J. Braz. Chem. Soc., Vol. 6, No. 1, 33-37, 1995.
Printed in Brazil.

0103 – 5053 $5.00 + 0.00

Electrochemical Studies of the Corrosion of 316L Stainless Steel Coated with Sol-Gel ZrO_2 Films

Pedro de Lima-Neto and Luis A. Avaca*

Instituto de Química de São Carlos, Universidade de São Paulo, C.P. 780, 13560-970 São Carlos - SP, Brazil

Mohamed Atik and Michel A. Aegerter

Instituto de Física de São Carlos, Universidade de São Paulo, C.P. 369, 13560-970 São Carlos - SP, Brazil

Romeu C. Rocha-Filho

Departamento de Química, Universidade Federal de São Carlos, C.P. 676, 13560-970 São Carlos - SP, Brazil

Received: April 30, 1994; October 10, 1994

Recobrimentos cerâmicos de ZrO_2 preparados pelo método sol-gel foram depositados sobre aço inoxidável 316L através de técnicas de imersão em soluções preparadas sob ultra-som, usando $Zr(OC_3H_7)_4$ como precursor e misturas de isopropanol, ácido acético glacial e água como solvente. Os recobrimentos foram densificados durante 2 h em temperaturas entre 450 e 800 °C. Curvas de polarização potenciodinâmicas e espectroscopia de impedância eletroquímica foram utilizadas para estudar o efeito dos diferentes recobrimentos sobre a corrosão do aço em soluções aquosas aeradas contendo 30 g dm^{-3} de NaCl. Os dados de impedância foram analisados através de ajuste gráfico usando funções de transferência de circuitos elétricos equivalentes. Ambas técnicas mostraram que existe um decréscimo apreciável da taxa de corrosão nas amostras com recobrimento, assim como a presença de uma descontinuidade no comportamento do sistema para os filmes tratados a 450 °C. Da análise dos circuitos equivalentes pôde-se concluir que os filmes tratados a 450 °C são bastante porosos, agindo simplesmente como uma barreira física entre o substrato e a solução. Para temperaturas de densificação maiores, o circuito equivalente deve incluir parâmetros extras relacionados a um efeito de porosidade no recobrimento análogo àquele observado em recobrimentos de tintas e sistemas semelhantes.

ZrO_2 sol-gel coatings were deposited on 316L stainless steel by dip-coating techniques, using a sol of $Zr(OC_3H_7)_4$ as a precursor and isopropanol, glacial acetic acid and water as the solvent prepared under ultrasound. The coatings were densified at temperatures ranging from 450 to 800 °C for 2 h. The influence of the different coatings on the corrosion behavior of steel in aerated aqueous solutions of 30 g dm^{-3} NaCl was studied by potentiodynamic polarization curves and by electrochemical impedance spectroscopy using transfer functions from electric equivalent circuits for the fitting of the data. Both techniques showed a significant decrease in the corrosion rate for the coated samples as well as a discontinuity in the behavior of the system for films densified at temperatures above 450 °C. From the equivalent circuit analysis it was concluded that the films densified at 450 °C are quite porous, acting simply as a physical barrier between the substrate and the solution. For higher densification temperatures extra parameters related to a coating porosity effect must be included in the equivalent circuit; this effect is similar to that observed with paint coatings and related systems.

Keywords: *sol-gel, corrosion, ZrO_2 films*

Introduction

Inorganic coatings of a ceramic nature have been extensively used for the chemical protection of stainless steel (SS) and other metals and alloys[1]. Previous studies[2,3] have shown that ZrO_2 films prepared by sol-gel methods with densification at high temperature (800 °C for 2 h) act as efficient corrosion protectors of 316L SS in NaCl and H_2SO_4 solutions. The substrate chosen (316L SS) is a material widely used in marine applications and its specific resistance to pitting is associated with a relatively high (2.0 - 3.0%) Mo content[4]. However, this resistance can be considerably reduced after heat treatment and/or welding due to Mo depletion in the vicinity of delta ferrite formed during this process[4]. Thus, the deleterious effect caused by high temperature could be minimized by the use of these coatings. Therefore, it seemed interesting to investigate the effect of protective ZrO_2 coatings on the corrosion behavior of 316L SS treated at different temperatures.

The studies mentioned above[2,3] were carried out through potentiodynamic polarization curves (PPC) at 1 mV s^{-1}, furnishing the corresponding corrosion parameters for the system, but they were not able to elucidate the way in which these films behave. Additionally, the effect of the densification temperature on the behavior of the ZrO_2 films was not investigated, although there is evidence that this parameter affects the structure and porosity of this type of coating[5]. On the other hand, the application of the electrochemical impedance spectroscopy (EIS) technique for this kind of corrosion study allows the use of transfer functions from equivalent electric circuits for the fitting of the experimental data. This approach allows the inference of some of the physical characteristics of the system under study. Therefore, the present work describes studies of the corrosion behavior in chloride solutions of 316L SS and 316L SS coated with sol-gel derived ZrO_2 films treated at different temperatures. The studies were carried out through PPC and EIS measurements on the different samples in NaCl aqueous solutions.

Experimental

ZrO_2 coatings having an average thickness of 0.5 μm were deposited on 316L SS plates (3 cm x 3 cm) by the dip coating technique, using $Zr(OC_3H_7)_4$ as the precursor and isopropanol, glacial acetic acid and water as the solvent prepared under ultrasound[5]. Densification of the films was performed at different temperatures in the range of 450 to 800 °C for 2 h. The resulting coatings were characterized by SEM, XRD and FTIR. Other details have been described elsewhere[5]. Electrochemical measurements were carried out in 30 g dm^{-3} NaCl aqueous air saturated solutions, at 25 °C, using an electrochemical cell with a Teflon sample holder that exposed only 3 cm^2 of the surface to the electrolyte. The auxiliary electrode was a Pt foil, and a saturated calomel electrode (SCE) was used as a reference. The instrumentation employed was: a) an EG&G PARC mod. 273 potentiostat controlled by the EG&G PARC M342 software for PPC; and b) an EG&G PARC mod. 273 potentiostat and a Solartron FRA mod. 1255 controlled by the EG&G PARC M388 software for EIS. The fitting of the EIS data was performed using the program "Equivalent Circuit" written by B. A. Boukamp.

Results and Discussion

Figure 1 shows the potentiodynamic polarization curves for 316L SS samples as received and heat-treated in air at different temperatures, while Fig. 2 shows the same curves for samples of 316L SS coated with ZrO_2 films densified for 2 h at 450, 600, 700 and 800 °C, respectively. The corresponding values of the corrosion potential (E_{cor}), polarization resistance (R_p) and corrosion rate (v_{cor}) are presented in Table 1.

Table 1. Values of the corrosion potential (E_{cor}), polarization resistance (R_p) and corrosion rate (v_{cor}) for stainless steel and stainless steel coated with ZrO_2 films densified for 2 h at the temperatures indicated.

Sample	Heat Treatment	$-E_{cor}$	R_p	v_{cor}
	T/°C	/V	/kΩ cm^2	/mpy
316L SS	–	0.39	80	0.08
316L SS	450	0.35	223	0.04
316L SS	600	0.28	134	0.23
316L SS	700	0.27	782	0.04
316L SS	800	0.27	37	0.50
316L SS + ZrO_2	450	0.31	1207	0.02
316L SS + ZrO_2	600	0.19	619	0.04
316L SS + ZrO_2	700	0.20	425	0.08
316L SS + ZrO_2	800	0.12	749	0.06

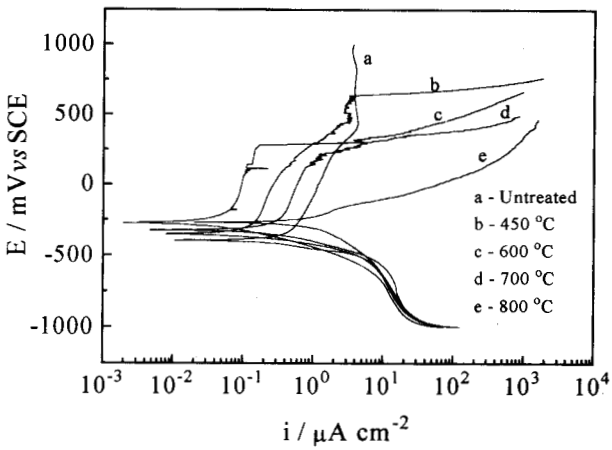

Figure 1. Potentiodynamic polarization curves at 1 mV s^{-1} in 30 g dm^{-3} NaCl solutions of 316L SS untreated and heat treated at different temperatures for 2 h.

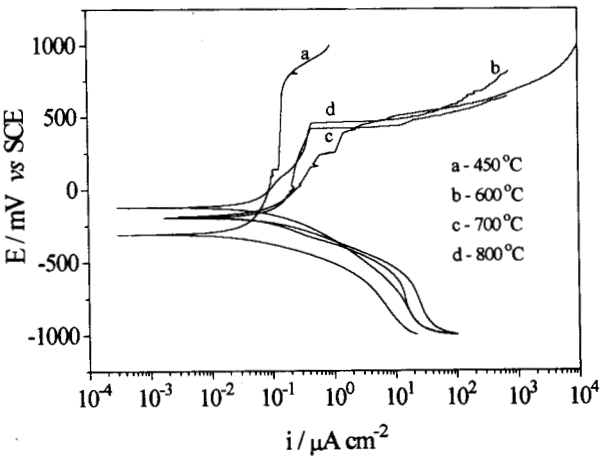

Figure 2. Potentiodynamic polarization curves at 1 mV s^{-1} in 30 g dm^{-3} NaCl solutions of 316L SS coated with ZrO_2 films densified at different temperatures for 2 h.

As expected[4], the results in Fig. 1 show that the sensitization of the SS by heat treatment leads to an increase in the corrosion rate (Table 1) that reaches a maximum at 600 °C, after which the chromium carbides formed tend to redissolve into the grains, as previously observed[6]. For the higher temperature (800 °C), the main effect observed is the total lack of pitting protection which was gradative for the other heat treatments. This is due to Mo depletion in the grains[4], resulting in a material extremely sensitive to both pitting and generalized or intergranular corrosion, thus showing a high v_{cor} value (Table 1). For the coated samples (Fig. 2) it is observed that although part of the original pitting protection is lost (shift of pitting potentials towards more negative values when compared with untreated SS), some of this property is present even for samples densified at 800 °C. Moreover, the corrosion rate remains low (Table 1) while the corrosion potential is shifted towards more noble values for the coated samples, in particular those densified at 800 °C. These are clear indications of the beneficial effect of the ZrO2 coatings on stainless steel substrates subjected to high temperature treatments.

Electrochemical impedance spectra were obtained at several potentials (and always more positive than the corrosion potential) for a large set of coated samples and for the untreated bare substrate. Figure 3 shows the spectra obtained at E = -0.30 V, -0.10 V and 0.10 V for a representative set of these samples. It should be noted that for each sample the impedance measurements were carried out from the most negative to the most positive potential, which means greater immersion time in the solution for increasingly more positive potentials.

The impedance behavior of the SS and of the coated SS samples densified at 450 °C can be described by the transfer function of an equivalent electric circuit analogous to the one commonly used to model coated metal-solution interfaces[7] (see Fig. 4a). In this modified Randles circuit[8,9], the capacitance of the double layer was replaced by a constant phase element (CPE_1), while R_s is the resistance of the surface film/solution interface, and R_{ct} the charge transfer resistance.

The behavior of the samples densified at temperatures greater than 450 °C can be described by the transfer function of a more complex equivalent electric circuit, involving a new constant phase element (CPE_2) related to the ZrO_2 film (see Fig. 4b). In this modified Mikhailowiskii equivalent circuit[8,9], R_f is the resistance of the ZrO_2 film.

The values of the different parameters in the transfer functions used to fit the data are listed in Tables 2, 3 and 4, where Q_1/a_1 and Q_2/a_2 are related to CPE_1 and CPE_2, respectively; in general, the agreement between the fitted and the experimental data was quite satisfactory ($\chi^2 < 4 \times 10^{-3}$). An analysis of the results shows that the parameters obtained through the two electrochemical techniques are consistent. So, the values of R_{ct} (Tables 2, 3 and 4) obtained by EIS are approximately of the same order of magnitude as the values of R_p (Table 1). Furthermore, the EIS data confirmed the discontinuity in the behavior of the samples densified at temperatures greater than 450 °C (whose fitting required the use of a more complex equivalent circuit), as already indicated by the larger displacement of E_{cor} from PPC experiments.

The EIS behavior of the coated SS sample densified at 450 °C indicates, when compared to that of the SS sample, that the film is discontinuous; thus, in practice it only reduces the exposed area of the SS substrate. On the other hand, the ZrO_2 film densification at temperatures greater than 450 °C leads to increasingly more compact films, which causes the appearance of a second EIS time constant related to porosity. This is clear in the phase angle *vs.* log$f$ plots (see Fig. 3), where a second capacitive contribution

Table 2. Values of the parameters associated with the transfer function of the electrical equivalent circuit (shown in Fig. 4a) used to fit the impedance behavior of the untreated stainless steel sample (see Fig. 3).

E/V	R_s/Ω	R_{ct}/MΩ	Q_1/ μF cm^{-2} $s^{\alpha-1}$	α1
-0.3	14	0.015	110	0.92
-0.1	14	0.080	91	0.92
0.1	14	0.22	74	0.93

Table 3. Values of the parameters associated with the transfer function of the electrical equivalent circuit (shown in Fig. 4a) used to fit the impedance behavior of the ZrO_2 coated stainless steel sample densified at 450 °C (see Fig. 3).

E/V	R_s/Ω	R_{ct}/MΩ	Q_1/ μF cm^{-2} $s^{\alpha-1}$	α1
-0.3	18	0.13	20	0.76
-0.1	18	1.7	28	0.74
0.1	18	2.9	24	0.76

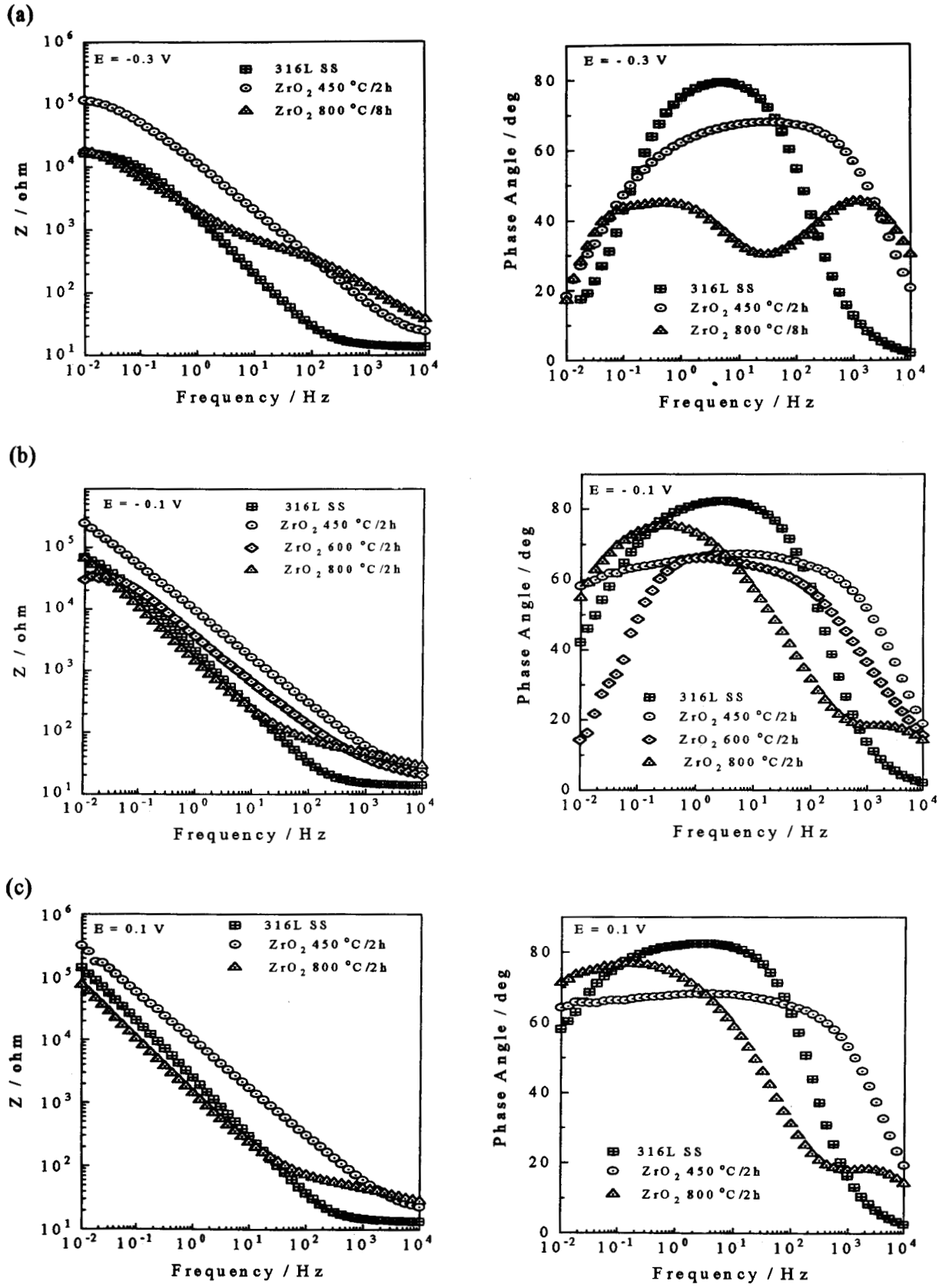

Figure 3. Impedance spectra obtained in 30 g dm^{-3} at different potentials of uncoated and ZrO_2 coated 316L SS densified at different temperatures for 2 h (as indicated).

Table 4. Values of the parameters associated with the transfer function of the electrical equivalent circuit (shown in Fig. 4b) used to fit the impedance behavior of the ZrO_2 coated stainless steel samples densified at 600 °C, 700 °C and 800 °C for 2 h (see Fig. 3).

Sample	E /V	R_s /Ω	R_f /Ω	R_{ct} /MΩ	Q_1 /μF cm^{-2} s$^{\alpha-1}$	α_1	Q_2 /μF cm^{-2} s$^{\alpha-1}$	α_2
600°C	-0.1	17	56	0.14	32	0.73	37	0.76
700°C	-0.1	15	17	0.07	50	0.66	3	0.89
700°C	0.1	17	77	0.26	8	0.88	23	0.64
800°C	-0.1	26	47	0.24	116	0.85	31	0.77
800°C	0.1	26	40	2.5	123	0.84	21	0.81
800°C	-0.3	22	534	0.03	155	0.63	17	0.71

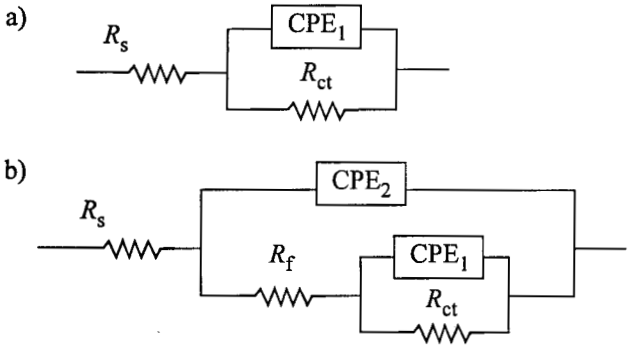

Figure 4. Equivalent electrical circuit used for the fitting of the impedance data: (a) modified Randles circuit; (b) modified Mikhailowiskii circuit.

evolves as the film densification temperature rises leading to a better defined porous film. A comparison of the EIS behavior of the films densified at 800 °C for 2 h and 8 h (see Fig. 3a) also indicates that the compactness of the film increases with the densification time; however, it should be pointed out that heat treatments for times longer than 2 h lead to less protective coatings, probably due to increased cracking as suggested by SEM observations.

These results, along with an evaluation of the corrosion behavior of the films when immersed in 30 g dm^{-3} NaCl solutions for long times (currently under way), will lead to a better understanding of the way the ZrO_2 sol-gel films act as protection coatings against the corrosion of heat treated 316L stainless steel.

Acknowledgments

The authors thank CNPq, FAPESP and CAPES for the support for this work.

References

1. D.A. Jones, *Principles and Prevention of Corrosion* (Maxwell-MacMillan, London, 1992).
2. P. de Lima Neto, M. Atik, M.A. Aegerter and L.A. Avaca, *J. Sol-Gel Sci. & Techn.* **1**, 177 (1994).
3. M. Atik, P. de Lima Neto, M.A. Aegerter and L.A. Avaca, *Proc. 44th ISE Meeting*, Berlin (1993).
4. A.J. Sedricks, *Corrosion of Stainless Steels* (John Wiley & Sons, New York, 1979).
5. M. Atik and M.A. Aegerter, *J. Non-Cryst. Solids* **147 & 148**, 813 (1992).
6. M. Atik, P. de Lima Neto, L. A.Avaca, M. A.Aegerter and J. Zarzycki, *J. Mater. Sci. Letters* **13,** 1081 (1994).
7. G.W. Walter, *Corrosion Sci.* **26**, 681 (1986).
8. I. Nowosz-Arkuszewska and M. Krawczyk, *Corrosion Sci.* **33**, 861 (1992).
9. E. Fréchette, C. Compère and E. Ghali, *Corrosion Sci.* **33**, 1067 (1992).