

ANTICORROSIVE NANOMATERIALS OF THE TYPE $\text{Zn}_3\text{Nb}_2\text{O}_8$ UNDOPED AND DOPED WITH TRIVALENT Er^{3+} IONS IN SALINE ENVIRONMENT

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Abstract

This study involves the depositions of metal-oxide films via the spin-coating method, using pseudo-binary $\text{Zn}_3\text{Nb}_2\text{O}_8$ oxides, both undoped and doped with Er^{3+} ions, synthesized hydrothermally on metallic substrates. Following the preparation of the thin films, electrochemical method were employed to evaluate their corrosion resistance and to validate their potential as corrosion inhibitors.

The tests were carried out using a Voltalab PGZ 402 potentiostat connected to a three-electrode electrochemical cell, with the working electrodes consisting of steels discs coated with the thin films. The working parameters included a potential range set between -1.3V and -0.6V and a scan rate of 1mV/s. The measurements were performed at a temperature of 23°C. The open circuit potential (OCP) of the modified electrodes was monitored for 30minutes prior to polarization. The corrosive medium used for the tests was a 0.3 M NaCl saline solution.

Introduction

Over time, zinc alloys like Zn-Ni and Zn-Co were developed to improve corrosion resistance, thanks to densely packed crystallographic planes and a more stable ionization environment. Additional improvements were achieved using protective porphyrin layers, amorphous oxide compounds, or pseudo-binary oxide nanomaterials [1].

Experimental

In order to obtain nanomaterials via hydrothermal synthesis, the following precursors were used, as follows:

Sample	Precursor 1	Precursor 2	Precursor 3	Molar ratio
1e	Nb_2O_5	$\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	Er_2O_3	1:3:0.2
2e	Nb_2O_5	$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$	Er_2O_3	1:3:0.2
3e	Nb_2O_5	ZnO	Er_2O_3	1:3:0.2
4a	Nb_2O_5	$\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	-	1:3
4e	Nb_2O_5	$\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	$\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	1:3:0.2
5a	Nb_2O_5	$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$	-	1:3
5e	Nb_2O_5	$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$	$\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	1:3:0.2
6a	Nb_2O_5	ZnO	-	1:3
6e	Nb_2O_5	ZnO	$\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	1:3:0.2

Table 1. Precursors used in the hydrothermal synthesis

Experimental condition using the hydrothermal method depended on temperature (240°C), time (12h) and pH (7). Thin films depositions were carried out on steel

discs(OL) with a diameter of 10 mm and a thickness of 2mm. The chemical compositions of OL used was as follows(wt.%):

Fe	Al	Cu	Si	Mn	Cr
98	0.0309	0.311	0.339	0.219	0.18
C	Ni	Mo	Pb	Nb	Ti
0.165	0.179	0.339	0.05	0.0023	0.005
Zn	V	W	P	S	Co
0.005	0.005	0.05	0.005	0.005	0.0138

Table 2. Chemical compositions of OL

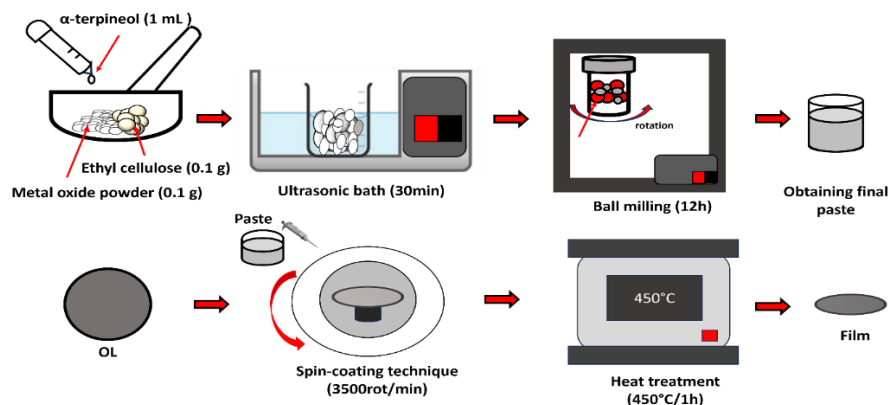


Figure 1. Schematic diagram of the thin film deposition process using the spin coating method

In the first stage, a paste was prepared by mixing 0.1g of metal oxide power with a matrix solution composed of 0.1g of ethyl cellulose and 1 mL of a α -terpineol in an agate mortar. To achieve proper homogenization of the mixture, the resulting solution was ultrasonicated for 30 minutes., followed by further processing in a planetary ball mill (Lab Mills 1 x QM) at a constant frequency of 40kHz for 12 hours.

In the second stage the films of undoped metal oxide ($\text{Zn}_3\text{Nb}_2\text{O}_8$) and doped (Er^{3+}) were then deposited onto low carbon steel substrates using the spin-coating technique. A homogeneous diluted paste of the metal oxide in ethanol was prepared and deposited onto the steel substrate at a rotation speed of 3500 rpm for 30 seconds. In order to remove the organic compounds used in the homogeneous solution (metal oxide- polymeric matrix) and to ensure proper adhesion of the oxide films to the steel substrates, a thermal treatment was applied at 450° C for 1 hour, with a heating rate of 2°C per minute.

Results and discussion

The OCP measurements presented in figure 2 (0.3NaCl) show that the coated electrodes stabilize with difficulty, reaching a quasi-stable state around 1500 seconds and displaying a non-uniform behavior, whereas the uncoated electrode stabilizes at approximately 1700 seconds. This results provides preliminary insights into the nature of the processes occurring at the metal/thin film-electrolyte interfaces.

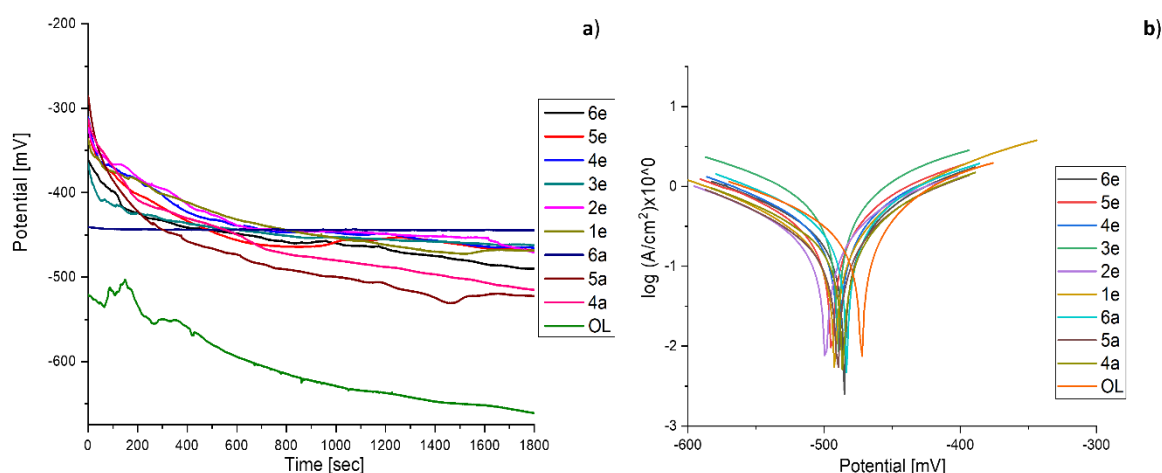


Figure 2. a) OCP measurements for the modified electrodes over 30 minutes: steel electrode, $Zn_3Nb_2O_8$, and $Zn_3Nb_2O_8:Er^{3+}$ in 0.3 M NaCl and b) Tafel curves for the modified electrodes after immersion of the steel electrode, $Zn_3Nb_2O_8$ and $Zn_3Nb_2O_8:Er^{3+}$ in 0.3 M NaCl for 30 minutes (notations according to Table 1)

Electrode	E (I = 0) (mV)	R _p (Ωcm^2)	i _{corr} (mA/cm ²)	β_a (mV)	β_c (mV)	v _{corr} (mm/Y)	IE (%)
OL	-389.14	68.20	3.8190	240.8	-251.5	21.27	-
1e	-553.2	15.75	1.8031	173.5	-189.8	15.049	52.79
2e	-577.0	8.81	1.6106	153	-139.7	11.879	57.82
3e	-433.2	27.74	1.1780	152.9	-122.2	9.393	69.15
4a	-426.9	5.33	2.0680	175	-128.9	18.831	45.84
4e	-563.0	14.51	1.6300	54.5	-61	10.591	61.34
5a	-512.2	9.95	1.9145	172.6	201.3	16.728	49.86
5e	-549.1	9.13	1.7328	155.3	-188.3	12.624	54.62
6a	-693.6	5.48	1.8068	223.9	-107.9	15.368	52.69
6e	-442.7	14.67	1.0841	109.6	-154.7	8.570	71.61

Tabel 3. Tafel parameters for electrodes analyzed after 30 minutes immersion in 0.3 M saline medium

In all analyzed cases of steel electrodes modified by spin coating deposition of thin films made from pseudo-binary oxides, an improvement in corrosion inhibition was observed. Moreover, it was found that the best IE value (71.61) was obtained when the layer was formed using the $Zn_3Nb_2O_8:Er^{3+}$ structure, synthesized by the hydrothermal method using: ZnO , Nb_2O_5 and $Er(NO_3)_3 \cdot 5H_2O$ as precursors in a saline medium. By analyzing the variation of corrosion potential and corrosion current as the inhibition efficiency increases (Table 3), it can be observed that the corrosion current decreases proportionally with the corrosion rate, while the corrosion potential shifts toward more cathodic values.

For all the deposits with materials obtained by the hydrothermal method and tested in saline environment, the polarization resistance (R_p) of the modified OL steel electrode increases. The best value recorded for the same test (6e).

The shift of the corrosion potential (E_{corr}) toward more negative values in the presence of undoped and Er^{3+} -doped $Zn_3Nb_2O_8$ is caused by the different nature of the electrochemically active species on the metallic surface (Zn, Nb, Er), in addition to Fe. The presence of Nb ions

together with Zn ions shifts the corrosion potential to more negative values (-389.14 mV), and the corrosion current density decreases from 3.8190 mA/cm² (bare steel) to 1.0841 mA/cm² in saline medium.

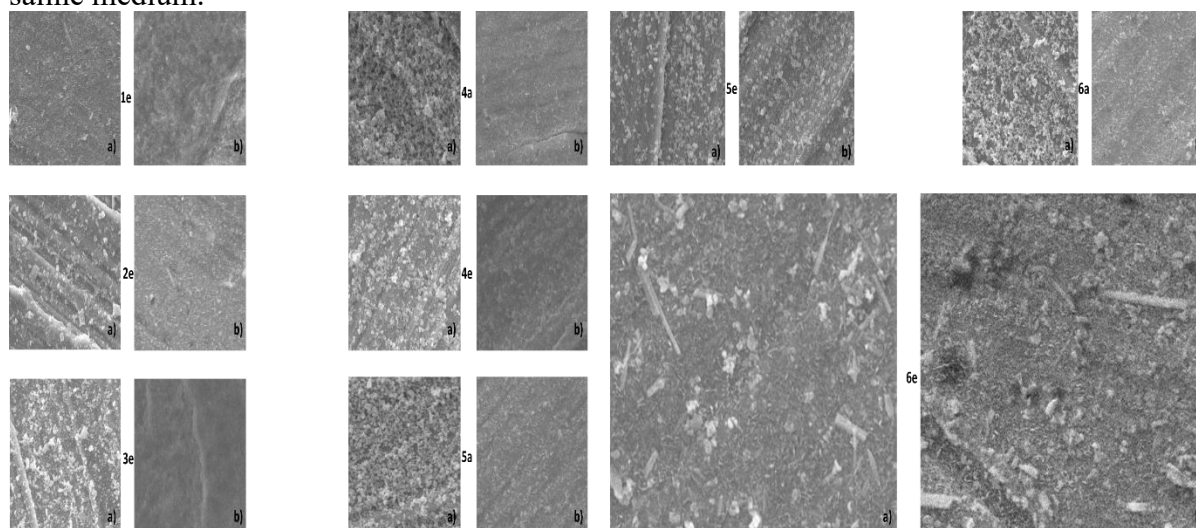


Figure 4. SEM images for the spin coated samples according to table 1 before (a) and after (b) corrosion tests in saline environment.

From the SEM images (Figure 4), it can be observed that doping the material with Er³⁺ ions leads to crystallization in the form of rod-like structures. SEM images of the doped and undoped oxides obtained by the hydrothermal method were taken at 12000x analysis magnification in medium vacuum.

Figure 5. shows the AFM images of the surfaces for each of the thin films deposited on the OL electrodes, measured before and after the corrosion tests, using the non-contact working mode. The measurements were performed in aggressive environments, namely 0.3 M NaCl.

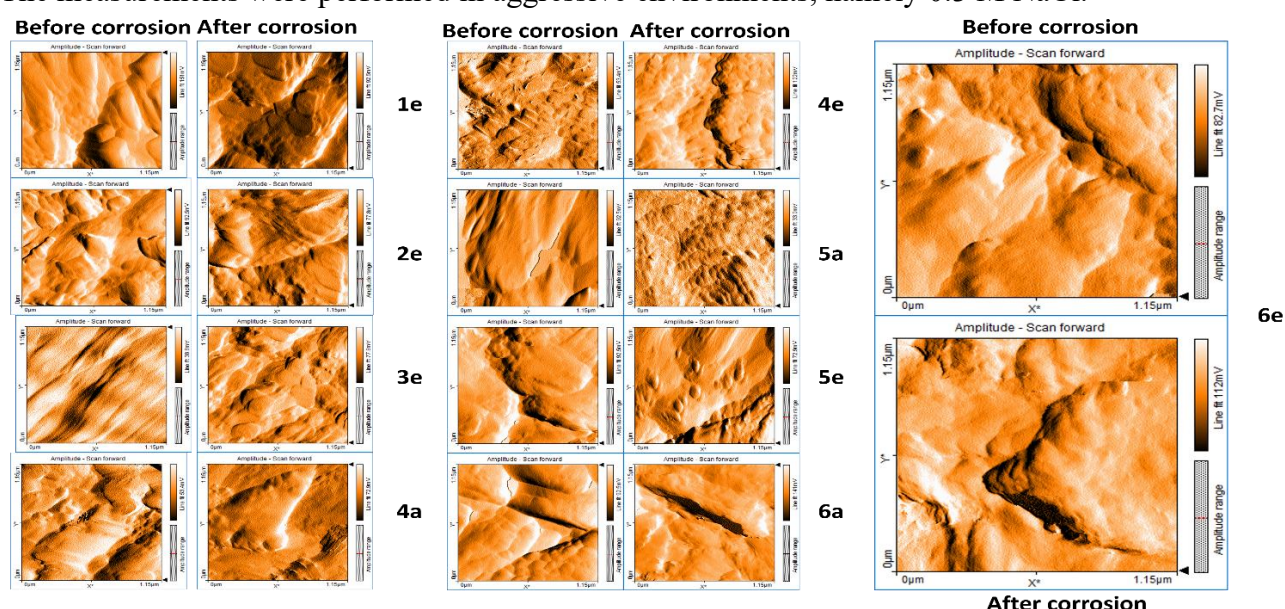


Figure 5. AFM images before and after corrosion tests for the samples deposited by spin coating according to table 1 before and after corrosion tests in saline environment

Electrode	Area (pm ²)	S_a before/ after 0.3 M NaCl (nm)	S_q before/ after 0.3 M NaCl (nm)	S_y before/ after 0.3 M NaCl (nm)
OL	1.326	11.281 / 46.154	16.405 / 56.855	-
1e		9.7957 / 35.209	12.368 / 44.446	750.43 / 265.12
2e		10.346 / 32.275	13.485 / 43.673	80.548 / 278.57
3e		14.307 / 21.176	18.6 / 26.795	132.59 / 161.51
4a		16.518 / 19.66	20.76 / 24.261	113.93 / 181.42
4e		16.867 / 40.598	20.20 / 47.235	120.15 / 222.63
5a		9.073 / 28.01	11.511 / 32.492	59.184 / 207.84
5e		19.384 / 30.724	24.772 / 38.124	150.18 / 236.23
6a		16.857 / 42.171	20.509 / 51.864	113.9 / 280.74
6e		22.186 / 33.844	27.499 / 251.94	156.57 / 251.94

Table 4. Nanoroughness of thin films obtained by spin coating technique

Using the Nanosurf®EasyScan 2 software, the nanoroughness of the monolayer thin films was calculated before and after the corrosion tests (Table 4).

Conclusion

Table 3 shows that the oxid corrosion inhibitor forms a barrier on the metal surface, reducing contact between the steel and saline environment, which ultimately decreases the corrosion rate. If a cathodic reaction occurs in the corrosion process, the corrosion potential becomes more negative (our case). The Tafel curves show that all thin films deposited as monolayer structures on electrodes exhibit lower corrosion current densities compared to the OL disk.

AFM microscopy reveals that after exposure to the saline environment, the thin films retain their material structure at the corrosion interface, though the morphology changes and aggregate size increases. This suggests that the corrosion inhibition mechanism in carbon steel relies on the physical protection provided by the compact and adherent pseudo-binary oxide layers at the steel interface.

The most distinct morphology (shown in Figure 4) was observed in sample 6e, synthesized using $\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, ZnO , and Nb_2O_5 as precursors. Notably, this sample also exhibited the highest corrosion protection efficiency in the tested environments

The corrosion protection mechanism of steel can be attributed to a physical/mechanical barrier effect. Correlating microscopic observations with electrochemical measurements, it is evident that $\text{Zn}_3\text{Nb}_2\text{O}_8\text{:Er}^{3+}$ layers obtained via the hydrothermal method act as an effective barrier against salt ion penetration, thereby protecting the steel surface.

Acknowledgements

This research was funded by a grant from the Ministry of Research, Innovation and Digitization, project number PN 23 27 01 02 INOMAT, 23-27 29N/2023 and partially by the project code PN-IV-P8-8.3-ROMD-2023-0227 within PNCDI IV.

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