Studies and researches regarding the obtaining of multifunctional nanocomposites coatings

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Abstract. The paper presents the preparation of ZnO - SiO₂ nanocomposite coatings by successive layers deposition using sol-gel method, dip-coating technique. The influence of the drawing speed and number of layers on the film morphology, optical properties and corrosion resistance were monitored. It has been found that the increase in drawing speed and the number of layers results in an increased film thickness and a modified film morphology by spherical restructuring. The films deposited on a glass substrate have a transparency ranging from 45-90% in the VIS-NIR range depending on the film thickness. In the case of non-transparent substrates, it has been found that these films diminish the reflectivity due to the surface morphology and the presence of ZnO nanoparticles that absorb some of the light radiation. The corrosion test has showed that all of the deposited films provide superior protection to the substrates.

1. Introduction
The field of thin films has grown spectacularly in recent years due to their use in many branches of science and technology. Their most important applications are in microelectronics, optoelectronics, telecommunications, computer industry, aerospace industry, mechanical parts manufacturing, machine parts and cutting tools.

Functional / multifunctional coatings are generally micronized or thin films in the order of nanometers which, in addition to a specific functionality such as electrical conductivity, optical reflexivity, anti-fouling, antibacterial action, etc., also provides additional protection (to corrosion, abrasion, erosion) and / or decorative functions.

Particular attention is now paid to achieving the smallest possible value-added coatings that have the least impact on the environment, able to apply easily, to adapt to the morphology of the surface and to ensure / increase safety and durability [1, 2, 3].

The sol-gel method is one of the most efficient chemical methods for obtaining thin nanocomposite films with SiO₂ matrices and represents an alternative to vacuum deposition methods.

In principle, the sol-gel method consists in forming a concentrated colloidal soil of oxides or metal hydroxides and converting it to a semirigid gel by one or more methods. The deposition of thin films by the sol-gel method is carried out in several stages: soil preparation, soil deposition on the substrate (with evaporation of the solvent) as a wet gel film, drying and stabilization of the deposited layer.

The dip-coating technique consists in immersing the substrate into the solution containing precursors (soil) and then taking it (drawing it) at a well-defined constant rate, to well-controlled temperature and atmospheric conditions [1-6].
Coatings and thin films obtained by this method are thermally or chemically stable, can transmit, absorb, or reflect radiation at a given wavelength, resist abrasion, erosion, or may constitute protective barriers (under alkaline and acidic environments) [1-3].

Nanocomposite coatings can be made on different substrates, such as steel, aluminum, copper or glass, depending on the application.

The paper presents a number of results obtained from the characterization of thinned nanocomposite films of ZnO-SiO$_2$ deposited on different substrates. The influence of the drawing speed and the number of layers on the film morphology, optical properties and corrosion resistance were monitored.

2. Experimental Conditions

2.1. Making films
Operational nanoparticles of ZnO (≤50nm) and a SiO$_2$ matrix were used for deposition purpose.

The steel and copper substrates (50x20 mm size) coated with thin films of ZnO-SiO$_2$ were polished and then subjected to ultrasonic cleaning for 10 minutes in acetone.

Aluminum substrates (50x20 mm size) were subjected to grinding, polishing, ultrasonic cleaning in acetone and alkaline pickling.

Glass substrates (20x20 mm size) were cleaned with ethanol and then dried.

The 2nd, 3rd and 4th layers of ZnO-SiO$_2$ were deposited on steel, copper, aluminum and glass substrates using dip-coating technique and different drawing speeds. After each deposited layer, the gel film was subjected to heat treatment by heating in a furnace (FN 055 Nüve type) at 65 °C for 45 minutes followed by a heating at 190 °C for 15 minutes. Cooling was done later with the oven.

The deposition regimes that were used are shown in Table 1.

2.2. Film characterization

2.2.1. Morphology of the deposited films
The microstructure of the deposited layers was obtained by optical microscopy using a Neophot 2 microscope.

2.2.2. Optical properties of the deposited films
The optical properties of the thin films were analyzed by a Perkin Elmer double Lambda 35 UV-VIS beam using the UV-WinLab software. The range of wavelengths in which this spectrophotometer is working is 190-1100 nm. The experiments were performed at room temperature.

2.2.3. Corrosion behavior of the deposited films
The tests were carried out in a corrosion chamber equipped with an automatic temperature measuring and control system, coupled with an evacuation system for the solution or condense which resulted during the tests. Samples were placed on plastic bars. The corrosion acceleration test in saline mist was performed according to SRISO 9227.

To conduct the test, the required solution was prepared at 35 ± 2° C from a quantity of sodium chloride so as to obtain a concentration of 50 ± 5 g/l. The pH of the saline solution was adjusted so that the pH of the solution collected in the spraying chamber ranged between 6.5 and 7.2. This was measured with a pH meter HI 991001, produced by "Hanna Instruments", also provided with a temperature indicator.

The corrosion test was carried out over a period of 96 hours at 35 °C. Initially the samples were degreased with alcohol weighed by analytical balance with an accuracy of 0.1 mg.

At the end of the test, the samples were removed from the chamber, the corrosion products were removed by washing with water and then dried. The analytical balance with an accuracy of 0.01 mg was subsequently used.
Table 1. The deposition regimes of ZnO-SiO₂ films

| Type of sublayer | Sample symbol | Drawing speed [cm/min] | Number of layers | Thickness of the deposited film [μm] |
|------------------|---------------|------------------------|------------------|-------------------------------------|
| Steel            | 2O₂           | 2                      | 2                | 1.176                               |
|                  | 2O₃           | 2                      | 3                | 1.839                               |
|                  | 2O₄           | 2                      | 4                | 2.502                               |
|                  | 10O₂          | 10                     | 2                | 1.313                               |
|                  | 10O₃          | 10                     | 3                | 2.014                               |
|                  | 10O₄          | 10                     | 4                | 2.715                               |
| Copper           | 2C₂           | 2                      | 2                | 0.606                               |
|                  | 2C₃           | 2                      | 3                | 1.269                               |
|                  | 2C₄           | 2                      | 4                | 1.932                               |
|                  | 10C₂          | 10                     | 2                | 0.758                               |
|                  | 10C₃          | 10                     | 3                | 1.459                               |
|                  | 10C₄          | 10                     | 4                | 2.16                                |
| Aluminum         | 2A₂           | 2                      | 2                | 0.735                               |
|                  | 2A₃           | 2                      | 3                | 1.398                               |
|                  | 2A₄           | 2                      | 4                | 2.061                               |
|                  | 10A₂          | 10                     | 2                | 0.798                               |
|                  | 10A₃          | 10                     | 3                | 1.499                               |
|                  | 10A₄          | 10                     | 4                | 2.2                                 |
| Glass            | 2S₂           | 2                      | 2                | 0.572                               |
|                  | 2S₃           | 2                      | 3                | 1.035                               |
|                  | 2S₄           | 2                      | 4                | 1.698                               |
|                  | 10S₂          | 10                     | 2                | 0.88                                |
|                  | 10S₃          | 10                     | 3                | 1.581                               |
|                  | 10S₄          | 10                     | 4                | 2.282                               |

3. Experimental Results

3.1. Morphology of the deposited films

As a result of the microscopic analysis, it has been observed that the obtained films are generally free of cracks, homogeneous and adherent as shown in Fig. 1.

Thus the obtained films exhibit high compaction because aggregation, gelling and drying (evaporation) occur almost simultaneously during the extremely short deposition on the substrate; the atmospheric vapor pressure controls evaporation of the solvent and the transformation of the soil into gel with the formation of a transparent film; the subsequent heat treatment produces gel densification and crystal formation (crystalline).

As also shown in Table 1, the thicknesses of the obtained layer varied depending on the substrate and deposition conditions as follows: 1.1-2.7 μm for the films deposited on steel, 0.7-2.2 μm for the ones deposited on aluminum, 0.6-2.1μm for copper and 0.3-2.2μm for those deposited on glass.

For the films with a thickness of less than 1 μm, it has been found that surface imperfections can cause some inhomogeneities. In the case of the films with a thickness greater than 1.5 μm, a film restructuring was noticed due to the spherical restructuring of the structures, most likely caused by the increase in superficial tension as seen in Fig. 2.

When increasing the drawing speed, correlated with the same number of layers, the thickness of the deposited film increased too.
Figure 1. Micrographs of film deposited at 2 cm / min rate on different substrates

Figure 2. Micrographs of film deposited at 10 cm / min rate on different substrates
3.2. Optical properties of the deposited films

It has been found that films with a small thickness of approx. 0.3-1.6 μm deposited on the glass substrates exhibit 75-90% transparency in the VIS-NIR range, and with those of larger thickness of 1.5-2.2 μm this decreases down to about 45-85%, as can also be seen from Fig. 3.

In the case of non-transparent substrates of steel, copper and aluminum, it has been observed that these films decrease reflectance due to the surface morphology and the presence of ZnO nanoparticles in the film composition that absorb some of the light radiation as highlighted by the reflectance spectra of Figs. 4 and 5. Decreasing surface roughness leads to improved reflectivity properties, which is particularly noticeable for aluminum and copper sublayers.

Figure 3. Transmission spectra of films deposited on glass substrates

Figure 4. Reflection spectra for film deposited at 2 cm / min rate on different substrates:
   a - steel b - copper and c - aluminum
3.3. Corrosion behavior of deposited films
Following the corrosion test in salt mist, after 96 hours, it has been found that the deposited films provide a corrosion protection superior to the substrates. The best corrosion behavior has been that of the films deposited on aluminum substrate where corrosion rate was between 0.1-14 mg/m²h, followed by those deposited on a copper substrate where corrosion rate has ranged between 0.5-35 mg/m²h, followed by those deposited on a steel substrate with a corrosion rate between 118-392 mg/m²h.

Corrosion rates for non-transparent substrates were 692 mg/m²h for steel, 125 mg/m²h for copper and 73 mg/m²h for aluminum.

However, it has been found that higher thickness films feature lower corrosion rate than the thinner ones where corrosion was more obvious. Thus, in the first case we can consider that there is a localized corrosion while in the second case the corrosion is generalized. These aspects can also be seen in figure 6.
4. Conclusions
As a result of characterizing ZnO-SiO₂ films deposited on different substrates, the following conclusions can be drawn:

a. The technique adopted is a low-cost, affordable method for obtaining oxide films, including conductive and transparent films, with performance similar to films obtained by physical methods;

b. The deposits made have resulted in homogeneous, compact films adhering to the substrate with thicknesses between 0.6-2.7μm;

c. The microstructural analysis of the deposited layers revealed that the films generally do not show cracks, but there are morphological differences depending on the type of the support and the thickness of the film; with increased layer thickness there is a decrease in roughness and a reorganization of the film by spherical restructuring due to the increase of the surface tensions;

Figure 6. Micrographs of films subject to corrosion
d. Increasing the drawing speed, as compared to the same number of layers, the thickness of the deposited film is increased;

e. Low-thickness films (0.3 – 1.6 µm) deposited on glass sublayer have a transparency of 75-90% in the VIS-NIR range, and those with a higher thickness (1.5 – 2.2 µm) it decreases to about 45-85%; In the case of non-transparent sublayers of steel, copper and aluminum, it is noticeable that these films decrease reflectivity due to the surface morphology and the presence of ZnO nanoparticles in the film composition that absorb some of the light radiation;

f. The corrosion test revealed the following: all deposited films, regardless of their thickness, provide superior corrosion protection to the substrates used; thicker layers exhibited a lower corrosion rate than thinner ones; the best corrosion behavior is found with films deposited on aluminum sublayers;

g. The ZnO-SiO₂ films deposited on steel and aluminum sublayers can be used for solar thermal devices, solar collectors and glass-coated ones for optoelectronic devices, transparent conductors, solar cells, sensors.

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