

# Oxygen-free deposition of ZrO<sub>2</sub> sol-gel films on mild steel for corrosion protection in acid medium

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Previous work from this laboratory the Instituto de Química de São Carlos has shown the effectiveness of sol-gel-derived ceramic coatings for the protection of stainless steel against corrosion in H<sub>2</sub>SO<sub>4</sub> [1–5] and NaCl solutions [6, 7]. The coatings used were ZrO<sub>2</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>-SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. In all the cases, a large degree of protection was achieved with corrosion rates in H<sub>2</sub>SO<sub>4</sub> diminishing by a factor of almost 6 for tests at room temperature [1–3] and 8.5 at 50 °C [4, 5]. Among the coatings, ZrO<sub>2</sub> was most efficient and, at the same time, the most easily prepared.

However, for practical applications it is important to study the deposition of ceramic coatings on mild steel (MS) substrates for the protection of this widely used material. Meanwhile, early attempts to deposit these films on MS surfaces following the conventional procedure resulted in discontinuous and non-adherent coatings. This was proved to be due to the simultaneous growth of iron oxides from the substrate.

In the meantime, one of the useful characteristics of the sol-gel method is related to the metal alkoxides used as precursors. These compounds contain a metal atom directly linked to sufficient oxygen atoms to produce the desired oxide without participation of the atmosphere. Therefore, it should be possible in principle to apply this technique for coating formation onto oxygen-reactive metal surfaces.

The aim of this work is to describe the conditions for ZrO<sub>2</sub> film formation on MS surfaces in the absence of oxygen to avoid chemical oxidation of the substrate and to promote adherent and protective films. The ZrO<sub>2</sub> coatings were deposited by dip coating using a sol preparation involving sonocatalysis [1–6]. The films were prepared through hydrolysis and polymerization of metal alkoxide solutions. This was followed by conversion to an oxide layer by heat treatment in a furnace with an argon atmosphere.

The substrate used was MS of composition 99.440 wt% Fe, 0.350 wt% Mn, 0.110 wt% Si, 0.023 wt% S and 0.018 wt% P. Samples of

30 mm × 15 mm × 1 mm size were mechanically cut from large foils and polished with successively finer grades of emery paper. Then, the samples were degreased ultrasonically in acetone, cleaned with distilled water and dried in air.

Zirconium isopropoxide (Zr(OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub>) diluted in isopropanol was used as the source of zirconia. The preparation procedure of the precursor solution and the coating deposition technique have been fully described elsewhere [5, 6]. The sol-gel films were densified for 2 h in a quartz-tube furnace with an argon atmosphere. The temperature was increased at a rate of 5 °C min<sup>-1</sup> up to the desired final value (500–800 °C).

The physical characterisation of the films was carried out at different stages of the densification process using infrared (IR) spectroscopy, scanning electron microscopy (SEM) and energy-dispersive X-

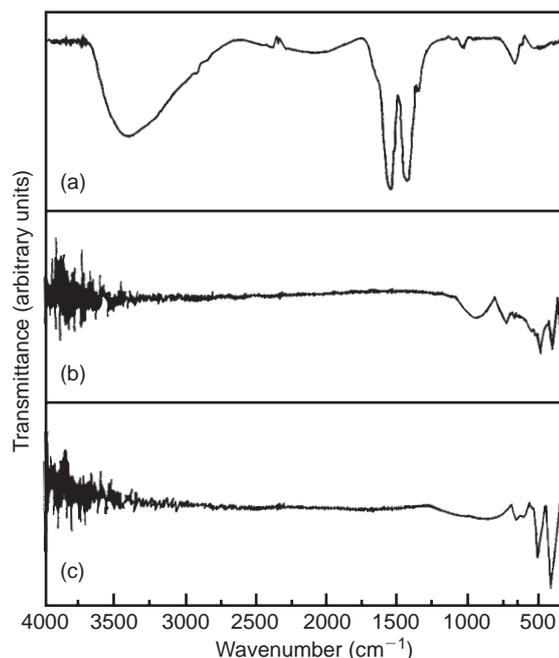


Figure 1 IR spectra for zirconia films deposited on MS: (a) after initial drying at 25 °C; (b) after heat treatment in an argon atmosphere at 700 °C; (c) after heat treatment in an argon atmosphere at 800 °C.

ray analysis (EDXA). These techniques allowed us to follow the decomposition of the organic material, to observe the surface and the cross-section of the coated samples and to confirm the presence of Zr in the deposited films, respectively.

The IR spectra were obtained using a Bomem Fourier transform spectrophotometer in the 400–4000  $\text{cm}^{-1}$  range by reflection at an incident angle of  $30^\circ$ . The morphology of the surface was examined using a Zeiss DSM 960 microscope. The chemical identification of the elements in the film was made using a Link Analytical QX-2000 instrument.

Electrochemical measurements were carried out by potentiodynamic polarization curves at  $1 \text{ mV s}^{-1}$  in deaerated  $0.5 \text{ M H}_2\text{SO}_4$  (Merck p.a.) aqueous (Milli-Q) solutions at  $25^\circ\text{C}$ . An electrochemical cell with a Teflon sample holder that exposed only  $1 \text{ cm}^2$  of the surface to the electrolyte was used. The auxiliary electrode was a Pt foil and a saturated calomel electrode (SCE) served as the reference. The work-

ing electrodes were the coated and the uncoated MS plates. A 273 PAR potentiostat linked to a micro-computer for data acquisition and handling through the 352 PAR corrosion measurements software was used for the electrochemical experiments.

Fig. 1 shows the IR spectra of the coated samples before and after densification for 2 h at 700 and  $800^\circ\text{C}$  in an argon atmosphere. In the spectrum of the dried sol-gel film (Fig. 1a) a large band can be observed at  $3500 \text{ cm}^{-1}$  corresponding to the OH group of water. Furthermore, two well-defined bands at  $1453 \text{ cm}^{-1}$  and at  $1578 \text{ cm}^{-1}$  corresponding to the asymmetric stretching of the Zr–O–C bond from the metallic precursor and one band at  $660 \text{ cm}^{-1}$  corresponding to the symmetric vibration of the Zr–O–Zr bond [8, 9] are also observed.

The spectra of the densified films (Fig. 1b and c) show the zirconium oxide formation on the MS surface. The vibrations corresponding to the OH groups and the Zr–O–C bonds have disappeared

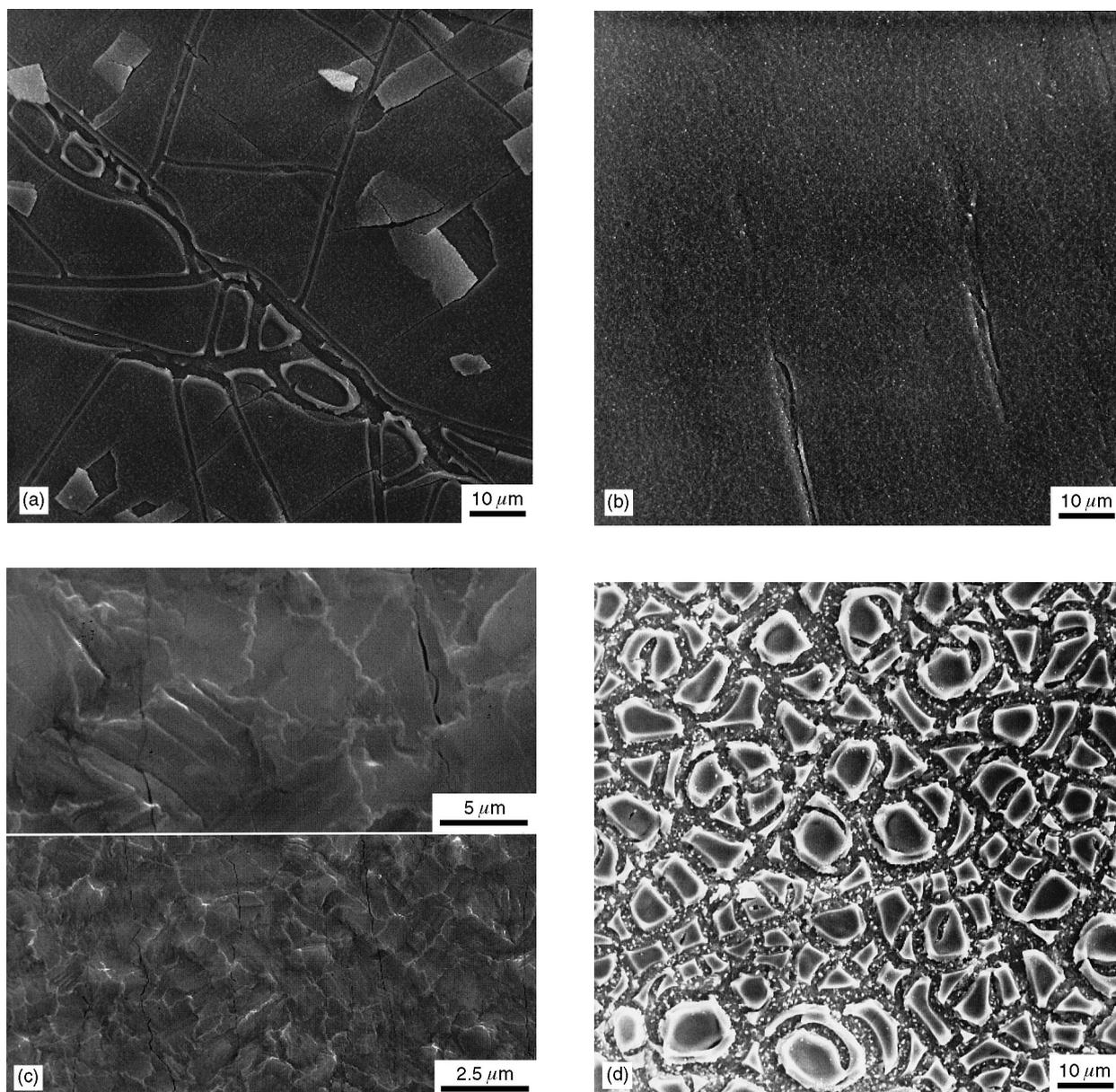


Figure 2 Scanning electron micrographs of MS samples coated with  $\text{ZrO}_2$  and heat treated for 2 h (a) (c) in an argon atmosphere at (a)  $600^\circ\text{C}$ , (b)  $700^\circ\text{C}$  and (c)  $800^\circ\text{C}$ , and (d) in an air atmosphere at  $800^\circ\text{C}$ .

completely while the band at  $660\text{ cm}^{-1}$  remains. The large vibration bands at  $510\text{ cm}^{-1}$  and  $390\text{ cm}^{-1}$  suggest the formation of  $\text{Fe}_2\text{O}_3$  [10, 11]. The analysis of these results demonstrates that the oxygen present in the alkoxide is sufficient for the densification of the zirconium oxide. It also indicates that the  $\text{ZrO}_2$  film is supported on a thin layer of oxides from the substrate. In fact,  $\text{ZrO}_2$  films have good adherence over iron oxide layers because they effectively interact, promoting the formation of Fe–O–Zr bonds [12].

The surface morphology evolution of the  $\text{ZrO}_2$  coatings deposited on MS and heat treated at different temperatures is presented in Fig. 2. It can be observed (Fig. 2a–c) that more compact films are obtained when the densification is carried out at higher temperatures. Thus, the film heat-treated at  $600\text{ }^\circ\text{C}$  (Fig. 2a) presents cracks on the surface while those densified at  $700\text{ }^\circ\text{C}$  (Fig. 2b) and  $800\text{ }^\circ\text{C}$  (Fig. 2c) are continuous. Additionally, Fig. 2c shows a surface film with well-defined grain boundaries. X-ray analysis of these samples revealed the presence of a mixture of monoclinic and tetragonal  $\text{ZrO}_2$  structures. This agrees with previously reported results [5, 13]. For comparison, Fig. 2d shows that the film heat treated for 2 h at  $800\text{ }^\circ\text{C}$  in an air atmosphere is discontinuous and non-adherent owing to the simultaneous growth of an iron oxide layer from the substrate. EDXA of the latter sample showed that  $\text{ZrO}_2$  is mainly located at the boundaries of the islands (clear regions) while the iron oxides are at the centre. Finally, SEM observations of the cross-section in coated samples densified at  $800\text{ }^\circ\text{C}$  show a homogeneous layer with an average thickness of  $0.7\text{ }\mu\text{m}$ .

Fig. 3 shows the potentiodynamic polarization curves of MS as received (curve a), heat treated for 2 h at  $800\text{ }^\circ\text{C}$  in an argon atmosphere (curve b) and coated with  $\text{ZrO}_2$  densified under the same conditions (curve c). This figure confirms that the presence of the coating alters the electrochemical behaviour of the MS substrate, both as received and after heat treatment without the coating. Hydrogen

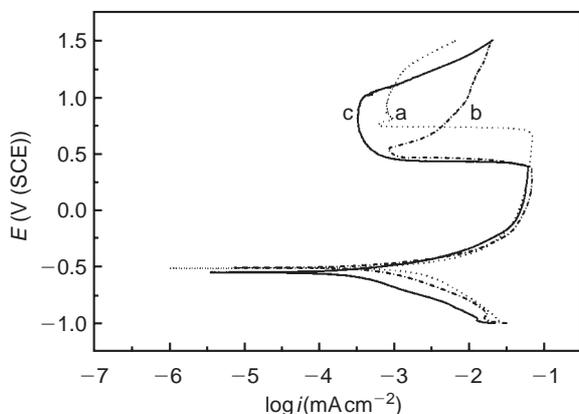


Figure 3 Potentiodynamic polarization curves reduced at  $1\text{ mV s}^{-1}$  in deaerated  $0.5\text{ M H}_2\text{SO}_4$  aqueous solutions at  $25\text{ }^\circ\text{C}$  on MS. Curve a, as received; curve b, heat treated at  $800\text{ }^\circ\text{C}$  for 2 h in an argon atmosphere; curve c, coated with  $\text{ZrO}_2$  densified at  $800\text{ }^\circ\text{C}$  for 2 h in an argon atmosphere.

TABLE I Corrosion parameters determined from the potentiodynamic curves for uncoated and coated MS samples heat treated for 2 h at different temperatures in an argon atmosphere: corrosion potential,  $E_{\text{corr}}$ , polarization resistance  $R_p$  and corrosion rate

Sample	Heat treatment temperature ( $^\circ\text{C}$ )	$E_{\text{corr}}$ (mV)	$R_p$ ( $\Omega\text{ cm}^2$ )	Corrosion rate (MPY)
MS	As received	494	24	1428
	500	532	18	1966
	600	525	17	2026
	700	536	19	1693
	800	516	53	436
MS/ $\text{ZrO}_2$	500	539	18	2243
	600	534	21	1434
	700	520	27	1005
	800	547	109	184

evolution is the reaction for the cathodic branch of all curves. The cathodic current density for the heat-treated MS is somewhat lower than that of the untreated substrate, as shown by curves b and a in Fig. 3. Additionally, the presence of the coating (curve c) shifts the cathodic current densities towards lower values. In all cases, the slope of the Tafel region is approximately constant, suggesting that the reaction mechanism remains unchanged. This indicates that the  $\text{ZrO}_2$  film acts as a physical barrier that diminishes the exposed area of the substrate to the electrolyte. This behaviour is very similar to that observed for the sol–gel-derived films on type 316L stainless steel in  $\text{H}_2\text{SO}_4$  solutions [1–5]. On the other hand, the shape of the anodic branch of the curves in Fig. 3 indicates that the coated sample has a better-defined passive region in the range  $0.5\text{--}1.0\text{ V (SCE)}$ , with current density values lower than those for both uncoated samples.

The electrochemical parameters, obtained from the data in Fig. 3, for the uncoated and coated samples heat treated for 2 h at different temperatures in an argon atmosphere are collected in Table I. It is worth noting that a direct heat treatment of MS at  $800\text{ }^\circ\text{C}$  under those special conditions greatly improves the corrosion resistance of this material. In addition, this table indicates that the coated samples heat treated up to  $700\text{ }^\circ\text{C}$  still have a high corrosion rate while that with the  $\text{ZrO}_2$  densified at  $800\text{ }^\circ\text{C}$  shows a value 7.8 times lower than measured for as-received MS.

The sol–gel method proved to be appropriate for depositing ceramic oxide films on MS substrates using an inert atmosphere. The film acts as a physical barrier than can increase the lifetime of the substrate by a factor of 7.8. This idea of chemical protection by ceramic oxide films can now be extended to other reactive materials since the coatings can be generated under oxygen-free conditions.

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