

Protective TiO₂–SiO₂ coatings on stainless steel sheets prepared by dip-coating

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One of the applications of the sol–gel process is to produce amorphous and crystalline oxide films. Their formation from alkoxide solutions on glass, ceramic or metallic substrates has been described in several publications [1–3].

Recently, works concerning the production and characterization of sol–gel thin films deposited on metallic substrates were presented at the 6th International Workshop on glasses and ceramics from gels, studying the properties of different coatings on steel [4–7].

Our work presents a systematic study of the thermal oxidation and the resistance to chemical attack of TiO₂–SiO₂ coatings using a sonocatalytic method [8–11]. These thin films were deposited on 316L stainless steel, from metal alkoxides Ti(OC₂H₅)₄ and Si(OC₂H₅)₄, and heated at high temperatures to convert gel film to oxides. The resistance to oxidation and chemical attack were respectively tested in air at 800 °C and in H₂SO₄ aqueous solutions at 89 °C.

The corrosion resistance of the films was evaluated by measuring the weight change as a function of time under different heat treatments and chemical treatments.

In these experiments, 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.

Ti(OC₂H₅)₄ and Si(OC₂H₅)₄ were used as sources of titania and silica. The sols were prepared by dissolving alkoxides in absolute ethanol (C₂H₅OH) to which a small amount of acetic acid (CH₃OOH) was added. The composition of the solution used in the experiments was: molar ratio $R = \text{Ti}(\text{OC}_2\text{H}_5)_4 / \text{Si}(\text{OC}_2\text{H}_5)_4$ varied from 0.1 to 1, 0.087 moles of acetic acid and 0.43 moles of absolute ethanol per mole of alkoxide.

The mixture was submitted to intense ultrasonic radiation (20 kHz) produced by a transducer. After 25 min the liquid became homogeneous and clear. The solutions used had compositions between $x = 10$ and 60 mol %, and were stable for about 5 weeks at room temperature.

Dip-coated samples were prepared by withdrawing the substrates from solution at a constant rate of 10 cm min⁻¹. The gel films were dried at 60 °C for 15 min and heated in a furnace at a given temperature in air for different times. The optimum heat-treatment conditions for TiO₂–SiO₂ film prepara-

tions were as follows: the temperature was increased at a rate of 5 °C min⁻¹ with two isothermal holdings, the first at 450 °C for 1 h and the second at 800 °C for 2 to 10 h.

Two tests were applied for measuring the corrosion. In test A the substrates were thermally treated at 800, 870 and 950 °C in an oxidizing atmosphere. The oxidation was obtained by measuring the weight gain. In test B corrosion was carried out by immersing the samples in a 15% H₂SO₄ solution at temperatures of 72, 82 and 89 °C. The determination of final corrosion was evaluated by weight loss measurements.

Fig. 1a–c illustrates the variation of weight gain as a function of corrosion time in air at different temperatures. It appears evident that the evolution of weight gain of uncoated samples increased linearly with increasing temperature and time. The apparent activation energy of the corrosion rate of uncoated stainless steel was calculated using the Arrhenius equation $v = v_0 \exp(-Ea/RT)$. Ea was found to be 25–30 kcal mol⁻¹ (Fig. 1e). In the case of samples coated with TiO₂–SiO₂ films of thickness 0.4 to 0.9 μm, no change in weight was observed during heating at 800 °C (Fig. 1d).

Fig. 2a–c shows the behaviour of stainless steel with time in 15% H₂SO₄ solution in a temperature interval of 72–89 °C. This shows that weight loss increases with time and temperature. During immersion treatment of substrates, data revealed that a linear relationship existed between the square of the weight loss and time. The activation energy of dissolution for uncoated substrates was found to be 27–32 kcal mol⁻¹ (Fig. 2f).

Some experiments were carried out by immersing the coated samples in a 15% H₂SO₄ solution at 89 °C for 40 h. It was observed that for coated stainless steel with film thickness of 0.4–0.9 μm, no chemical attack was detected (Fig. 2e).

X-ray analyses of uncoated and coated substrates were made using a Philips diffractometer with a characteristic CuK_α radiation. It can be seen from Fig. 3a that 316L stainless steel shows three distinct peaks with d values of 0.208, 0.18 and 0.127 nm, which correspond to the cubic phases of the alloy containing Cr, Fr and Ni.

Some samples were heat-treated at 800 °C for 20 h. Their diffraction spectra show peaks with d values of 0.49, 0.36, 0.297, 0.267, 0.253, 0.169, 0.167 and 0.149 nm. The crystalline phase formed was an

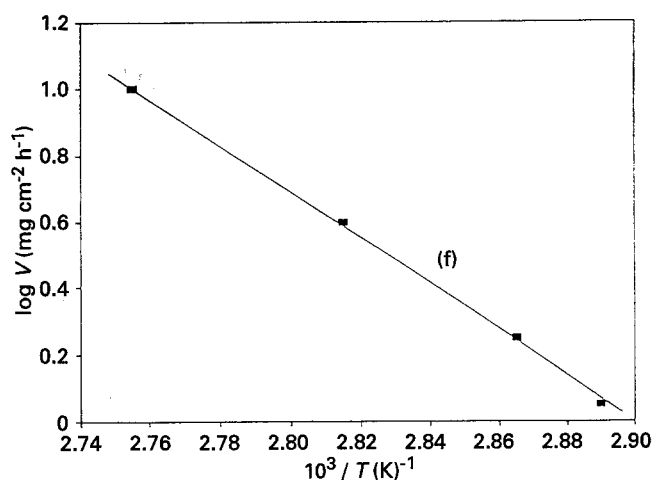
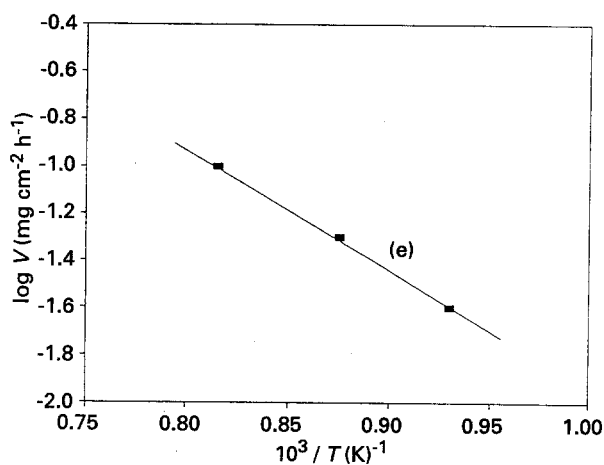
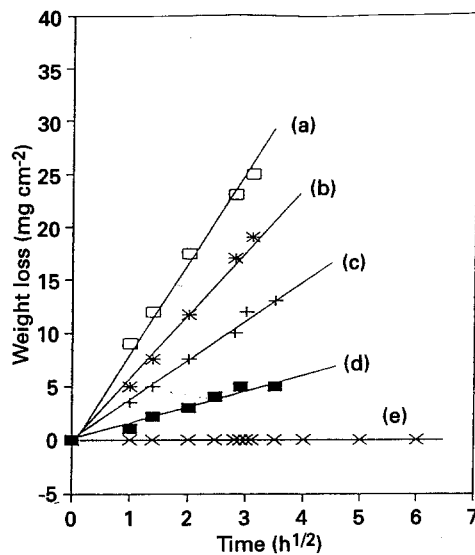
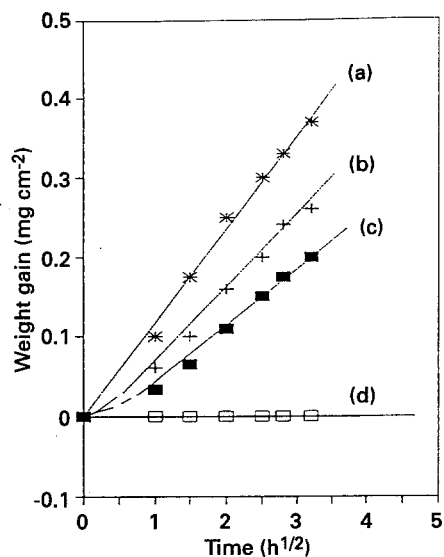


Figure 1 Thermal oxidation of stainless steel sheets: isothermal results for uncoated substrates at (a) 950 °C, (b) 870 °C and (c) 800 °C, (d) samples coated by $\text{TiO}_2\text{-SiO}_2$ of thickness 0.4–0.9 μm after oxidation in air at 800 °C and (e) logarithm of velocity against the inverse of temperature for uncoated stainless steel, $E = 25\text{--}30 \text{ kcal mol}^{-1}$.

Figure 2 Chemical durability of stainless steel in 15% H_2SO_4 solution: uncoated samples after immersion at (a) 89 °C, (b) 82 °C, (c) 76 °C and (d) 72 °C, (e) coated stainless steel of thickness 0.4–0.9 μm treated in 15% H_2SO_4 solution at 89 °C and (f) logarithm of velocity against the inverse of temperature for uncoated stainless steel tested in 15% H_2SO_4 solution at different temperatures.

intimate mixture of cubic and hexagonal Cr_2O_3 (Fig. 3b).

After treatment in 15% H_2SO_4 solution at 89 °C for 20 h, the peaks of the stainless steel decreased in relative intensity (Fig. 3c).

Coated substrates of composition 30 $\text{TiO}_2\text{--}70\text{SiO}_2$ heated at 800 °C for 15 h showed no change in relative intensity of peaks, indicating no oxidation of the coated samples following heat treatment (Fig. 3d), but additional peaks were observed at 0.276, 0.23 and 0.131 nm corresponding to orthorhombic titania (anatase). Similar results were obtained when the coated samples were tested in 15% H_2SO_4 solution at 89 °C for 40 h (Fig. 3e).

A Fourier transformation infrared (FTIR) spectrometer with a 400–4000 cm^{-1} range was used to obtain high resolution spectra of coatings; the measurement was obtained by reflection at an incident angle of 30°.

Fig. 4a shows the spectra of 30 $\text{TiO}_2\text{--}70\text{SiO}_2$ films deposited on 316L stainless steel as dried at 25 °C.

Near 1070, 800 and 460 cm^{-1} vibrations of SiO_4 tetrahedra were observed in SiO_2 structures, corresponding to absorption bands of Si–O–Si asymmetric band stretching modes of the “rigid cage”, asymmetric band stretching modes of the “breathing” and symmetric bond bending O–Si–O bands [12]. The presence of 1450 and 1650 cm^{-1} bands correspond to mixtures of Si–O–C and Ti–O–C. The absorptions due to the C–H and OH groups were respectively observed near 3680–3860 cm^{-1} and 3210 cm^{-1} .

However, bands were found at 940 and 680 cm^{-1} which were attributed to vibrations of Si–O–Ti [13].

After firing at 450 °C for 2 h, bands characteristic of Si–O–Si and Si–O–Ti appear and there was no change in relative intensity (Fig. 4b). With an increase in temperature other bands of C–H, OH and mixture of Si–O–C, Ti–O–C disappeared. These strong absorptions decreased with increasing temperature, and disappeared completely at 800 °C

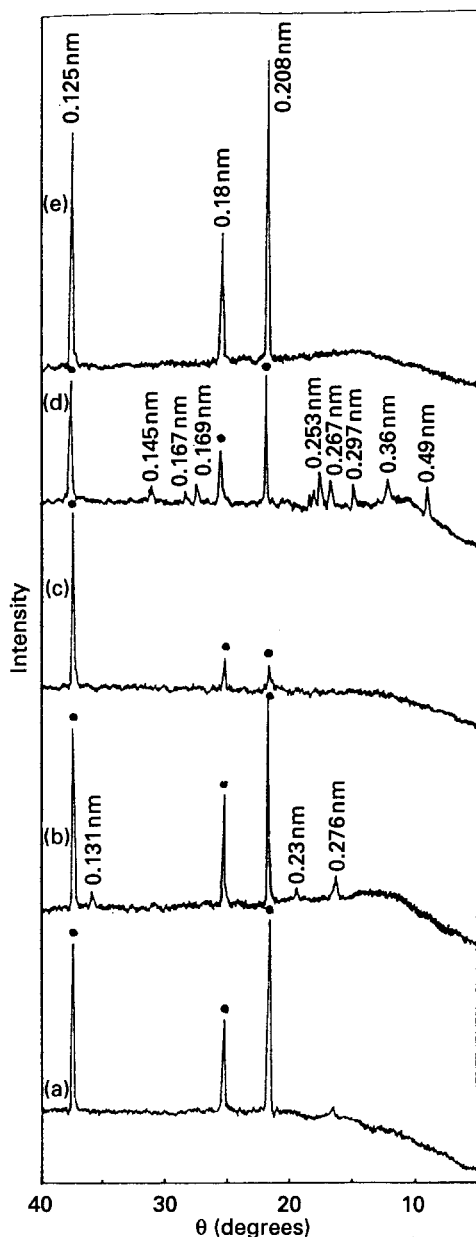


Figure 3 XRD patterns of uncoated and coated substrates: stainless steel (a) as cleaned, (b) heat treated at 800 °C in air for 20 h, (c) after treatment in 15% H₂SO₄ solution at 89 °C for 20 h, (d) coated with 30TiO₂-70SiO₂ films kept at 800 °C in air for 15 h and (e) coated with 30TiO₂-70SiO₂ films after acid attack at 89 °C for 40 h.

(Fig. 4c). Vibrations of Si-O-Si and Si-O-Ti bonds were observed. A similar spectrum was also obtained after treatment of 30TiO₂-70SiO₂ in 15% H₂SO₄ solution at 89 °C for 40 h (Fig. 4d).

The morphology of the surface was examined by scanning electron microscopy (SEM; JSM-6300F). Fig. 5a shows a photomicrograph of the as received stainless steel surface. The same sample heated for 20 h in air at 800 °C showed growth of crystals, which was confirmed by XRD analysis (Fig. 5b). Fig. 5c shows the stainless steel surface after immersion in 15% H₂SO₄ solution at 89 °C. Fig. 5d shows a micrograph of thin film 30TiO₂-70SiO₂ deposited on stainless steel and heated at 800 °C for 15 h. The resulting coating was homogeneous, with dense structure. Fig. 5e is an electron micrograph of

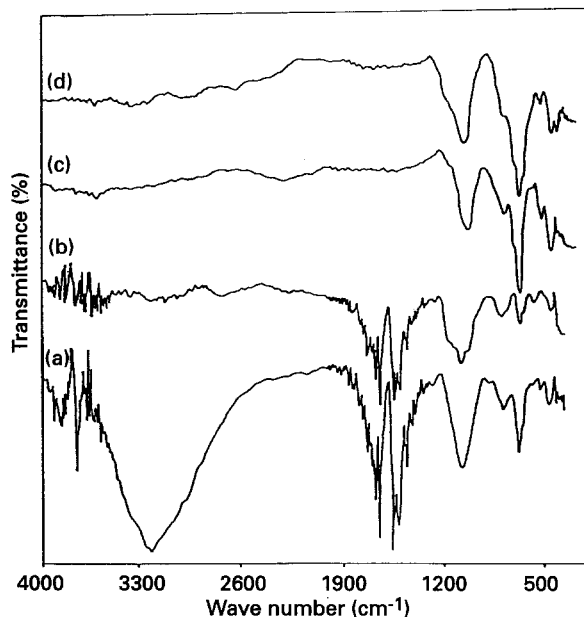


Figure 4 IR spectra of 30TiO₂-70SiO₂ films deposited on 316L stainless steel: (a) as dried at 25 °C, (b) after firing at 450 °C for 2 h, (c) after oxidation in air at 800 °C for 15 h and (d) after treatment in 15% H₂SO₄ solution at 89 °C for 40 h.

the coated surface treated in 15% sulphuric acid at 89 °C for 40 h. Fig. 5f gives the edge of a 50TiO₂-50SiO₂ film after heating at 800 °C. In this case the film thickness is about 0.6 μm.

The corrosion behaviour of 316L stainless steel was investigated by corrosion measurements after oxidation in air at high temperature and immersion in 15% H₂SO₄ solutions (Figs 1 and 2). Comparing uncoated and coated samples, it may be observed that substrates with thin films had a good resistance against thermal oxidation and presented a chemical durability for up to 40 h. Results of X-ray analysis show that stainless steel coated with TiO₂-SiO₂ reveals the crystalline phase of titania (anatase) formed during oxidation in air. With a single film, no oxidation and no acid corrosion was detected. Single film appears to have resistance to oxidation and acid attack (Fig. 3). Using a FTIR for the analysis of TiO₂-SiO₂, the formation of mixed Ti-O-Si bond in the resultant film was found (Fig. 4). SEM micrography (Fig. 5a-c) shows the change in microstructure of the surface of 316L stainless steel after oxidation and acid attack. During the same experiment with coated samples, no weight change was observed (Fig. 5d-f).

In this work, sol-gel coatings obtained from sonocatalysed hydrolysis of alkoxides were deposited on stainless steel by the dip-coating method. The study clearly shows that this new sol-gel method may be used to promote homogenization of gels of the *x*TiO₂-(100-*x*)SiO₂ system. The resulting films densified at 800 °C; they are crystalline with an orthorhombic structure of titania. It was found that these coatings provide a significant protection of the metal substrate against air oxidation for at least 15 h at 800 °C and against H₂SO₄ chemical attack for at least 40 h at 89 °C.

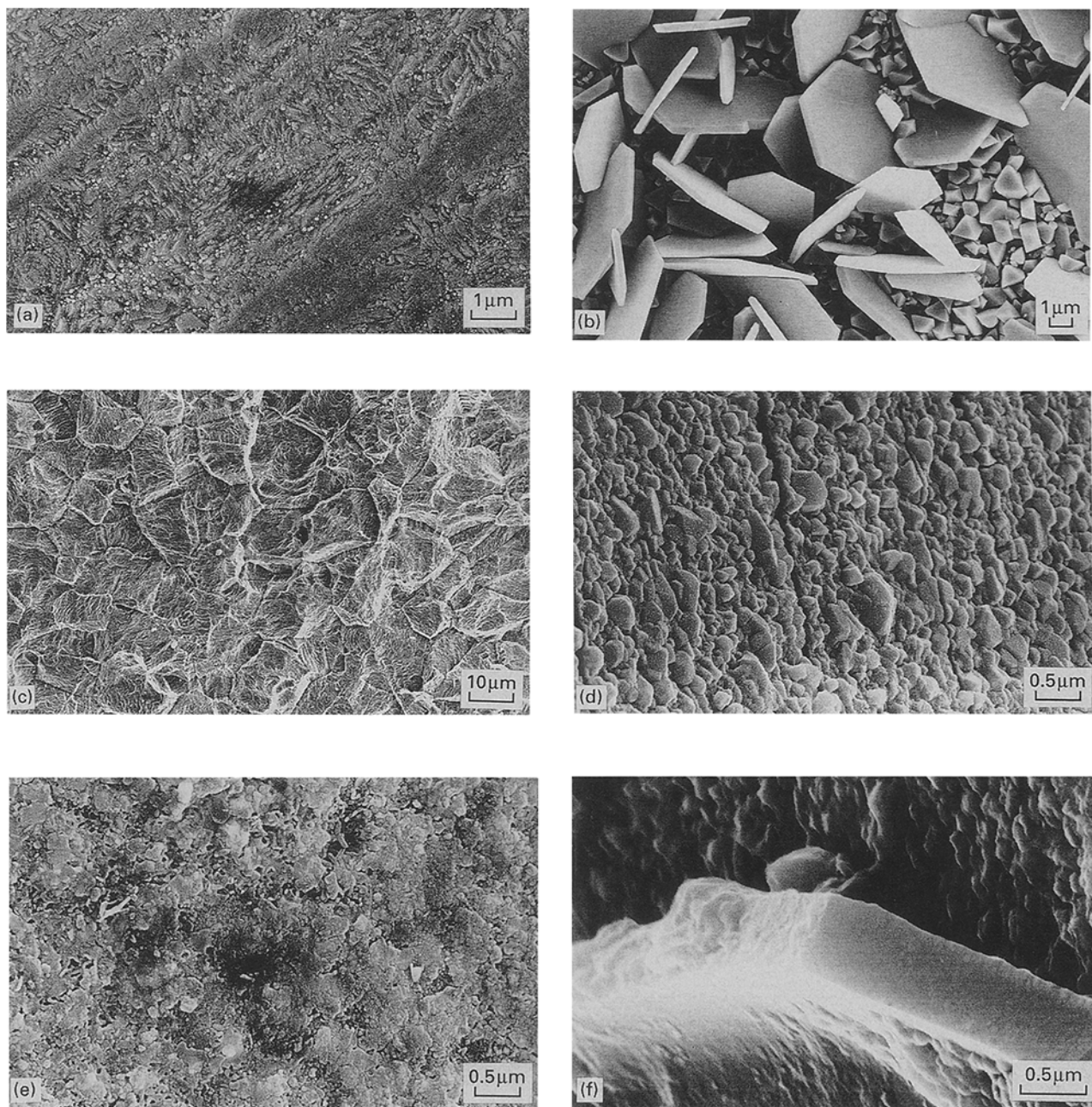


Figure 5 SEM micrographs of (a–c) 316L stainless steel (a) as cleaned, (b) heated in air at 800 °C for 20 h and (c) treated in 15% H₂SO₄ solution at 89 °C for 15 h, (d, e) 30TiO₂–70SiO₂ film deposited on stainless steel (d) after oxidation in air at 800 °C for 15 h and (e) after heating at 800 °C for 2 h and treating in 15% H₂SO₄ solution for 40 h and (f) the edge of a 0.6 μm thick 50TiO₂–50SiO₂ film after heating in air at 800 °C for 10 h.

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