact with acidic medium, the thin films retain the structure of the material that comes into direct contact with the corrosion medium, but the morphology is different and the size of the agglomerates is larger.

Conclusion

It was found that the best corrosion inhibition values IE = 93.3% for spin coating were obtained when the layer was made for the $Zn_3Nb_2O_8:Er^{3+}$ type structure obtained first by the solid-state method using $Zn(NO_3)_2x4H_2O$, Nb_2O_5 and $Er(NO_3)_3x5H_2O$ as precursors in an acidic medium, which managed to provide a smooth, non-porous and uniformly coated surface. From the AFM measurements it can be seen that the corrosion inhibition mechanism of carbon steel is based on the physical protection caused by the compact and adherent layers made by the pseudo-binary oxide at the interface with the steel.

Acknowledgements

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