

Study on the Corrosion Resistance of Sn/Zr_{0.74}Y_{0.16}Ti_{0.10}O_{2.8} Composite Coatings Electrodeposited on Carbon Steel in Acidic Medium

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In this work the corrosion resistance of Sn/Zr_{0.74}Y_{0.16}Ti_{0.10}O_{2.8} composite coatings electrochemically co-deposited from SnCl₂ solutions containing 4-amino-N-(1,3-thiazole-2-yl) benzenesulphonamide was evaluated and compared to the pure Sn coatings one. The corrosion resistance in 0.1 M HCl solution was investigated using two electrochemical techniques: Tafel polarisation and electrochemical impedance spectroscopy (EIS). The surface morphology was examined using a metallographic microscope. Tafel polarisation showed that the insertion of Zr-based mixed oxide (Zr_{0.74}Y_{0.16}Ti_{0.10}O_{2.8}) in solution disrupts the cathodic reaction and reduces in a significant manner the anodic reaction, leading to a considerable decrease of corrosion currents. The polarization resistance values obtained from Nyquist diagram confirm a much better protection of carbon steel in the presence of Zr-based mixed oxide. The microscopic images show the presence of distinct layers on carbon steel surface in the absence and presence of Zr-based mixed oxide.

Keyword: tin, electrodeposition, corrosion resistance

The composite material can be described as a mixture of materials specially designed for satisfying certain technological requirements, improving the desired properties of the components and reducing the undesirable properties of the same materials.

The main objective in developing the production of composites is to provide performant characteristics and properties, beyond the known limits for metallic and nonmetallic materials commonly used.

The metal matrix composite materials is an area of great interest, the composite layers providing superior electrical [1], optical [2-4], magnetic [5,6], mechanical [7-9] physical and chemical properties (e.g. excellent wear resistance and corrosion resistance) [10-14] to the surfaces.

There are fewer papers concerning Ni/Al₂O₃ coatings. Such coatings are highly abrasion and heat resistant and have quite good anticorrosion properties [15-17].

Most of the recent papers on composite coatings deal with nickel coatings containing SiC and TiO₂. The incorporation of the SiC nano-particulates leads to the changes in the morphology, microhardness and wear resistance of the nano-composite coatings as compared to the nickel coatings [18,19]. The effect of TiO₂ nanoparticles on the structure of the nickel matrix was investigated, evidencing the correlation between inhibition and its effect on morphological features of electrodeposits under an extended region of electrodeposition conditions such as pH of the bath, current density and TiO₂ loading [20].

The aim of this work was to investigate the corrosion resistance of composite Sn/ZrO₂-based mixed oxide coatings obtained from 0.25 M SnCl₂ solutions in 0.1 M HCl containing the ZrO₂-based mixed oxide (Zr_{0.74}Y_{0.16}Ti_{0.10}O_{2.8}) in the presence of 0.1 M 4-amino-N-(1,3-thiazole-2-yl) benzenesulphonamide (TBSA).

Experimental part

Tin (Sn) and composite (Sn/Zr_{0.74}Y_{0.16}Ti_{0.10}O_{2.8}) coatings were electrochemically deposited from a 0.25 M SnCl₂ solution in 0.1 M HCl in the presence of 0.1 M 4-amino-N-(1,3-thiazole-2-yl) benzenesulphonamide (TBSA), and from

a 0.25 M SnCl₂ solution in 0.1 M HCl containing the ZrO₂-based mixed oxide (Zr_{0.74}Y_{0.16}Ti_{0.10}O_{2.8}) in the presence of 0.1 M TBSA, respectively. Fluka reagents were used.

The electrodepositions and the corrosion tests were performed using electrochemical techniques such as Tafel polarisation and electrochemical impedance spectroscopy (EIS).

Before and after electrochemical investigations the surfaces of the Sn coatings and Sn/Zr_{0.74}Y_{0.16}Ti_{0.10}O_{2.8} coatings were examined under a microscope.

Nanostructured zirconia-based ceramic material has been synthesized by a Pechini method at Faculty of Chemistry, University of Craiova and previously reported [21].

The electrochemical experiments were performed in a conventional three-electrode cell, by using a platinum auxiliary electrode (1 cm²), an Ag/AgCl reference electrode and a carbon steel plate (2 cm²) as working electrode, having the following composition: C = 0.1%, Si = 0.035%, Mn = 0.4%, Cr = 0.3%, Ni = 0.3% and Fe - balance.

Prior to electroplating, the carbon steel electrode was polished with metallographic paper, washed in distilled water, degreased in acetone and dried in warm air. During the electrodeposition process, the solution and suspension were mechanically stirred at about 600 rpm. For each sample five measurements were carried out, taking into account the most reproducible results.

The electrochemical investigations were carried out using a computer-controlled VoltaLab 40 potentiostat/galvanostat with a VoltaMaster 4 software.

The surfaces of the electrodes were examined using a metallographic microscope Euromex with Canon camera.

Results and discussions

The electrodeposition polarization curves.

Tin coatings and Sn/ZrO₂-based mixed oxide coatings were electrochemically deposited by linear potentiometry.

The electrodeposition was performed in the potential range of -300 mV to -600 (vs. Ag/AgCl), with a 10 mV/s scan rate. The polarization curves obtained after 4 minutes of electrode immersion at open circuit are shown in figure 1.

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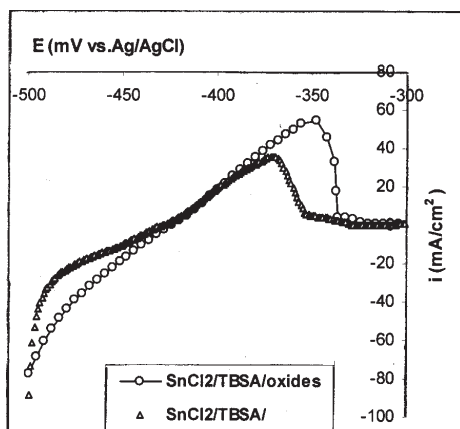


Fig. 1. Polarization curves for electrochemical deposition of Sn and Sn/zirconia-based mixed oxide

It can be noticed from figure 1 that in the absence of Zr-based mixed oxide, the polarization curve has a passive range until a potential of -352 mV. This behaviour can be ascribed to the TBSA film formed at the electrode/electrolyte interface.

Knowing the fact that tin is reduced on a potential of -335 mV vs. Ag/AgCl, we can appreciate that under experimental data the metal electrodeposition occurs in the potential range of -368 mV to -500 mV. Also, in this potential range other competing reactions could be involved leading to the formation and deposition of SnO₂.

TBSA film formed at the interface may prevent the oxidation of Sn²⁺ to Sn⁴⁺ by forming short-lived complexes, temporary linking Sn, facilitating its subsequent reduction. The polarization curve obtained in the same experimental conditions, but in the presence of mixed oxide, looks slightly modified; the passive field maintains until -336 mV and the electrodeposition potential shifts towards a more positive value (-347 mV). This can be attributed to a change of interface layer, possibly formed in this case from the adsorbed TBSA, which contains other molecules from the investigated system. Cathodic drop of the curve is slower and occurs in -347 mV ÷ -500 mV range, being assimilated to Sn electrodeposition. The change in the polarization curve can be explained by the appearance of the oxide molecules in the electrodeposited layer.

The corrosion behaviour of the electrodeposited coating in 0.1 M HCl solution

Tafel polarization

In Tafel region, the polarisation curves were measured in the potential range -700 mV to -400 mV, with a scan rate of 10 mV/s. The polarisation curves obtained after 10 min of immersion are presented in figure 2.

The performed tests showed that:

- addition of zirconia-based mixed oxide into initial solution leads to a shift of corrosion potential towards more positive values;

- the shift of the corrosion potential towards more positive values is correlate with a significant corrosion current decrease;

- the presence of zirconia-mixed oxide in the solution significantly disturbs cathodic reaction and reduces the anodic reaction in a considerable manner;

- the corrosion currents presented in table 1 were calculated using VoltaMaster4 software at smoothing 9, calcule zone 120 and segment 80 mV.

- the protection efficiency, P (%) was calculated using the following relation:

$$P = \frac{i_{corr}^0 - i_{corr}}{i_{corr}^0} \cdot 100 \quad (1)$$

where:

i_{corr}^0 and i_{corr} are the corrosion current densities of the carbon steel surface in the absence and presence of zirconia-based mixed oxide.

It can be noticed that the protection efficiency in the presence of mixed oxide exceeds 85%, which implies a high corrosion resistance. This can be explained by the appearance at the metal/solution interface of a layer with a different composition from the one obtained in the absence of oxide. It can be assumed that this layer has a relative uniformity, is adherent, compact and modifies the electronic transfer at the interface.

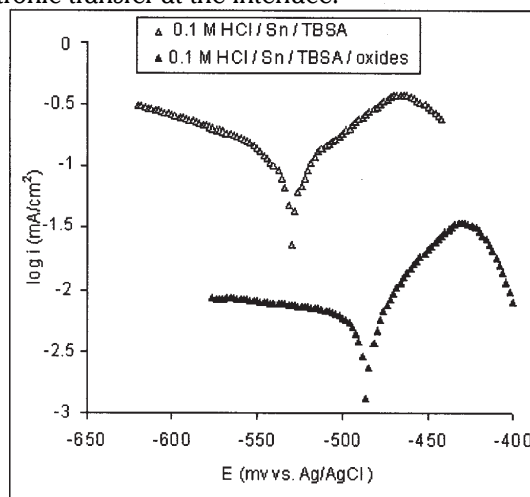


Fig. 2. Tafel diagram for tin coating and composite coating after corrosion in 0.1 M HCl solution

Table 1

ELECTROCHEMICAL CORROSION PARAMETERS OF PURE TIN AND COMPOSITE Sn/Zr_{0.74}Y_{0.16}Ti_{0.10}O_{2.8} COATING IN 0.1 M HCl SOLUTION OBTAINED FROM TAFEL POLARIZATION

Parameters	E _{cor} (mV)	i _{cor} (μA/cm ²)	P (%)
Coating			
Sn coating	-530	76.5	0
Composite coating	-486	11.21	85

Electrochemical impedance measurements

Electrochemical impedance measurements for all investigated samples in 0.1 M HCl solution were carried out at the open circuit potential in the frequency range from 10⁵ to 10⁻¹ Hz, with a value of 10 mV for the amplitude. In figure 3 Nyquist plots of impedance spectra of investigated coatings in 0.1 M HCl at room temperature are shown. A more pronounced frequency arc was obtained for the sample coated with composite layer. Moreover, a shift towards lower frequency of this contribution when oxides nanoparticles were incorporated into tin matrix can be noticed. This behaviour is usually assigned to changes in density and composition of electrode coating. For the description of EIS measurements an equivalent circuit is suggested in figure 3, where (R_s) is the solution resistance of the bulk electrolyte and (C_{dl}) represents the double layer capacitance of the electrolyte at the metal surface. (R_p) is the polarization resistance of the metal. The impedance parameters derived from EIS measurements and respective fitting results are given in table 2 and figure 3, respectively. The fitting results show that R_s and C_{dl} decrease, while R_p

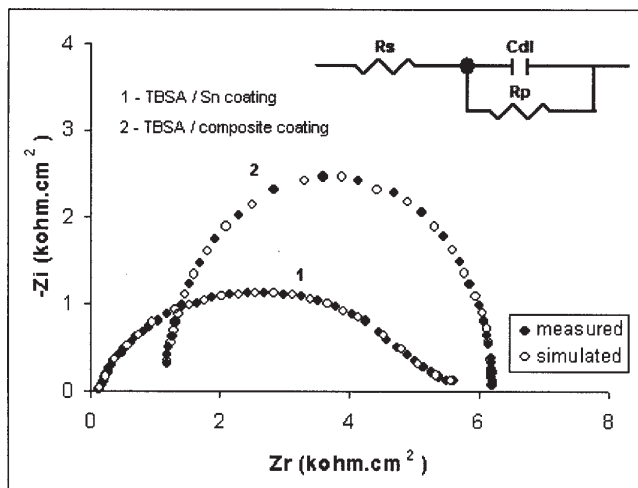


Fig.3. Nyquist plots of impedance spectra: 1- tin coating; 2 - composite coating

Parameters	R_s ($k\Omega.cm^2$)	R_p ($k\Omega.cm^2$)	C_{dl} ($\mu F/cm^2$)	P (%)
Sn coating	0.002	0.135	117.9	0
Composite coating	0.0015	1.205	59.4	88.7

Table 2
ELECTROCHEMICAL CORROSION PARAMETERS
OF PURE TIN AND COMPOSITE Sn/
 $Zr_{0.74}Y_{0.16}Ti_{0.10}O_{2-\delta}$ COATING IN 0.1 M HCl
SOLUTION OBTAINED FROM EIS

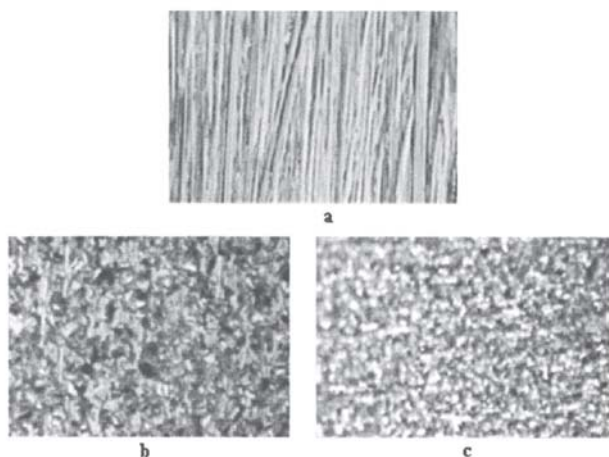


Fig.4. Microscopic images of: a – carbon steel, reference sample; b - electrodeposited tin coating; c- electrodeposited Sn/ZrO₂-mixed oxide composite coating before the corrosive processes

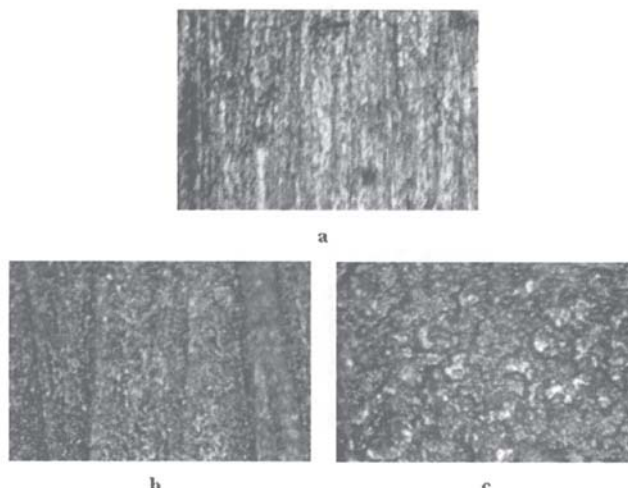


Fig.5. Microscopic images of: a – carbon steel, reference sample; b - electrodeposited tin coating; c- electrodeposited Sn/ZrO₂-mixed oxide composite coating after the corrosive processes

increases, suggesting an increase in the protection efficiency.

The protection efficiency (P) was determined by the following relationship:

$$P = \left(1 - \frac{R_p^0}{R_p} \right) 100 \quad (2)$$

where R_p and R_p^0 represent the polarization resistances in the presence and absence of mixed oxide.

Table 2 shows that the presence of mixed oxide leads to an approx. 89% protection efficiency, in good agreement with the one obtained from Tafel polarization.

Surface Characterization

The microscopic images of the surface coatings before the corrosive processes are presented in figure 4.

In figures 4b and 4c, the formation of specific electrodeposited layers was evidenced; it is difficult to assess that they would be characteristic of a metal or an oxide. In a previous work concerning the electrodeposition of Sn in the presence of TBSA, Mossbauer spectroscopy revealed that the metallic tin percentage is higher than the oxide percentage [21]. In case of electrodepositions from solutions containing Zr-based mixed oxide (fig. 4c), the layer uniformity is more obvious and the feature of a metallic nucleation, forming a matrix in which certain oxide particles are embedded, is relatively nuanced. It might indicate that the surface morphology shown in the case of solutions containing Zr-based mixed oxide (fig. 4c) is significantly different and denser than that obtained in SnCl₂ solutions/TBSA (fig. 4b).

The microscopic images obtained after the corrosion processes in 0.1 M HCl are presented in figure 5.

In case of carbon steel random spread corrosion spots can be noticed (fig.5a). In „b” and „c” cases the texture is modified and the corrosion spots have a low intensity.

Conclusions

In this work the corrosion behaviour of tin coatings and Sn/ZrO₂-based mixed oxide composite coatings was evaluated.

The polarization curve obtained in the presence of mixed oxide presents a passive region until -336 mV and the electrodeposition potential shifts towards more positive values (-347 mV). Cathodic drop of the curve is slower and occurs between -347 mV ÷ -500 mV range, being assimilated to Sn electrodeposition. The change in the polarization curve can be attributed to the incorporation of the oxide molecules in the electrodeposited layer.

The Tafel curves showed that the presence of zirconia-based mixed oxide leads to a shift of corrosion potential towards more positive values, which is correlated with a significant corrosion current decrease.

The resistance corrosion values, obtained from Nyquist plot, confirm a highly protecting capacity. The gradual presence of the oxide molecules on the substrate is characterized in the impedance diagram, by an increase in the capacitive loop, knowing the fact that R_p increases with decreasing of C_{dl}.

Microscopic images confirm the fact that in case of electrodepositions from solutions containing Zr-based mixed oxide (fig. 4c) the layer uniformity is more apparent and the feature of a metallic nucleation, forming a matrix in which are embedded certain oxide molecules is relatively nuanced. Also after corrosion the surface texture modified without corrosion spots being noticed.

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