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Sb/SnO_2 NANOSTRUCTURED ANTICORROSIVE COATINGS ON METALS

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ABSTRACT. The paper reports on the structural and mechanical properties of ATO (Antimony doped tin dioxide) thin coatings obtained by the by sol-gel one step multiple-dip coating technique on Ti, Cu and stainless steel substrates. Surface morphology, microstructure, composition, roughness and hardness of the obtained coatings were determined by using SEM (Scanning Electron Microscopy), AFM (Atomic Force Microscopy), EDX (Energy Dispersive X-ray Microanalysis) and XRD (X-ray Diffraction) mesurements. Corrosion resistance was evaluated from corrosion potential measurements in 0.5 M H_2SO_4, 0.5 M NaOH and 0.5 M NaCl solutions. Adherent, nanostructured ATO coatings with long term corrosion resistance were obtained on all types of metal substrates.

Keywords: *ATO, nanostructured thin coating, microstructure, roughness, hardness, corrosion resistance.*

INTRODUCTION

Coating is a covering that is applied to the surface of a substrate in order to improve properties such as appearance, adhesion, corrosion resistance, wear resistance, optical transparency and gas sensitivity.

The choice of coating materials is strongly related to their chemical composition, purity, crystallinity, thermal stability, adhesion while the coating technologies must fulfill requirements related to complexity, overall cost and envinronment safety.

The conventional coating methods intended for metals corrosion protection such as plating with Cr, Ni, Zn, show several drawbacks such as: high energy consumption, discharge of process effluents containing hazardous chemical species, expensive technologies for effluents purification [1].

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A modern approach of coating is by using the nanostructured thin film technologies. Nanostructured inorganic or mixed inorganic-organic materials became of interest for many areas in the last decades [2].

Among the techniques used for preparing thin films, sol-gel seems to be prefered due to the large variety of precursors composition, many processing options, generation of many complex micro- and nanostructures, low thermal stress of the substrate, simple coating procedures. This technique was used with a wide variety of substrates: glass, ceramics, metals, polymers [3-5].

The use of nanostructured ATO thin films as protective coatings for glass or metals is based on their outstanding properties such as high mechanical resistance, very good chemical stability and antistatical properties [6-9].

The paper presents the obtaining procedure of ATO nanostructured thin coatings deposited on metal substrates, namely Ti, Cu and stainless steel by sol-gel one step multiple-dip coating technique. The results regarding the structural and mechanical characteristics of the obtained coatings (surface morphology, microstructure, roughness, hardness) and corrosion behavior are shown.

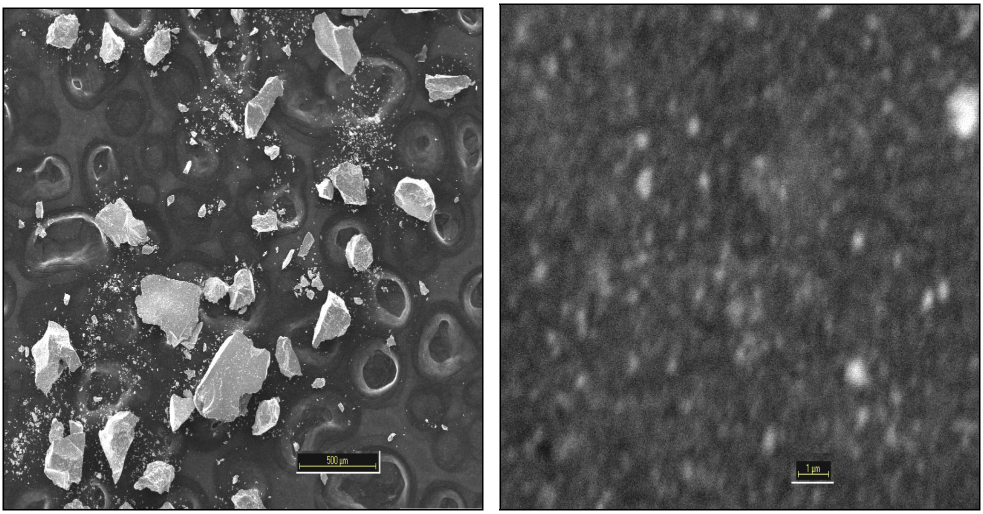
RESULTS AND DISCUSSIONS

It is a well know the fact that the mechanical, electrochemical and long term stability of a coating is strongly influenced by the coating quality expressed in terms of uniformity, microstructure, cristalinity, constituent particles size, roughness, hardness and adherence.

The ATO thin films intended for protective coatings must fulfill the same quality requirements. When ATO coatings are prepared by sol-gel dip coating technique, these characteristics depend on preparation conditions such as: composition of the precursor (dopping degree), number of dippings, annealing temperature [10].

The surface morphology of the ATO coatings prepared according the experimental conditions described, was investigated by SEM. The images were taken for the ATO coatings obtained after air drying at 60^0C only and annealing, as well (figures 1-3).

The SEM images show that, in all cases, annealing leaded to more uniform, compact and free of crack coatings and good conformal coverage of the substrate surface. Also, one may observe that the ATO coating on Cu substrate is formed of larger particles while the coatings on Ti and stainless steel substrates appear to be formed of smaller particles having comparable dimensions.



a **b**

Figure 1. SEM images of ATO coating on Ti:
a) after air drying at 60^0C; b) after annealing

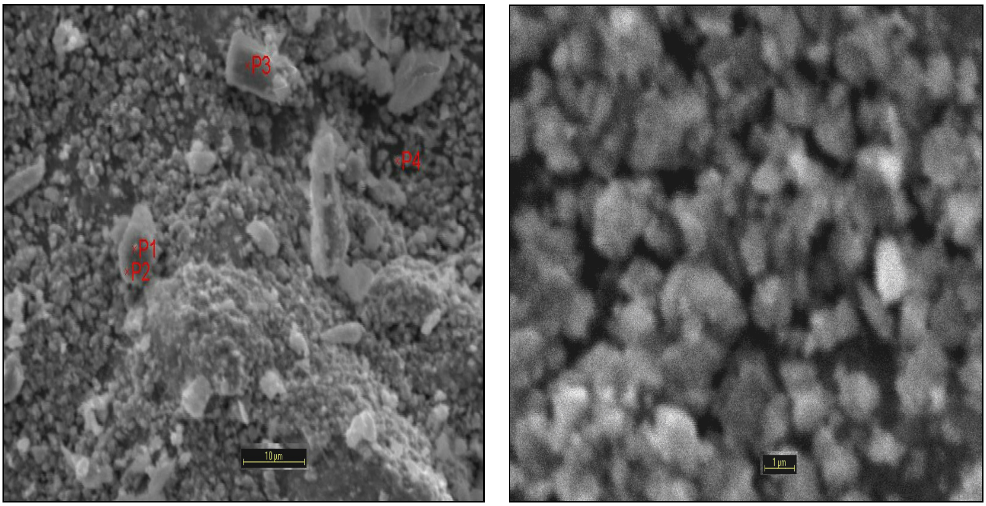


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Figure 2. SEM images of ATO coating on Cu:
a) after air drying at 60^0C; b) after annealing

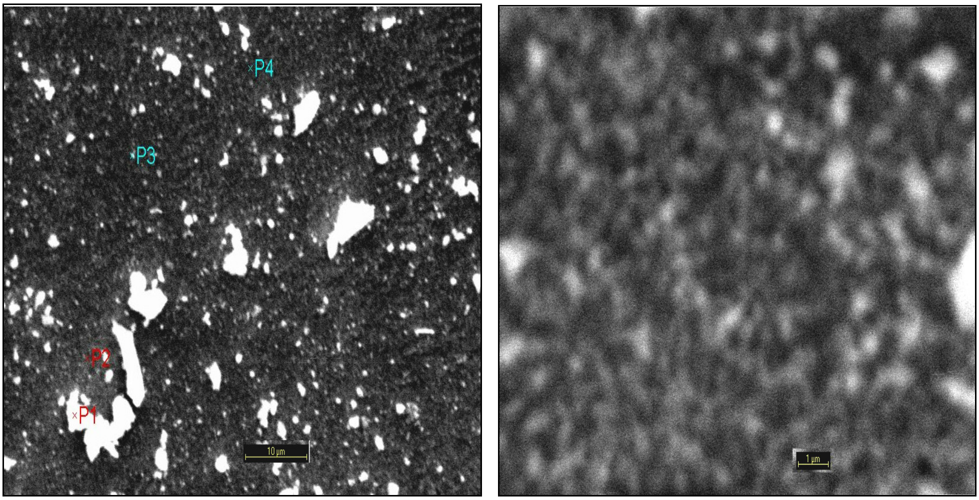

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Figure 3. SEM images of ATO coating on stainless steel:
a) after air drying at 60^{0}C; b) after annealing

The XRD patterns taken for the coatings obtained after annealing confirmed their polycrystalline structure and showed diffraction peaks belonging to the tetragonal rutil structure of SnO_2 with a preferred orientation along the plane (101) while the ATO coatings obtained after air drying only show an almost single crystalline structure (figure 4).

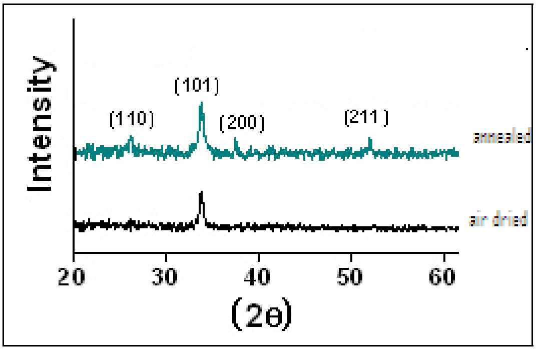

Figure 4. XRD spectra for the air dried only and annealed ATO coatings on stainless steel substrate

Also, the XRD patterns didn't show any difference in the crystalline structure of the ATO coatings related to the nature of the substrate. The grain sizes were calculated by using the Scherrer's equation and are presented in table 1.

The composition of the annealed ATO coatings was determined by EDX analysis. A typical spectrum is shown in figure 5.

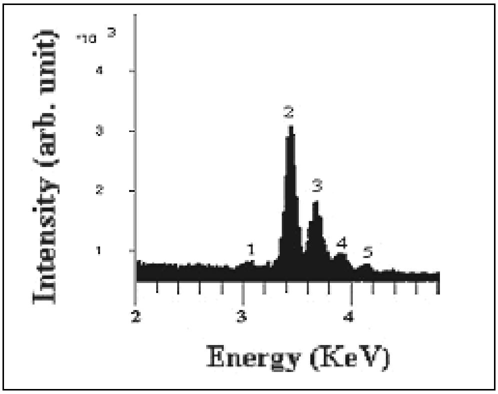

Figure 5. EDX spectrum of annealed ATO coating deposited on Ti

The appearance of the peaks at 3.045 keV (Sn L_1-peak 1), 3.444 keV (Sn $L_{\alpha1}$-peak 2), 3.905 keV (Sn $L_{\beta2}$ – peak 3), 4.101 keV (Sb $L_{\beta2}$-peak 4) and 4.248 keV (Sb $L\gamma_1$-peak 5) which are characteristic lines of Sn and Sb confirmed the presence of both elements in the ATO coating.

Surface roughness and hardness have a major impact on the corrosion resistance of the coating. For the annealed ATO coatings these parameters were determined from AFM measurements on the basis of height images obtained in tapping mode (figure 6) and nanoidentation, respectively. The obtained results are summarized in table 1.

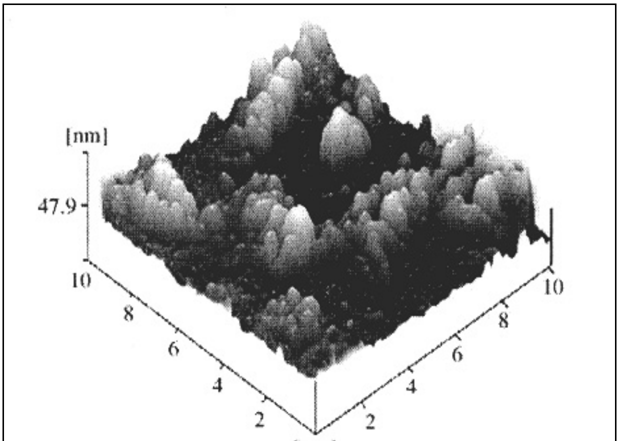

Figure 6. AFM image of ATO coating on Ti substrate

Table 1. ATO coatings physical characteristics

Substrate	Physical characteristics		
	Particle size [nm]	**Roughness** [min-max]	**Hardness** [MPa]
Stainless steel	95	12-150	5,3 ± 0,05
Copper	120	45-330	3,4 ± 1,2
Titanium	72	12-130	5,9 ± 1,1

The data in table 1 show that the ATO coatings obtained on Ti and stainless steel show comparable mechanical characteristics while the coating on Cu differ with respect to particle size, roughness and hardness. The determined data are in good agreement with the information provided by SEM images and with literature data which shows that with grain size decreasing, the hardness of the coating increases [11].

The corrosion resistance of the ATO coatings was evaluated by recording the corrosion potential in 0.5 M H_2SO_4, 0.5 M NaOH and 0.5 M NaCl solutions for 120 days. A typical overall variation of the corrosion potential is shown in figure 7.

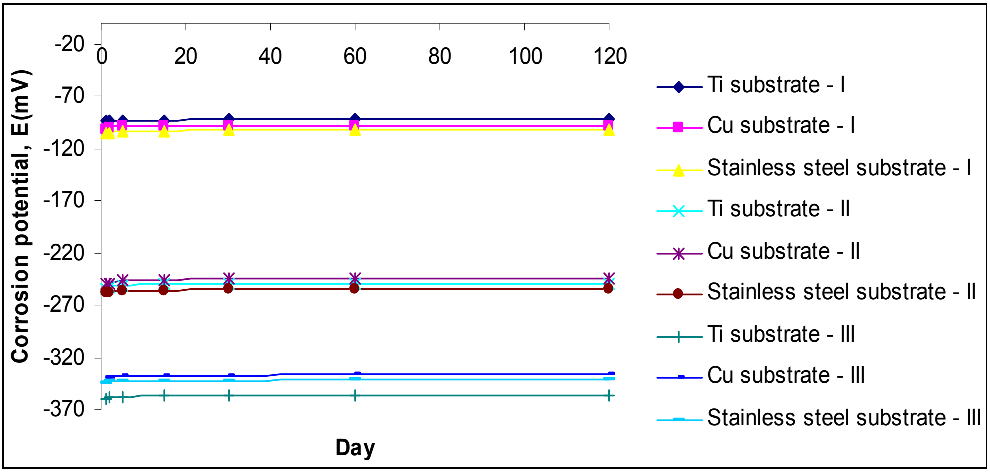

Figure 7. Variation of the corrosion potential (work electrode: annealed ATO coating deposited on Ti, Cu or stainless steel substrate): I - 0.5 M H_2SO_4; II - 0.5 M NaOH; III - 0.5 M NaCl.

The data in figure 7 show a very small long term variation of the corrosion potential (2-4 mV) which indicates a passive behaviour of the ATO coating in the chemical media under investigation. No significant behaviour differences were observed as a function of substrate nature and ATO coating roughness and hardness.

CONCLUSIONS

ATO thin coatings on metal substrates (Cu, Ti, stainless steel) were prepared by sol-gel multiple-dip coating technique and their physical, mechanical and corrosion resistance was examined by SEM, XRD, EDX, AFM and corrosion potential measurements.

The SEM measurements revealed that the coatings are more uniform and also free of cracks after annealing. Also, the ATO coatings on Cu substrate are formed of larger particles than the coatings on Ti or stainless steel.

XRD patterns showed the polycrystalline structure of the annealed ATO coatings with diffraction peaks belonging to the rutil structure of SnO_2. No difference in the crystalline structure related to the nature of the substrate was observed. The grain sizes belong to the nanoscale (70-120 nm), the coatings on Ti and stainless steel containing smaller particles, their size being 72 nm and 95 nm, respectively. By using EDX measurements, on the basis of the characteristic lines, it was established that Sn and Sb are present in the ATO coatings chemical composition.

Roughness and hardness measurements showed comparable values for the ATO coatings on Ti and stainless steel substrates while those on Cu substrate showed higher roughness and lower hardness, which is in good agreement with the information provided by SEM images and the calculated grain sizes.

The corrosion potential measurements for a period of 120 days showed the passive behaviour of the ATO coatings with no significant difference in the corrosion potential evolution related to the nature of the substrate or roughness and hardness of the ATO coating.

By using sol-gel multiple-dip coating technique, nanostructured ATO thin coatings were prepared on Cu, Ti and stainless steel substrates with long term corrosion resistance.

EXPERIMENTAL SECTION

Reagents and materials

$SnCl_4 \cdot 5H_2O$, (Sigma), $SbCl_3$ (Fluka), etanol (Fluka), tartaric acid (Fluka), H_2SO_4 (Fluka), NaOH (Fluka), NaCl (Fluka), reagent grade.

The metal substrates made of Ti, Cu, stainless steel plates 20x20x0.8 mm^3, were treated with H_3PO_4 2 M at 60Cº for 15 min, followed by washing with distilled water and acetone and drying in air for 15 min. This cleaning procedure slightly increases surface roughness and subsequently, improves the coating ahesion to the substrate.

Obtaining of ATO coatings

The sol was obtained from a precursor with the following composition: 100 ml 0.2 M $SnCl_4$ and 15 ml 0.5 M $SbCl_3$ both in ethanol. The precursor was stirred for 1.5 hours with tartric acid.

The coatings were obtained by one step multiple-dip coating using a Nima Tensiometer. The substrates were immersed into the sol with 10 mm/min constant speed and withdrawn in the same conditions. The operation was repeated 10 times. The coated substrates were dried 30 min at 60Cº. An second series of coatings was prepared following the same procedure but instead of air drying only they were annealed for 15 minutes at 350^0C too.

Characterisation of ATO coatings

The surface morphology of both air dried only and annealed coatings was investigated by SEM on a HITACHI electron microscope.

Crystalline structure and composition were estabilished by XRD and EDX measurements by using a Philips PW 3710 diffractometer with Cu-Kα source. The scanning range was $20\text{-}60^0$.

Roughness and hardness were determined by AFM and nanoindentaion measuremnts with a Veeco Dimension 3100 Atomic Force Microscope with a Nanoidenter III controler.

Evaluation of ATO coatings corrosion behaviour

Half-cell potential measurements were performed in a classic two electrode cell by using as work electrode the coated substrates and as reference electrode a Ag/AgCl, KCl sat. (Radiometer, France). The corrosion potential was recorded by using an Infinitron, model 800, high impedance voltmeter.

The measurements were done in 0.5 M H_2SO_4, 0.5 M NaOH and 0.5 M NaCl solutions during 120 days, with everyday reading of the potential.

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