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Characterizations of coatings obtained by dip coating from sol-gel suspensions

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This research paper shows the conformation of coatings of the SiO_2-TiO_2-ZrO_2system synthesized by the sol-gel method from Si$(OC_2H_5)_4$, Ti$(OBu)_4$ y Zr$(OC_3H_7)_4$, which mean precursors, EtOH and water, and 2,4-pentanodione. They were deposited on stainless steel substrates AISI 304 by dip-coating in mono-layer, bi-layer and tri-layer. They were used as concentrations of the precursors Si 10% Ti 70% Zr 20% and Si 10% Ti 20% Zr 70%, which them conform the system. It was also studied the influence of the coatings on the anticorrosive behavior of the substrate in a solution of HCl to 3% by means of Electrochemical Impedance Spectroscopy (EIS) and power-dynamic curves of polarization. Additionally, it was carried out a study on adhesion of the coatings to the substrate and a study on micro-hardness of the system substrate-coatings. It was also found that the values of the electrochemical parameters changed substantially with the number of layers deposited on the substrate.

Keywords: Corrosion; sol-gel; electrochemical techniques; stainless steel; adhesion.

Este trabajo muestra la conformación de películas cerámicas del sistema SiO_2-TiO_2-ZrO_2sintetizadas por el método sol-gel a partir de Si$(OC_2H_5)_4$, Ti$(OBu)_4$ y Zr$(OC_3H_7)_4$ como precursores, como solvente EtOH y agua y, como acomplejante 2,4 pentanodiona. Fueron depositadas sobre sustratos de acero inoxidable AISI 304 mediante inmersión (dip-coating) en monocapa, bicapa y tricapa. Se utilizaron como concentraciones de los precursores Si 10% Ti 70 % Zr 20 % y Si 10% Ti 20 % Zr 70% que conforman el sistema. Se estudió la influencia de los recubrimientos sobre el comportamiento anticorrosivo del sustrato en una solución de HCl a una concentración del 3% mediante las técnicas de Espectroscopía de Impedancia Electroquímica (EIS) y curvas potenciodinámicas de polarización. Adicionalmente se realizó un estudio sobre la adhesión de los recubrimientos al sustrato, y un estudio sobre microdureza del sistema sustrato-recubrimiento**.** Se encontró que los valores de los parámetros electroquímicos cambian sustancialmente con el número de capas depositadas sobre el sustrato.

Descriptores: Corrosión; sol-gel; técnicas electroquímicas; acero inoxidable; adhesión.

PACS: 61.66.Fn; 62.20.Qp; 68.35.Ct; 81.20.Fw

1. Introduction

The main characteristic of stainless steel is its high resistance to corrosion [1], but when getting in contact with Cl^- and Br^- they undergo of pitting [2]. The Sol-gel is one of the methods of synthesis of materials that presents great interest at the present time [3,4]; by means of this method it is possible to obtain ceramic coatings that act as an anticorrosive barrier [5,6]. Research projects carried out on this topic have indicated that Sol-gel method has allowed applying binary systems (SiO_2-TiO_2 y SiO_2-ZrO_2) on stainless steel substrates AISI/SAE 304 and has allowed to diminish the attack of corrosive agents [7,8]. This research paper shows the testing of the anticorrosive characteristics of the ceramic coatings in monolayers, bilayers and trilayers, by means of a ternary system SiO_2-TiO_2-ZrO_2 [9,10].

2. Experimental procedures

The multi-component system SiO_2-TiO_2-ZrO_2 was applied on steel substrates AISI/SAE 304 of 3.5 cm $\times$ 2.5 cm $\times$ 0.32 cm, to metallographic polish, taken the grease out of to ultrasound with acetone and dried with hot air. The following step was to synthesize the films by dip-coating, being used a speed of 3.67 cm/min, previous elaboration of the stable sol. The sols in the concentrations of the precursors Si/Ti/Zr: 10/70/20 and Si/Ti/Zr: 10/20/70 were conformed with a time of aging of 280 hours, approximately. In Fig. 1 the process for the conformation of stable sols is described.

The sintering of the films was carried out at a speed rate of 2°C/min, in the following stages: For monolayers: the temperature rises from 20 to 300°C staying constant during one hour, soon it is taken to 400°C and it is stabilized by half an hour. For bilayers: the temperature rises from 20 to 100°C staying constant during one hour, soon it is taken to 200°C and it is stabilized by half an hour. For trilayers: the temperature rises from 20 to 50°C staying constant during one hour, soon it is taken to 100°C again and it is stabilized by half an hour.

The Electrochemical Impedance Spectroscopy (EIS) was done with equipment by Gamry Instruments; this device consisted of three electrodes, an electrode of reference (Ag/AgCl), a counter-electrode of platinum and an electrode of work that was the piece to be tested. The sweeping frequency included a rank between 0.1 Hz and 10^5 Hz. The amplitude of the used sinusoidal signal is of 10 mV, in an area of exhibition of 0.2 cm^2 using HCl to 3% with pH = 2.83 as work solution. The diagrams of Tafel were obtained in a rank of potential of -0.2 to 0.2 V with a sweeping of 0.5 mV/s. The measures of micro-hardness on the substrate and the coatings were carried out through a digital micro-durometer

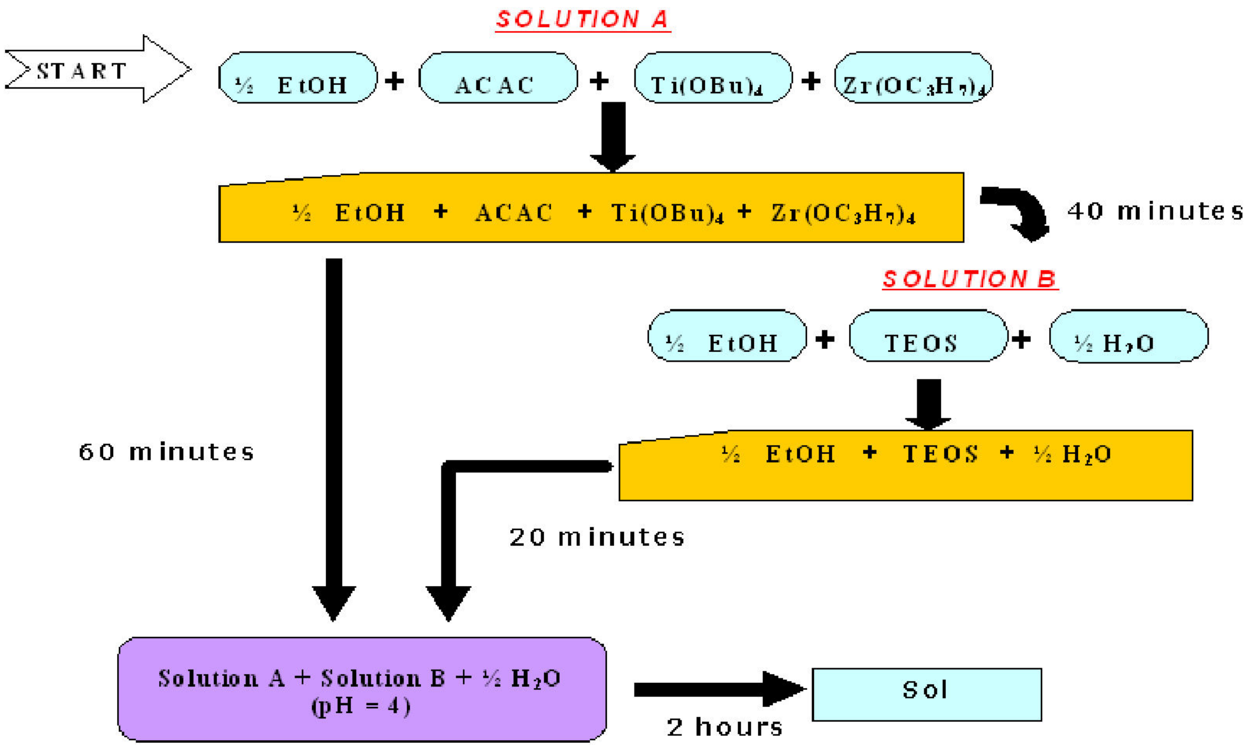

FIGURE 1. Diagram for the adequate preparation of the sol.

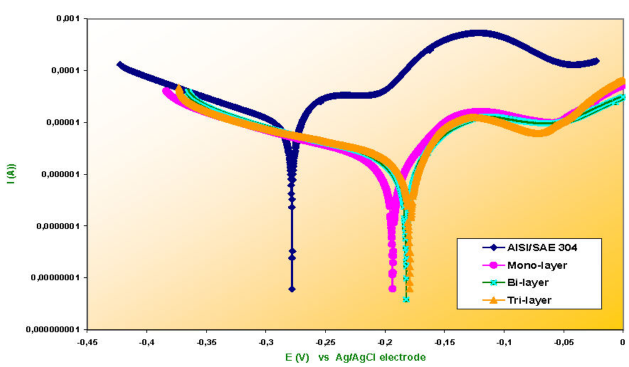

FIGURE 2. Diagrams of Tafel for the Si/Ti/Zr: 10/70/20 concentration.

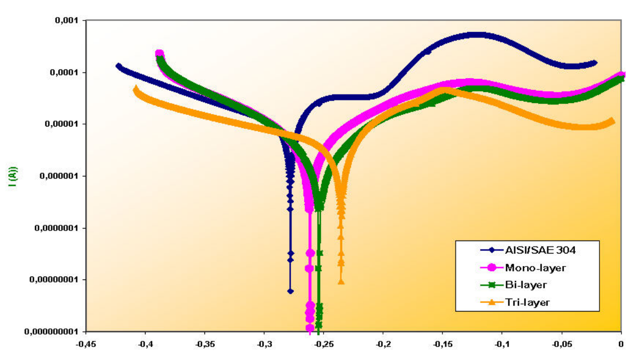

FIGURE 3. Diagrams of Tafel for the Si/Ti/Zr: 10/20/70 concentration.

TABLE I. Values of corrosion currents.

Concentration	$I_{corr}(\mu A)$		
	Mono-layer	Bi-layer	Tri-layer
Si/Ti/Zr: 10/20/70	41.5	23.8	8.00
Si/Ti/Zr: 10/70/20	3.27	2.02	1.87
AISI/SAE 304		57.6	

model HVS 1000, applying a compression load of 98 mN with a time of contact of 20 s. For the determination of the coatings adhesion, the procedure developed and patented by the company DAIMLER BENZ under the norm N° 81 was used, applying the method of Rockwell C. For this test a compression load of 150 kg was applied on the coating, with a conical diamond indenting with 120° and a radius of 0.2 mm.

3. Results and discussion

3.1. Diagrams of Tafel

The graphs of Figs. 2 and 3 revealed the diagrams of Tafel for the Si/Ti/Zr: 10/70/20 and Si/Ti/Zr: 10/20/70 concentrations, and their comparison according to the substrate. The variation of the corrosion potentials of the ceramic films was also observed according to the corrosion potential of the substrate. In general, the corrosion potential tended to take more positive values as it increases to the number of coatings deposited on the substrate.

TABLE II. Values of corrosion speed.

Concentration	Corrosion speed(mpy)		
	Mono-layer	Bi-layer	Tri-layer
Si/Ti/Zr: 10/20/70	95.69	54.74	18.43
Si/Ti/Zr: 10/70/20	16.45	7.53	4.31
AISI/SAE 304		132.6	

TABLE III. Values of resistance to polarization.

Concentration	$R_p(\Omega)$		
	Mono-layer	Bi-layer	Tri-layer
Si/Ti/Zr: 10/20/70	211.1	261.8	419.5
Si/Ti/Zr: 10/70/20	867.8	1800	2500
AISI/SAE 304		147.4	

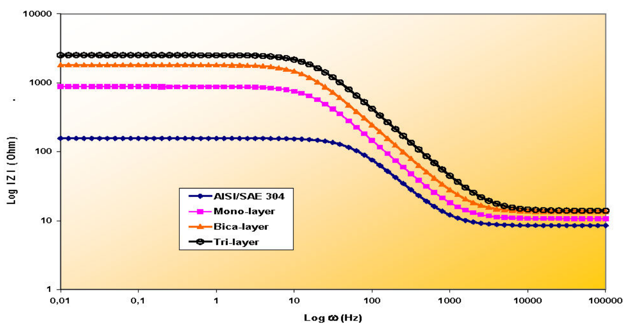

FIGURE 4. Diagrams of Impedance (Bode) for the Si/Ti/Zr: 10/70/20 concentration and the substrate.

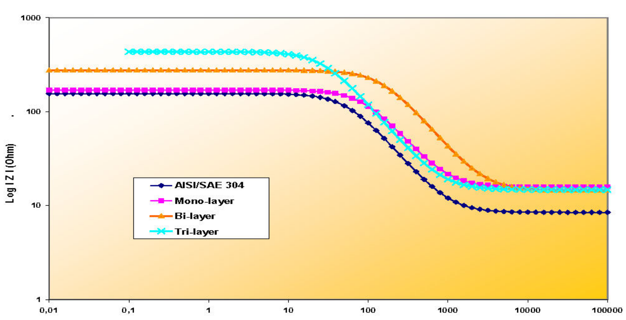

FIGURE 5. Diagram of Impedance (Bode) for the Si/Ti/Zr concentration: 10/20/70 and the substrate.

Additionally, to complement the analyses, in Table I the values of corrosion current (Icorr) were transformed. The study of the tendency of the parameters previously mentioned allowed the evaluation of the inter-phase behavior each stage.

In Figs. 2 and 3 it is observed that the films presented potentials near zero (0) and this behavior stays for the films of each concentration. An important characteristic to stand out in Fig. 2 is the little variation in corrosion potential in the second and third ceramic films. Because of the previous coating, the third layer significantly did not contribute to increase the corrosion potential, unlike Fig. 3, in which the third layer showed a good contribution to the diminution of the corrosion potential.

When comparing Tables I and II, which were obtained from Figs. 2 and 3, revealed directly a proportional behavior between the corrosion current and the corrosion speed, the greater corrosion current the greater corrosive attack undergoes the substrate.

3.2. Electrochemical impedance spectroscopy (EIS)

The EIS analysis was centered, mainly, in determining the values of polarization resistance R_p. This parameter determined the resistance that the coating opposed to the ion passage from the work solution to the substrate, preventing it from corrosion. In general terms, when a coating registered a high value of polarization resistance it was possible to conclude that it was a good anticorrosive protector.

The results obtained when carrying out the EIS analyses are observed in the graphs of Figs. 4 and 5. These graphs revealed the behavior of the substrate and the different coatings in front of a corrosive agent that is the HCl solution. It was appraised that the resistance to the work solution (Rs) had a value average of 12.74 Ω. The values of Rp for mono-layer, bi-layer and tri-layer are registered in Table III, respectively. In the same table the tendency of the values of polarization resistance was appraised to be increased in relation to the number of applied layers.

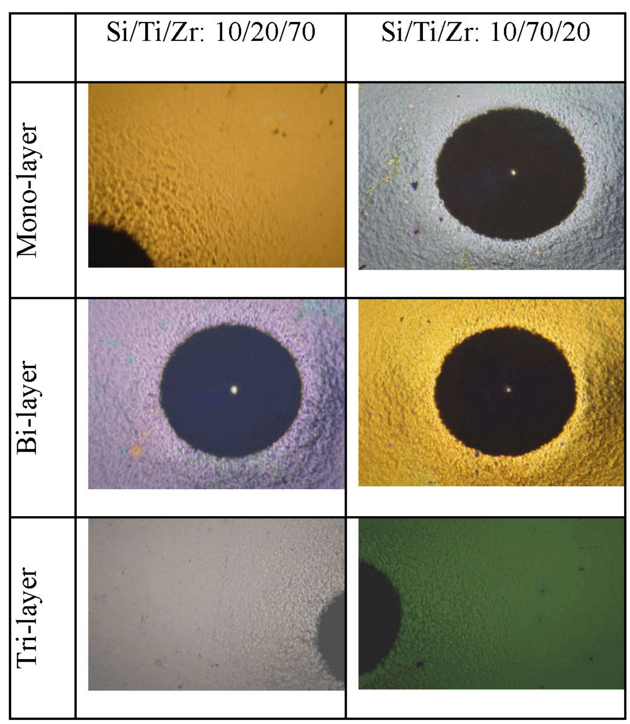

FIGURE 6. Adhesion Testing.

TABLE IV. Values of micro-hardness

Concentration	Micro-hardness (HV)		
	Mono-layer	Bi-layer	Tri'layer
Si/Ti/Zr: 10/20/70	271	336	359
Si/Ti/Zr: 10/70/20	337	365	447
AISI/SAE 304		249	

3.3. Adhesion

In Fig. 6 the adhesion of the coatings is evaluated according to its concentration and number of deposited layers. The analysis was centered in determining the type of deterioration that undergoes the coating around the track of the indenting unity. As a result, a rank of G2 adhesion is gotten for all the coatings when confronting itself with the pattern that defines the highest degree in G1. This result, although comparative, allows affirming that the multi-component coatings enhance the mechanical properties of the substrate due to the formation of strong connections in the inter-phase film substrate.

3.4. Micro-hardness

In Table IV the values of micro-hardness for each one of the coatings and the substrate are registered. These values are the average of five indentations in each case. The study reveals that the two concentrations improve the micro-hardness of the substrate-coating system, especially, the obtained films of the Si/Ti/Zr: 10/70/20 concentration.

4. Conclusions

With the ceramic coatings obtained by the methodology Sol-gel, specially the one of Si/Ti/Zr: 10/70/20 concentration, it is searched to protect steel AISI/SAE 304 of attacks by corrosive agents who contain Cl^- ions. For the two studied concentrations it is observed that: the greater number of ceramic layers deposited on the substrate the lesser the corrosion speed. This allows improving the useful life of steel AISI/SAE 304.

The application of the ceramic films of the multicomponent system to the substrate AISI/SAE 304, and especially in the Si/Ti/Zr: 10/70/20 concentration, it increases, to a great extent, the micro-hardness of the inter-phase substrate-coating.

For the two concentrations a high degree of adhesion of the ceramic films is obtained to the substrate AISI/SAE 304.

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