Ultrasonic spray pyrolysis synthesis of Al, Zr, and Ti oxides multishell

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Abstract. In recent years, core shell nanoparticles have received increased attention due their possible applications in catalysis, biology and materials science. Solid micro-particles with a nanostructure of concentric multilayers were obtained with spray pyrolysis technique. In this work we present the synthesis and characterization of 1 to 10 layers of micro-spheres deposited on commercial brass sheet. Each layer is formed by three films: the first one is made of aluminum oxide, the second of zirconium oxide and the last film of titanium oxide. The films were deposited by the ultrasonic spray pyrolysis technique using organometallic salts of aluminum, zirconium and titanium, employing N, N-dimethylformamide as solvent. Scanning electron microscopy micrographs of 7 and 10 layers shows details about the formation of the layers. The micro-spheres are compacted in a homogeneous and uniform film, whose hardness increases with the number of layers.

1. Introduction

Multiple concentric layers have received increased attention due their applications on several fields. Nanostructured semiconducting metal oxides can be used in gas/vapour sensing technology [1]; concentric spheres of dielectric materials with different refractive index have been studied as 3D photonic band gap structures [2, 3] and notable optical properties of metal/dielectric core/shell nanoparticles have been reported due to their potential applications in dynamic light scattering for biological and molecular recognition, light trapping in thin-film silicon, organic solar cells [4], and photocatalysis [5]. In all these structures, their properties depend on the mechanical, thermal, dielectric and chemical attributes of the materials, and the thickness of the layers used. The ultrasonic spray pyrolysis technique (USP) has been recognized as an excellent method to prepare structures of various morphologies, such as dense and hollow spherical particles, rod-like particles, and thin films [6]. This process allows controlling characteristics such as morphology, layer size and chemical component purity of the structures.

The spray pyrolysis process requires a container with a precursor solution, which must be atomized and carried by a gas with a controlled flow rate directed into a chamber in which the drops are evaporated and decomposed into solid particles. Both, the electric heating system with a controlled temperature and the deposit substrate are localized at the bottom of the chamber. Several factors, such as the precursor, the solvent, the deposition time and the temperature, affect the morphology and the size of the film. For
example, the $\text{Al}_2\text{O}_3$ crystalline films have been obtained by ultrasonic spray pyrolysis using Aluminum acetylacetonate ($\text{Al}($acac$)_3$) dissolved in N, N-dimethylformamide (N, N-DMF) with a substrate temperature in the range of 500–650 °C during deposition of the films [7], whilst nanoporous aluminum oxide ($\text{Al}_2\text{O}_3$) particles were obtained by spray pyrolysis from aluminum nitrate ($\text{Al}($NO$_3$)$_3$9H$_2$O) and sodium chloride NaCl solutions deposited at 550 °C. On the other hand, research on USP has found that the precursor concentration plays a predominant role in the determination of the ZrO$_2$ particle size [8]. A similar model was elaborated to predict the zirconia particles size in function of the concentration of the precursor substance, based on the fact that the concentration affects the drying time of the drop and the diffusion distance, in which the chemical homogeneity is maintained before precipitation [9].

2. Experimental details
The layers were composed of three films: aluminum oxide, zirconium oxide other and titanium oxide. Each film was deposited by USP. The precursor substance was X-acetylacetonate, with X as Aluminum, Zirconium or Titanium (Alfa-Aesar) dissolved in N, N-dimethylformamide (Merk) (N, N-DMF). The conditions of the ultrasonic pyrolysis process are shown in Table 1. In the first column we show the concentration of X-acetylacetonate in N, N-DMF; in the second one we show the flow rate of the air carrier, and in the third one the temperature of deposition controlled in the Sn bath, next the deposit time, and in the last column the nozzle-substrate distance.

The multilayer coating was performed by deposition of individual films in the conditions described in the Table 1. The films were deposited on a brass substrate to apply a tension test. Each layer was composed by three films of $\text{Al}_2\text{O}_3$, $\text{ZrO}_2$ and $\text{TiO}_2$, respectively. Multilayer samples were obtained with one to ten layers of coating. Measurements of Vickers microhardness (Micromet, 2000), profilometry (Dektak 3) and tension test (Universal machine of mechanical test, INSTRON 1125) were made on each multilayer sample.

The chemical composition of the multilayers was determined by an energy dispersive scan. Analysis of the coating surface was made using microphotographs (optical microscope Olympus MG-3 and electronic microscope ZEISS SUPRA 55PV). With the purpose of observing the effect that the coatings had in the mechanical properties. The tension tests were performed at a slow crosshead speed, using samples with $N(\text{Al}_2\text{O}_3, \text{ZrO}_2, \text{TiO}_2)$ layers, for $N$ (1, 3, 5, 7, 10)

| Table 1. Parameters of films deposition. |
|-----------------------------------------|
| **Concentration (mol)** | **Flow rate (ml/min)** | **Temperature (°C)** | **Deposit time (s)** | **N-S distance (cm)** |
|-------------------------|------------------------|----------------------|----------------------|----------------------|
| Aluminum                | 0.10                   | 1990                 | 550                  | 60                   | 0.8                  |
| Zirconium               | 0.08                   | 1990                 | 500                  | 60                   | 0.8                  |
| Titanium                | 0.06                   | 1450                 | 500                  | 60                   | 0.8                  |

3. Results and discussion
The chemical composition of the coating with $10(\text{Al}_2\text{O}_3, \text{ZrO}_2, \text{TiO}_2)$ layers has an oxygen excess with respect to the oxides stoichiometry (Table 2). This excess is due to the deposition technique. The X-ray pattern for each coating indicates a dominant amorphous microstructure. The coating $10(\text{Al}_2\text{O}_3, \text{ZrO}_2, \text{TiO}_2)$ has an average thickness of 6.8 microns.
The evaluation of mechanical properties of the thin coating allows us to glimpse their potential applications to the aerospace, chemical and energetic industries [10]. Hardness measurements show that the micro-hardness increases with the number of layers deposited on the brass, thus, for uncoated brass, an average value of HV 68.0 was obtained, which increases up to HV 268.9 for the sample with 10 layers. Figure 1 shows the mechanical properties of samples for a different number \( N \) of layers. Results of microhardness and tensile tests are included. In the left plot, we can observe an exponential relation between the Vickers number and the number of layers. The maximum microhardness of 2.64 GPa is obtained with 10 layers, which is within the range of microhardness measurements of films obtained by the dip coating and sputtering processes; 0.7 GPa for granular \( TiO_2 \) films deposited on soda-lime glass substrates [11], and 17-19 GPa obtained in \( Al_2O_3/TiO_2 \) multilayers with a high degree of uniformity deposited on sapphire substrates [12]. The multilayer effect on the mechanical properties can be determined through the elastic modulus. From the elastic region of the relationship between the stress \( \sigma \) and the strain \( \epsilon \), the Young’s modulus \( E = \frac{\sigma}{\epsilon} \) was obtained for each sample. The elastic modulus increases with the number of layers, a logarithmic behaviour is observed in the right plot of figure 1. Nevertheless, practically in the onset of test the coatings were fractured. In order to compare the effect of the multilayer coating on the mechanical properties of the brass sheet, the values at room temperature of the elastic modulus \( E \) for oxides of aluminum, zirconium, and titanium reported in the database of material properties (MakeitFrom.com) are shown in the Table 3.

| Element       | At %  |
|---------------|-------|
| Zirconium     | 15.6  |
| Aluminum      | 23.1  |
| Titanium      | 3.14  |
| Oxygen        | 58.6  |

Table 2. Chemical composition of the coating with 10 layers.

The optical micrographs show in general coatings with a homogeneous surface, without fractures and with few defects. Scanning electron micrographs for 1, 7 and 10 layers coatings are shown in the figure 2. In the images the granular structure of the coating is revealed, and can be observed that the granules diameter increases with the number of layers. The sequence of photographs, according to the resolution and type of layers, shows the morphological changes associated with the growth kinematics of the layers. In those images the spherical shape of the granules is clearly observed. At the right, the fracture of a spherical structure can be observed.

Table 3. Young’s modulus \( E \) at room temperature.

| Element       | \( E \) (GPa) |
|---------------|--------------|
| Zirconium oxide | \( ZrO_2 \) | 190-200 |
| Aluminum oxide  | \( Al_2O_3 \) | 220-370 |
| Titanium oxide   | \( TiO_2 \) | 293   |
| Uncoated brass     | \( Sn \) | 110   |
| Coating with 10 layers | \( 10(Al_2O_3,ZrO_2,TiO_2) \) | 320   |

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Figure 1. Variations of the microhardness (left) and the Young’s modulus (right) with the number layers.

Figures 3 and 4 show high-resolution micrographs of the coatings surface with 7 and 10 layers respectively, for samples after the tension test. Both figures show details of nanostructured spherical multilayers. A nested spherical shape with approximate diameter $1.2 \mu m$ in the coating with 7 layers is identified, and other one with an approximate diameter of $3.6 \mu m$ is observed in the coating with 10 layers. The spherical multilayer structures show only two films in each layer with an approximate thickness of $85 - 90 nm$, so we can suppose than only two components are present in the nested concentric structures. The nested shape could be performed by effect of the surface tension if a drop envelopes a particle deposited previously, so the evaporation of the volatile component within the drop had to occur on the substrate. This hypothesis is difficult to verify, since multiple variables affect the drying drop morphology [13]. Among these factor are the solution characteristic such as surface tension, liquid density, viscosity, precursor concentration and operating parameter such as heating temperature, rate of evaporation, mass of solute, among other.

Figure 2. Scanning electron micrograph for 1, 7, and 10 layers. The scale bar sizes are 200 nm, $1\mu m$ and $1 \mu m$ respectively.

Theoretical models based on the physicochemical properties of the components of the solution have been used to study the thermodynamic and hydrodynamic of the system during the evaporation and drying stages in spray pyrolysis [14]. Also, considering the complexity of the problem, dimensionless studies have been proposed to simplify the constitutive equations of the process [15].

In figures 3 and 4, two types of multilayer shells can be observed. In figure 3, in the $7(Al_2O_3,ZrO_2,TiO_2)$ coating, the nested structure has 7 layers with an approximate mean thickness $\alpha = 86 nm$, where, $d_1 = 66 nm$ and $d_2 = 20 nm$ are the size along the radial direction of the first and the second film, which could be $Al_2O_3/ZrO_2$. In figure 4, in the $10(Al_2O_3,ZrO_2,TiO_2)$ coating, the nested structure has 10 layers with an approximate mean thickness $\alpha = d_1 + d_2 = 180 nm$, where $d_1 = 160 nm$ and $d_2 = 20 nm$ are the size along the radial direction of the first and the second film respectively, which could be $Al_2O_3/TiO_2$ or $ZrO_2/TiO_2$ if the atomic percent of the chemical composition shown in the Table 2 is considered.
4. Conclusions

Microhardness and tension tests were applied to coatings over brass with 1 to 10 layers; each layer is composed by three different films. This films were deposited one by one using the ultrasonic spray pyrolysis technique. The microhardness and the Young’s modulus of the coating brass show an effective and significant increase with the number of layers, therefore the ultrasonic spray pyrolysis technique has shown to be useful for the production of coverages at low cost, resulting in good mechanical properties. This coatings can be used to cover fragile materials that works in harsh conditions. The coatings were fractured by the tension tests, and the breaking of some granules of the coating was induced. The scanning electron micrographs show microspheres with a periodic nanostructure composed by concentric layers of two films. This result show that, by using the deposit conditions introduced in this work, the ultrasonic spray pyrolysis technique can be employed to design periodic concentric layers nanostructures, which can be used as electronic and photonic devices for different applications.
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