

CORROSION RESISTANT ZrO_2 SOL-GEL COATING ON STAINLESS STEELM. ATIK^{*,**} AND M.A. AEGERTER^{**}^{*} Laboratoire de Science des Matériaux Vitreux, Université des Sciences et Techniques du Languedoc, Place E. Bataillon, 34060 Montpellier, France^{**} Instituto de Física e Química de São Carlos, Universidade de São Paulo, Cx. Postal 369, 13560 São Carlos, SP, Brazil.

ABSTRACT

Corrosion resistant Sol-Gel ZrO_2 coatings deposited by dip coating technique on 316 L stainless steel sheets have been fabricated utilizing sonocatalysed precursors sols prepared from zirconium alkoxide $Zr(OC_3H_7)_4$, isopropanol, glacial acetic acid and water. Their composition varied between 0,025 to 0,9 mol/l ZrO_2 . The coatings have been characterized by X-ray diffraction, IR optical reflection, ellipsometry and scanning electron microscopy. When densified under a slow heat treatment thin coatings exhibit outstanding corrosion resistance as no weight change has been observed after 24 h chemical attack in H_2SO_4 aqueous solution at 81°C and 10 h oxidation treatment in air at 800°C. Thick films as well as films densified under rapid heat treatments tend to crack and are less corrosion resistant.

INTRODUCTION

Zirconia (ZrO_2) is a well known material which has superior properties such as high mechanical strength, chemical durability, alkali resistance, heat resistance against oxidation and refractoriness. Its use to prepare coatings on glass substrates has been reported with emphasis directed toward the understanding of the hydrolysis, polymerization and sintering processes as well as the obtention of good optical properties such as transparency and high reflection [1-4].

Very few reports have been published concerning the obtention and the characterization of ZrO_2 Sol-Gel thin films deposited on metallic substrates [5,6]. The stability and the optical appearance of ZrO_2 films coated on stainless steel sheets have been found strongly dependent of the choice of the sol precursors; the use of zirconium alkoxides leads to less stable films than Zr tetraoctylate and Zr tetrakis(acetylacetonate).

The oxidation resistance was tested in air at 800°C showing that the weight increase of a 130 nm thick coating of ZrO_2 on stainless steel sheet was not less than one half of that of the substrate alone after a 10h test [6].

Several works were recently presented at the 6th International Workshop on "Glasses and Ceramics from Gels" studying the properties of mullite coating on carbon steel [7], borosilicate on mild steel [8], methyltrialkoxysilane (MTOS) on steel [9] and ZrO_2 on stainless steel [10].

This paper presents a systematic study of the durability against chemical attack and thermal oxidation of zirconia thin coatings prepared from zirconium propoxide, isopropanol and water sols which have been previously sonocatalyzed and then deposited by dip coating technique on 316L stainless steel sheets. The corrosion resistance of the films was evaluated by measuring the weight change as a function of time under different heat and chemical treatments.

EXPERIMENTAL

Zirconium sols were prepared by dissolving zirconium propoxide $Zr(OC_3H_7)_4$ in isopropanol (C_3H_7OH) and adding under ultrasonic irradiation (sonicator W385 Heat Systems-Ultrasonics, Inc., 20 kHz) glacial acetic acid and excess water to complete the hydrolysis. The ultrasonic procedure was carried on

until obtaining clear and transparent sonosols. The resulting sols were then left undisturbed for four weeks at room temperature.

The substrates were 316L stainless steel sheets, degreased ultrasonically in acetone. They were dipped into the solutions and withdrawn at a speed of 10 cm/min and then dried at 40°C for 15 minutes. The samples were then heat treated at 400°C for 1 hour in air to remove the organic residues.

Two tests have been applied for measuring the oxidation and corrosion resistance:

Test A: the samples were first densified at various temperatures and then placed in a 15% H_2SO_4 aqueous solution at 72-89°C for different periods of time (up to 32 hours). The determination of the total chemical corrosion was determined by measuring the weight loss of the samples due to a slow leaching of the coatings.

Test B: the oxidation test was carried out in air typically at 800°C for 2 to 10 hours. The oxidation was determined by measuring the weight increase of the coated sheets resulting from the formation of various oxide compounds.

RESULTS AND DISCUSSION

The thickness of ZrO_2 films deposited on 316 stainless steel and densified after a heat treatment in air at 800°C for 9 h is shown in figure 1 as a function of the ZrO_2 sol concentration. The values have been measured by ellipsometry (Rudolf S 2000); they increase linearly with the concentration of ZrO_2 .

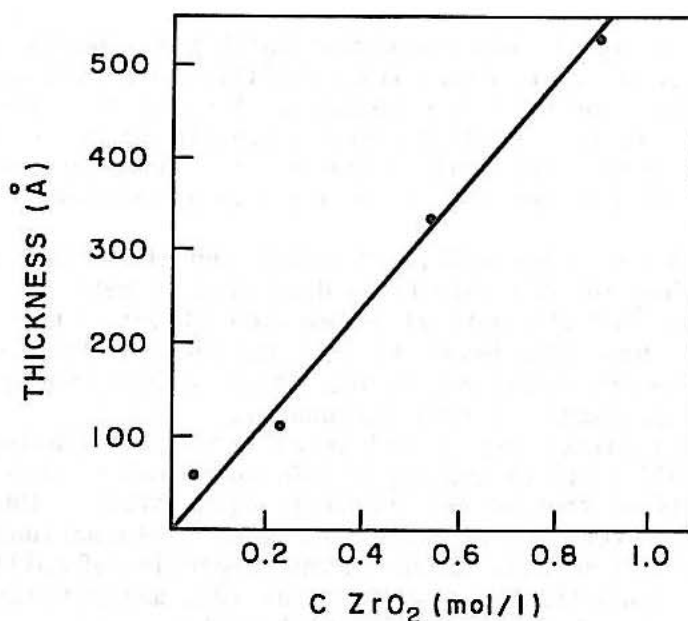


Fig. 1. Thickness of single layers of ZrO_2 deposited on both sides of 316L stainless steel sheet by dip coating technique ($v=10$ cm/min) and then densified in air at 800°C during 9 h versus ZrO_2 sol concentration.

Measurements of reflection in the IR region of unsintered samples show characteristic OH bands at ~ 3600 cm^{-1} , Zr-O-C groups at 1476.8 and 1452.4 cm^{-1} and Zr-O-Zr at 665.7 cm^{-1} . During sintering the OH and Zr-O-C bands disappear and the Zr-O-Zr band increases strongly. X-ray diffraction data has confirmed that the films densified at 800°C have the tetragonal ZrO_2 structure (111 peak at $d=2.98\text{\AA}$).

The effect of air oxidation on samples prepared with different ZrO_2 sol concentration (and consequently different film thickness) is shown in figure 2. All the samples have been heat treated at 800°C during 6 h but their sintering has been realized either under a rapid heating process (RHP, direct

introduction of the samples in preheated furnace) or a slow heating process (SHP, 5°C/min from 25 to 800°C with 1 h holding time at 400°C to complete the elimination of the organic compounds). The rate of oxidation, observed as a weight gain, increases with the ZrO₂ sol concentration for RHP while no weight change is observed using SHP. Apparently the oxidation resistance does not depend of the solution concentration or film thickness but is probably linked to the films morphology and their structural homogeneity. Thermal stresses, cracks, etc. are likely to develop during a rapid heating, particularly for thicker coatings.

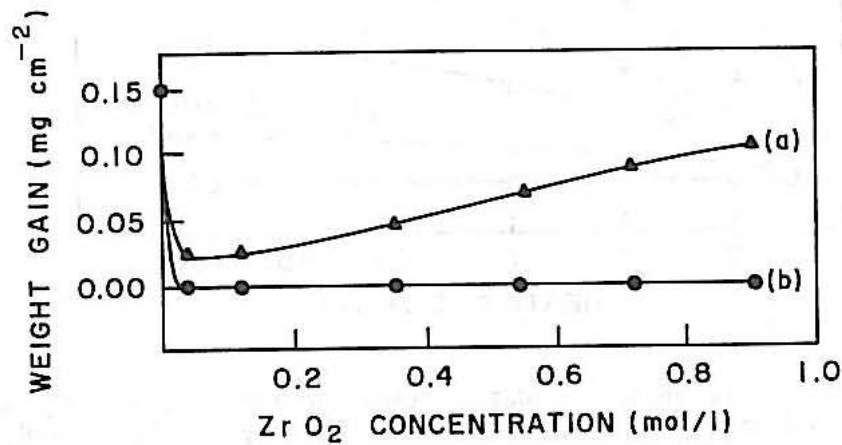


Figure 2. Weight increase of ZrO₂ coated 316L stainless steel measured after air oxidation treatment at 800°C/6 hrs versus ZrO₂ sol concentration a) rapid heating process b) slow heating process (see text).

The effect of time on the oxidation treatment is shown in figure 3. Curve a, b and c show the weight gain of uncoated samples at 950, 870 and 800°C, which is seen to increase with the temperature. ZrO₂ coating of 35 nm thickness tested at 800°C sintered under RHP (curve d) shows a reduction of the oxidation rate and confirms that this fast densifying process introduces defects which impede a perfect protection. The effect is more pronounced for thicker coatings.

The samples sintered under SHP do not exhibit any weight gain up to 8 h heat treatment (thickness of 35 nm) and up to at least 10 h for smaller thicknesses confirming the above conclusions.

Figure 4 shows two SEM micrographs taken for 5,5 nm thick ZrO₂ sintered using both processes. The surface rapidly heated and kept only 10 minutes in the furnace at 800°C shows clearly regions where oxidation can take place easily. On the contrary the surface slowly heated and kept 9 hours at 800°C is smoother and is better protecting the substrate.

Figure 5 shows a series of measurements made at high temperature indicating that the films have however a limited protection and do not protect the stainless sheet indefinitely. These results clearly show that the films only delay the oxidation process and that, after a certain time or for higher temperatures, the films are not efficient at all.

The chemical corrosion in H₂SO₄ aqueous solution is shown in figure 6 where the weight loss of the samples is plotted as a function of time for different experimental conditions.

The weight loss of uncoated samples (curve a, b, c) increases with time and temperature. The weight loss of coated samples sintered under SHP shows a drastic reduction which depends of the thickness of the films. Thick coatings (≥ 55 nm) provide protection up to 10 h and thin coatings (<40 nm)

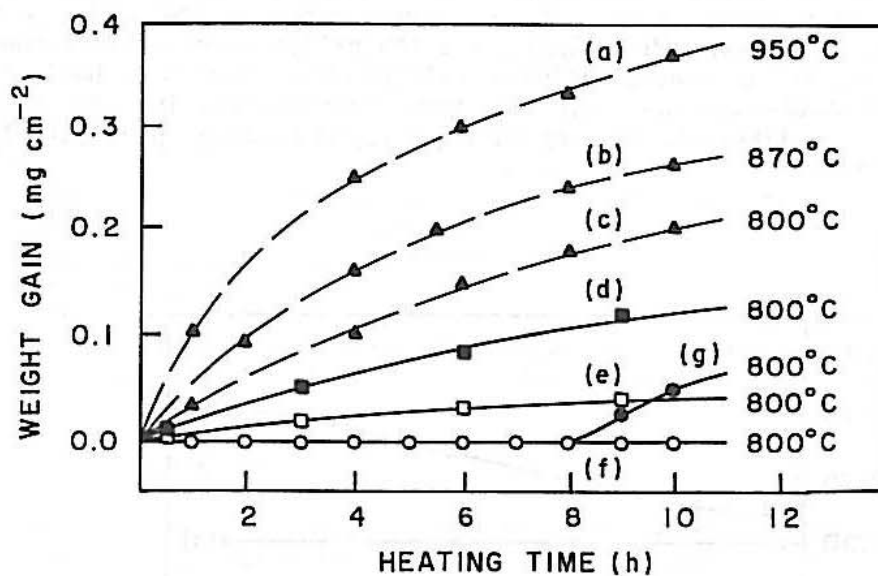


Figure 3. Weight gain versus oxidation time in air. a), b), c) uncoated substrates tested at 950, 870 and 800°C respectively, d) 35 nm ZrO_2 coated sample sintered under RHP and tested at 800°C, e) idem for 5,5 nm coating, f) and g) 5,5 and 35 nm respectively coated samples sintered under SHP and tested at 800°C.

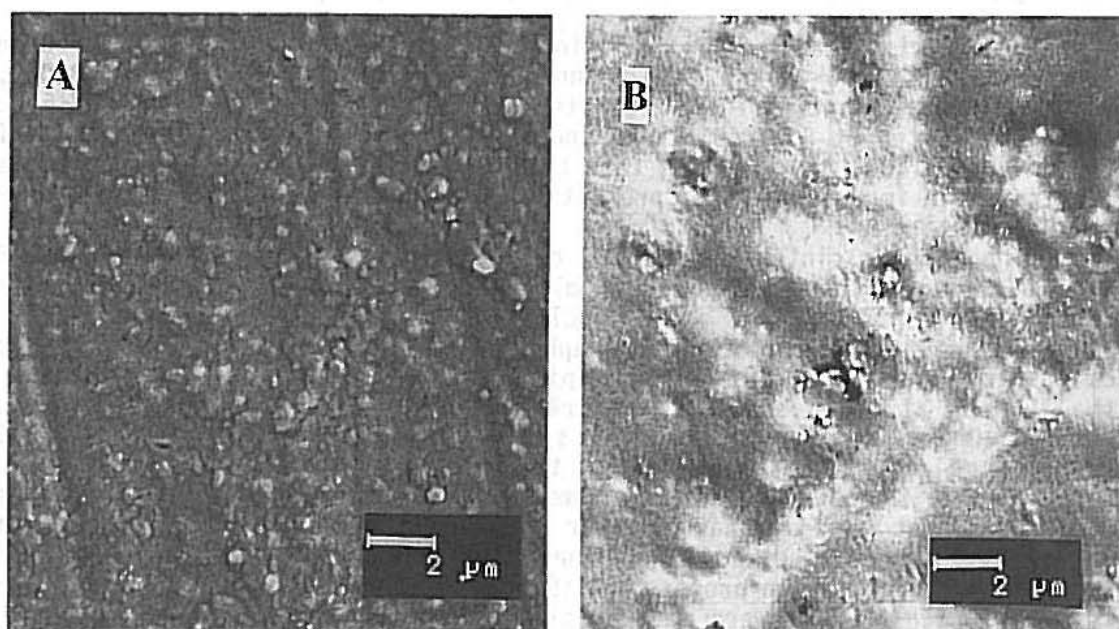


Figure 4. SEM micrographs of 5,5 nm thick ZrO_2 coating a) sintered under SHP and kept at 800°C during 9 h; b) sintered under RHP and kept 10 min at 800°C.

do not present any chemical attack up to 24 h at 81°C. No test has been realized for coatings sintered under RHP. The figure once again shows that the

SHP leads to much more homogeneous coatings. However thicker coatings, even densified under SHP, present a chemical corrosion after a certain time of treatment.

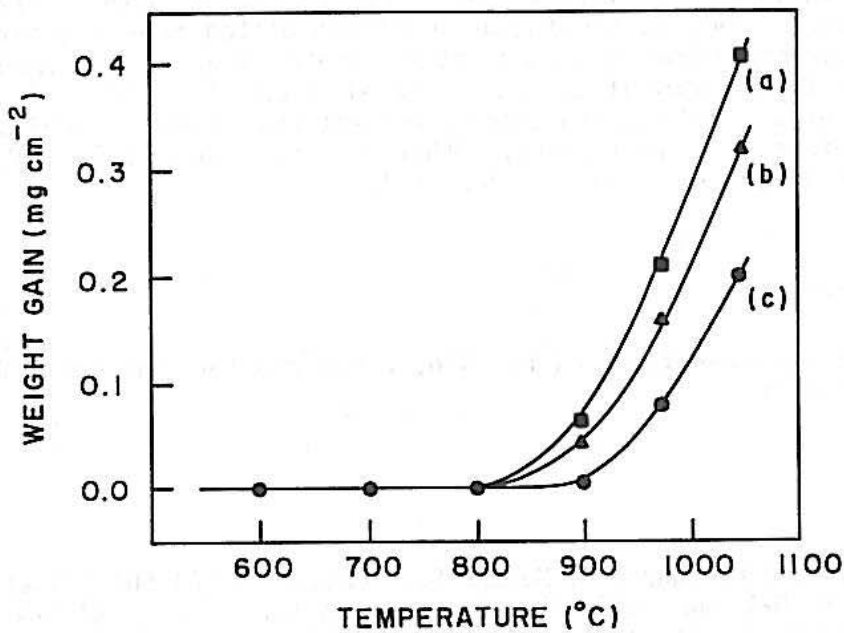


Figure 5. Weight gain of 5,5 nm ZrO_2 coating sintered under SHP, measured after oxidation in air at different temperatures. Time of heat treatment a) 9h, b) 6h, c) 3h.

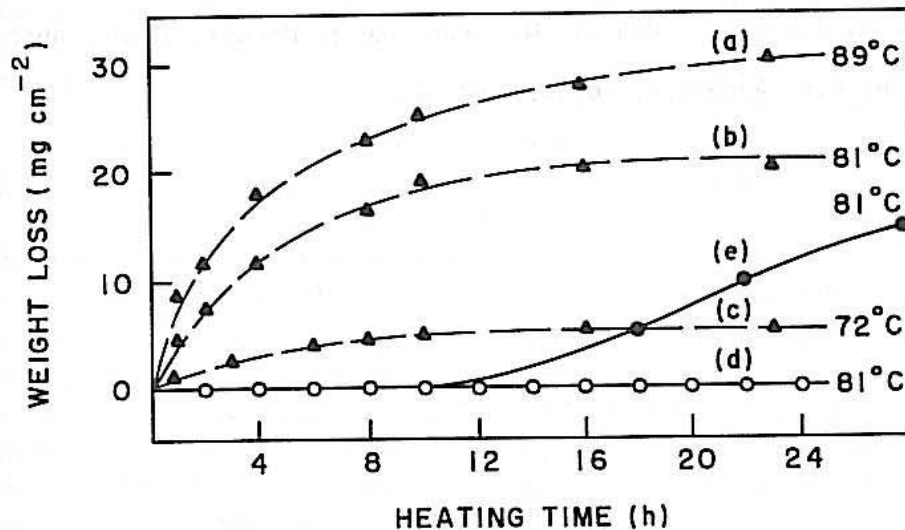


Figure 6. Weight loss of samples as a function of immersion time in 15% H_2SO_4 aqueous solution. a), b) and c) uncoated samples tested at 72, 81 and 89°C respectively d) ZrO_2 coated substrate sintered under SHP and tested at 81°C with films having a thickness <40 nm; e) same as d) but for a film of 55 nm.

CONCLUSION

Sol-gel ZrO_2 coatings obtained from sonocatalyzed hydrolysis of Zr propoxide have been deposited on 316L stainless steel sheet by dip coating technique. The films densified at $800^\circ C$ are crystalline with a tetragonal structure. When slowly sintered under a $5^\circ C/min$ heated rate they provide an outstanding corrosion protection against air oxidation up to at least 10 hours at $800^\circ C$ and H_2SO_4 chemical attack up to at least 24 h at $81^\circ C$. Films densified under a rapid heating process present cracks and thermal stresses and are therefore less protective. Other systems such as $SiO_2, Al_2O_3, SiO_2-Al_2O_3$ and SiO_2-TiO_2 are presently under study.

ACKNOWLEDGEMENTS

This research has been financed by CNPq, Finep and the Program RHAE - New Materials (Brazil).

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