

Sol–Gel Thin Films for Corrosion Protection

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Abstract: The preparation of sol–gel coatings with specific chemical functions offers potential advantages over traditional methods as it offers tailoring of their structure, texture and thickness and allows the fabrication of large coatings. The chemical protection of 316L stainless steel has been verified for ZrO_2 , $\text{TiO}_2\text{--SiO}_2$ and $\text{Al}_2\text{O}_3\text{--SiO}_2$ coatings. The anticorrosion behavior of the films have been characterized in acidic and basic media by weight and loss, electrochemical techniques, XRD and FTIR and SEM spectroscopic techniques. Analysis of the data indicates that the films act as geometric blocking layers against exposure to the corrosive media and increase drastically the lifetime of the substrate (for instance up to 10 for stainless steel).

1 INTRODUCTION

Sol–gel processing is a viable means of preparing glass, ceramics and thin films through hydrolysis and condensation of metal alkoxides in organic solvents.^{1–4} Compared with conventional techniques, the sol–gel method has several advantages because many multicomponent oxides can be prepared with a higher degree of chemical purity and easier control of stoichiometry.

The application of ultrasonic radiation to sols is a very convenient technique to produce various types of materials at low temperatures as well as monoliths, coatings, ceramic composites, ceramic–ceramic composites and glasses.^{5–8} The preparation of zirconia, silica–titania and silica–alumina coatings on 316L stainless steels using this technique is used in our group, mainly to provide corrosion prevention on metallic and glass substrates. The electrochemical corrosion tests indicate that all these oxide films increase the protection of metal against air corrosion (tested up to 800°C), acid attack (tested up to 80°C) and in aqueous NaCl solutions.^{9–13}

In the present work, the coatings were deposited on 316L stainless steel substrates by dip-coating technique from alkoxides as precursors using the application of ultrasound irradiation. Corrosion tests to assess their performance

as protection against corrosion were performed using a potentiodynamic polarization technique in aqueous 3% NaCl and in deaerated 15% H_2SO_4 solutions and to act as a geometrical blocking layer.^{9–13} The structure of the coated films was characterized by X-ray diffraction, FTIR and SEM spectroscopies.

2 EXPERIMENTAL

The substrate used was 316L stainless steel of composition (wt%): 67.25 Fe, 18.55 Cr, 11.16 Ni, 2.01 Mo, 0.026 Cu, 0.15 Si and 0.028 C. Samples ($3.0 \times 1.5 \times 0.1$ cm) were mechanically cut from large foils and then degreased ultrasonically in acetone. This material was chosen taking into account the heat treatment necessary for the densification of the coatings (see below). Therefore, a low carbon content steel was judged more convenient since it is less susceptible to sensitization which might promote an enhanced corrosion.¹⁴ In addition, 316L SS is a material widely used in chemical industry environments.¹⁵

Zirconium isopropoxide $\text{Zr}(\text{OC}_3\text{H}_7)_4$ diluted in isopropanol ($\text{C}_3\text{H}_7\text{OH}$) was used as source of zirconia. Following the dissolution of the zirconium alkoxide in isopropanol, glacial acetic acid (CH_3COOH) was added to the solution. An excess of water was then also added under

ultrasound (sonicator Heat Systems Ultrasonics W385, 20 kHz) to complete the hydrolysis until a clear and transparent sonosol was obtained. The concentration of the starting alkoxide solutions was 0.5 mol/l and the volume ratios $\text{H}_2\text{O}/\text{C}_3\text{H}_7\text{OH}$ and $\text{H}_2\text{O}/\text{CH}_3\text{COOH}$ were equal to 1 and 2, respectively.

Binary compositions in the system $\text{TiO}_2\text{--SiO}_2$ and $\text{Al}_2\text{O}_3\text{--SiO}_2$ have been prepared using tetraorthotitanate $\text{Ti}(\text{OC}_2\text{H}_5)_4$, tetraethylorthosilicate $\text{Si}(\text{OC}_2\text{H}_5)_4$ and aluminum sec-butate $\text{Al}(\text{OC}_4\text{H}_9)_3$ as sources of titania, silica and alumina. The compositions of the solutions were 30 TiO_2 –70 SiO_2 and 25 Al_2O_3 –75 Si_2O_2 (mol%). The sols were prepared at room temperature by dissolving the alkoxides in absolute ethanol $\text{C}_2\text{H}_5\text{OH}$ (0.43 mol of absolute ethanol per mol of alkoxide) to which was added 0.087 mol of acetic acid CH_3OOH . The mixture was submitted to intense ultrasonic radiation. After 25 min the liquid became homogeneous and clear and remained stable for about five weeks at room temperature when kept in a closed vessel.

Coating of the substrates has been done by the dip-coating process, withdrawing the substrates from the solution at a constant rate of 10 cm min^{-1} . The gel films were dried at 60°C for 15 min and then densified in a furnace in an air atmosphere. The heat-treatment protocol for coatings preparations was the following: the temperature was raised at a rate of 5°C min^{-1} with isothermal holdings, first at 450°C for 1 h and then at 800°C for 2 h. The thickness of the films varied from 0.4 to 0.6 μm depending on the composition of the solution.

The electrochemical measurements were carried out with freshly prepared samples in aqueous 3% NaCl and in deaerated 15% H_2SO_4 solution at room temperature using a computerized PAR 273 Potentiostat/Galvanostat. A saturated calomel electrode (SCE) was used as reference and a Pt foil served as the auxiliary electrode. The working electrodes were immersed 1 cm into the solution. The potentiodynamic polarization curves have been obtained mainly on a PAR 273 potentiostat. They were initiated at –0.7 V and scanned in the anodic direction at 1 mV s^{-1} . The data were analyzed with the PAR model 342 Corrosion Measurements Software.

X-ray diffractograms of the coated substrates have been obtained with a Philips diffractometer with the characteristic CuK_α radiation.

A Bomen FTIR spectro was used to obtain high resolution spectra of the coatings in the range (400–4000 cm^{-1}); the measurements were performed by reflection at an incident angle of 30°.

The morphology of the surfaces was examined by scanning electron microscopy (Jeol JSM-6300F and Zeiss 960).

3 RESULTS AND DISCUSSION

The X-ray diffraction results of ZrO_2 indicate that the films densified at 800°C have the tetragonal structure as evidenced by the peak at $d = 2.89 \text{ \AA}$;⁹ however 70 SiO_2 –30 TiO_2 coatings are crystalline showing anatase crystallites in an amorphous silica matrix¹² while 75 SiO_2 –25 Al_2O_3 coatings are amorphous.

The FTIR measurements obtained with the sintered samples of zirconia show a characteristic Zr–O–Zr band at 665.7 cm^{-1} and details of these analyses can be found elsewhere.⁹ The principal bands observed with 70 SiO_2 –30 TiO_2 coatings are located near 1070, 800 and 460 cm^{-1} and attributed to vibrations of SiO_4 tetrahedra in the SiO_2 structure; they correspond to absorption bands of Si–O–Si. Other bands, located at 940 and 680 cm^{-1} are attributed to vibrations of Si–O–Ti.¹⁶ For 75 SiO_2 –25 Al_2O_3 coatings, the vibrations of SiO_2 have been obtained at 1100, 808 and 470 cm^{-1} . Other bands can be seen near 1070, 658 and 526 cm^{-1} . The band at 1070 cm^{-1} corresponds to an Al–O–Si vibration and the bands at 658 and 526 cm^{-1} are assigned to Al–O vibrations.

Figure 1 shows the potentiodynamic polarization curves of ZrO_2 , 70 SiO_2 –30 TiO_2 and 75 SiO_2 –25 Al_2O_3 coated and uncoated 316L stainless steel (as reference) measured in aqueous 3% NaCl solution at room temperature. At high current all the cathodic branches are practically

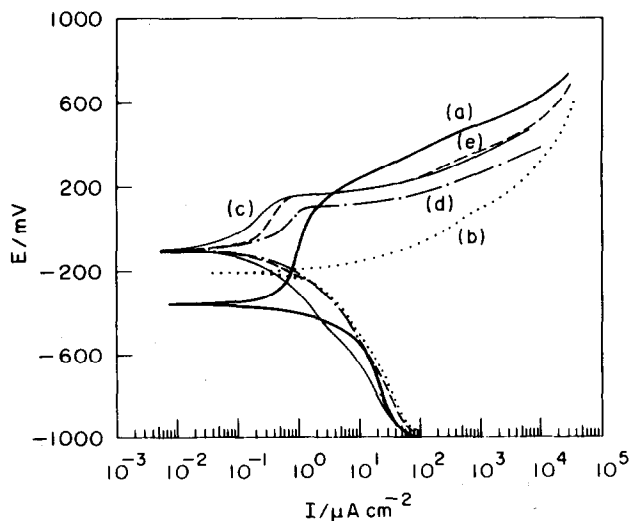


Fig. 1. Potentiodynamic polarization curves measured in aqueous 3% NaCl solution at 25°C for 316L stainless steel; (a) uncoated and untreated, (b) uncoated but heat treated at 800°C for 2 h, (c) coated with ZrO_2 (800°C/2 h), (d) coated with 75 SiO_2 –25 Al_2O_3 (800°C/2 h), and (e) coated with 70 SiO_2 –30 TiO_2 (800°C/2 h).

Table 1. Electrochemical corrosion parameters derived from the polarization curves obtained at room temperature with an aqueous NaCl (30 g/dm³) test solution; $-E_{\text{cor}}$: corrosion potential (mV vs SCE), R_p : polarization resistance (k Ω cm²), CR: corrosion rate (mil per year, MPY)

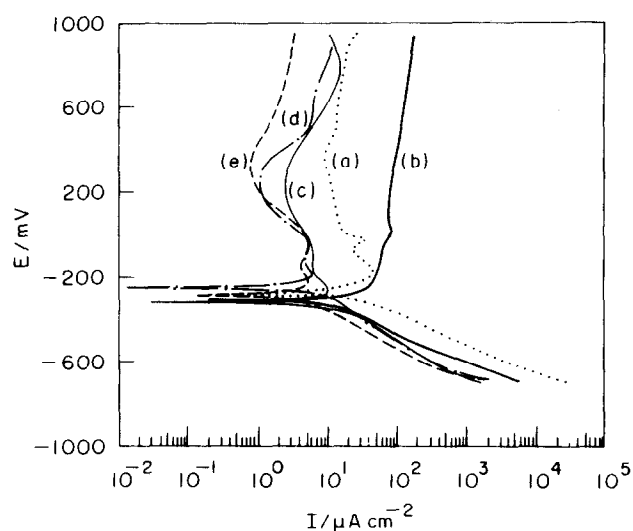
Sample	$-E_{\text{cor}}$ (mV)	R_p (K Ω cm ²)	CR(MPY)
316L as received	344	57.6	0.23
316L heat treated at 800°C/2 h	201	18.4	0.89
316L + (ZrO ₂); 800°C/2 h	89	198	0.13
316L + (30TiO ₂ -70SiO ₂); 800°C/2 h	94	289	0.07
316L + (25Al ₂ O ₃ -75SiO ₂); 800°C/2 h	98	153	0.10

superimposed, probably due to a limiting current controlled by oxygen diffusion in the NaCl solution. The presence of the coating however increases the values of the corrosion potential toward more anodic values and causes change in the anodic branches of the curves which show a region of quasi-passive behaviour.

Table 1 lists the electrochemical parameters obtained from the polarization curves for uncoated and coated 316L stainless steel immersed in 3% NaCl solution. The value of the corrosion potential E_{cor} (mV), the polarization resistance R_p (k Ω cm²) and the corrosion rate CR (mil per year = MPY) were determined by extrapolation of the Tafel lines. The results of the coated samples were better than those obtained with the substrate without coatings. The E_{cor} values of untreated and treated substrates without coatings are -344 and -201mV, respectively, whereas for ZrO₂, 30TiO₂-70SiO₂ and 25Al₂O₃-75SiO₂ coatings deposited on 316L stainless steel, the values are -89, -94, -98 mV, respectively. The corrosion rate of the coatings (CR) are typically 10 times smaller than that of 316L substrate. Obviously this fact is extremely interesting for practical applications.

Figure 2 shows the potentiodynamic curves of the same samples in deaerated 15% H₂SO₄ solution at 25°C. It is apparent that these curves exhibit a typical spontaneous passivation characteristic. The presence of the films on the substrates are very effective in reducing the critical current density for passivation (i_{cp}). A reduction in i_{cp} results in an increase of ease of passivation. Thus the corrosion current density (i_{cor}) of these coatings decreases. The curves obtained with 70SiO₂-30TiO₂ and 75SiO₂-25Al₂O₃ coatings

show that these compositions were more effective than ZrO₂ in increasing the corrosion resistance of the 316L stainless steel exposed to 15% H₂SO₄. The polarization resistance R_p for these coatings is about 9 times higher than that of the substrate without films. Also, the value of the corrosion rate, CR, is about five and two times lower than that of untreated and treated 316L stainless steel, respectively. All these coatings are more effective in increasing the corrosion resistance of 316L stainless steel substrates exposed in 15% H₂SO₄ solution. The electrochemical corrosion parameters derived from the polarization curves (Fig. 2) are given in Table 2.

**Fig. 2.** Potentiodynamic polarization curves obtained at room temperature in deaerated 15% H₂SO₄ acid for; (a) stainless steel as received; (b) stainless steel heat treated at 800°C/2 h, coated substrate with (c) ZrO₂, (d) 75SiO₂-25Al₂O₃, and (e) 70SiO₂-30TiO₂ (all heat treated at 800°C/2 h).**Table 2. Corrosion parameters determined from the potentiodynamic curves measured in 15% H₂SO₄ solution at room temperature: corrosion potential $-E_{\text{cor}}$ (mV); polarization resistance R_p (k Ω cm²) and corrosion rate CR (mil per year, MPY)**

Sample	$-E_{\text{cor}}$ (mV)	R_p (K Ω cm ²)	CR(MPY)
316L as received	286	1.80	11.5
316L heat treated at 800°C/2 h	306	1.45	5.0
316L + (ZrO ₂); 800°C/2 h	308	10.5	3.4
316L + (30TiO ₂ -70SiO ₂); 800°C/2 h	291	10.72	2.2
316L + (25Al ₂ O ₃ -75SiO ₂); 800°C/2 h	240	4.96	3.37

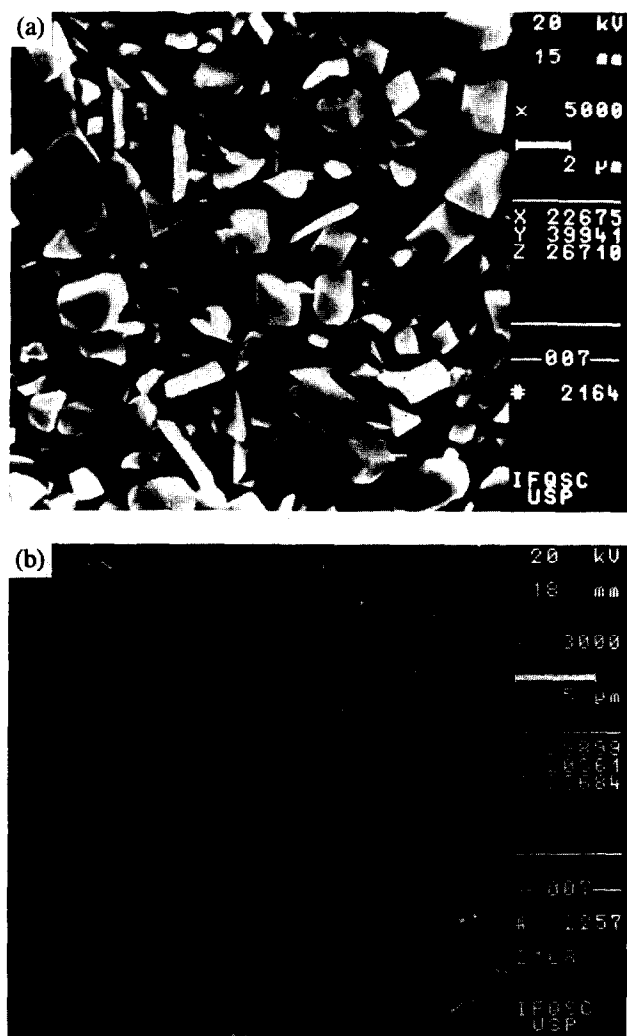


Fig. 3. (a) SEM micrograph of 316L stainless steel heat treated at 800°C for 2 h showing small crystals at the surface. (b) SEM micrograph of a ZrO_2 film on 316L stainless steel heat treated at 800°C for 2 h.

Figure 3(a) shows the texture of 316L stainless steel after heat treatment at 800°C for 2 h. Small crystals grow at the surface. Figure 3(b) shows the micrograph of a thin film of ZrO_2 deposited on 316L SS and heated in air at 800°C for 2 h. The resulting coating is dense and homogeneous, without appearance of cracks.

4 CONCLUSION

Sonocatalysis performed during the preparation of sols provides an interesting method for the prepa-

ration of thin coatings on 316L stainless steel. The study clearly shows that with a single dip-coating, thin films of composition ZrO_2 , 70SiO_2 - 30TiO_2 and 75SiO_2 - $25\text{Al}_2\text{O}_3$ act very efficiently as corrosion protectors of these metallic substrates in aqueous NaCl and acid media at room temperature. The films increase the lifetime of the substrate by a factor of up to 10 in 3% NaCl and 5 in 15% H_2SO_4 solutions.

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