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Tribological properties of $Bi_xTi_yO_z$ films grown via RF sputtering on 316L steel substrates

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Abstract
In this paper, we present the results obtained in surface chemical analysis, morphological characterization and evaluation of tribological properties of coatings of amorphous bismuth titanate ($Bi_xTi_yO_z$) deposited on substrates made of 316L stainless steel using rf sputtering technique. The chemical elemental analysis was performed using Auger electron spectroscopy (AES), the morphology of the coatings was determined by atomic force microscopy (AFM). Measures of friction coefficient and wear rate were obtained by ball on disc test. EEA analyses allowed to establish that the first 10 nm of the coatings are comprised probably of $Bi_4Ti_3O_{12}$ and Ti_2O_3, AFM measurements indicate that the coatings have an average roughness of 22.28nm and grain size of 50nm. Finally, the tribological tests established that the coefficient of friction and wear rate of the coated steel has similar values to the bare steel.

Keywords: Amorphous titanate, spectroscopy, tribology.

Propiedades tribológicas de Películas de $Bi_xTi_yO_z$ producidas por RF sputtering sobre sustratos de acero 316L

Resumen
En este trabajo se presentan los resultados obtenidos en el análisis químico superficial, la caracterización morfológica y evaluación de las propiedades tribológicas de recubrimientos de titanato de bismuto amorfo ($Bi_xTi_yO_z$) depositados sobre sustratos de acero inoxidable 316L utilizando la técnica de pulverización catódica rf. El análisis químico elemental se realizó por medio de espectroscopia de electrones Auger (EEA), la morfología de los recubrimientos se determinó mediante microscopia de fuerza atómica (MFA). Las medidas del coeficiente de fricción y la tasa de desgaste fueron obtenidas mediante pruebas de bola sobre disco. Los análisis de EEA permitieron establecer que los primeros 10 nm de los recubrimientos están formados probablemente por óxidos de $Bi_4Ti_3O_{12}$ y Ti_2O_3, las medidas de AFM indican que los recubrimientos tienen una rugosidad promedio de 22.28nm y un tamaño de grano de 50nm. Finalmente, las pruebas tribológicas establecieron que el coeficiente de fricción y la tasa de desgaste del acero recubierto tiene valores similares al acero desnudo.

Palabras clave: Titanato amorfo, espectroscopia, tribología

1. Introduction

Ferroelectric thin films are of interest in many fields, such as the electronic and microelectronic industries, and in particular those that deal with bismuth titanate (BIT), which is a ceramic material that has a high Curie temperature, good resistance to fatigue, and interesting photocatalytic properties, which allow it to be useful in devices such as non-volatile memories, capacitors, and optical memories [1]. These coatings can be deposited through sputtering to obtain a high density, compact and homogeneous material [2,3]. It is important to note that there are numerous papers in the scientific literature that show the technological and industrial applications of BIT, but there is insufficient data regarding

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its tribological behavior. During the last few years many phases of bismuth titanate have been synthesized using various techniques, for instance chemical solution decomposition (CSD)[4], reactive sintering [5], and RF magnetron sputtering [6,7], obtaining diverse stoichiometric of BIT, but in general these types of films grow in an amorphous structure¨ [8].

In the present paper, bismuth titanate (BixTiyOz) was deposited on 316 stainless steel substrates via RF magnetron sputtering. The microstructural characterization showed that they were amorphous films, and their tribological properties such as resistance to wear and the coefficient of friction were determined. The results showed that these films exhibit a protecting effect that generates a reduction of the rate of wear when compared to the substrate.

2. Experimental Method

The dimensions of the 316L stainless steel substrate were 19.00mm x 3.00mm; the surface was prepared by mechanical grinding with sandpaper from number 300 to 1200 and Alumina (Al2O3) with a grain size of 0.02µm. The substrates were cleaned using 50 mL of deionized water in ultrasound for 10 minutes. The samples were dipped into 50 mL of acetone in order to remove the organic compounds. Finally, the same process was undertaken using butanol until a clean surface was obtained.

The ceramic BIT coatings were prepared from a target of Bi4Ti3O12 (99.9%, Plasma Materials,) using a CIT rf Alcatel HS 2000 sputtering system with a balanced magnetron 101.6 mm in diameter, described in a previous paper [9]. The deposition time for the films was 45 minutes. An rf electrical power of 150W and an argon atmosphere with a working pressure of 7.5x10-3mbar were used. The temperature of the substrate was varied between 300 and 400°C, and a voltage bias of -280V was applied during the deposition.

The microstructure of the BIT coating was determined using an MFP-3D-BIO atomic force microscope with a resolution of 0.5 nm. The obtained images were made at 1µm2 in non-contact mode. Igor pro software was used for the acquisition of data about the preciseness and the particle sizes. For the elemental chemical analysis, an Omicron Auger spectrometer was used, working at 3.0 keV.

3. Results and Discussion

3.1. Chemical and morphological characterization

Fig. 1 shows the chemical composition of the surface obtained through Auger electron spectroscopy. The spectrum allows us to find peaks belonging to the atomic transitions for BiN6O45O45 [10] at 103.1eV, Ti L3M23M23 and Ti L23M23V at 382.4 eV [11] and 417.0eV [10], respectively, O KL1L23 and O KVV at 491.2[10] and 511.6eV [13], respectively, and CKVV at 266 eV [10].

The energies associated with the oxygen peaks have been reported by Humbert [14] as titanium dioxide (TiO_2). Moreover, taking into account that the kinetic energy of metallic bismuth is 102.0eV and that the experimental energy shift is 1.1eV, this could indicate that the Bi was forming an oxide.

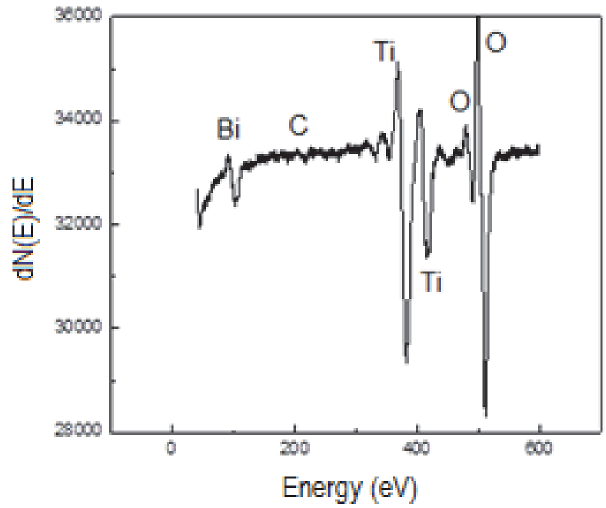

Figure 1. AES spectrum of $Bi_xTi_yO_z$ coatings for samples grown at 350°C and 150W.
Source: Authors

Table 1.
Chemical composition of BiTiO coatings.

Element	(% at)
Bismuth	8.0
Titanium	32.0
Oxygen	60.0

Source: Authors

The semi-quantitative analysis made from the line intensity and sensitivity factors at 3 keV [10] allowed for establishing that the films have the following chemical composition (see Table 1).

According to the values of atomic concentration of the surface, the chemical composition of the coatings was a mixture of $Bi_4Ti_3O_{12}$ and Ti_2O_3. The formation of titanium trioxide is not in accordance with that reported by Humbert [14], since, as mentioned above, this author associated the results found in TiO_2 powders.

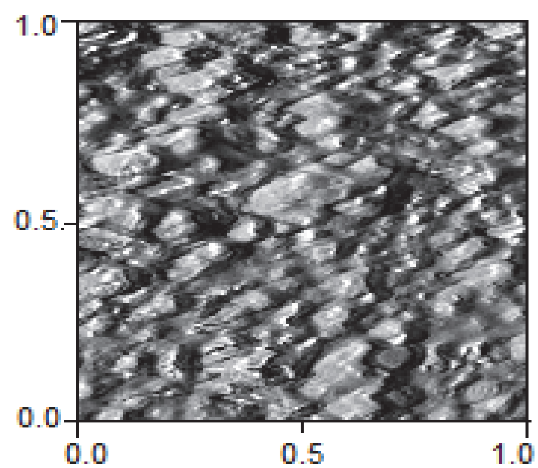

Figure 2. AFM micrograph of $Bi_xTi_yO_z$ coating.
Source: Authors.

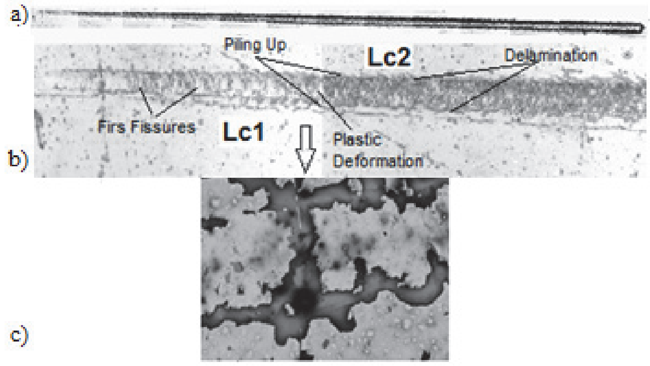

Figure 3. Adherence test for the $Bi_xTi_yO_z$ coating.
Source: Authors.

Fig. 2 shows the morphology of the surface of the $Bi_xTi_yO_z$ coating, where it is possible to see that there is a preferential direction of growth of the grains that formed the coating, which allows us to establish that the growth mechanism is due to the formation of isles. The grain size and roughness obtained in this film were 50nm and 11.28nm, respectively.

3.2. *Adherence and coefficient of friction*

A scratch test was performed under the ASTM C1624-05 standard. Fig. 3 shows the different zones and effects of this test, which had a length of 8mm produced by an applied load of the ascending type. a) is a 200x magnification of an optical microscope image where we see the first fissure (LC1), plastic deformation, and delamination, and b) is a SEM micrograph, where it is possible to observe, in more detail, the delamination (Lc2), plastic deformation, and initial fissures of the coating.

The cracks that are observed are due to a normal load and the displacement of the indenter, since this is a ceramic compound that is fractured, causing micro-cracks that are known as buckling of the lining, which occurs at 2N of load. Due to the fact that the application of the load was progressive, it is possible to see a split that occurs approximately at 4N. Fig. 4 shows the curves of the coefficient of friction made at 2500m for the substrate of 316L stainless steel and the bismuth titanate film.

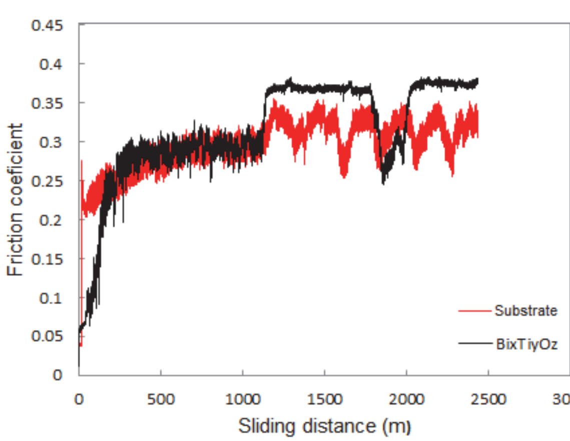

Figure 4. Representative curve of the wear coefficient the $Bi_xTi_yO_z$ coatings.
Source: Authors.

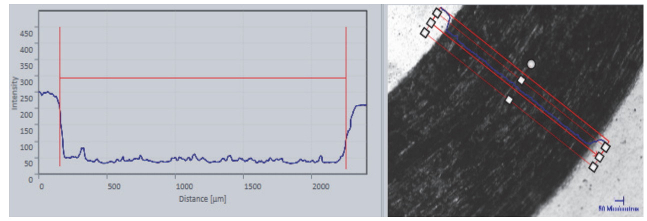
Figure 5. Width of the wear track on films of $Bi_xTi_yO_z$ after 2420m.
Source: Authors.

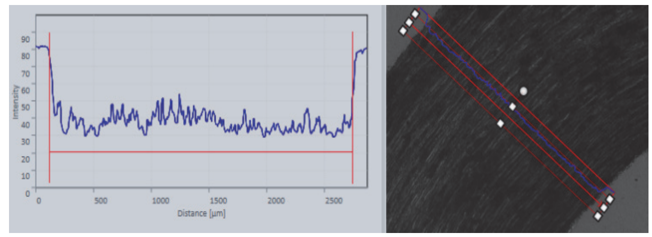
Figura 6. Width of the wear track on substrate SS 316L after 2420m.
Source: Authors.

The results allow us to establish that in the first 250m, the coefficient of friction of the substrate was approximately 4.6 times higher than the coefficient of friction of the coating. This result can be explained because the rough edges of the substrate were polished; from 250m to 1100 m, the values of the two coefficients are very similar. After 1200m, the coefficient of friction of the coatings was higher than that of the substrate, which is probably due to the action of the dry lubricant of bismuth.

Figs. 5 and 6 show the measurements of the width of the wear track in five different areas. Using these measurements, the average width of the wear track, the volume, and the rate of wear were calculated. These values were determined using ZEN 2011 software. The widths of the tracks allow us to observe that for the same distance travelled, the track of the wear test with the coating is thinner and softer than the track of the substrate.

These results show that bismuth acts as a dry lubricating agent. Fig. 7 shows the calculation of the rate of wear.

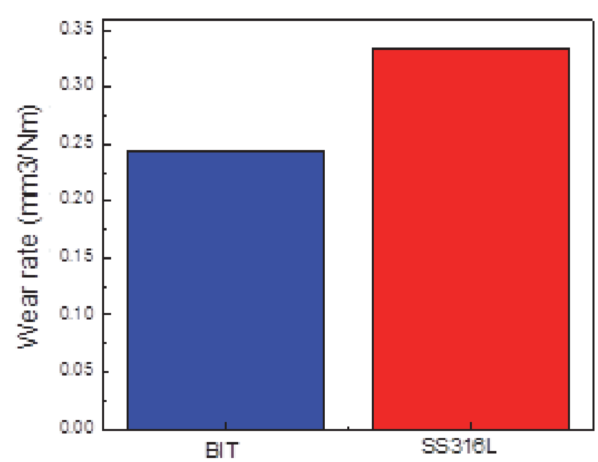

Figure 7. Calculation of the rate of wear after 2420m.
Source: Authors.

The values of these rates allow us to establish that a substrate coated with BIT has a lower rate of wear than an uncoated substrate. This result indicates that BIT exhibits good tribological behavior.

4. Conclusions

Bismuth oxide films were grown via RF magnetron sputtering. Chemical analysis showed that the surface of the films was composed of TiO_2 and $Bi_4Ti_3O_{12}$. Tribological tests showed that the adherence exhibited a critical value at 4N, since at this load, the films were delaminated. Moreover, the coefficient of friction and rate of wear of the films were less than those of the substrate.

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