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Corrosion Protection of A36 Steel with SnO₂ Nanoparticles Integrated into SiO₂ Coatings

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Received: 20 February 2020; Accepted: 30 March 2020; Published: 14 April 2020



Abstract: Tin oxide (SnO₂) nanoparticles were successfully added to silicon oxide (SiO₂) coatings deposited on A36 steel by the sol-gel and dip-coating methods. These coatings were developed to improve the performance of corrosion protection of steel in a 3 wt % NaCl solution. The effects of modifying the SnO₂ particle concentration from 0–7.5 vol % were investigated by polarization resistance, Tafel linear polarization, and electrochemical impedance spectroscopy (EIS). The formation of protective barriers and their corrosion inhibition abilities were demonstrated. It was found by electrochemical studies that all of the coated samples presented higher corrosion resistances compared with an uncoated sample, indicating a generally beneficial effect from the incorporation of the nanoparticles. Furthermore, it was established that the relationship between the SnO₂ content and the corrosion inhibition had parabolic behaviour, with an optimum SnO₂ concentration of 2.5 vol %. EIS showed that the modified coatings improved barrier properties. The resistance for all of the samples was increased compared with the bare steel. The corrosion rate measurements highlighted the corrosion inhibition effect of SnO₂ nanoparticles, and the Tafel polarization curves demonstrated a decrease in system dissolution reactions at the optimal nanoparticle concentration.

Keywords: corrosion; SnO₂ nanoparticles; SiO₂ coating

1. Introduction

In order to protect metallic devices from corrosive environments, a relatively simple approach is to avoid direct contact between the environment and the exposed surface. Therefore, ceramic barriers have been developed from oxides due to their excellent thermal and chemical stability [1,2]. However, most of the analysed coatings have been deposited on stainless steel (SS), despite their natural tendency to passivate. For example, TiO_2 [3,4], ZnO [5], SnO_2 [6,7], SiO_2 [8], ZrO_2 [9,10], $CuAlO_2$ [11], and NiO [12] ceramics have been studied and in all cases improved the corrosion resistance. The properties of these coatings have been studied by electrochemical techniques in aggressive environments, such as simulated body fluid and solutions of NaCl and H₂SO₄. Despite these promising results, there is little information on the use of these ceramics as protection on carbon steels, which are used more frequently and present an onerous industrial problem due to failures caused by their generally very low resistance. For this type of steel, only ZnO [13], ZrO₂ [14], and TiO₂ composites [15,16] have been analysed and shown to yield an improvement in its anticorrosion properties.



For preparing coatings, one of the most promising corrosion prevention approaches has been to use sol-gel films prepared by a dip-coating technique, which produces materials with significant chemical stability, oxidation control and good adhesion [17–19]. This process offers potential advantages because it modifies the properties of surfaces through low-temperature treatment without altering the original strength and toughness of the substrates while achieving good homogeneity and allowing the use of compounds that do not introduce impurities into the final product [8,20].

Furthermore, recent evidence suggests that the incorporation of nanoparticles into sol-gel systems increases the corrosion protection because they act as fillers and decrease the porosity, modifying the layer and improving its barrier properties [17,21,22]. Therefore, particles such as TiO_2 , SiO_2 , Fe_2O_3 , and CeO_2 have been used and were found to improve wear, corrosion resistance, and mechanical properties [23–25].

Of all analysed ceramics, SiO_2 emerged as one of the most promising coatings since it presents excellent properties of hardness and resistance to wear and corrosion when applied in various kinds of materials [26,27]. Likewise, tin oxide (SnO₂) is a versatile material which has found applications in different fields, including coatings [28,29], sensors [30], and fuel cells [31], among others. The application of SnO₂ for corrosion protection has been shown to achieve good resistance when deposited on 304 stainless steel, demonstrating that the corrosion current density for SnO₂-coated 304 SS was significantly decreased in a corrosive environment [7].

The purpose of this study was to produce SiO_2 coatings with dispersed SnO_2 nanoparticles using the sol-gel and dip-coating techniques for the protection of a common carbon steel and to study the effect of the SnO_2 concentration on the corrosion resistance of the system when it is in contact with an aggressive solution of NaCl.

2. Materials and Methods

2.1. SnO₂ Nanoparticles Preparation

For the preparation of the tin oxide particles, the following materials were used: stannous oxalate 0.35 M (SnC₂O₄) was used as the precursor, citric acid 1.16 M (C₆H₈O₇·H₂O) was used as the catalyst, triethanolamine 1.08 M (TEA, N(CH₂CH₂OH)₃) was added dropwise as the dispersion agent and ethanol (C₂H₅OH) was used as the solvent. Using the sol-gel method and heat treatment, tin oxide nanoparticles were obtained as a powder. Five samples were prepared. Each was heat-treated for 1 h at different temperatures (300, 450, 600, 800, and 1000 °C) in order to analyse the structural evolution of SnO₂ with the aim of obtaining impurity-free nanoparticles.

2.2. SiO₂ Sol-Gel Synthesis

The coating solution was obtained using the sol-gel method. Tetraethyl orthosilicate 0.35 M (TEOS) was used as the chemical precursor and water and ethanol were used as solvents, while NH_4OH 0.038 M was added to the solution as a catalyst. The solution was stirred for 12 h to allow hydrolysis and condensation reactions to occur, in accordance with the method of Domínguez-Crespo [32]. Later, the SnO₂ particles were added at 0, 1%, 2.5%, 5%, and 7.5% by volume and the sol was stirred for 30 min in an ultrasonic bath for dispersion.

Typically, the addition of catalysts increases the hydrolysis rate. The mechanism of hydrolysiscondensation of TEOS is directly affected by the category of the catalyst present. TEOS condenses rapidly and hydrolyses slowly in acidic conditions, while it experiences rapid hydrolysis and slow condensation in alkaline conditions. Therefore, the reaction time was shortened by the NH₄OH catalyst [33].

2.3. Steel Substrate Preparation

A36 carbon steel with a nominal chemical composition of 0.24 wt % Si, 0.5 wt % Mn, 0.05 wt % P, 0.05 wt % S and 0.18 wt % C was used as the substrate. The samples were machined to dimensions of

 $25.4 \text{ mm} \times 50.8 \text{ mm} \times 1.6 \text{ mm}$. They were ground using SiC abrasive paper with grit sizes from 320 to 600 in order to increase their rugosity. Then, all specimens were cleaned using an ultrasonic bath over three rinsing steps (detergent solution, distilled water, and acetone) to remove residual grease.

2.4. Coatings

The deposition of coatings was realized by the dip-coating technique with a withdrawal rate of $2.5 \text{ cm} \cdot \text{min}^{-1}$. Each layer of the deposition was followed by a thermal treatment of 15 min at 120 °C and 20 min at 450 °C to form a dense film and remove organic compounds. The thickness was increased to 1.13 µm (thickness was measured by the perfilometer technique using a Bruker contour GT Inmotion 3D perfilometer, Billerica, MA, USA) by performing a total of five depositions, since thin layers might have cracked during drying, which would have resulted in low corrosion resistance performance. In contrast, multilayer coatings had the advantage of producing even coverage and providing high corrosion resistance [33].

2.5. Characterization Methods

2.5.1. X-ray Diffraction and Scanning Electron Microscopy

X-ray diffraction (XRD) powder patterns were obtained using a Bruker D8 ADVANCE diffractometer (Bruker Corporation, Billika, MA, USA) using Cu K α radiation over a 2 θ range from 20° to 80°. Scanning electron microscopy (SEM) was carried out on the coatings and powders using a JEOL JXA-8530F microscope (JEOL Ltd., Tokyo, Japan).

2.5.2. Electrochemical Measurements

Electrochemical techniques, including electrical impedance spectroscopy (EIS), polarization curves, and Tafel analysis were used to study the protection characteristics of the coatings.

The electrochemical measurements were carried out in a Potentiostat/Galvanostat Model 263A (EG&G Instruments, Champaign, IL, USA) using a three-electrode cell consisting of a working electrode (A36 carbon steel, surface area 1 cm²), a platinum auxiliary electrode, and a reference electrode (saturated calomel electrode). Prior to the electrochemical measurements, the samples were kept in the solution for 60 min in order to stabilize the free corrosion potential (E_{corr}). Potentiodynamic polarization was undertaken from $E_{corr} \pm 250$ mV at a scan rate of 1 mV/s. Electrochemical Impedance Spectroscopy (EIS) measurements were made in the range 0.1 to 10 Hz. The analysis was performed at room temperature (20 °C) and 3 wt % NaCl solution with pH 5.5 was used as electrolyte.

3. Results and Discussion

3.1. Structure of SnO₂ Particles

Figure 1 presents the X-ray diffraction patterns of SnO₂ particles annealed at different temperatures. The XRD pattern at 300 °C shows that the crystallization process has begun, as the presence of SnO₂ characteristic peaks is observed. From 450 °C, it is clear that the SnO₂ phase is obtained, however, at 29.87° (*) a peak corresponding to a romarchite (tetragonal) structure (SnO JCPDS 96-901-2141) was detected. SnO is a metastable phase due to its oxygen deficiency [34], so it transforms into the more stable SnO₂ phase at temperatures above 200 °C [35,36]. The SnO disappeared completely after 800 °C, as shown in Table 1. The results regarding the SnO content in the samples were obtained by X'Pert High Score Plus software (version 4.8) using the XRD patterns. These results suggest that the oxidation of tin atoms was probably incomplete during heat treatment, leading to the coexistence of the second phase (SnO) in the powder [37]. All the other diffraction peaks are in good accordance with the standard sample of cassiterite (tetragonal) SnO₂ (JCPDS 96-900-9083). To ensure the purity and presence of single-phase SnO₂, a powder treated at 1000 °C was used to prepare the coatings.



Figure 1. X-ray diffraction patterns for samples of tin oxide (SnO₂) annealed at 300, 450, 600, 800, and 1000 °C for 1 h.

Samples	Grain Size (nm)	% SnO	
SnO2-450 °C	11.5 ± 1.02	10	
SnO2-600 °C	15.8 ± 2.02	5	
SnO2-800 °C	18.9 ± 2.20	1	
SnO ₂ -1000 °C	25.7 ± 3.17	0	

Table 1. Grain sizes of SnO₂ particles.

The grain sizes were estimated by Scherrer's equation, as listed in Table 1. The results correspond with those of the study by Agrahari [38], who also observed that the grain size of SnO_2 particles increased with increasing calcination temperatures. In the current study, a grain size of 11.5 nm was obtained at 450 °C, increasing up to 25.7 nm at 1000 °C. The calcination temperatures play a significant role in determining the size of the SnO_2 nanoparticles synthesized via the sol-gel method [39]. Previous studies indicate that the grain size distribution has an important role in determining the corrosion behaviour of materials. Improved corrosion resistance is exhibited with decreasing grain size in NaCl media [40]. However, in H₂SO₄ solutions, having a higher grain boundary density accelerates corrosion due to the absence of passive processes, and the corrosion resistance decreases with decreasing grain size. The difference in experimental results in corrosion behaviour can be reasonably explained by the positive or negative effect of high-density grain boundary densities in different corrosive media, so that the nano-crystal deposited coating has a high density of nucleation sites for passive films, leading to a high fraction of passive layers and low corrosion rates [40–42].

3.2. Morphological Study of SnO₂ Particles

According to the XRD results, the grain size increases proportionally with the temperature. Meanwhile, the agglomeration also increases, as has been shown in some previous studies [38,43]. In the SEM micrograph shown in Figure 2, particle agglomeration is clearly observed, with aggregate diameters in the range of 100 to 800 nm. This behaviour occurs because the sol-gel and calcination processes are prone to nanoparticle clustering, resulting in poor dispersion. The use of a solvent is beneficial for the dispersion of nanoparticles [24]. In this work, to determine the particle size, SnO₂ was

dispersed in ethanol and measurements were obtained in the range of 14 to 69 nm with $d_{50} = 23$ nm using the dynamic light scattering (DLS) technique. The distribution of the particle sizes is shown in Figure 3, which presents a mono-modal distribution with a strong tendency toward smaller-sized particles (11–13 nm). On the other hand, with respect to morphology, spherical forms are observed, which is considered an advantage because they have better fluidity and fewer contact interfaces than more irregular particles. When vibrated, smaller particles can occupy vacancies, and thus spherical particles are more easily close-packed [39]. Therefore, if the particles are nanometric in size, it is expected that nucleation occurs and more zones exist that prevent the passage of the current applied to the system for the corrosion test.



Figure 2. SEM image of tin oxide (SnO₂) nanoparticles annealed at 1000 °C.



Figure 3. Particle size distribution obtained by dynamic light scattering.

3.3. Surface Morphology of SiO₂ Coating with SnO₂ Nanoparticles

SEM imaging was conducted to obtain qualitative information about the coating's surface morphology. Figure 4a shows the image of the SiO_2 coating modified with SnO_2 nanoparticles. For comparison, the SEM image of an unmodified SiO_2 coating (Figure 4b) is also included.

The micrographs show that the film is homogeneous, continuous, and free of cracks. The clearer points in Figure 4a correspond to SnO_2 nanoparticles.



Figure 4. SEM images of SiO_2 coatings (a) with SnO_2 nanoparticles and (b) absence of SnO_2 nanoparticles.

3.4. Corrosion Behaviour of SiO₂ Coatings with SnO₂ Nanoparticles

The efficiency of the coatings was analysed by different electrochemical tests in a 3 wt % NaCl solution at room temperature. First, the results of polarization resistance for all the samples are presented. In previous research [21,33,44], it was reported that silane coatings provided very good barrier properties and improved corrosion protection compared to bare steel substrates. Previous results also suggested that the coatings provided a protective layer for defects formed in the steel. Increased protection was observed when particles were added to the coating because this promoted self-healing through the partial recovery of protective properties of the coated system when damaged [45]. The most suitable way to evaluate self-healing is by forming an artificial defect on the surface and monitoring the electrochemical behaviour using the polarization resistance technique. Each electrochemical measurement was repeated with three independent samples under the same conditions in order to demonstrate repeatability and reproducibility; therefore, the mean values and standard deviations of the results are reported. Tafel analysis and electrochemical impedance were used to complement the polarization resistance tests and determine the corrosion resistance of the coatings in the presence and absence of SnO₂ nanoparticles in the NaCl solution at room temperature.

3.5. Polarization Resistance

Polarization resistance (*R*p) is defined as the slope of the potential current density plot at the corrosion potential [24]. Then, I_{corr} was used to calculate the inhibition efficiency (*IE*%) using the following relationship, where I_0 and I_i are the current densities in the absence and presence of the coating, respectively [46].

$$IE\% = \frac{I_{\rm o} - I_{\rm i}}{I_{\rm o}} \times 100\tag{1}$$

The protective properties are also dependent on the coating composition [47]. According to the corrosion potential data, the bare A36 steel ($E_{corr} = -702.83 \pm 0.17$ mV) presented a high tendency to react compared with the coated samples, and a relation was found with the corrosion resistance due to the I_{corr} values obtained. For the coated samples, the corrosion resistance initially increased up to 64.2% and then decreased as the concentration of SnO₂ nanoparticles went up. However, all coated samples presented better corrosion resistance than the uncoated substrate. This effect can be attributed to the fact that when modifying the surface with a coating, the ions of the corrosive solution must first diffuse through this barrier. This behaviour has been observed in similar systems, such as silica coatings on galvanized steel with different concentrations of Ce and CeO₂ nanoparticles during polarization in a 3.5% NaCl solution. Ceria nanoparticles have the ability to change the silane solution chemistry,

promoting the formation of reactive silanol groups, and of more condensed species in a more stable and protective layer of zinc oxides and hydroxides formed in the alkaline environment [21,25].

For the samples prepared with different amounts of SnO_2 particles, better corrosion resistance was obtained at a SnO_2 concentration of 2.5 vol % compared with the non-coated substrate. The electrochemical parameters obtained in this analysis and *IE*% calculated are presented in Table 2.

SnO ₂ Concentration (vol %)	E _{corr} (mV)	I _{corr} (μA·cm ⁻²)	<i>R</i> p (Ω)	IE%
A36 Steel (Bare)	-702.83 ± 2.09	24.24 ± 0.17	896.66 ± 6.36	-
0	-639.52 ± 3.01	23.15 ± 0.36	939.38 ± 14.49	4.5
1	-597.81 ± 0.76	13.82 ± 0.22	1572.54 ± 25.09	43
2.5	-521.20 ± 8.66	8.68 ± 0.35	2507.92 ± 102.24	64.2
5	-636.78 ± 0.42	18.79 ± 0.19	1156.73 ± 11.61	22.5
7	-656.46 ± 2.06	20.16 ± 0.02	1078.06 ± 1.28	16.8

Table 2. The corrosion parameters obtained from polarization resistance measurements.

3.6. Tafel Analysis

The polarization Tafel method was applied to analyse the inhibitor efficiency of the coatings. Figure 5 represents typical anodic and cathodic potentiodynamic polarization curves for carbon steel carried out in the absence and presence of SiO₂ coatings with various concentrations of SnO₂ particles. The figure shows that in saline solutions, the presence of SnO₂ in the coating on the metal's surface shifts both the anodic and cathodic sections of the Tafel plots to lower values of current density at all investigated SnO₂ particle contents. The corrosion current density decreased from 25.43 μ A·cm⁻² for the bare A36 steel to 6.01 μ A·cm⁻² for the most effective coating (2.5 vol %). These results indicated that the coatings displayed better barrier properties in the NaCl environment and inhibited the reactions associated with corrosion processes [23]. The same trends found in the resistance polarization test results were also observed in this analysis. In this case, the plots show that the curve corresponding to 2.5 vol % of SnO₂ nanoparticles had a smaller slope than for other samples and therefore had a decreased current density.



Figure 5. Polarization curves obtained in a 3 wt % NaCl solution for A36 steel with SiO₂ coatings in the absence and presence of SnO₂ nanoparticles.

The electrochemical parameters, including the corrosion potential (E_{corr}), current density (I_{corr}), polarization resistance (Rp), and inhibition efficiency (IE%) are listed in Table 3.

SnO ₂ Concentration (vol %)	E _{corr} (mV)	$I_{\rm corr}$ ($\mu { m A~cm^{-2}}$)	IE%
A36 Steel (Bare)	-606.64	25.43	-
0	-640.24	24.18	4.9
1	-561.52	18.62	26.8
2.5	-447.49	6.01	76.4
5	-619.72	18.90	25.7
7	-518.22	24.10	5.2

Table 3. The corrosion parameters obtained from the polarization Tafel method.

3.7. Impedance

Figure 6 shows Nyquist plots of A36 steel in a 3 wt % NaCl solution modified with SiO₂ coatings in the absence and presence of different concentrations of SnO_2 nanoparticles. When the steel is immersed in a solution, EIS will detect the NaCl solution and form a resistive solution [46]. The Nyquist plots of all samples show only one capacitive loop in the entire frequency range. According to the EIS results and visual inspection, the plots are composed of large, unfinished semicircular arcs. This shape is attributed to the charge transfer process in the electrode/electrolyte interface. Charge transfer resistance is the resistance offered by the metal atom to become ionized when in contact with the electrolyte (R1), and the coating resistance is denoted by R2. In addition, a constant phase element (CPE1) is used as a substitute for a double-layer capacitor to fit the impedance data of the interface between an electrode and the surrounding electrolyte [40].



Figure 6. Nyquist plots of the composite coatings in the absence and presence of different concentrations of SnO₂ particles from EIS measurements in NaCl media.

Silica coatings improve the corrosion resistance due to the formation of protective oxides that act as a barrier to oxygen diffusion to the metal surface [27]. As shown in Figure 6, the Nyquist plots of the coatings in the NaCl solution exhibit an increasingly large semicircle with additional SnO₂ nanoparticles. The corresponding R2 values also increase evidently, however, the same behaviour was obtained, so the test indicates that there is an ideal concentration of SnO₂ for corrosion protection.

The R2 value of the 2.5 vol % sample is higher than the R2 value of the bare substrate. Therefore, the curve corresponding to SiO_2 -2.5 vol % SnO_2 should exhibit better corrosion protection performance in the NaCl solution. An equivalent electric circuit is generally used to interpret EIS data. The data of impedance was analysed by ZView software to calculate the equivalent circuit parameter values,

which are listed in Table 4. The calculated adjustment values confirm the results obtained by Rp and indicate the positive influence that can be achieved with the precise SnO_2 concentration. The simplified equivalent circuit is shown in the inset of Figure 6. The presence of SnO_2 particles in the SiO₂ coating promotes an increase in the low-frequency impedance, resulting in the inhibition of corrosion efficiency compared to the bare A36.

SnO ₂ Concentration (vol %)	R1 (Ω)	R2 (Ω)	CPE1 (µF/cm ²)	IE%
A36 Steel (bare)	28.36	675.5	0.0012	-
0	29.72	779.9	0.0013	13.4
1	27.7	1563	0.0011	56.8
2.5	30.78	1935	0.0008	65.1
5	29.42	862.9	0.0013	21.7
7	29.17	913.9	0.0009	26.1

Table 4. The corrosion parameters obtained from EIS.

In the study by Yang [7], a modified sample exhibited high stability in the test solution when the SnO_2 was applied as a film on stainless steel, increasing the impedance values with respect to the bare 304 stainless steel. They demonstrated that SnO_2 is an effective barrier to inward penetration and that it reduced the corrosion of the substrate [7].

In order to get a better understanding of the corrosion behaviour of the coated samples, the inhibition efficiencies obtained from the three methods were compared (Figure 7). It is clear that for all three electrochemical techniques, the coating efficiency follows the same trend for each concentration compared with the substrate. All the coatings present protective corrosion properties for the A36 steel. Apparently, the coating layer on the surface of the carbon steel prevented iron from reacting with the corrosive media in all of the study cases. The results also indicated that the SiO₂ coating material should completely isolate the substrate from the corrosive media so that no electrochemical reactions occur at the coating-substrate interface. From this viewpoint, a good protective coating should be as dense as possible so that the poor anticorrosion ability in some coatings may have been due to the presence of pores which allowed the corrosive media to penetrate through.



Figure 7. Comparison of IE% plots produced from the results for each corrosion test.

On the other hand, it is known that the electrode potential of Fe is more negative than that of SnO₂. The nanoscale pores in the coating allow seawater to penetrate through, leading to severe corrosion at the coating-substrate interface via the formation of an SnO₂–Fe galvanic cell. A possible mechanism for the above significant improvement in anticorrosion ability of the composite coating might be related to the satisfactory sealing of the pores in the coating by SnO₂ nanoparticles, as suggested by Dongyun Yu in previous work using TiO₂ and/or ZnO nanoparticles in composite coatings for improved corrosion protection on carbon steel [15].

In addition, it is demonstrated here that the optimal efficiency occurred at an SnO_2 nanoparticle concentration of 2.5 wt %. When the concentration increases or decreases about this value, the *IE*% decreased as well. Although the value of the inhibitor efficiency depends on the electrochemical test used, it is clear that the addition of SnO_2 particles had a beneficial effect on the corrosion protection of A36 steel.

4. Conclusions

In order to improve its corrosion resistance, carbon steel was successfully coated with SiO_2 by the sol-gel method. It was found that adding SnO_2 nanoparticles to the coating had a great influence on the sol-gel film formation and thus on the stability of the coated substrates in corrosive media. The investigation showed that the incorporation of tin oxide (IV) in sol-gel SiO₂ coatings helped protect A36 steel from corrosion. All of the coatings tested provided a barrier that inhibited corrosion. Very low and very high SnO_2 concentrations led to a reduction in inhibition, and the optimum concentration of SnO_2 nanoparticles was found to be 2.5 vol %.

Author Contributions: A.K.A.-G., A.G.M.-R. and J.M.-P. conceived of the presented idea; A.K.A.-G. developed the theory and methodology; Á.d.J.M.-R., J.M.-P., J.G.G.-S. and A.L.P.-F. verified the analytical methods and supervised the findings of this work. All authors discussed the results and contributed to the final manuscript. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Instituto Politécnico Nacional.

Acknowledgments: The authors would like to acknowledge the facilities granted in the use of the LIDTRA and LICAMM infrastructure, as well as the technical assistance of Daniela Moncada and Adair Jimenez.

Conflicts of Interest: The authors declare no conflict of interest.

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