

Corrosion resistant sol–gel ZrO_2 coatings on stainless steel

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Corrosion resistant ZrO_2 coatings on 316L stainless steel sheets have been fabricated utilizing sonocatalysis of precursors sols. The solutions were prepared from zirconium alkoxide $Zr(OC_3H_7)_4$, isopropanol alcohol, glacial acetic acid and water, and submitted to ultrasonic agitation. Their composition varied between 0.025 and 0.9 mol/l ZrO_2 . Single thin films were thermally treated between 40 and 1100°C in unoxidizing atmosphere. The coatings characteristics were determined by X-ray diffraction, optical reflection, ellipsometry and scanning electron microscopy. At temperatures higher than 700°C, the films are polycrystalline with a tetragonal structure and show a blue–green color. Depending on the composition, the thickness varied from 5.5 to 35 nm. When treated under a slow and controlled heating rate, the ZrO_2 films with the smallest thickness show outstanding corrosion resistance to acid attack and to oxidation as no weight change was observed after 30 h treatment in H_2SO_4 at 81°C or 10 h treatment in air at 800°C. The thicker films as well as the films treated with a rapid heating rate tend to crack during the densification process and are less corrosion resistant.

1. Introduction

Dense thin films of ZrO_2 were prepared on stainless steel substrates by hydrolysis and polycondensation reactions of metal alkoxide precursors, using the dip-coating technique. Sol–gel dip-coating is very useful for modifying a large surface area and to provide substrates with new active properties [1,2]. ZrO_2 films can be used for protection of metal substrates from attack by acid and oxidation [3–8].

The solutions prepared from zirconium alkoxide with the application of ultrasound were found to be stable and to yield a high degree of homogeneity. It is possible for a high purity oxide to be easily obtained and yield homogeneous coatings of a high quality. The heat resistance of substrates was obtained at higher temperatures and longer times.

This study aims at producing ZrO_2 coatings of good chemical durability via the sol–gel process with the application of ultrasonic treatment. The resistance of the films is evaluated from the results of weight gain and weight loss measurements [9,10].

2. Experimental

Zirconium isopropoxide $Zr(OC_3H_7)_4$ diluted in isopropanol (C_3H_7OH) was used as the source of zirconia. The sonocatalysis technique consists in submitting the alkoxide–alcohol mixture to the action of intensive ultrasound (20 kHz) produced by a transducer immersed in the mixture [11–13]. Following the dissolution of zirconium alkoxide in isopropanol, glacial acetic acid (CH_3COOH) was added to a solution homogenized with ultrasonic irradiation. After 20 min, a homogeneous mixture was obtained. Under ultrasound, excess water was added to complete the hydrolysis until a clear and transparent sonosol was obtained. The solutions used had concentrations between 0.025 and 0.9 mol/l ZrO_2 . The volume ratios H_2O/C_3H_7OH and H_2O/CH_3COOH were respectively equal to 1 and 2. The hydrolysis reaction was sonocatalyzed and then the resulting solution was left undisturbed for four weeks at room temperature.

The substrates were stainless steel sheets, 316L, which were degreased ultrasonically in acetone. The substrates were then dipped into the solutions and withdrawn at a speed of 10 cm/min

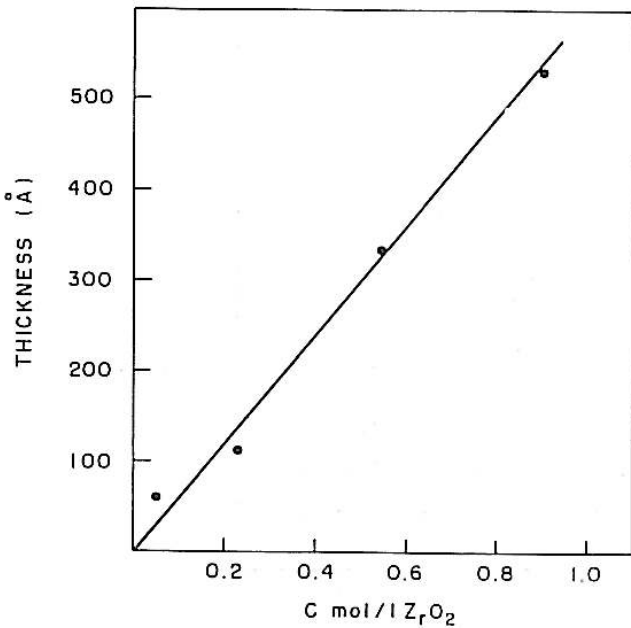


Fig. 1. Thickness of ZrO_2 films deposited on stainless steel sheet and densified at $800^\circ C$ for 9 h (low heating rate) vs. concentration of ZrO_2 sol (withdrawal speed = 10 cm/min).

and then dried at $40^\circ C$ for 15 min. After drying at about $70^\circ C$ for 15 min, the samples were heated to $400^\circ C$ at $3^\circ C/min$ for 1 h to remove the organic residues and oxidized in air between 400 and $900^\circ C$ at a heating rate of $5^\circ C/min$ to obtain adherent coatings.

Two tests were applied for measuring the oxidation and corrosion resistance.

(1) Test A: before corrosion the stainless steel sheets with ZrO_2 coating were heated at $400^\circ C$ for 1 h and fired at $800^\circ C$. The attack of acid on stainless steel with different coatings was studied and the weight loss was recorded after different times for various concentrations. The samples densified were placed in a 15% H_2SO_4 solution at 72 – $89^\circ C$ for different periods of time (up to 32 h). The determination of total corrosion was evaluated by weight loss measurements.

(2) Test B: the oxidation testing was carried out directly at $800^\circ C$ for 2–10 h. The oxidation was evaluated by measuring the increase in weight of the coated sheets when they were heated in air.

The resulting ZrO_2 films thickness were measured by ellipsometry. X-ray diffractometer was used to determine the structure of the coatings. Spectra of coated films was carried out with a FTIR spectrometer by the reflection method with an incident angle of 30° . The surface of ZrO_2 films was observed by scanning electron microscopy (SEM).

3. Results

Figure 1 illustrates the variation of film thickness, measured by ellipsometry, deposited on

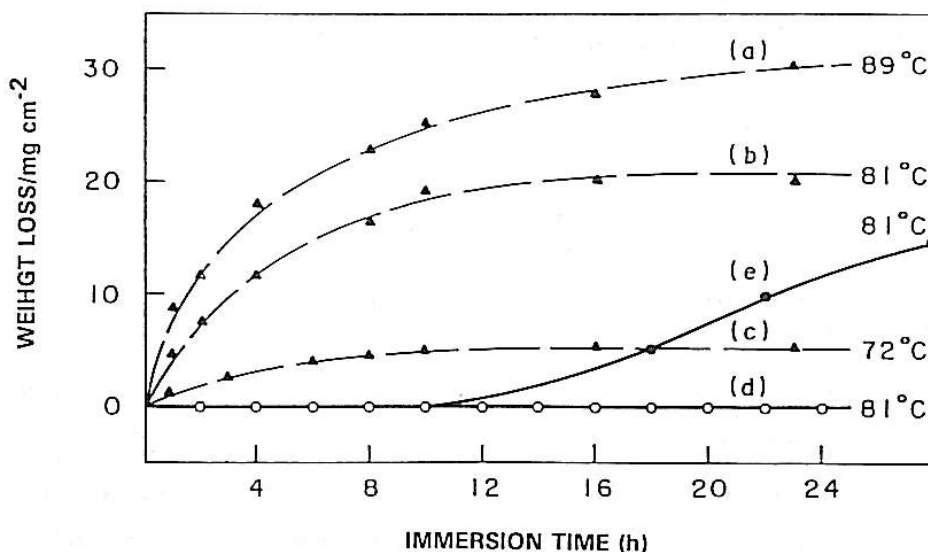


Fig. 2. Weight loss (mg/cm^2) of 316L stainless steel sheets measured as a function of immersion time in 15% H_2SO_4 at different temperatures for: (a)–(c) uncoated samples tested at 89, 81, and $72^\circ C$, respectively; and (d) and (e) ZrO_2 coated substrates densified at $400^\circ C/1$ h and $800^\circ C/1$ h (low heating rate), respectively, and tested at $81^\circ C$. (d) Film thickness $5 < e < 40$ nm. (e) Film thickness 55 nm.

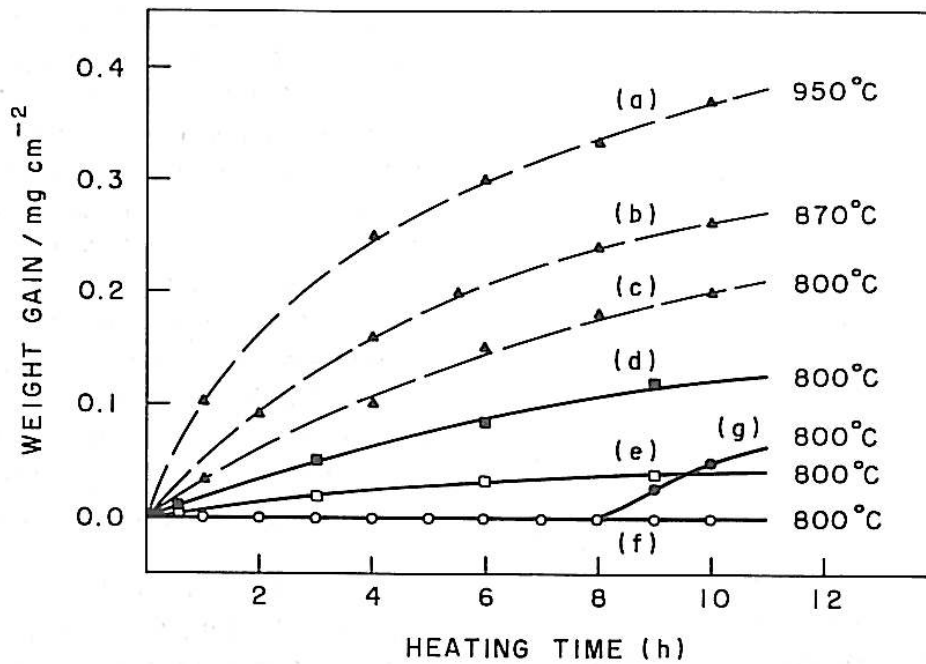


Fig. 3. Weight gain (mg/cm⁻²) of 316L stainless steel sheets measured as a function of the time of isothermal oxidation treatment in air at different temperatures. (a)–(c) Uncoated substrates tested at 950, 870 and 800°C, respectively. (d)–(g) ZrO₂ coated substrates tested at 800°C. (d) Film thickness 35 nm. (e) Film thickness 5.5 nm and rapid heating process (samples inserted directly at 800°C). (f), (g) Same films under slow heating process (400°C/1 h and 800°C).

316L stainless steel after heating at 800°C for 9 h. The thickness increased linearly with the concentration of ZrO₂. The thickest film obtained by single coating was about 55 nm for a ZrO₂ concentration of 0.91 mol/l.

Figure 2, curves (a)–(c) show the evolution of weight loss as a function of corrosion time in 15% H₂SO₄ solution at different temperatures. It is clear that for the samples without coatings the

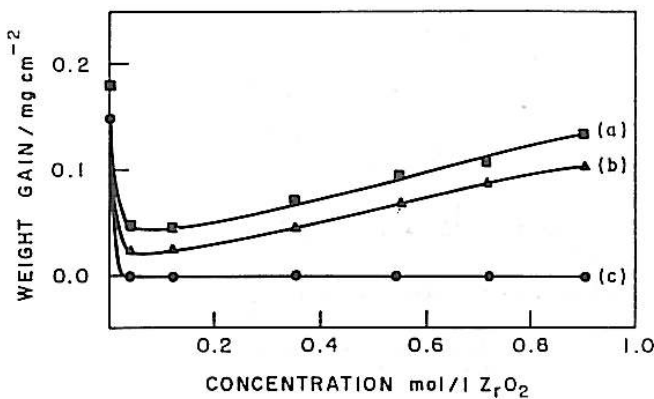


Fig. 4. Weight gain of ZrO₂ coated 316L stainless steel measured after oxidation treatment at 800°C vs. sol concentration of ZrO₂. (a) Rapid heating process (800°C/9 h). (b) Rapid heating process (800°C/6 h). (c) Slow heating process (400°C/h and 800°C/6 h).

weight loss increased with the temperature and time. However, as shown in fig. 2(d) and (e) the substrates coated with ZrO₂ films present a protective barrier against acid attack. ZrO₂ films reduce the effect of acid attack and the maximum

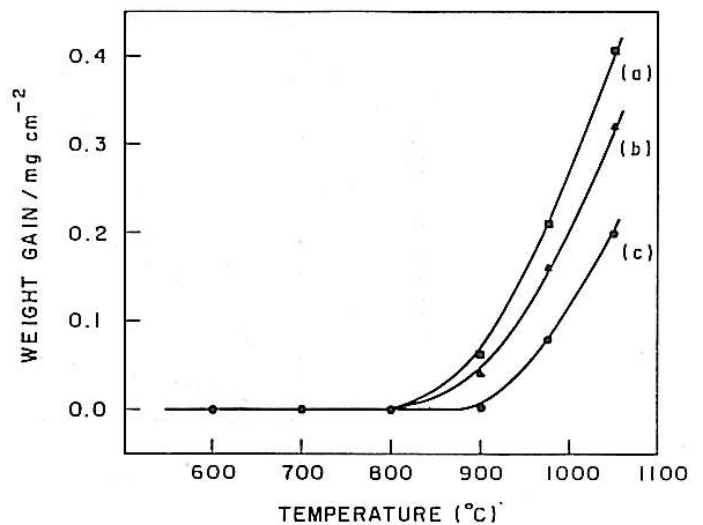


Fig. 5. Weight gain of 5.5 nm thick ZrO₂ coated 316L stainless steel sheets measured after non-oxidation treatment in air for 3, 6 and 9 h vs. oxidation temperature. The film was previously slowly densified at 800°C for (a) 9 h, (b) 6 h and (c) 3 h.

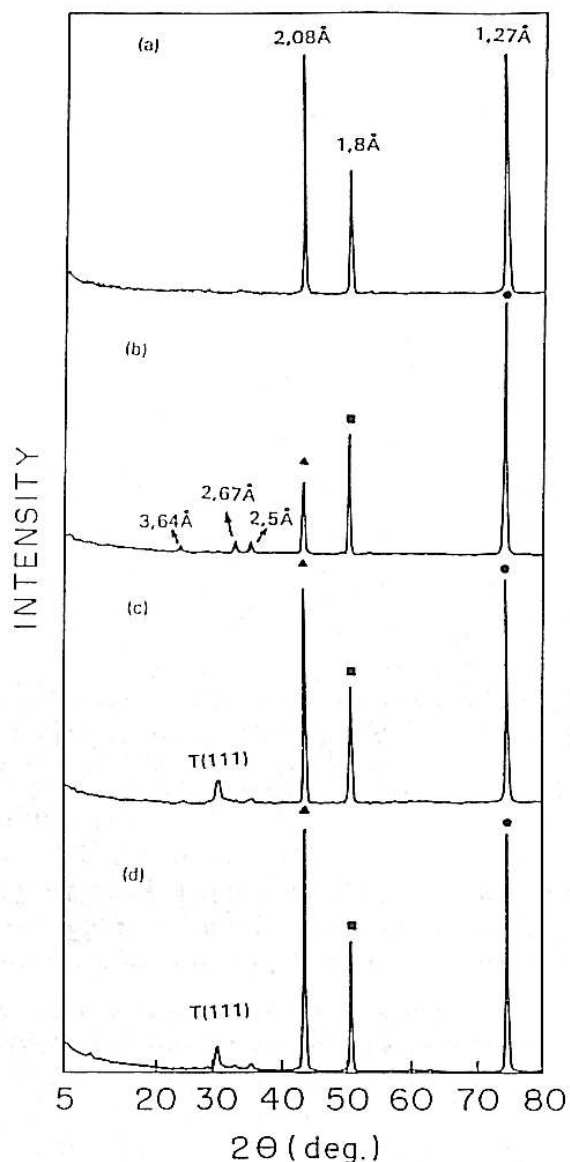


Fig. 6. X-ray diffraction of stainless steel sheets measured after different heat treatments. (a) As-received (uncoated). (b) Uncoated but oxidized in air at (400°C/1 h + 800°C/9 h). (c) 5.5 nm ZrO₂ coated (densification under slow heat treatment) after oxidation at 800°C for 9 h. (d) 5.5 nm ZrO₂ coated (densification under slow heat treatment) after densification at 800°C for 1 h, then tested in 15% H₂SO₄ solution at 81°C for 9 h.

value of weight loss was 15 mg cm⁻² for 32 h. For thickness < 40 nm, no chemical attack was observed on coated substrates (fig. 2(d)). At thickness greater than 40 nm, coating provided protection for up to 10 h (fig. 2(e)).

The general corrosion phenomena of these stainless steels at high temperatures can be evaluated from the experimental data. It may be observed that the extent of surface oxidation can be

determined by the apparent weight gain. Comparing uncoated and coated substrates (fig. 3(a)–(g)), the weight of the coated samples remains almost unchanged, whereas uncoated samples showed significant weight gain. These tests were performed on samples heated to test temperature at 5°C/min with a 1 h hold at 400°C.

For coated samples, the protection of metal was found to provide resistance against thermal oxidation.

The thermal oxidation of coated samples inserted directly into a heated furnace for oxidation testing is shown in fig. 4. The rate of thermal oxidation increased with the concentration of ZrO₂ in the initial solutions. This was attributed to greater thermal stresses present in the thicker coatings obtained at higher concentrations. The effect of solution concentration is also shown in fig. 4. The solution concentration had no effect on samples slowly heated to test temperatures.

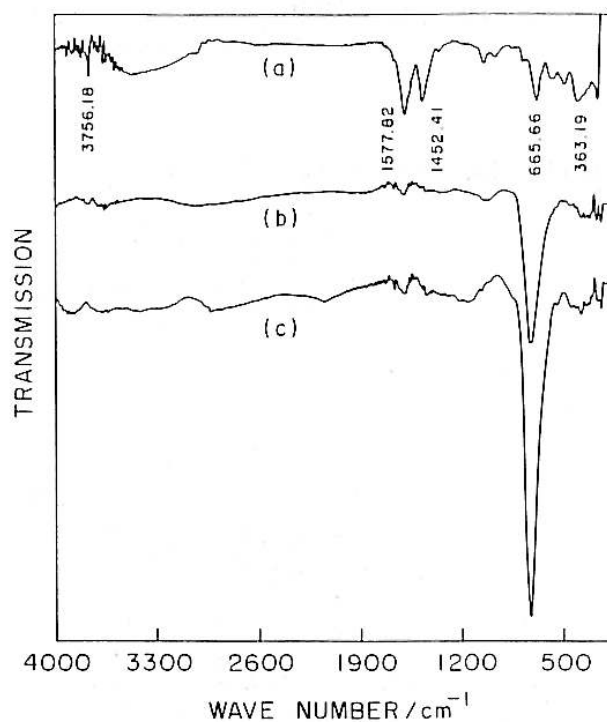


Fig. 7. IR spectra of films prepared on stainless steel. (a) After deposition without heat treatment. (b) Densified under slow heat treatment and under oxidation in air at 800°C for 9 h. (c) Densified under slow heat treatment and oxidized at 800°C for 1 h, and tested in 15% H₂SO₄ solution at 81°C for 9 h.

It was shown that the thin coatings had a good chemical durability and present a good resistance against oxidation and acid corrosion. When the thickness was > 40 nm, destruction of the coatings on the side surfaces was observed and the

corrosion resistance decreased. The different corrosion behavior of coating to oxidation depended on the process of densification.

As seen in fig. 5, the effect of various temperatures on coated samples prepared from solution

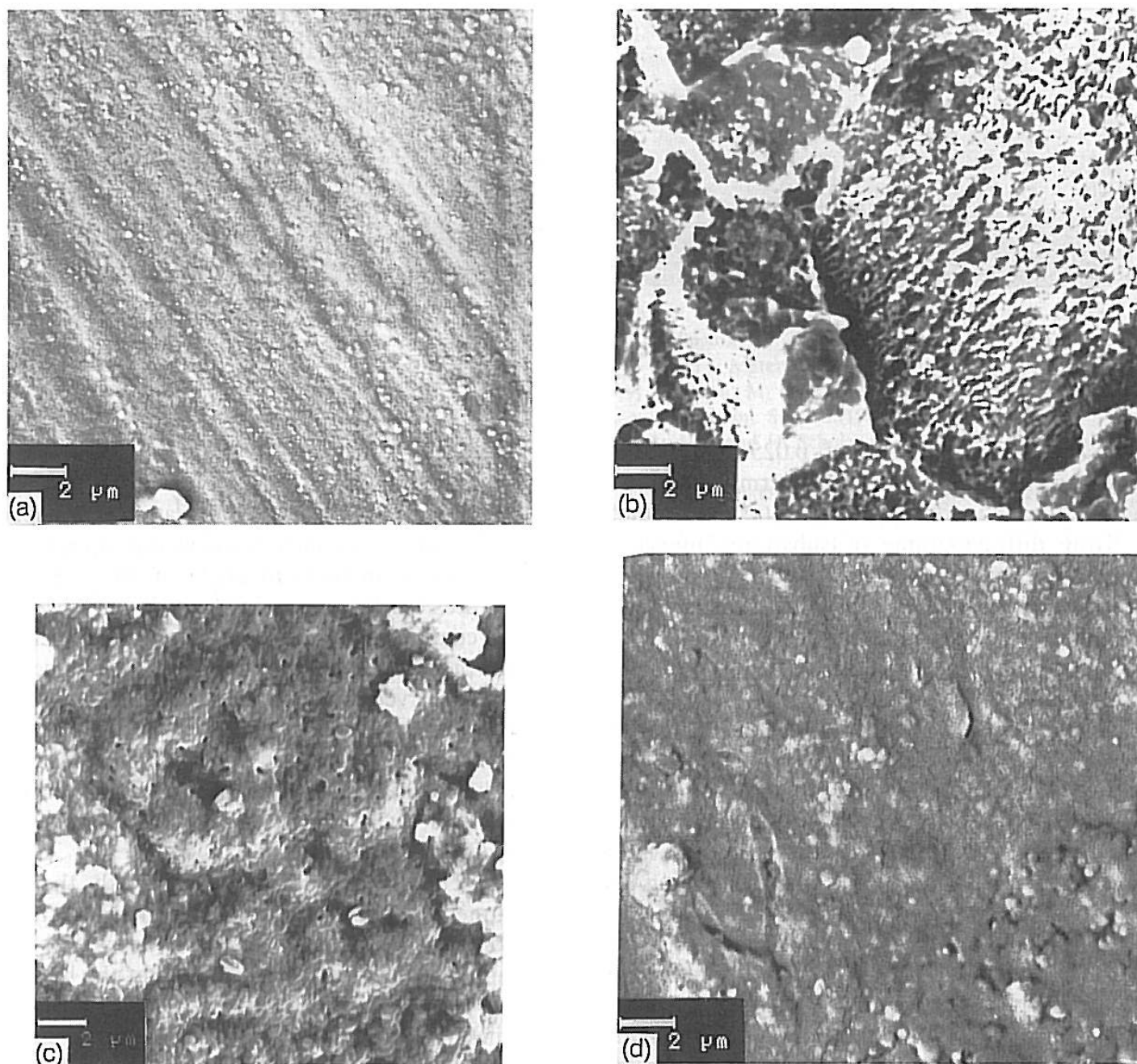


Fig. 8. SEMs of (a) uncoated stainless steel sheet, as-received (b) uncoated 316L stainless steel after acid attack in 15% H_2SO_4 solution at 81°C for 9 h, (c) uncoated stainless steel but oxidized in air at 800°C for 9 h, (d) ZrO_2 film (thickness 5.5 nm; slow heat treatment) deposited on stainless steel after oxidation in air at 800°C for 9 h, (e) ZrO_2 film (thickness 5.5 nm) of coated stainless steel but inserted directly into a pre-heated furnace at 800°C for 10 min, and (f) 5.5 nm ZrO_2 film coated after oxidation at $800^\circ\text{C}/1$ h (slow heat treatment) and tested in 15% H_2SO_4 solution at 81°C for 9 h.

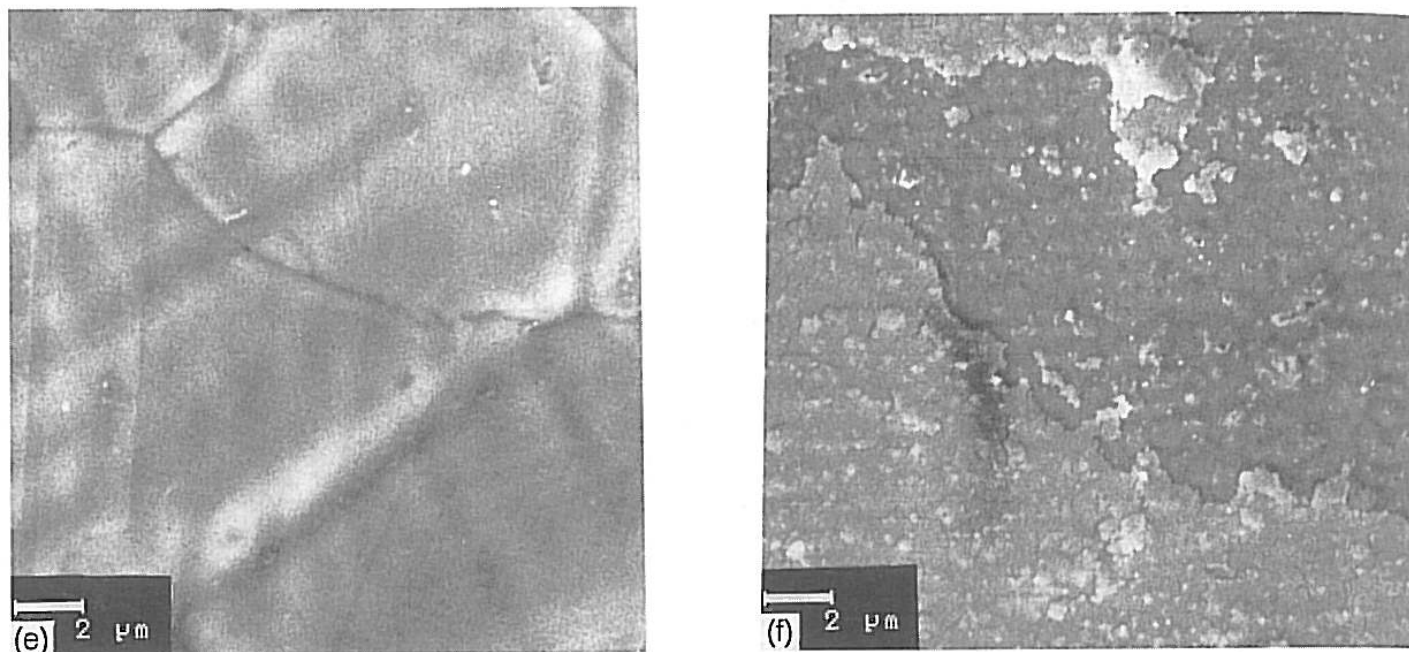


Fig. 8. (continued).

with ZrO_2 concentration of 0.025 mol/l. The weight gain obtained during thermal oxidation increased with increasing temperature and time.

X-ray diffractograms of substrates uncoated and coated are shown in fig. 6. The patterns were obtained by using a Philips diffractometer with a characteristic Cu K α radiation. The results of uncoated stainless steel specimens showed three distinct peaks with d values of 2.08, 1.8 and 1.27 Å which correspond to the cubic (Cr + Fe + Ni) phase (fig. 6(a)).

Following heat treatment of stainless steels at 800°C for 9 h in air, the first peak decreased in intensity and there exist another peaks which appears to $d = 3.64, 2.67$ and 2.5 Å providing the Cr_2O_3 formation (fig. 6(b)).

Stainless steels coated with ZrO_2 films and heated at 800°C for 9 h, showed additional X-ray diffraction peaks at 2.98 Å corresponding to tetragonal zirconia (fig. 6(c)). However, the coated stainless steels showed no change in relative intensity of the cubic metal peaks, indicating no oxidation of the coated samples following heat treatment.

After treatment in H_2SO_4 solution at 81°C/9 h, similar results were obtained (fig. 6(d)). The

ZrO_2 coating appeared as protective barrier against oxidation and acid corrosion.

Using a Fourier transformation IR spectrophotometer, the measurement was obtained by reflection at an incident angle of 30°. Figure 7 illustrates the IR absorption spectra for the ZrO_2 films coated on stainless steel sheets from zirconium propoxide with thermal treatment. The IR bands observed can assigned as follows.

(i) At room temperature and before firing, the bands at about 1453–1578 cm^{-1} were observed, which are characteristic of Zr–O–C. The absorption band due to Zr–O–Zr was observed near 666 and 363 cm^{-1} .

(ii) The evolution of spectra, with thermal treatment of the samples, showed that the strong absorption due to the Zr–O–C decreased and disappeared with firing time and that the band of Zr–O–Zr increased strongly with firing time.

(iii) The absorption characteristic of Zr–O–Zr was observed even after treatment in 15% solution of H_2SO_4 for 9 h at 81°C.

The morphologies of the stainless steel sheets with and without films were investigated by scanning electron microscopy. Figure 8(a) shows the microstructure of stainless steel sheet surface.

However, the surface obtained after acid attack showed granular microstructure (fig. 8(b)). When the sample was exposed to oxidation, the surface was found to be inhomogeneous and etch-pits were formed (fig. 8(c)).

Figure 8(d) gives the homogeneous film, which was deposited on stainless steel by a single dip-coating. It was shown that the coating heated at 800°C for 9 h has an ultrafine and dense microstructure.

A crack occurred during thermal treatment when the samples were inserted directly into a preheated furnace at 800°C for 10 min (fig. 8(e)).

Figure 8(f) shows the surface of coated samples after acid attack for 9 h. Scanning electron micrographs shows homogeneity of coating.

4. Conclusion

Using the sol-gel method, ZrO_2 coatings were obtained from sonocatalyzed hydrolysis of alkoxides on stainless steel substrates. By heat treatment, these films crystallize yielding tetragonal ZrO_2 coatings. It was shown that the ZrO_2 films provided corrosion protection of metal substrates. It was interesting that, by the technique using ultrasonic processing, other systems such as

$SiO_2-Al_2O_3$ and SiO_2-TiO_2 in which resistance is strong can be easily prepared.

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