Ormocer (ZrO_2-PMMA) Films for Stainless Steel Corrosion Protection

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Abstract. The chemical protection of 316 L stainless steel coated with ORMOCER coatings of polymethylmethacrylate (PMMA) and ZrO_2 has been verified. The coatings were dip-coated on the substrates from sols prepared by mixing zirconium propoxide ($ZrOC_3H_7)_4$, isopropanol (C_3H_7OH), glacial acetic acid (CH_3COOH), polymethylmethacrylate and water under application of ultrasounds. The films were heat treated between 40 and 300°C in air up to 20 h. Their morphology was studied by electron scanning microscopy (SEM). Their anticorrosion behavior was analysed in $0.5M$-H_2SO_4 solutions through potentiodynamic polarization curves at room temperature.The influence of the sol preparation, coating composition as well as of the duration and temperature of heat treatments on the corrosion parameters is reported. The films act as geometric blocking layers against the corrosive media and increase the lifetime of the substrate up to a factor 30.

Keywords: ormocer, coatings, chemical protection, stainless steel, PMMA-ZrO_2, corrosion

1. Introduction

Sonocatalyzed sol-gel coatings of ZrO_2, SiO_2, SiO_2-TiO_2 and SiO_2-A_2O_3 compositions deposited on stainless steel present a high resistance to corrosion [1–5]. Their properties were studied by gravimetric and electrochemical techniques, under oxidizing atmosphere (up to 800°C) and into NaCl and H_2SO_4 aqueous solutions, respectively. All these films increase the protection of the metallic substrates.

Recently, the sol-gel method has been used to develop a new class of materials called polycerams or ormocers [6, 7]. A key factor is the incorporation of organic groups linked to the inorganic backbone formed by hydrolysis and condensation of alkoxides. The possibility combining properties of organic and inorganic networks in an unique material is an old challenge starting with the beginning of the industrial era. These new systems show interesting properties with respect to applications in optics, electronics, ionics, mechanics and biology.

The present study reports on the corrosion protection in acidic media ($0.5M$ H_2SO_4) of hybrid coatings of PMMA-ZrO_2 composition deposited on 316L stainless steel by dip-coating technique using essentially sonocatalyzed sol. The influence of the preparation and composition of the starting solutions and coatings heat treatment on the corrosion parameters are investigated.

2. Experimental Procedure

The PMMA-ZrO_2 ORMOCER sol was prepared by first diluting commercially available zirconium isopropoxide $Zr(OC_3H_7)_4$ in isopropanol (C_3H_7OH) to which was added glacial acetic acid (CH_3COOH). The concentration of the starting alkoxide solution was 0.5 mol/l and the volume ratios H_2O/C_3H_7OH and H_2O/CH_3COOH were 1 and 2, respectively. The solution was homogenized with ultrasound irradiation produced by a transducer immersed in the mixture (Heat Systems Ultrasonics W 385 Sonicator, 20 kHz). Water with polymethylmethacrylate (PMMA, with molecular weight ~400 000) was then added under ultrasound to complete the hydrolysis until a clear and transparent sonosol was obtained. The relative volume of PMMA in the sol was estimated in relation to the total volume of PMMA and Zr propoxide and was varied between 0 and 100%. The resulting sols can be kept for five weeks at room temperature without gelification.

The 316L stainless steel substrates (30 mm × 20 mm × 0.4 mm) chosen for this study had the following composition (weight%): 67.25 Fe, 18.55 Cr, 11.16 Ni, 2.01 Mn, 0.026 Cu, 0.15 Si and 0.28 C. They were degreased ultrasonically in acetone and rinsed with distilled water. They were dipped into the solution and withdrawn at a speed of 10 cm/min. The gel coated substrates were dried in ambient atmosphere for 15 min and then heat-treated between 40 and 300°C in air for different heating times to obtain adherent and dense coatings. The thickness of one PMMA-ZrO_2 coating after heat-treatment in air at 300°C for 10 hours was about 0.2 μm, as determined with a Taylor Hobson Talystep.

The potentiodynamic polarization curves were carried out in deaerated (0.5*M*) H_2SO_4 at 25°C using a computerized PAR model 273 Potentiostat/Galvanostat with specimens having 1 cm^2 test area. A saturated calomel electrode (SCE) was used as reference and a Pt foil served as the auxiliary electrode. The potentiodynamic measurements were initiated at −0.7 V vs. SCE and scanned continuously in the anodic direction at 1 mVs^{-1}. The data were analysed with the PAR 342 corrosion measurements software, which furnishes several electrochemical parameters of the system under study.

The composition and the morphology of the coatings have been analysed using a Zeiss 960 scanning electron microscope (SEM) coupled to a QX 2000 EDX analyser.

3. Results and Discussion

Figure 1 shows typical results of potentiodynamic polarization curves obtained with uncoated stainless steel (a) and substrates coated with ormocer film of different compositions labelled in volume % of PMMA and heat-treated at 200°C for 10 hours (b, c, d). The curves show that the PMMA-ZrO_2 coatings affect both the cathodic and anodic branches and exhibit typical active to passive characteristics. In the cathodic branches, which correspond to the hydrogen evolution reaction $2H^+ + 2e^- \rightarrow H_2$, the slope of the reaction is maintained, but the value of the corrosion currents for the coated samples (b, c, d) are clearly shifted to smaller values, indicating that the films act as geometric blocking layers against exposure to the corrosive media. The anodic branches show that all coatings have a strong effect on the current density in the passive region. For 63 vol% PMMA the current values are reduced by almost

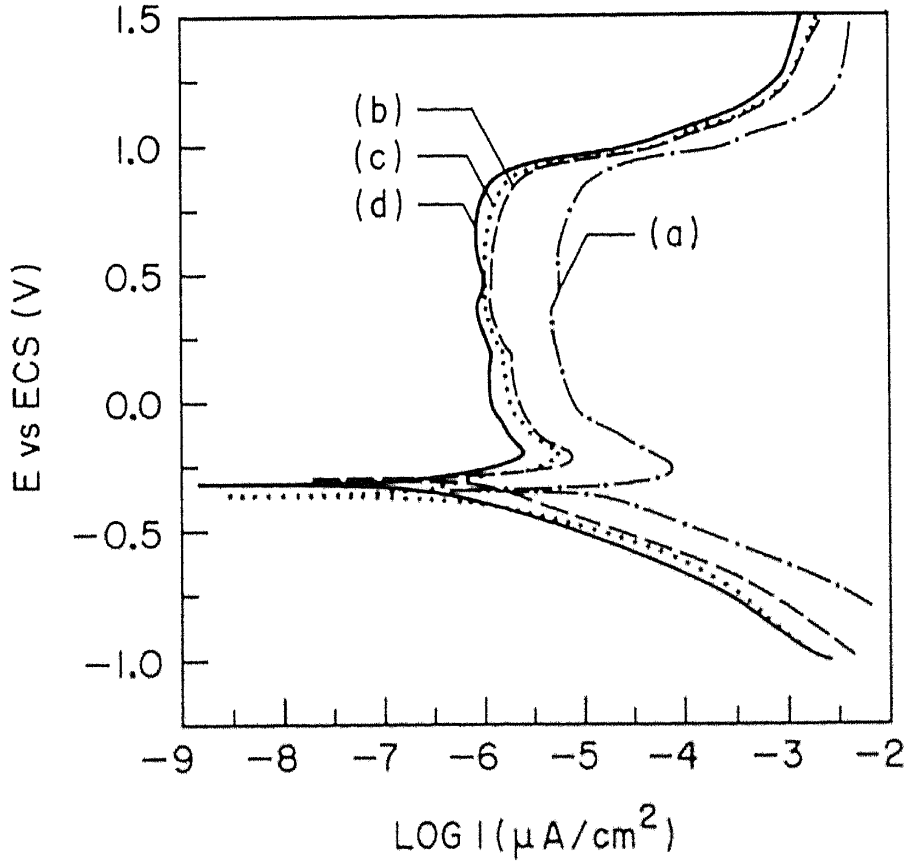

Figure 1. Potentiodynamic polarization curves measured in deaerated 0.5*M* aqueous H_2SO_4 at 25 C: (a) uncoated and untreated 316L stainless steel; SS coated with PMMA-ZrO_2 with heat treatment at 200 C for 10 hours with PMMA (in vol%) of 26% (b), 51% (c) and 63% (d)

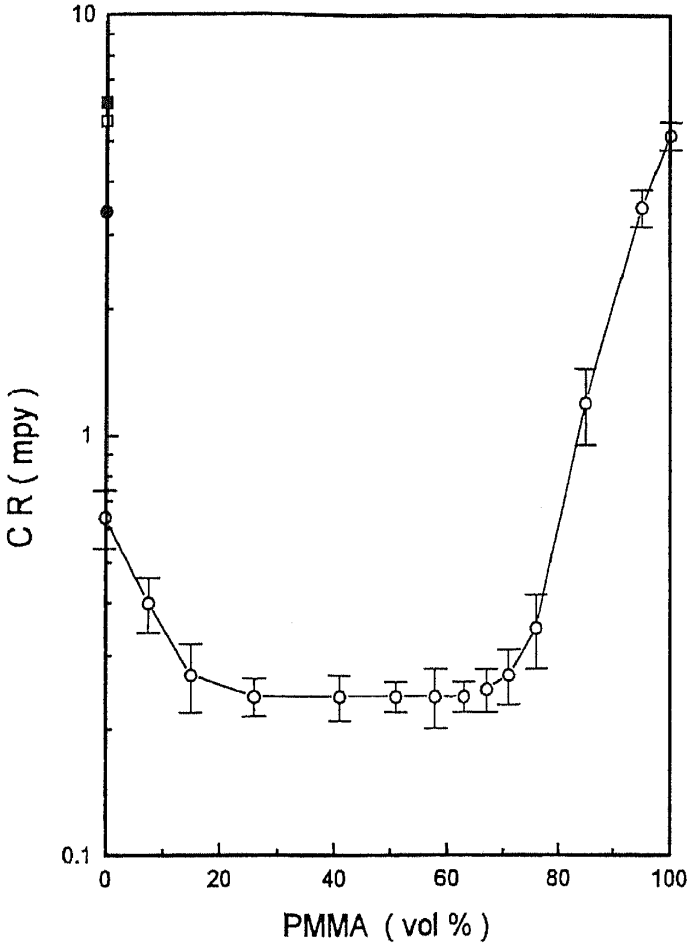

Figure 2. (○) Corrosion rate, CR (mpy), of PMMA-ZrO_2 coatings heat-treated at 200°C/10 h measured in 0.5*M* H_2SO_4 solution at 25°C as a function of the PMMA content (vol%). (■): Same for as received stainless steel (without any coating), (□): Same for stainless steel heat treated at 200°C/10 h (without coating) and (●): SS coated with pure ZrO_2 at 800°C/2 h in air and measured in 15% H_2SO_4 [4].

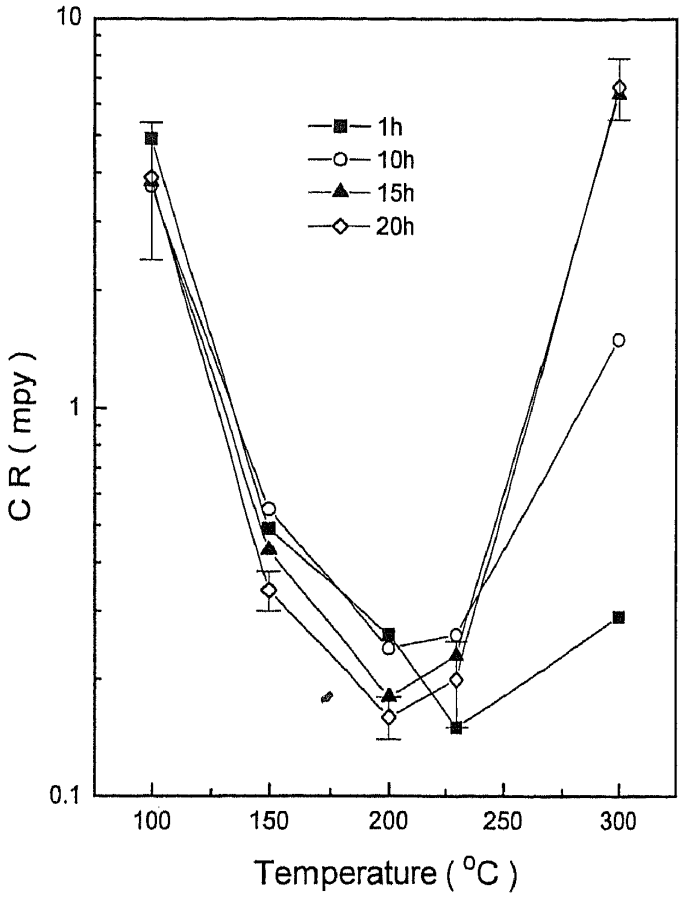

Figure 3. Variation of the corrosion rate, CR (mpy), measured in 0.5*M* H_2SO_4 solution at 25°C of 316L stainless steel coated with PMMA(63 vol%)-ZrO_2 vs heat treatment temperatures for different heat-treatment time in air.

one order of magnitude. The critical current density i_c for passivation is also reduced indicating that the coating increases the ease of passivation.

The corrosion rate of the ormocer coatings heat-treated at 200°C for 10 hours in air was investigated as a function of the sol PMMA-ZrO_2 composition and is shown in Fig. 2. Pure zirconia coatings present a value of the corrosion rate equal to 0.65 mpy. Hybrid PMMA-ZrO_2 coatings well protect the metallic surface in the range 20 < PMMA < 70 vol%, where the corrosion rate is lower and pratically constant (0.25 mpy). At the present stage, it is worthwhile to compare these results with the value of 3.4 mpy reported for crystalline ZrO_2 coatings densified at 800°C for 2 h in air and tested in 15% H_2SO_4 solution (concentration three times higher) [4]. The values for the ormocer coatings are considerably lower and these materials protect better this stainless steel substrate. In relation to an as received substrate the corrosion rate is reduced from 7.5 to 0.25 mpy. The resistance of stainless steel to corrosion is therefore increased by a factor ~30. Substrates coated with amounts of PMMA larger than 80% in volume show higher corrosion rate and pure PMMA coatings do not protect the substrates at all.

The influence of the time and temperature of the heat treatment of the coatings on the corrosion rate was determined for films prepared from a sol having a 63 vol% PMMA and the results are shown in Fig. 3. The coatings heat-treated at low temperature present a high corrosion rate and are probably not densified and/or polymerized. The same samples heat-treated in air at temperature higher than 250°C do not present a good resistance against corrosion and rapidly deteriorate if the heat treatment time is increased. The lowest corrosion rates were found for coatings heat-treated between 200 and 230°C with a treatment of 20 to 1 h respectively. Table 1 summarizes some of the best results of the electrochemical corrosion parameters derived from the polarization curves. Coatings heat treated at 230°C present the lowest corrosion rate and increase the lifetime of the substrate by a factor of about 30. These coatings are more effective in increasing the corrosion

Table 1. Corrosion parameters determined from the potentiodynamic curves for stainless steel 316L and SS coated with PMMA(63 vol%)-ZrO_2 at 200 and 230°C for 10 hours measured in (0.5*M*) H_2SO_4 solutions at 25°C: corrosion potential E_{corr} (mV); polarization resistance R_p (KΩcm^2) and corrosion rate CR (mills per year. MPY).

Sample	$-E_c$ (mV)	R_p (KΩcm^2)	C.R. (MPY)
316L (SS) as received	298	0.7	7, 5
SS + ZrO_2 + PMMA(200°C/10 h)	335	96, 8	0, 13
SS + ZrO_2 + PMMA(230°C/10 h)	357	49, 19	0, 39

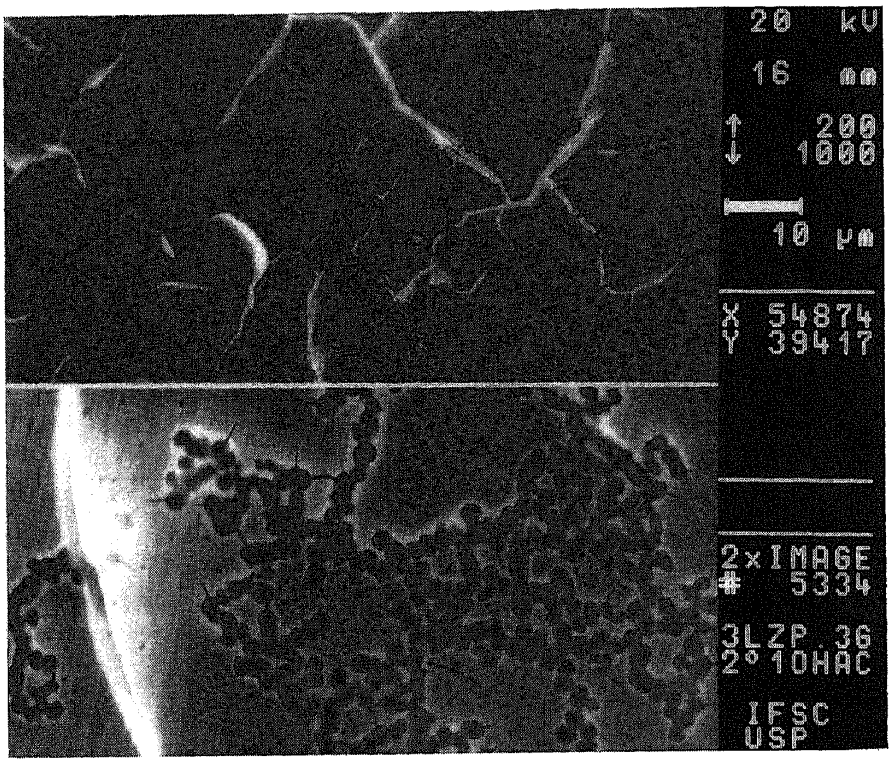

Figure 4. SEM micrographs (upper part) and EDX mapping of Zr (lower part) micrographs of a PMMA(63 vol%)-ZrO_2 coatings heat-treated at 200°C for 10 h. The white dots in the lower picture indicate Zr location.

(*Continued on next page.*)

resistance of the substrates exposed to H_2SO_4 solution than those coated with a sol-gel pure crystalline ZrO_2 layer [8] heat-treated at 800°C, since the layers are no longer porous.

The morphology of the surfaces was examined by scanning electron microscopy (SEM) and EDX analysis (Fig. 4). The upper part is a SEM micrograph of an hybrid coating PMMA(63 vol%)-ZrO_2 after heat-treatment at 230°C for 10 h and shows that the coating is made of large particles (black dots) imbedded in an amorphous structure. The lower part is an EDX mapping of Zr (white dots) which reveals that the above large particles are in fact essentially polymeric. These particles grow with the temperature and heat-treatment time and are already present as deposited coatings, either aglomerated as in the picture or dispersed. Measurements are underway to determine if the presence of these particles is due to a too high molecular weight of the PMMA (400 000), an effect of the ultrasonic irradiation which through cavitation phenomena may already polymerize the PMMA into particles or a poor initial dissolution of PMMA. These almost pure polymeric particles are not desirable and their elimination should decrease the values of the corrosion rate to much lower values. These particles act as weak spots for the corrosion since pure PMMA material does not protect against corrosion in acidic media (Fig. 2). Figure 5 shows the modification of the morphology of the coating observed by SEM for an ormocer coating heat-treated at 200°C and 300°C. The origin of the deterioration of the coatings at 300°C already discussed (Fig. 3) is clearly revealed by the presence of cracks which act as connecting pathways for the corrosive media.

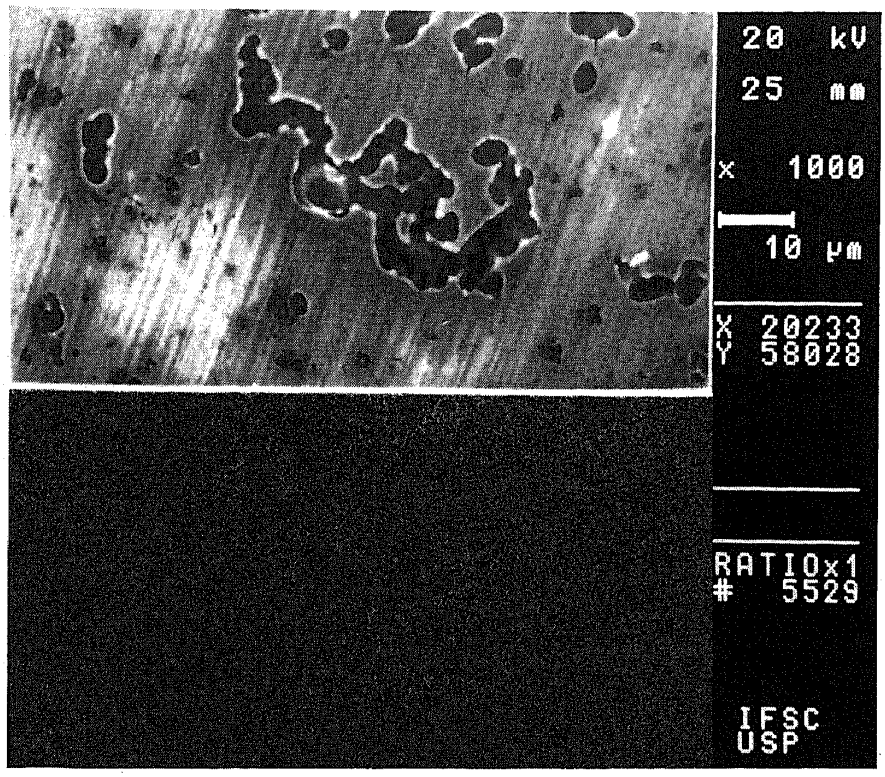

Figure 4. (*Continued.*)

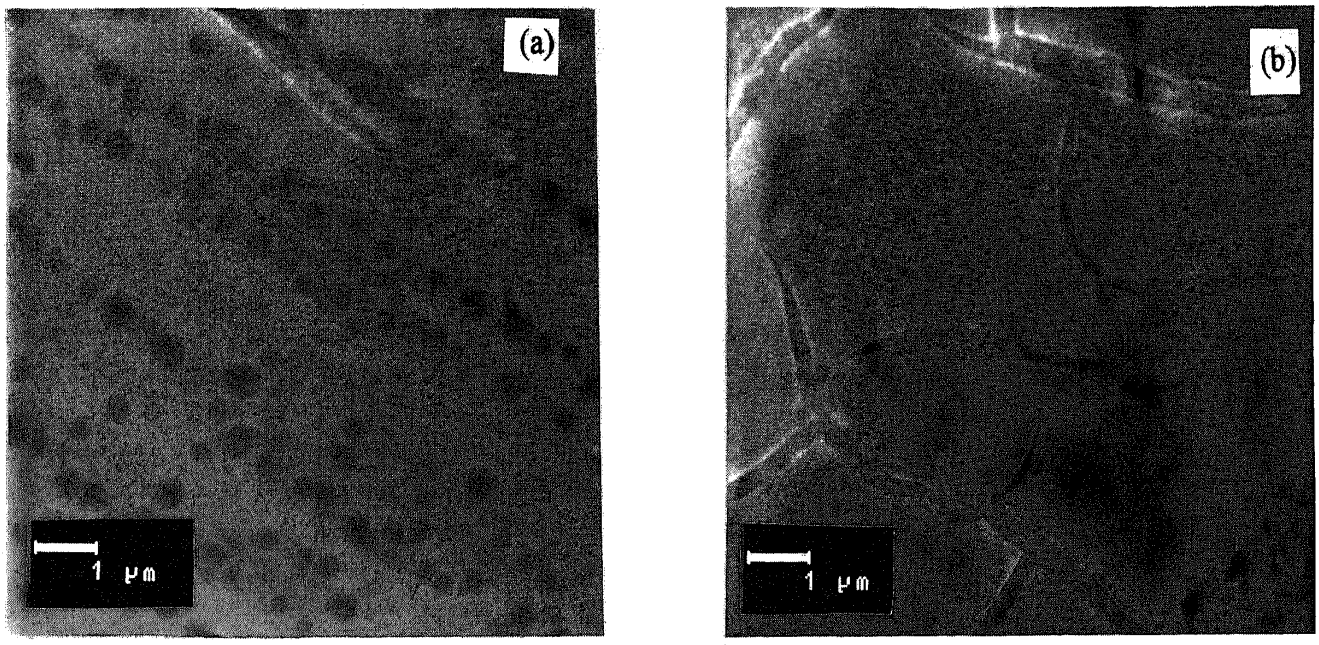

Figure 5. SEM micrographs of PMMA(63 vol%)-zirconia film after heat-treatment in air at 230 (a) and 300°C (b) for 10 h, respectively.

4. Conclusion

Hybrid PMMA-Zirconia sols were synthesized under ultrasonic irradiation and used to dip-coat ormocer coatings on 316L stainless steel. Coatings heat treated in air between 200 and 230°C for 1 to 10 h respectively increase the corrosion resistance of the substrate in the aggressive (0.5*M*) H_2SO_4 acid solution. The lifetime of an as received substrate is increased by a factor of 30. The presence of micrometer size polymeric particles (still of unknown origin) is probably a limiting factor of the corrosion resistance as these particles are weak spots for the corrosive attack. A lifetime increase higher than 30 should be obtained by a better control of the sol preparation. Nevertheless these coatings are better than those of pureZrO_2 which had to be densified

at 800°C/2 h [4]. However the presence of polymeric species limits the use of these ormocer coatings to temperatures not higher than 250°C.

Acknowledgments

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