

Improvement of Corrosion Resistance of Stainless Steel by $\text{ZrO}_2\text{-SiO}_2$ Sol-gel Coatings

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Abstract. $\text{ZrO}_2\text{-SiO}_2$ coatings deposited on 316 L stainless steel were prepared to protect chemically the substrates by sol-gel process using $\text{Zr}(\text{OC}_3\text{H}_7)_4/\text{Si}(\text{OC}_2\text{H}_5)_4$ as precursors. The influence of the $\text{ZrO}_2\text{-SiO}_2$ coatings on the corrosion resistance of the 316 L stainless steel was evaluated with the potentiodynamic polarization curves in deaerated 15% H_2SO_4 solutions at 25, 40 and 50 °C. Comparative test was performed on uncoated one. The values of the electrochemical parameters explain how. $\text{ZrO}_2\text{-SiO}_2$ films increase the resistance of stainless steel against corrosion.

1. Introduction

Inorganic coatings with a vitreous structure have been used as protective coatings for metals and alloys [1]. They improve the chemical and physical properties of the metal surfaces against corrosion and wear without altering the original properties of strength and toughness of the substrate [2]. Traditionally, ceramic coatings have been employed for extending the life on service of steels exposed to oxidation conditions up to 850 °C [2]. Coatings of SiO_2 , TiO_2 and ZrO_2 have been used in different corrosive environments, and can efficiently protect alloyed steels and super-alloys up to 1100 °C. SiO_2 inhibits well corrosion in a wide range of pH [3]. SiO_2 film can be also considered potential candidates for protecting corrosive applications. However, SiO_2 film tends to lose strength by alkali [4]. ZrO_2 is a well-known material that has excellent properties, such as high mechanical strength, chemical durability, and alkali resistance and can be used to protect chemically metal substrates from acid and oxidations [5]. The dip coating is one of the most promising applications of the sol-gel process [6]. This method offers potential advantages over traditional techniques, because coatings with various single component and multi-component oxides have already been elaborated at low temperature [7,8].

In this work, we present the results of an electrochemical corrosion study of $\text{ZrO}_2\text{-SiO}_2$ film on the 316L stainless steel prepared by dip-coating. The corrosion characteristics of the samples were evaluated through potentiodynamic polarization curves obtained in deaerated 15% H_2SO_4 solutions at 25, 40 and 50 °C.

2. Experimental Procedure

$\text{ZrO}_2\text{-SiO}_2$ coatings were obtained by dissolving $\text{Si}(\text{OC}_2\text{H}_5)_4$ and $\text{Zr}(\text{OC}_3\text{H}_7)_4$ in $\text{C}_2\text{H}_5\text{OH}$. The molar ratios of $\text{ZrO}_2/\text{SiO}_2$ were 30/70 and 50/50. The molar ratio of H_2O , $\text{C}_2\text{H}_5\text{OH}$ and $\text{HCl}/\text{alkoxide}$ was 50, 1.0 and 0.3, respectively. $\text{Si}(\text{OC}_2\text{H}_5)_4$ was at first partially hydrolyzed by dropping it into the solution of HCl , $\text{C}_2\text{H}_5\text{OH}$ and $\text{H}_2\text{O}/\text{Si}(\text{OC}_2\text{H}_5)_4$, of which the molar ratio was 0.3, 1 and 1, respectively. After this solution was stirred for 120 min, $\text{Zr}(\text{OC}_3\text{H}_7)_4$, the residual HCl , $\text{C}_2\text{H}_5\text{OH}$ and H_2O were added drop by drop, and then stirred for 120 min at 25 °C. The $\text{ZrO}_2\text{-SiO}_2$ films were coated by dipping

(withdrawn at 10 ± 0.1 cm min) on polished 316 L stainless steel sheets, which were previously cleaned in ultrasonic bath, rinsed with ethanol and heated at 500°C for 1 h. This treatment oxidizes slightly surface. The oxidation enhances the adhesion of the coating. After being dried for 30 min at 50°C , they were heated at 500°C for 1 h.

The cross sections of ZrO_2 - SiO_2 films were observed using SEM. The content of ZrO_2 - SiO_2 in film was done by the electrochemical measurements which are convenient and precise methods to evaluate the corrosion of a material in a given mediums. The chosen mediums were 1, 2 and 3 M of aqueous NaCl solutions. It has been carried out with freshly prepared samples in deareated 15% H_2SO_4 solutions at 25, 40 and 50°C using a computerized PAR 273 Potentiostat/Galvanostat. A saturated calomel electrode (SCE) was used as reference and a Pt foil served as the auxiliary electrode. The working electrodes were immersed 1 cm into the solution. The potentiodynamic measurements were initiated at -0.7 V and scanned continuously toward the anodic direction at 1 mV/s.

3. Results

ZrO_2 - SiO_2 films heated at 500°C for 1 h were amorphous. At higher temperature, crystalline ZrO_2 of tetragonal form was precipitated in the films.

Fig. 1 shows SEM micrographs of the cross section of ZrO_2 - SiO_2 films heated at 500°C for 1 h. The thickness of ZrO_2 - SiO_2 films were about 0.5 and $0.8\ \mu\text{m}$. ZrO_2 - SiO_2 films was crack free and had smooth surface, which was coated on the 316 L stainless steel sheet after a single deposition and heat treatment (Fig. 1 (a, b)). ZrO_2 - SiO_2 film heated at 500°C , of which the thickness is $\geq 1.0\ \mu\text{m}$, presented cracks (Fig. 1 (c)) However, ZrO_2 - SiO_2 coatings, of which the thickness is thinner than $0.8\ \mu\text{m}$, were continuous and visually crack free.

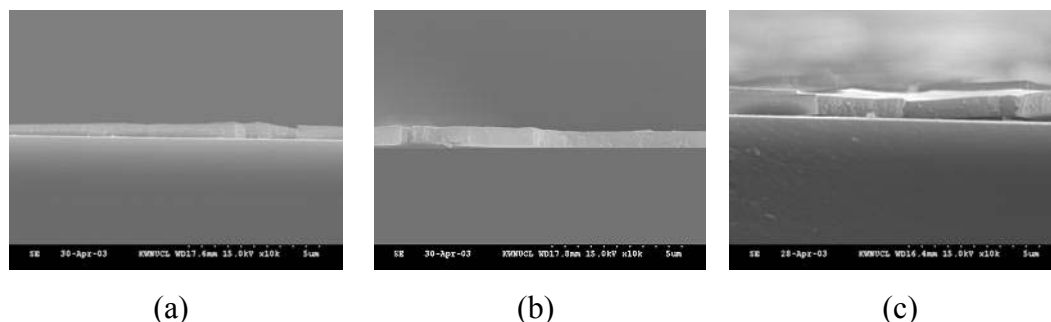


Fig. 1. SEM micrographs of cross section of ZrO_2 - SiO_2 films heated at 500°C for 1 h.
 (a) 30ZrO_2 - 70SiO_2 coating, (b) 50ZrO_2 - 50SiO_2 coating ($0.8\ \mu\text{m}$) and
 (c) 50ZrO_2 - 50SiO_2 coating ($>1.0\ \mu\text{m}$ of thickness).

The measurements of electrochemical corrosion in deareated 15% H_2SO_4 was made with a $0.8\ \mu\text{m}$ thickness of film. On the surface of thicker coatings were cracks.

Fig. 2 shows polarization curves measured with 316L stainless steel (SS) uncoated and untreated; A, SS uncoated but heated at 500°C for 1 h; B, SS coated with 30ZrO_2 - 70SiO_2 ; C, SS coated with 50ZrO_2 - 50SiO_2 ; and D Investigation in deareated 15% H_2SO_4 solutions at 25, 40 and 50°C . The analysis of these results shows that the coatings affect both the cathodic and anodic branches of the curves [1,2]. In the cathodic branches, the slope of the cathodic reaction is maintained, but the values of the current for coated samples are smaller than the values for the uncoated samples. It indicates that

the corrosion mechanism remains unchanged and the film acts, therefore, as a geometric blocking [3]. The anodic branches of the polarization curves show that the coating has a strong effect on the current density in the passive region, and diminishes the current value of uncoated and untreated stainless steel by roughly one order of magnitude, except for the polarization curve obtained at 50 °C, where the anodic current in the passive region is the same as that of uncoated but heat-treated stainless steel [4].

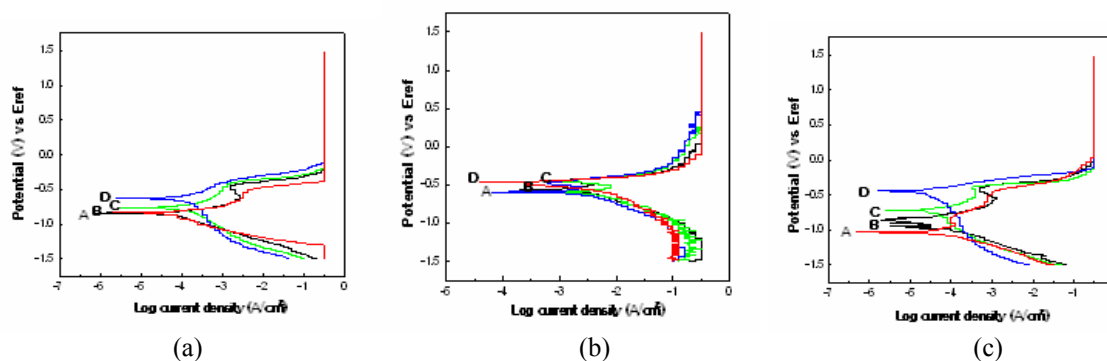


Fig. 2. Potentiodynamic polarization curves measured in deaerated 15% H₂SO₄ solutions at 25 (a), 40 (b) and 50 °C (c) for 316 L stainless steel. A; uncoated and non-heated, B; uncoated but heat-treated, C; 30ZrO₂-70SiO₂ coating and D; 50ZrO₂-50SiO₂ coating.

Table 1. Corrosion parameters determined by the potentiodynamic curves measured for 316 L stainless steel, which was uncoated and untreated, and uncoated and heat-treated at 500 °C for 1 h in deaerated 15% H₂SO₄ solutions at 25, 40 and 50 °C

Samples	Temperature (°C)	$-E_{corr}$ (mV vs. SCE)	R_p (kΩ cm ²)	CR (MPY)
316L SS	25	336	10.50	11.9
	40	337	8.84	47.8
	50	340	7.23	56.2
316L SS*	25	315	28.53	10.7
	40	321	16.27	21.4
	50	318	14.30	41.5
30ZrO ₂ -70SiO ₂	25	282	43.63	8.9
	40	290	35.26	13.4
	50	292	28.23	24.2
50ZrO ₂ -50SiO ₂	25	243	65.42	5.8
	40	244	53.27	8.3
	50	256	33.40	15.2

$-E_{corr}$; corrosion potential, R_p ; polarization resistance, CR(mills per year, MPY); corrosion rate.

*: 316 L Stainless steel with heat-treated at 500 °C for 1 h.

The combined cathodic and anodic effects of the coatings on the corrosion behavior of 316 L stainless steel are summarized in Table 1. In all cases, the experiments were repeated several times, and the results, which were reported for 316 L stainless steel uncoated and untreated and ZrO₂-SiO₂ coatings, correspond to mean values of at least three independent measurements, which showed small

variation (e.g., ± 5 mV for E_{corr}). For instance, the corrosion rate (CR) of the coated stainless steel is about 5.8 times lower than that of substrates at 40 °C. In the case of 30ZrO₂-70SiO₂ coating (>1 µm), the results were not reproducible. This must be a consequence of the cracks present in the coating [6]. Sol-gel coatings of ZrO₂-SiO₂ prepared from sols and deposited by a dip-coating technique on 316 L stainless steel protect the metallic substrate against acid corrosion. The film is shown to act as a geometric blocking layer and increases the life-time of the substrate by a factor up to 5.8 at 40 °C. These oxide films can be used by the chemical and construction industries.

4. Conclusion

ZrO₂-SiO₂ coatings deposited on 316 L stainless steel were prepared by sol-gel process using Zr(OC₃H₇)₄/Si(OC₂H₅)₄ as precursors to protection chemically the substrates. The influence of the ZrO₂-SiO₂ coatings on the corrosion resistance of the 316 L stainless steel was evaluated by the potentiodynamic polarization curves in deaerated 15% H₂SO₄ solutions at 25, 40 and 50 °C. Comparative test was performed on uncoated one. Sol-gel coatings of ZrO₂-SiO₂ prepared from sols and deposited by a dip-coating technique on 316 L stainless steel protect the metallic substrate against acid corrosion. The film is shown to act as a geometric blocking layer and increases the lifetime of the substrate by a factor up to 5.8 at 40 °C. These oxide films can be used by the chemical and construction industries.

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