Sol-Gel Deposition of ZrO_2 Films in Air and in Oxygen-Free Atmospheres for Chemical Protection of 304 Stainless Steel: A Comparative Corrosion Study

F. PERDOMO L.
Instituto de Química de São Carlos, Universidade de São Paulo, C.P. 780, 13560-970 São Carlos (SP), Brazil; and Departamento de Materiales, Universidad del Valle, Cali, Colombia

P. DE LIMA-NETO
Instituto de Química de São Carlos, Universidade de São Paulo, C.P. 780, 13560-970 São Carlos (SP), Brazil; and Departamento de Química Analítica e Físico-Química, UFC, Fortaleza, CE, Brazil

M.A. AEGERTER
Instituto de Química de São Carlos, Universidade de São Paulo, C.P. 780, 13560-970 São Carlos (SP), Brazil; and Institut für Neue Materialien-INM, Saarbrücken, Germany

L.A. AVACA
Instituto de Química de São Carlos, Universidade de São Paulo, C.P. 780, 13560-970 São Carlos (SP), Brazil

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Abstract. ZrO_2 coatings for corrosion protection were deposited on 304 stainless steel by sol-gel method using zirconium propoxide as precursor and densified in air and in oxygen-free (argon or nitrogen) atmospheres. XRD and IR data of the films were practically independent of the atmosphere used in the densification step showing that the ceramic oxide is properly formed from the precursor. The corrosion behavior of the stainless steel substrate was studied by potentiodynamic polarization curves in the absence and the presence of ZrO_2 coatings prepared in air, argon or nitrogen. The coatings extended the lifetime of the material by a factor of almost eight in a very aggressive environment, independently of the preparation procedure. The possibility of depositing pure or mixed oxide films by sol-gel methods in the absence of additional oxygen will allow the preparation of specific coatings onto oxygen-reactive substrates.

Keywords: sol-gel coatings, ZrO_2, oxygen-free densification, corrosion protection, 304 stainless steel

1. Introduction

Pure and mixed sol-gel derived oxide films have been widely studied in our laboratories as coatings for corrosion protection of steel as well as catalysts for some selected electrode reactions. In those studies, ZrO_2, SiO_2, SiO_2-TiO_2 and SiO_2-Al_2O_3 have shown to effectively protect 316L stainless steel (SS) against corrosion in H_2SO_4 [1–5] and NaCl solutions [6, 7]. On the other hand, $RuIrO_2$ layers deposited on titanium proved to be very active and stable materials for the oxygen evolution reaction in acid solutions [8]. In all cases, a conventional methodology was used for the preparation of the coatings. In particular, the heat-treatment necessary for the densification of the material was carried out in an open furnace.

Meanwhile, recent studies [9] have described a new methodology developed for the deposition of ZrO_2 sol-gel coatings on mild steel using an oxygen-free argon atmosphere to avoid unwanted initial oxidation of the surface. The electrochemical behavior of the coated samples in 0.5M H_2SO_4 was also reported and the coatings showed to be an effective physical barrier that can increase the lifetime of the substrate, as in previous cases [1–7]. This new methodology is appropriate to deposit ceramic or catalytic oxide films on oxygen-reactive metal surfaces because metal alkoxides or acetyl-acetonates are used as precursors. These molecules contain a metal atom directly linked to enough oxygen atoms to produce the desired oxide without the participation of additional oxygen from the atmosphere. Therefore, the deposition of ceramic coatings on stainless steels for corrosion protection in aggressive media could profit from these principles by avoiding the initial formation of oxide layers on the surface.

The objective of this work is to study the formation of ZrO_2 coatings on 304 SS surfaces in air and in oxygen-free furnace atmospheres and to compare the corrosion behavior of the different coated samples in 0.5M H_2SO_4 solutions at 25°C. The 304 SS was chosen because it is a widely used material for industrial applications that combines a reasonable corrosion resistance with a good formability [10] being, at the same time, less expensive than the 316L SS previously studied. In addition, the 304 SS is much less reactive to oxygen than mild steel [9] thus allowing the preparation of the coatings under both experimental conditions and the comparison of the corrosion behavior of the samples.

2. Experimental

2.1. Substrate

The substrate used was AISI 304 stainless steel of composition (wt%): 70.94 Fe, 0.07 C, 1.74 Mn, 0.033 P, 0.018 S, 0.45 Si, 8.16 Ni and 18.59 Cr. Samples of $30 \times 15 \times 1$ mm were mechanically cut from large foils and polished with successively finer grades of emery paper. After that, the samples were degreased ultrasonically in acetone, cleaned with distilled water and dried in air.

2.2. Preparation of the Films

Zirconium propoxide $Zr(OC_3H_7)_4$ diluted in isopropanol was used as the source of zirconia. The ZrO_2 coatings were deposited by dip-coating using a sol preparation involving sonocatalysis [1–4]. The films were prepared through hydrolysis and polymerisation of the metal alkoxide solution. The preparation procedure of the precursor solution and the coating deposition technique are fully described elsewhere [5, 6]. The films were initially dried at 60°C for 15 min and then densified for 2 h in a quartz-tube furnace with either air, argon or nitrogen flowing through it slowly. The temperature was increased at a rate of 5°C min^{-1} up to the desired final value (700 or 800°C). The resulting coatings were very homogeneous and continuous, showing an average thickness of 0.7 μm as revealed by lateral SEM pictures of cut samples.

2.3. Physical Characterization

The evolution of the chemical bonds during the process of formation of the ZrO_2 films was followed by IR reflection measurements at an incident angle of 30° using a Bomem Fourier Transform Infrared (FTIR) spectrophotometer. X-ray diffraction measurements (XRD) were carried out on the films densified at 800°C using a Rigaku Rotaflex 200B diffractometer with a characteristic CuK_α radiation ($\lambda = 1.5405$ Å) and a symmetric setup. Energy Dispersive X-ray analysis (EDX) of the coatings was carried out in a Link Analytical QX-2000 instrument using a tilt angle of 75° to minimize the interference of the substrate.

2.4. Electrochemical Measurements

The electrochemical measurements were carried out to study the influence of the densification conditions on the corrosion behavior of coated and uncoated samples in deaerated 0.5M H_2SO_4 solutions at 25°C. An electrochemical cell with a Teflon sample holder that exposed only 1 cm^2 of the sample surface to the electrolyte was used. The auxiliary electrode was a Pt foil and a saturated calomel electrode (SCE) served as reference. Potentiodynamic polarization curves were obtained at 1 mV s^{-1} in the range of -1.0 to 1.5 V vs. SCE using a mod 273 computerized EG&G/PAR potentiostat/galvanostat controlled by the EG&G/PAR M352 corrosion software.

3. Results and Discussion

The formation of the ZrO_2 coatings under the different furnace atmospheres studied here is illustrated by

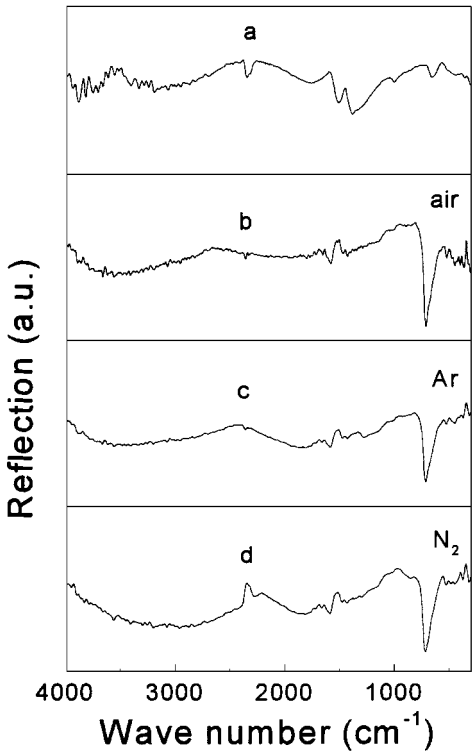

Figure 1. IR spectra for zirconia films deposited on 304 SS: after initial drying in air at 60°C (a) and after heat treatment in: air (b), argon (c) and nitrogen (d) atmospheres.

the results presented in Fig. 1. The IR spectra of the samples show the evolution of the chemical bonds in the coatings with the densification process at 800°C for 2 h in air, argon and nitrogen.

In the dried sol-gel film (Fig. 1(a)), the wide band at around 3000–3500 cm^{-1} corresponds to the OH group of water and the bands at 1453 and 1578 cm^{-1} to the asymmetric stretching of the Zr─O─C bond from the metallic precursor. The band at 710 cm^{-1} reveals the symmetric vibration of the Zr─O─Zr bond [11] already present at this stage. The spectra of the densified films (Figs. 1(b)–(d)) show that the vibration corresponding to the Zr─O─C bond disappears almost completely while the band at 710 cm^{-1} grows in intensity and is very well defined after the heat treatment. The remarkable similarity between the spectra of the different samples (Figs. 1(b)–(d)) strongly suggests that the ZrO_2 coating is properly formed even in the absence of O_2 during densification.

Due to the small thickness of the films, the X-rays diffractograms were dominated by the peaks coming from the substrate. Thus, strong signals were observed for values of 2Θ equal to 74.68, 50.76 and 43.56 degrees corresponding to the planes [220], [200] and [111] of phase centered cubic $Cr_{0.19}Fe_{0.7}Ni_{0.11}$, respectively (12). The main peak arising from the ZrO_2 coating was much smaller but very distinct, appearing at 2Θ equal to 30.16 degrees. This corresponds to the [111] plane of tetragonal ZrO_2 ($d = 2.96$ Å). In all cases, the XRD response of the system was practically independent of the atmosphere used for the densification step. The surface formation of ZrO_2 was further confirmed by EDX analysis of tilted samples that practically showed a single and very large zirconium peak.

Potentiodynamic polarization curves were recorded in 0.5M H_2SO_4 at 25°C to compare the corrosion behavior of uncoated and coated 304 SS samples densified at 700 and 800°C for 2 h using different furnace atmospheres. Figures 2 and 3 illustrate the effect of temperature for ZrO_2 densified in air. The responses of samples of 304 SS as received and after heat-treatment under the same conditions are also included for comparison.

These figures show that the presence of the ZrO_2 film on the 304 SS shifts the cathodic currents densities towards much lower values but the slope of the straight line is practically unaltered. This fact strongly suggests that the mechanism for the hydrogen evolution reaction remains unchanged and the coatings is acting as a physical barrier that diminishes the active area for reaction. In the anodic branch of the curves, the presence of ZrO_2 lowers the current density of the passive region by almost one order of magnitude for the sample densified at 800°C (Fig. 3, curve a). On the other hand, the value of the passive current density of the coated sample heat-treated at 700°C is nearly the same as that of 304 SS as-received (Fig. 2, curves a and b), indicating that the film is much less compact at this temperature. These results confirm previous studies [1–7, 9] indicating that in most cases 800°C is the best temperature for the densification of sol-gel protective coatings. In the same passive region, the heat-treated bare samples (curves c in Figs. 2 and 3) show current densities higher than the untreated substrate, revealing changes of the material during the heat-treatment. The potentiodynamic polarization curves for uncoated and coated 304 SS samples heat-treated in oxygen-free atmospheres (Argon and Nitrogen) were qualitatively very similar to those presented in Figs. 2 and 3.

The corrosion parameters derived from the electrochemical measurements for the whole set of samples studied here are collected in Table 1.

This table shows that, in most cases, the ZrO_2 films densified at 800°C are more efficient protective coatings than those densified at 700°C. The corrosion

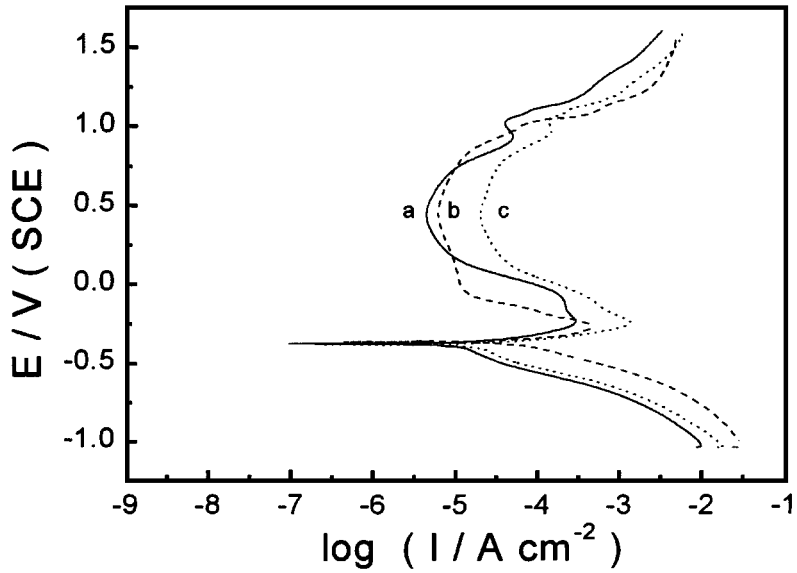

Figure 2. Potentiodynamic polarization curves recorded at 1 mV s^{-1} in deaerated 0.5M H_2SO_4 aqueous solutions at 25°C on 304 SS: coated with ZrO_2 densified at 700°C for 2 h in air atmosphere (a); as-received (b) and; uncoated but heat treated at 700°C for 2 h in air atmosphere (c).

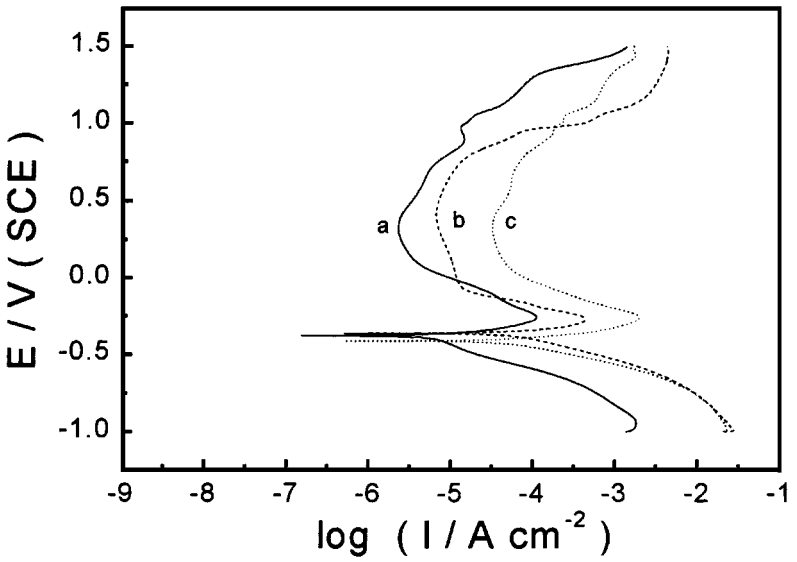

Figure 3. Same as Fig. 2, but ZrO_2 densified at 800°C.

rates for the samples with films densified at 800°C for 2 h in either Nitrogen or air atmospheres (i.e., 3.8 mpy) are almost 8 times lower than for the original material. In the case of Argon at 800°C, the measured corrosion rate is rather high while the corrosion potential is close to that of the uncoated samples. These facts suggest cracking of the film with the consequent exposure of the steel surface. Finally, it is worth noticing that the decrease in corrosion rates is exclusively due to the coatings on the 304 SS surface and not to a combination of the presence of film with the heat treatment. This is because the uncoated 304 SS samples heat-treated

Table 1. Corrosion parameters derived from potentiodynamic curves for uncoated and coated 304 SS samples heat treated at 700 and 800°C for 2 h in air, argon and nitrogen atmospheres; corrosion potential (E_{cor}), polarization resistance (R_p) and corrosion rate (v_{cor}).

Sample	Furnace atmosphere	Heat treatment (°C)	$-E_{cor}$ (mV)	R_p (kΩ cm^{-2})	v_{cor} (mpy)
304 SS[a]			361	0.3	29.0
304 SS	Air	700	376	0.7	6.9
304 SS	argon	700	395	0.2	21.3
304 SS	Nitrogen	700	376	0.4	10.0
304 SS	Air	800	383	0.7	7.2
304 SS	Argon	800	414	0.4	24.2
304 SS	Nitrogen	800	412	0.3	26.9
304 SS/ZrO_2	Air	700	363	0.6	5.3
304 SS/ZrO_2	Argon	700	376	0.8	4.7
304 SS/ZrO_2	Nitrogen	700	373	0.5	6.8
304 SS/ZrO_2	Air	800	371	1.2	3.8
304 SS/ZrO_2	Argon	800	400	0.9	6.9
304 SS/ZrO_2	Nitrogen	800	370	1.3	3.8

[a]304 SS as-received.

in Argon and in Nitrogen do not show a significant decrease in corrosion rate when compared to the 304 SS as-received. The observed decrease in corrosion rate for the 304 SS heat-treated in air at either 700 or 800°C is possibly due to the growth of resistant oxide films that are not formed if oxygen is absent.

4. Conclusions

Two main conclusions can be drawn from these studies. Firstly, the sol-gel derived ZrO_2 films act as very effective coatings for the protection of 304 stainless steel against corrosion in aggressive environments. The lifetime of that steel can be extended by a factor of almost eight in the presence of the coating thus conferring the 304 SS characteristics found only in much more expensive materials.

The second and more important conclusion is that the alkoxides used as precursors in the sol-gel method contain sufficient oxygen to allow the proper formation of ZrO_2 films in oxygen-free atmospheres. Therefore, the sol-gel method can be used for the deposition of pure and mixed oxide films with specific characteristics even on oxygen-sensitive substrates. This will certainly enlarge the field of application of the sol-gel methodology.

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