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Characterization of the anticorrosive properties in bismuth-titanate films obtained by the sol-gel method

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Abstract. Sol-gel synthesis has been used since 1950 to prepare oxides. The method is attractive because the processes of obtaining the oxides are developed at room temperature; products with high purity and homogeneity are obtained, and allow the combination of several types of oxides: silicon, zirconium, titanium, aluminum, bismuth, and cerium. Sol-gel has been used to make ceramic composites with anticorrosive properties on stainless steel substrates. A class of stainless steel widely used in biomedical applications, especially in the treatment of fractures, 316L is its low economic cost relative to other materials such as titanium. Once the steel implant is inside the human body it comes into contact with body fluids that contain chloride ions. The fluid-implant interaction develops a corrosive process on the metal surface. The corrosive products of iron diffuse in the body causing tissue damage. As a possible solution to this problem, the objective of the investigation was to obtain a bismuth-titanium oxide using the sol-gel method and apply it on 316L stainless steel substrates. Bismuth nitrate pentahydrate and titanium tetrabutoxide were used as precursors. The anticorrosive response was evaluated in a simulated physiological solution, Ringer's solution, by electrochemical impedance spectroscopy and potentiodynamic polarization curves. It is concluded that the coatings function as a corrosion barrier preventing the chloride ions Ringer's solution reach the metal surface.

1. Introduction

AISI 316L stainless steels are characterized by good resistance to corrosion, malleability, weldability and biocompatibility. These properties make it a functional and versatile material in the chemical, naval, petrochemical, pharmaceutical, food and biomedical industries [1-2]. Under certain environmental conditions, the anticorrosive properties can be considerably affected by degrading the material by pitting due to contact with chloride ions Cl^- and/or sulfide ions S^2 [3-7]. One of the most important applications of 316L steel is related to surgical implantology, due to its low cost compared to other materials such as titanium. Steel implants are considered a public health problem because when they have been introduced into the human body they are subjected to the corrosive environment of the physiological fluids in contact. When the corrosive attack of iron diffuses into the body, its excess can cause hemosiderosis (an increase of iron in the tissue without alteration of its structure or function), or hemochromatosis (tissue damage) [8-12].

The objective of this investigation was to obtain bismuth titanate ceramic coatings using the sol-gel method on 316L stainless steel substrates using bismuth (III) nitrate pentahydrate and titanium tetrabutoxide as precursors. Three proportions of the precursors, bismuth/titanium (Bi/Ti), were studied (Bi/Ti: 20/80), (Bi/Ti: 50/50) and (Bi/Ti: 80/20) to determine the effect of precursor concentrations on the effectiveness of anticorrosive barrier of coatings.

The results of this work can have a positive effect in Colombia and the world, by using steels coated with bismuth-titanium layers in surgical implantation. Coated steel implants are cheaper compared to titanium; this feature reduces economic costs to the health sector. Equally importantly, that by coating 316L stainless steel with bismuth/titanium films, implanted patients improve their quality of life by eliminating dissolution iron in his body. Therefore, the results of the study directly address a public health problem benefiting the neediest communities. From the scientific and technological development point of view, this research starts for new studies in the field of biocompatible coatings.

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 $(NO_3)_3$ $5H_2O$ (Alfa Aesar, 98%). As solvents 2-ethoxyethanol (Aldrich, 99%) and glacial acetic acid (Aldrich, 99.7 %). In addition, as a complexing agent ethanolamine (Aldrich, 98%), the systems studied were (Bi/Ti: 80/20), (Bi/Ti: 50/50) and (Bi/Ti: 20/80).

The films were formed by spin coating at a speed of 1500 rpm on substrates 316L stainless 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 for one hour.

The electrochemical impedance spectroscopy tests (EIS) were developed in a three-electrode cell: Ag/AgCl reference electrode; platinum electrode as a counter electrode; working electrode substrate-coating system with an exposure area of 1 cm^2. The test solution was Ringer´s solution at 37 °C. Frequency ranges from 0.01 Hz to 100 kHz. scanning potential of 10 mV. The EIS data were analyzed by fit to a proposed equivalent electric circuit model and constituted by capacitances and resistances, with the Gamry Echem Analyst software and with the nonlinear method of least squares method based on iterations.

The Tafel polarization assays were carried out in a three-electrode cell: 1) Ag/AgCl reference electrode, 2) platinum as counter-electrode and 3) sample as electrode work. The analysis area was 1 cm^2, the scanning was 1 mV/s in Ringer´s solution. The range of scanning potential from -200 mV to 200 mV with respect to the corrosion potential (Ecorr). Speeds and corrosion potentials were obtained by extrapolation of Tafel using a GAMRY Instruments potentiostat-galvanostat 3000. The study was carried out using the Echem Analyst program. The equipment has a voltage resolution of 20 V and a current of 1 fA. The immersion time before the test was 45 minutes. For each coating three potentiodynamic tests were performed. Corrosion current density (icorr) and corrosion potential values are determined by the Tafel extrapolation method using the Gamry Echem Analyst software 5.3.

3. Results and discussions

3.1. Polarization potentiodynamic curves

Figure 1 reveals the Tafel diagrams of bismuth / titanium films in the three study concentrations (Bi/Ti: 80/20), (Bi/Ti: 50/50) and (Bi/Ti: 20/80), and its comparison with respect to the 316L substrate. The polarization curves obtained allow us to find the values of the anodic and cathodic slopes. These parameters allow the determination of corrosion current densities and corrosion rate in thousandths of inches per year (mpy) using the Sterm-Geary equation. In Tafel polarization curves,

Figure 1, it is observed that for all films the corrosion potentials were more positive with respect to the substrate. This behavior is due to the improvement of the thermodynamic stability of the metal surface. In addition, when analyzing the behavior of corrosion currents, it is observed that the coated specimens had always-lower Icor values with respect to the substrate 316L. Corrosion rates were therefore always lower in the films than in the substrate (Table 1), which indicates that the Bi/Ti coating improved the kinetic behavior of the specimens against corrosive processes. On the other hand, in the Tafel curves obtained, it is observed that none of the samples presented passivation zones in the applied potential range.

In general, corrosion potentials tend to be more positive as the concentration of the titanium compound increases, the behavior observed for films (Bi/Ti: 20/80) as shown in Table 1. This indicates the electrochemical behavior nobler. To set the values of the potential parameters of corrosion, the corrosion current, and the corrosion rate will allow knowing the behavior of the coating-substrate interface in each case. It is noted that all coatings indicate more positive corrosion potential values than the value found for the 316L stainless steel substrate.

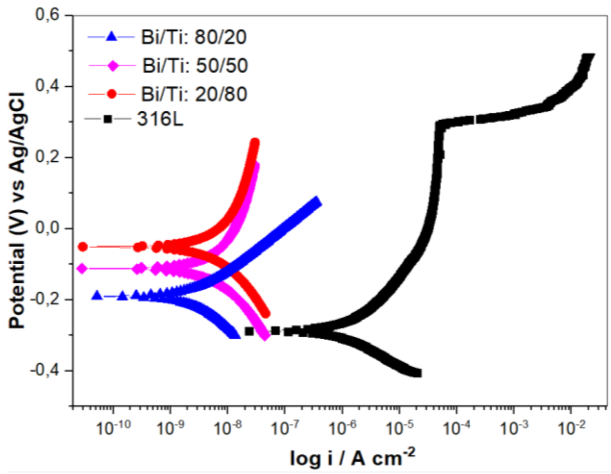

Figure 1. Potentiodynamic polarization curves for coatings of bismuth titanate and 316L substrate.

It can be seen, in Figure 1, that all the curves that represent the coatings are on the curve corresponding to the 316L stainless steel, indicating that the corrosion potential of these is more positive and therefore there is a lower tendency to suffer corrosion in a saline medium. It is also observed that these curves are displaced to the left that allows inferring that the current corrosion density is lower in the coatings with respect to the substrate. It is noteworthy that some concentrations have a better anticorrosive performance than others; this is concluded by comparing the results of the values of corrosion potential and corrosion current for the concentrations studied, as shown in Table 1.

In Figure 1 several parameters can be observed that appear in the anodic polarization curve: a) the primary passivation potential (Epp) is the potential at which the current density begins to decrease or reach to be constant over a finite range of potential, said current is called primary passivation current density (ipp). b) The depletion potential (Ea) is the potential where the current increases with the increase in potential. c) The passive region is the portion of the curve between Epp and Ea. d) the portion of the potentiodynamic polarization curve, where the potentials are less than the Epp (more negative) is called the active region of the curve. e) The portion of the curve where the potentials are greater than Ea is called the transpassive region of the curve.

Quantities such as Epp, Ea and the width of the passive region can be used to characterize corrosion behavior and evaluate how a passive film protects the metal from corrosion. Uniform corrosion and sometimes-pitting corrosion occur in the active region. Very little corrosion or any type of corrosion occurs in the passive region and pitting corrosion can occur in the transpassive region.

The corrosion behavior for a given curve is determined by the shape of the curve, the presence or absence of Epp, Ea and of a passive region.

Table 1. Values of the Tafel parameters for the films and the substrate.

Sample	Icor (nA)	Ecor (V vs Ag/AgCl)	Corrosion rate (mpy)
(Bi/Ti: 20/80)	110.04	-0.056	12.37×10^{-3}
(Bi/Ti: 50/50)	150.20	-0.103	24.46×10^{-3}
(Bi/Ti: 80/20)	176.10	-0.195	35.78×10^{-3}
Substrate 316L	840.70	-0.352	880.80×10^{-3}

As for corrosion rates, it was found that coatings with low concentrations of titanium tetrabutoxide precursor and high concentrations of bismuth nitrate show high corrosion rates. This behavior is explained because the coatings have a greater tendency to the formation of bismuth oxides in the sintering process. The oxides thus constituted, please the appearance of cracks and pores by which the ions present in the working solution, when the test is carried out, without greater resistance to the surface of the substrate.

3.2. Electrochemical impedance spectroscopy

Figure 2 and Figure 3 show the Nyquist diagrams for coatings in concentrations (Bi/Ti: 80/20), (Bi/Ti: 50/50) and /Bi/Ti: 20/80). The working solution used was Ringer's solution that simulates the conditions of human body fluids.

The EIS analysis focuses mainly on determining the values of polarization resistance (Rp). Polarization resistance is the resistance at which the coating opposes the passage of ions from the working solution to the substrate. The high resistance to polarization indicates greater protection of the substrate against the corrosive attack of Ringer's solution. This condition states that the coating offers good corrosion protection.

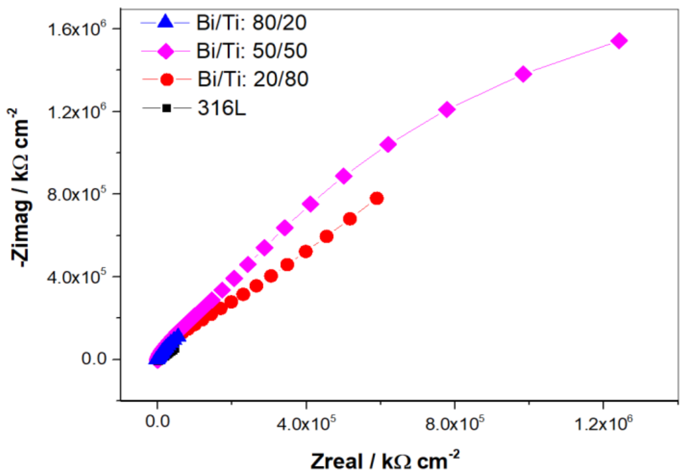

Figure 2. Polarization potentiodynamic curves for bismuth/ titanium films and the 316L stainless steel substrate.

In Figure 2, a similar trend is seen between the graphics of the coatings. Comparing the results with that obtained for the substrate 316L, an improvement in the anticorrosive properties of stainless steel due to the effect of the coating can be observed. There are no inductive arcs. The behavior is capacitive coupled to low frequencies; it is not ideal for the contribution in the real axis and can be explained with the elements of constant phase. It is also important to note that the behavior of Nyquist diagrams infers the existence of very dense coatings with minimal porosity or surface imperfections that can cause load transfers. This condition is explained because at low frequencies there is no evidence of diffusion processes of the electroactive species present due to concentration gradients at the interface of the coating-electrolyte and coating-substrate. The open graphs demonstrate the existence of high values in polarization resistance and, therefore, low corrosion rates, which is corroborated with the analysis by Tafel. It is evident that the coatings have corrosion protection due to the inclusion of titanium in the system which seems to favor the protective properties of the layers.

The behaviors described in Figure 2 is modeled with the equivalent circuit shown in Figure 3. The equivalent circuit is related to a metallic substrate coated with layers of ceramic material. It consists of the following elements: the resistance of the solution (Rsol) corresponds to the resistance offered by the working solution. For this case Ringer's solution, resistance to polarization (Rpo), constant phase element (Cc) of the porous outer layer or coating, constant phase element (Ccor) representing the double layer of Helmholtz, and resistance of the ceramic coating or the porous outer layer (Rcor).

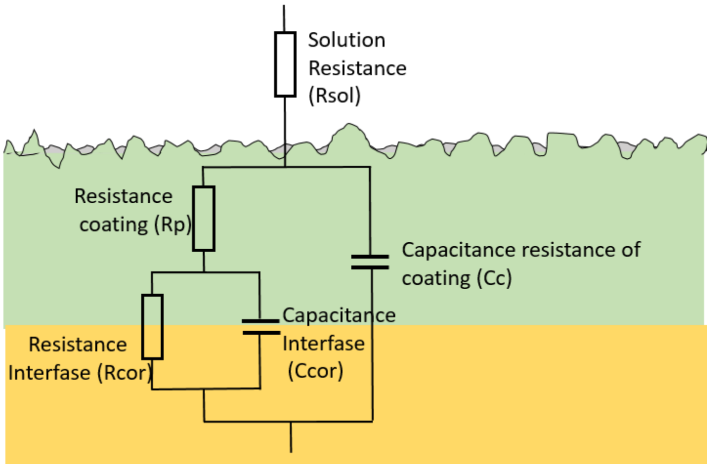

Figure 3. Equivalent electrical circuit.

The values of the parameters or constituent elements of the equivalent circuit for each of the coatings studied as a function of the type of molar concentration are recorded in Table 2. From the information reported in this table, an average value is established for the resistance to the solution of work, Ringer's solution, of 213.6 Ω.

Table 2. Values of equivalent circuit parameters for bismuth/titanium films.

Sample	Rsol (Ω cm^2)	Rpo (Ω cm^2)	Rco (Ω cm^2)	Ccor (μF cm^{-2})	n	Cc (μF cm^{-2})	m
(Bi/Ti:20/80)	230.9	296.2x10^3	100.9	740.4x10^{-9}	458.6x10^{-3}	325.7x10^{-9}	952.6x10^{-3}
(Bi/Ti:50/50)	211.0	2.1x10^6	441.1	879.2x10^{-9}	995.6x10^{-3}	217.6x10^{-9}	973.5x10^{-3}
(Bi/Ti:80/20)	199.0	1.9x10^3	425.4	18.9x10^{-18}	526.3	5.7x10^{-6}	688.2x10^{-3}

4. Conclusions

According to the results of this study, and from its discussion and analysis, the following main conclusions can be drawn: 1) the optimization of the sintering conditions of the bismuth titanate films allowed obtaining dense films with little micropore formation depending on the concentration of the precursors. The influence of the high concentrations of titanium tetrabutoxide on the good densification characteristics of the coatings was determined. 2) The anticorrosive characterization by potentiodynamic polarization curves shows that coatings with a high content of titanium tetrabutoxide (titanium precursor) improve the response to corrosive attack, with respect to the substrate, when they are immersed in Ringer's solution.

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