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Effect of the number of layers on surface topography of bismuth-titanium coatings

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Effect of the number of layers on surface topography of bismuth-titanium coatings

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Abstract. The objective of this research is to perform a topographic characterization by atomic force microscopy of the surface of bismuth titanate (Bi/Ti) coatings varying the number of layers deposited on the substrates, considering that there were not results of reported studies in which these precursors were used. It is important to analyze the surface behavior of these coatings as a first phase of future researches to establish the viability of possible uses and applications in biomedical industry. The films were synthesized by the sol-gel method from bismuth nitrate pentahydrate and titanium tetrabutoxide. Subsequently, by means of the spin-coating technique, the coatings were deposited on 316L stainless steel in monolayer and bi-layer, as this type of steel has been widely used for medical applications due to its good compatibility. The roughness values of each of the coatings were also determined. It is concluded that there is a relationship between the topography of the surface and the roughness values of the films with respect to the concentration of the precursors, the number and the speed of centrifugation of the layers deposited on the substrate. High concentrations of titanium tetrabutoxide effect on the good densification characteristics of the coatings.

1. Introduction

The sol-gel process is a chemical synthesis method initially used for the preparation of inorganic materials [1,2]. This process defines conformation of ceramic materials from routes of chemical polymerization of components in liquid state, sol, at low temperature (environment). Currently, the sol-gel technique allows products of very different characteristics to be obtained according to the path followed to obtain them. It provides an alternative route for the production of ceramic materials and glass. Compared with traditional methods, the sol-gel route offers a large number of important advantages that make the method interesting for the design of materials with the necessary properties for specific applications, achieving with this great versatility a growing application. The industrial applicability of the sol-gel process has focused mainly on the preparation of thin films that allow improving and modifying the properties of the different substrates [3-6].

The 316L austenitic stainless steel is used by several industries due to its excellent corrosion resistance in many aqueous and atmospheric environments [7-11]. It has also been widely used as a substrate for depositing films to improve properties such as corrosion resistance, hardness and wear resistance; evidencing that coatings do optimize the performance of 316L stainless steel, in addition to evidencing the need for a surface morphology that favors adhesion and cell growth [10].

This work will to contribute to the solution of the corrosion problem by means of the synthesis of a ceramic material based on compounds of bismuth and titanium (Bi/Ti) by the sol-gel method, obtaining a protective anticorrosive film on the 316L stainless steel substrate and characterizing the surface of these coatings. This will allow new knowledge to be generated regarding the possibility of using Bi/Ti films on 316L stainless steel substrates for various industry needs.

The characterization focuses on establishing the influence, in the surface homogeneity, of the sols according to the concentration of the precursors, the number of layers deposited on the 316L stainless steel substrate and the centrifugation speeds used in the forming process by the technique of spin-coating.

Spin-coating technique allows obtaining dense coatings with good adhesion of films to substrate. For 316L stainless steel, spin-coating technique has demonstrated better advantages that dip-coating technique. This behavior is most likely due to high viscosity of the sol. With dip-coating technique when removing the stainless-steel substrate of the sol, abrupt dehydration of solvents that make it up is not presented, this makes the film drains and does not adhere to the substrate. After the sintering process, the coatings obtained are very thick, because the difference between the thermal expansion coefficients of the film and the substrate of poor quality coatings are obtained [12].

2. Materials and methods

The precursors used in this study were titanium (IV) butoxide-Ti $(OBu)_4$ (Aldrich, 98%) and bismuth nitrate (III) pentahydrate $Bi(NO_3)_3 \cdot 5H_2O$ (Alfa Aesar,98%). As solvents 2-ethoxyethanol (Aldrich, 99%) and glacial acetic acid (Aldrich, 99.7%). And as a complexer ethanolamine (Aldrich, 98%), the systems studied were (Bi/Ti: 80/20), (Bi/Ti: 50/50) and (Bi/Ti: 20/80). The methodology of conformation of stable sols is detailed in previous investigations [7,8]. The films were formed by spin-coating at a speed of 1500 revolutions per minute (rpm) and 4000 rpm on substrates of 316L steel of dimensions 2 cm x 2 cm x 0.4 cm.

The sintering of the films was carried out at a heating rate of 1 °C/min allowing the controlled elimination of the organic components present in the films. The thermal process is established from the initial temperature of 25 ºC to 300 ºC and is stabilized at this temperature for one hour, later, heating is resumed up to 400 ºC and for half an hour it is balanced.

To evaluate the topography of coatings equipment "NaioAFM-nanosurf" was used in contact mode.

3. Results and discussion

In addition to assessing the topography, the atomic force microscopy (AFM) technique allows determining the surface roughness values of each of the samples studied. In Figure 1 the topography of the substrate is shown.

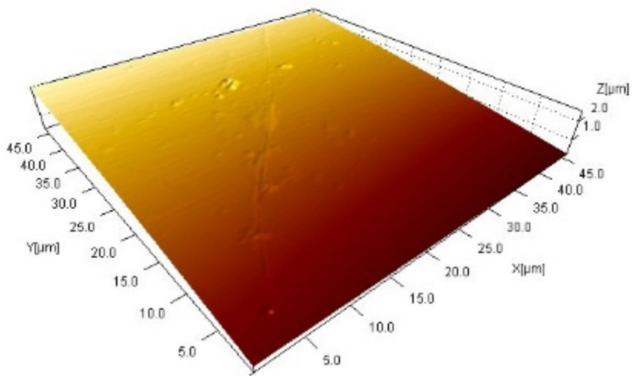


Figure 1. AFM micrograph 316L substrate.

Figure 1 shows a slightly homogeneous surface with some imperfections caused by the polishing and conditioning process to deposit the coatings. Figure 2, Figure 3 and Figure 4 correspond to the results by AFM of the surface characteristics of the coatings of the system concentrations (Bi/Ti:

20/80), (Bi/Ti: 50/50), and (Bi/Ti: 80/20), respectively. To facilitate the comparative study, representative areas of 45 µm x 45 µm were considered.

Specifically, Figure 2 presents the AFM micrographs for coatings of the Bi/Ti system in a concentration of the precursors (Bi/Ti: 20/80), of which monolayer and bilayer coatings were formed, varying the spin speeds at 1500 rpm and 4000 rpm. When comparing the superficial behaviors of the films and the substrate (Figure 1), considerable variation is observed in the topography and, therefore, in the roughness values. At a speed of 1500 rpm, the monolayer as the bilayer has irregular surfaces with a high degree of roughness, due to the growth of bismuth oxides. For speed of 4000 rpm the coatings, especially the monolayer, show a very homogeneous surface with low roughness. In the bilayer, it is evident that, when another film is superimposed, the roughness changes and as a result, a very regular topography is obtained. The roughness values for the different coatings are recorded in Table 1.

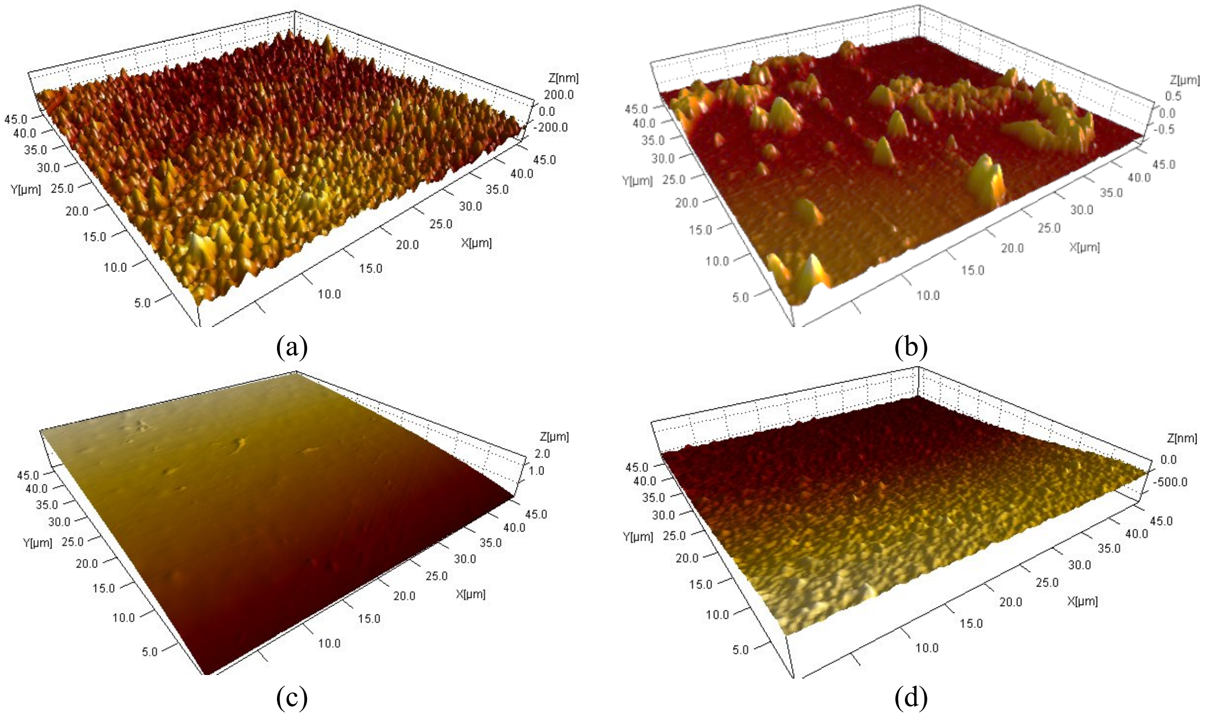
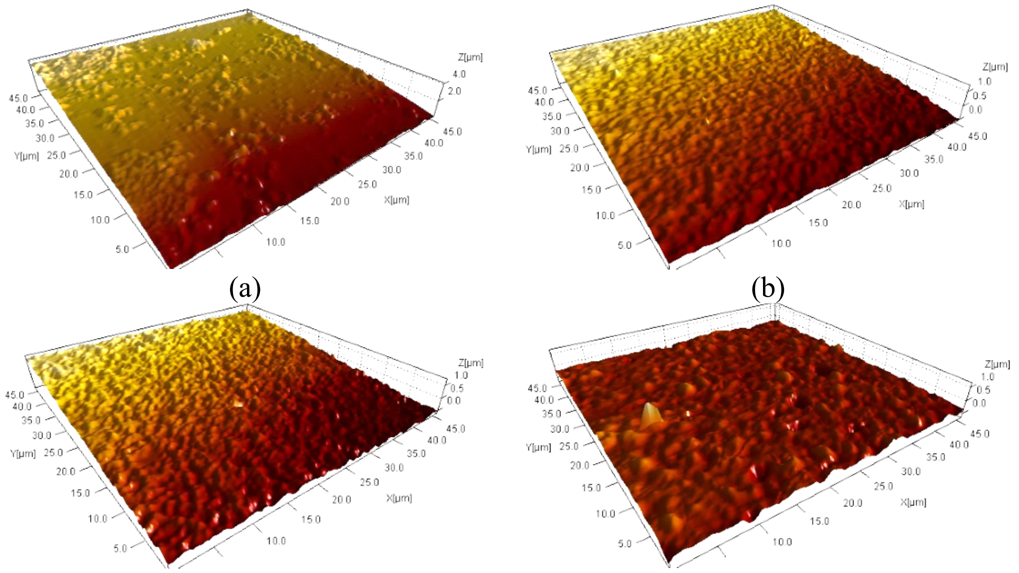


Figure 2. [Bi/Ti: 20/80] coatings, (a) monolayer 1500 rpm, (b) bilayer 1500 rpm, (c) monolayer 4000 rpm and (d) bilayer 4000 rpm.

Figure 3 shows the AFM micrographs for conformal coatings of the concentration (Bi/Ti: 50/50). Rough surfaces with variations in their value are observed as shown in Table 1. From the results, it is possible to infer that the best surface uniformity is presented for coatings obtained at 4000 rpm. Additionally, it is observed that the films are compact because the formation of cracks or pores is not evident.

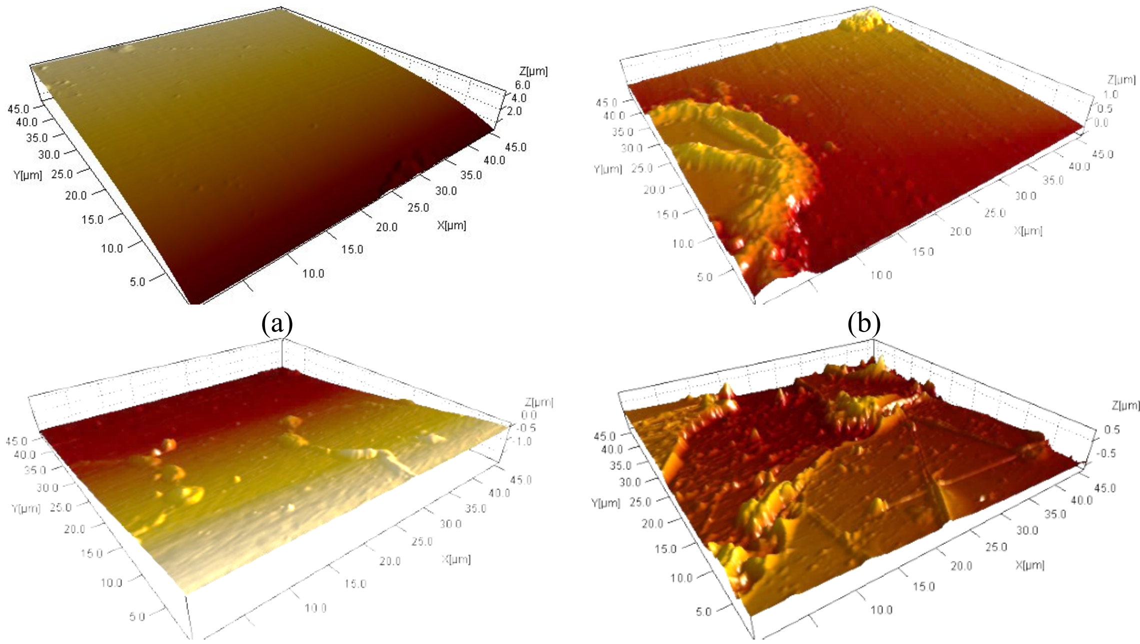
Continuing with the analysis, Figure 4 presents the surface images by AFM of the films formed from the stable sun with a concentration of the precursors (Bi/Ti: 80/20). It is observed that the coatings are the most homogeneous of all the concentrations studied. The films have quite smooth surfaces and few oxide incrustations as shown in Figure 4(a), Figure 4(b) and Figure 4(c). The lowest roughness value is demonstrated by the monolayer obtained at 1500 rpm. Figure 4(d) corresponds to the bilayer coating at 4000 rpm, superficial cracks and quite superficial irregularity are observed. The roughness values found for the coatings are recorded in Table 1.

The Table 1 shows the roughness values for the coatings of the Bi/Ti system, depending on the concentration of the precursors, the speed of centrifugation and the number of layers.



(a) (b) (c) (d)

Figure 3. [Bi/Ti: 50/50] coatings, (a) monolayer 1500 rpm, (b) bilayer 1500 rpm, (c) monolayer 4000 rpm and (d) bilayer 4000 rpm.



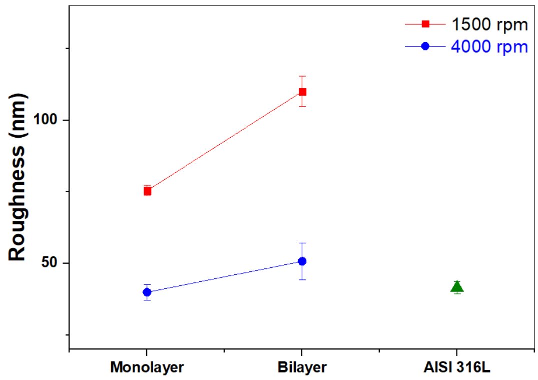
(a) (b) (c) (d)

Figure 4. Bi/Ti: 80/20 coatings: (a) monolayer 1500 rpm, (b) bilayer 1500 rpm, (c) monolayer 4000 rpm and (d) bilayer 4000 rpm.

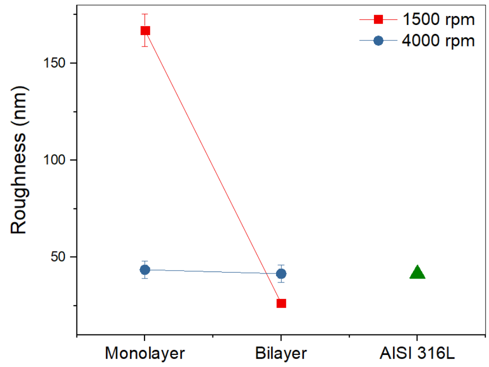
Table 1. Roughness values of Bi/Ti films by concentration, speed of production and number of layers.

	Roughness (nm)			
Bi/Ti	Monolayer		Bilayer	
	1500 rpm	4000 rpm	1500 rpm	4000 rpm
20/80	75.4±3.8	39.9±2.0	110.0±5.5	50.7±2.5
50/50	167.0±8.4	43.6±2.2	26.3±1.3	41.5±2.1
80/20	35.3±1.8	55.0±2.8	106.0±5.3	128.0±6.4

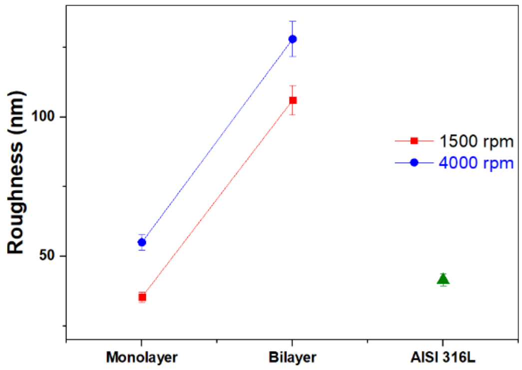
The Figure 5 shows the trends in the roughness values determined for each of the coatings based on (1) the concentration of the precursors with which the sols were synthesized, (2) the centrifugation speeds selected in the process formed by the spin-coating technique and (3) the number of layers applied to the 316L stainless steel substrate.



(a)



(b)



(c)

Figure 5. Roughness graph for Bi/Ti coatings, (a) (Bi/Ti: 20/80), (b) (Bi/Ti: 50/50) and (c) (Bi/Ti: 80/20).

With respect to Figure 5(a) it can be affirmed that in the coatings of the Bi/Ti system with concentration (Bi/Ti: 20/80) the roughness is greater for low spin speeds and, otherwise, high spin speeds allow coatings to be obtained with low roughness values. This characteristic is related to the final thickness of the coatings, where it is established that low centrifugation speeds, in spin-coating, influence the conformation of films with greater thickness than in the case of high speeds. It is also evident that the roughness of the bilayers is greater than in the monolayers depending, as mentioned above, on the forming speeds of the coatings.

The difference in roughness between the observed and the quantified is that the average roughness is estimated as a value of the arithmetic average of the absolute values of the heights and y(x) measured from a central line. Studies have shown [9] that average roughness can be calculated mathematically.

When comparing the roughness graph for films of the concentration (Bi/Ti: 50/50), Figure 5(b) with the respective micrographs, Figure 3, it is concluded that there is no clear correspondence of the qualitative with the quantitative in this type of coatings; situation that could be explained as follows: at a speed of 1500 rpm it can be observed that the surface of the monolayer is quite irregular with totally flat areas and zones with oxides incrustations. This superficial irregularity leads to high values of roughness. As a consequence of the application of the bilayer, the coating covers the flat areas and it is about homogenizing the surface but maintaining high values of roughness, which reaffirms the tendency of the bilayers to present greater roughness than the monolayers.

As regards the films of the concentration (Bi/Ti: 80/20), as shown in Figure 5(c), the bilayers show an increase in roughness with respect to the monolayers regardless of the centrifugation speed selected in the conformation of the coating. It is evident that coatings at 4000 rpm show greater roughness than those obtained at 1500 rpm, as corroborated by the AFM micrographs in Figure 5.

In some cases, roughness values lower than those reported for the substrate are indicated, such as coatings (Bi/Ti: 80/20) in monolayer at 1500 rpm and (Bi/Ti: 20/80) in monolayer at 4000 allowing infer that, under some circumstances, the application of the coatings homogenizes the substrate surface of the imperfections, such as scratch marks, typical of the metallographic polishing process to which the blanks were subjected before the forming process of the thin films.

4. Conclusions

The optimization of the sintering conditions of the Bi/Ti films allowed obtaining dense films with little formation of pores and cracks depending on the co-concentration of the precursors, the number of layers and the speeds of centrifugation.

The influence of the high concentrations of titanium tetrabutoxide on the good densification characteristics of the coatings was determined. The characterization by means of the AFM technique of the Bi/Ti coatings demonstrates the influence of the concentration of bismuth nitrate on the final topography of the films.

Acknowledgment

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References

[1] Bautista-Ruiz J, Aperador W, Delgado A and Díaz-Lagos M 2014 *Int. J. Electrochem. Sci.* **9** 4144
[2] Brinker C and Scherer G 1990 *Sol-gel science: The physics and chemistry of sol-gel processing* (San Diego: Academic Press Inc)
[3] Kartavtseva M 2007 *Thin Solid Films* **515** 6416
[4] Veber A, Kunej S, Cerc R and Suvoriv D 2020 *Journal of the European Ceramic Society* **30** 2475
[5] Veber A, Kunej S and Suvorov D 2010 *Ceramics International* **36** 245
[6] Sánchez C, Livage J, Henry M and Babonneau 1998 *Journal of Non-Crystalline Solids* **100** 65
[7] Bautista-Ruiz J, Aperador W and Caicedo J 2018 *Indian Journal of Science and Technology* **11** 1
[8] Bautista-Ruiz J, Ruiz E, Duque J, Aperador W and Olaya J 2016 *Int. J. Chem. Sci.* **14** 1447
[9] Hinojosa M and Reyes M 2001 *Revista Ingenierías* **11** 27
[10] Bordji K, Jouzeau J, Mainard D and Payan E 1996 *Biomaterials* **17** 491
[11] Bülbül F, Altun H, Ezirmik V and Kücük Ó 2013 *Journal of Engineering Tribology* **227** 629
[12] Bautista-Ruiz J, Olaya J and Aperador W 2016 *Journal of Physics: Conference Series* **687** 012030