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An efficient protection of stainless steel against corrosion: Combination of a conversion layer and titanium dioxide deposit

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ABSTRACT

In the present work, a novel process has been developed to improve the corrosion properties of ferritic stainless steels. Titanium oxide coatings have been deposited onto stainless steel by sol–gel process after a pre-functionalization of the substrate in a conversion bath. Gel titania was prepared by hydrolysis of a titanium butoxide through a sol–gel process. Duplex systems "conversion layer/uniform TiO_2 coating" have been prepared on stainless steels using a dipping technique and thermal post-treatments at 450 °C. The preparation of sol–gel coatings with specific chemical functions offers tailoring of their structure, texture and thickness and allows the fabrication of large coatings. The morphology and structure of the coatings were analysed using scanning electron microscopy with field effect gun (SEM-FEG), Mass spectroscopy of secondary ions (SIMS) and X-ray diffraction (XRD). The anticorrosion performances and the ageing effects of the coatings have been evaluated in neutral and aggressive media by using several normalized tests.

The results show that the conversion layer was not sufficient to protect steel but sol–gel TiO_2 coatings, anchored on the metal substrate via the conversion layer, show good adhesion with the substrate and act as a very efficient protective barrier against corrosion. So, duplex layers with TiO_2 nanoparticle coatings on steels exhibit an excellent corrosion resistance due to a ceramic protective barrier on metal surface. Analysis of the data indicates that the films act as geometric blocking layers against exposure to the corrosive media and increase drastically the lifetime of the substrate.

1. Introduction

An increased resistance of metals and alloys to corrosion is generally obtained by the formation of a protective layer isolating the substrate from the surrounding oxidant atmosphere. A variety of protective ceramic coatings, such as nitrides, carbides, silicides or transition metal oxides, have been deposited on steel [1–4]. Coatings with very low electronic conductance, such as SiO_2, non-conducting Al_2O_3, mixed-oxide coatings (TiO_2, SiO_2, and Al_2O_3) have been reported to protect efficiently metals against corrosion. TiO_2 coatings have been proposed [5–8] and show a good corrosion resistance. However these coatings present a low adhesion to the metal substrate at high temperature.

The formation of a conversion layer previous to coating deposition may represent a solution to this problem. For example, conversion layers obtained by chemical treatment may have a high surface area

and an interesting morphology with micropores and cavities in a large size range [9,10]. Such a microstructure helps to anchor further deposits [11], and various layers can be deposited by different methods on top of the conversion coating [10–12]. Moreover, subsequent thermal treatment may induce a reaction between compounds of the conversion layer and the deposit [12,13] and, further enhance adhesion.

We have recently proposed a simple, inexpensive and efficient method for the deposition of anatase TiO_2 films with controlled thickness on a functionalised stainless steel [13]. This method involves two chemical steps followed by thermal treatments. In the first chemical step, the substrate surface was functionalized by a

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Table 1
Chemical composition of ferritic stainless steel (wt.%)

Fe	Cr	Al	Si	Ti	Mn	Ni	Cu	Mo	Nb
82.36	16.31	0.09	0.38	0.01	0.2	0.33	0.41	0.08	0.11

Table 2
Conditions for the conversion treatment

Bath composition			Temperature
H_2SO_4	$Na_2S_2O_3$, $5H_2O$	C_3H_4O	60 °C
0.93 M	0.005 M	0.06 M	

Table 3
Various steps in a cycle of the severe test

1 cycle (24 h)	Temperature (°C)	Atmosphere
4 h	60	Wet
1 h	35	Dry
4 h	60	Wet
1 h	35	Dry
6 h	60	Wet
2 h	35	Dry
3 h	60	Wet
3 h	35	Dry

conversion treatment in an acid bath with suitable additives. The following heat treatment led to an increased crystallinity of the conversion coating. In the second chemical step, TiO_2 was deposited onto the functionalised stainless steel surface by a sol–gel method and a final thermal treatment induced crystallization of the TiO_2 anatase form. The major interest of this material is its multifunctionnality because it was mainly developed for its potential application to the photocatalytic degradation of organic pollutants in aqueous solutions, as TiO_2 (especially in its anatase form) is a well-known photocatalyst for water and air treatment [14].

The present work had two objectives: i) to study the influence of the method of preparation of the conversion layer on the morphology and the chemical composition of the layer; ii) to evaluate the corrosion resistance of duplex conversion layer/titanium dioxide deposits on F17 stainless steel. Since highly oxidizing species are produced by irradiation of TiO_2, the resistance to corrosion of the newly developed

supported catalyst had to be tested under aggressive oxidizing conditions. To this aim, two industrial and normalized test methods were performed: the test under wet atmosphere and the salt spray test [15].

2. Experimental

2.1. Material

The conversion coatings were prepared on a ferritic F17 stainless steel. The chemical composition of this material is given in Table 1. Substrates were in the form of 0.5 mm thick samples (3 cm×2 cm).

2.2. Conversion coating

Conversion coatings were obtained by chemical oxidation of the stainless steel substrate in an acidic solution containing additives such as thiosulphate and propargyl alcohol in order to control the growth of the coating and to obtain microporous morphology with high surface area. Conditions of the conversion treatment are presented in Table 2. The influence of the treatment duration has been investigated in detail in this work. The period of immersion of the sample in the conversion bath varied between 1 and 30 min.

After the treatment, the samples were rinsed in demineralised water, then dried at 60 °C for 15 min. In order to stabilise the coating, they were treated at 450 °C for 2 h. We have chosen 450 °C for a treatment temperature, because this temperature gives optimal results for the (subsequent) thermal treatment of the TiO_2 sol–gel deposit (see below).

2.3. Sol–gel process

0.1 mol of titanium(IV) butoxide was dissolved in 1 mol of absolute ethanol under argon atmosphere and refluxed for 12 h. 0.05 mol of 2,4-pentanedione and 0.01 mol of double distilled water were added dropwise under vigorous stirring. After refluxing for several hours, the
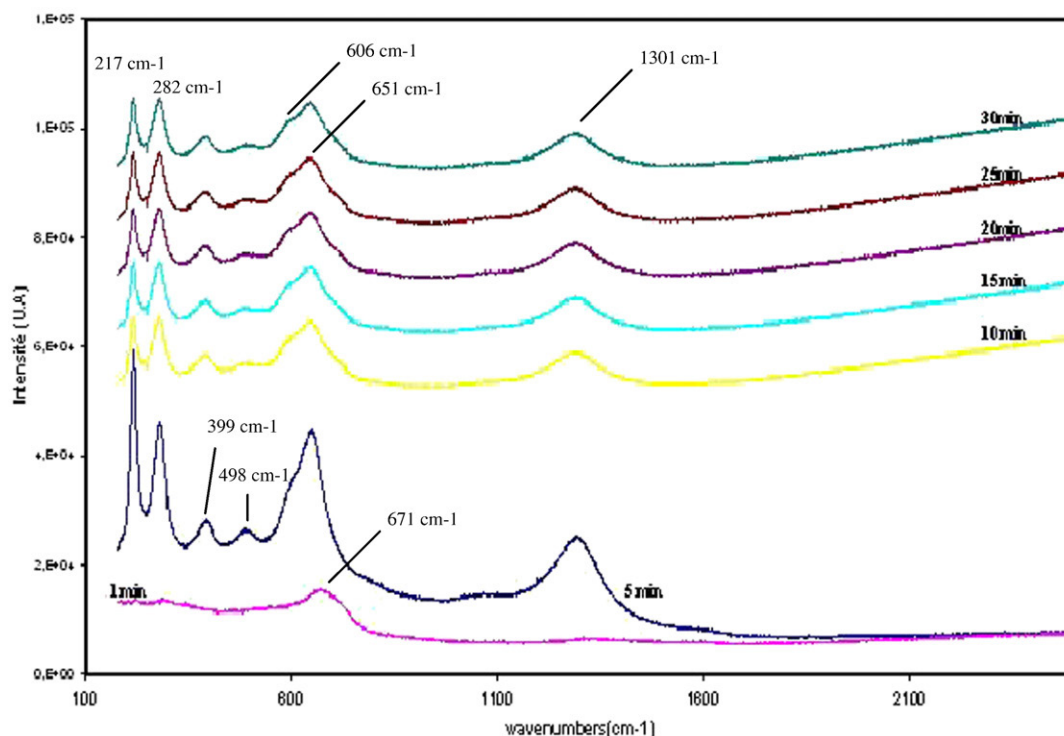

Fig. 1. Raman spectroscopy of the conversion coating between 1 min and 25 min of immersion in the bath of treatment.
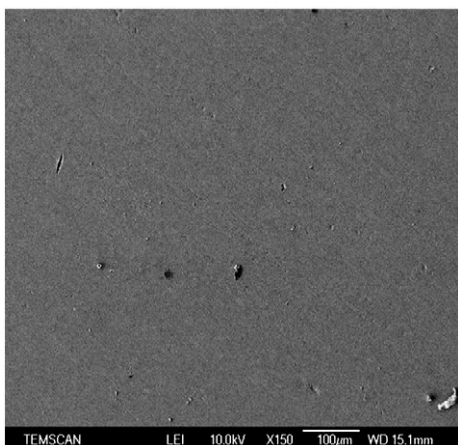
Fig. 2. SEM images of F17 stainless steel.

profiles were obtained in an inert atmosphere by bombardment using a cesium ion gun by secondary ions mass spectroscopy (SIMS). X-ray diffraction measurements were performed on a Seifert XRD 3003 TT using the Cu Kα radiation (λ=1.545 Å). Raman measurements were performed on a LabRAM-HR800 spectrometer (Jobin Yvon). The spectra were obtained at room temperature using the 632.8 nm line of a He–Ne laser. The incident beam was focused onto the conversion coating through the ×100 optical microscope objective, giving a spot size of ~1 μm^2. The back-scattered light was collected through the same objective, dispersed (single-grating spectrograph, 1800 grooves mm^{-1}, f=80 cm) and then imaged onto a CCD detector (Andor DU420-OE).

Scanning electron micrographs were registered on a JEOL JSM 6700F scanning electron microscope equipped with field effect gun. The B.E.T. method was used to determine the specific surface area of the coating in order to evaluate the coating reactivity.

2.5. Corrosion tests

The salt spray test is a standardized test method used to study corrosion resistance of coated samples. It is an accelerated and severe test that produces a corrosive attack on the samples and allows prediction of the suitability of the coating as a protective finish. These tests have been used for more than 90 years as accelerated tests in order to determine the degree of protection provided by both inorganic and organic coatings on a metallic substrate. The neutral salt spray (fog) test (ASTM B117) [15], developed several years ago in order to simulate a corrosive marine environment, is perhaps the most commonly used test for material or product specifications and qualifications in industry. The apparatus for testing consists of a closed testing chamber, where a salted solution (3% NaCl, pH 6.8) is sprayed by means of a nozzle. The temperature of the salt spray chamber is controlled to maintain 35(±2)°C within the exposure zone of the closed chamber. The volume of the chamber used in this work

clear solution was concentrated by solvent distillation. An amorphous and translucid gel was obtained. It contained enough alcohol to avoid ageing and could therefore be stored unchanged for several weeks [16]. The TiO_2 coating was processed by the dip-coating process. Xerogel coatings were then submitted to a two stage thermal treatment. In the first stage the catalyst system was dried at 100 °C, whereas in the second stage the desired crystalline anatase phase was obtained after calcination at 450 °C.

2.4. Characterisation methods

Both secondary Raman spectroscopy and X-ray diffraction were used to analyse the samples structure at each stage of the process : in the initial state of the stainless steel substrates, after formation of the conversion layer and after coating of titanium dioxide. The metalloid
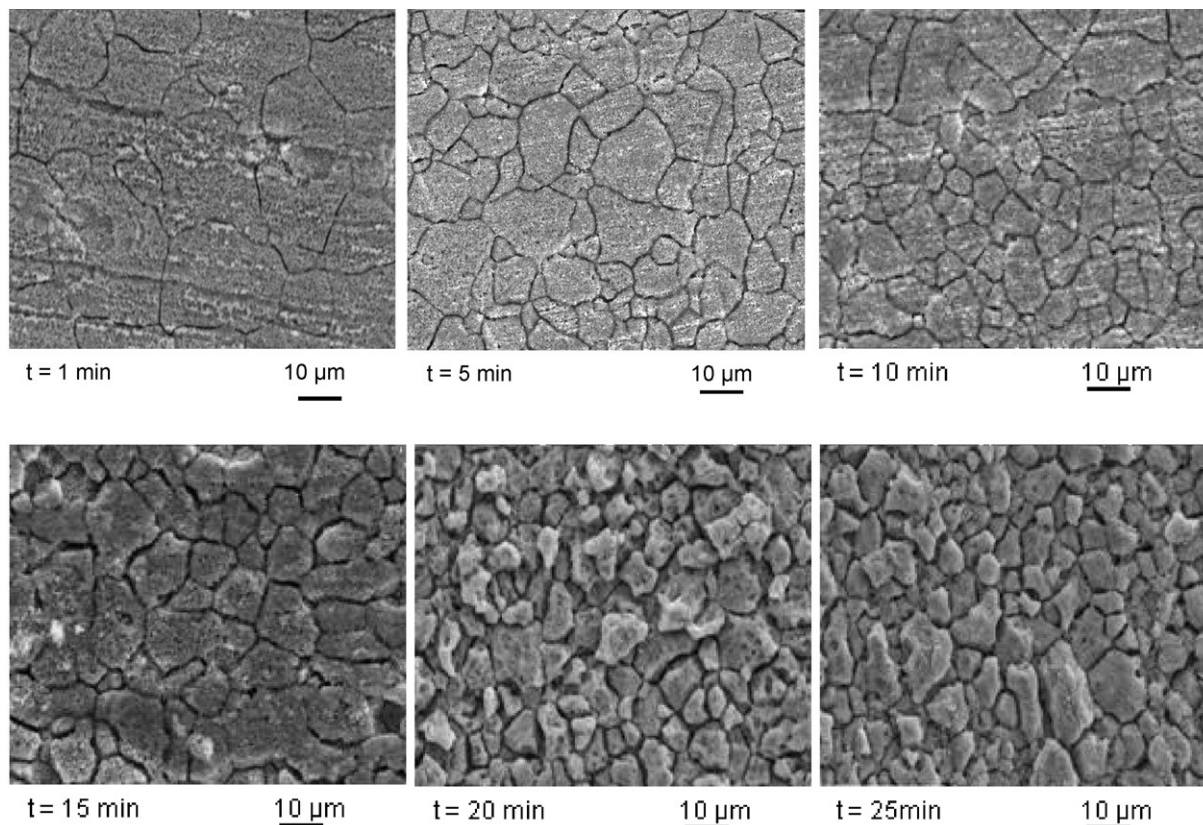

Fig. 3. SEM images of F17 stainless steel after conversion treatment at 1 min to 25 min.
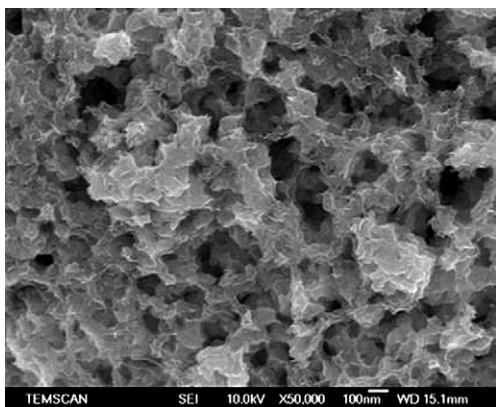
Fig. 4. SEM-FEG micrographs of the conversion layer after 25 min of chemical treatment.

was 400 L. The samples were observed for appearance of the first traces of corrosion or red rust and was regularly weighted during the exposure to quantify the progress of the corrosion process (balance accuracy = 10^{-4} g). The test was stopped after 8 days (192 h) or 20 days (500 h).

The "Normalized test under wet atmosphere", best known under the European test method, DIN Standard 50017 (KFW modified, Table 3), is a severe measurement of corrosion resistance. The samples to be tested are prepared and placed in a specially designed unit called a Test Cabinet. In the soft Test, samples are exposed to a succession of 10 cycles. A cycle includes three steps: 6 h in a wet saturated atmosphere at 40 °C followed by 2 h under dry atmosphere at 30 °C and 16 h under dry atmosphere at 25 °C. The samples are weighted before and after each cycle. During the wet atmosphere step, an environment of 100% relative humidity is maintained by heating water in a steam generator. In the severe test, a cycle is divided into several steps of variable duration, temperature and humidity as indicated in Table 3.

3. Results and discussion

3.1. Influence of the immersion time in the conversion bath

In a previous publication [13], we have described an original method to obtain duplex conversion layer/TiO_2 coatings on a stainless steel substrate with good adhesion. This new material (steel/conversion layer/TiO_2) has been prepared to be used as a photocatalyst for the degradation of organic pollutants in water. The surface functionalization by a conversion treatment of steel is a primordial step because morphology and chemical composition characteristics of the layer will influence the TiO_2 adhesion and probably the photocatalytic activity.

Previous studies [17] have shown that the immersion time in the conversion bath could be an important factor influencing the specific surface area. Therefore, we have investigated the effect of this parameter on both the morphology and on the chemical composition of the conversion layer. 7 samples were prepared and their immersion time in the treatment bath was varied from 1 to 30 min. For each sample, the chemical composition was analyzed by Raman spectroscopy and the morphology characterised by scanning electron microscopy (SEM).

After 1 min of treatment, the Raman spectrum showed a broad signal located at 671 cm^{-1}, which is assigned to the E_g mode in Fe_3O_4 [18], thus indicating that magnetite was formed in a short time period in the conversion layer (Fig. 1). After 5 min of treatment, the Raman signal-to-noise ratio improved considerably and seven peaks could be distinguished at 1301(m), 651(m), 606(sh), 498(w), 399(w), 282(m) and 217(s) cm^{-1}. Longer immersion times (5 < t ≤ 25 min) do not significantly change Raman data (relative intensities of signals are roughly constant, Fig. 1). This result shows that the spectral signature of the surface of the material remains unchanged after 5 min of treatment. Peaks at 651 and 498 cm^{-1} are assigned to E_g and T_{2g} modes in Fe_3O_4, respectively [19]. The decrease in the E_g mode frequency from 671 (after 1 min of treatment) to 651 cm^{-1} (after 5 min of treatment) may result from an increasing substitution of iron ions by chromium ions when increasing the immersion duration. Other modes at 1301, 606 (E_g), 399 (E_g), 282 (E_g), and 217 (A_{1g}) cm^{-1} are attributed to α-Fe_2O_3 by comparison with literature data [20]. In summary, magnetite was formed first. After 5 min in the conversion bath, peaks related to α-Fe_2O_3 appeared in addition to those of Fe_3O_4 and longer immersion periods did not alter the chemical composition of the conversion layer. This result was confirmed by X-ray diffraction analysis.

In contrast, an important effect of the immersion time on the morphology of the conversion coating was observed by SEM, as shown in Figs. 2 and 3.

A SEM image of the stainless steel substrate before conversion treatment is presented in Fig. 2. Between 1 min and 10 min of treatment (Fig. 3), a uniform and homogeneous surface was obtained, however the conversion layer was smooth and not porous. After 15 min of conversion treatment, the layer started to thicken and became increasingly porous (Fig. 3). After 25 min, the layer presented an homogeneous aspect with high roughness; it consisted of organized crystallites with sizes in the range from 8 to 15 μm and with a pore distribution between a few nanometers and a few micrometers (Fig. 4). This particular morphology (rough, very porous and nanostructured) appeared very adequate for a subsequent deposition of TiO_2 by a sol–gel process, because it was associated to a high specific surface area (500 m^2/m^2).

Titanium dioxide was deposited by the sol–gel method on this pre-functionalised support. The roughness measurements coupled with
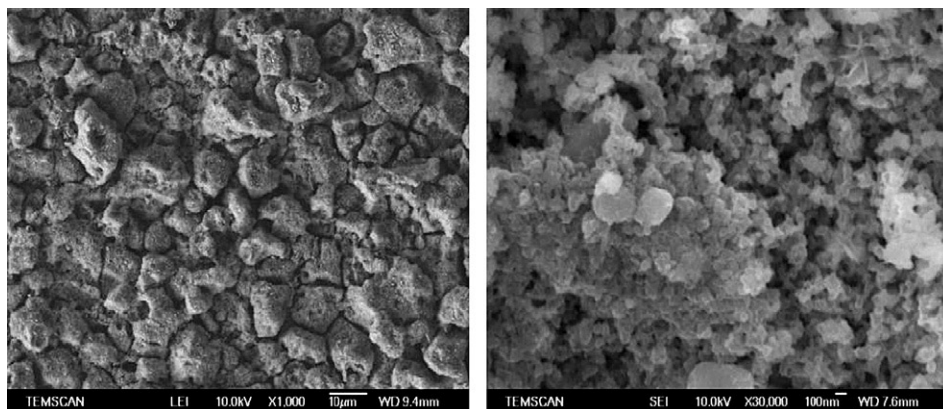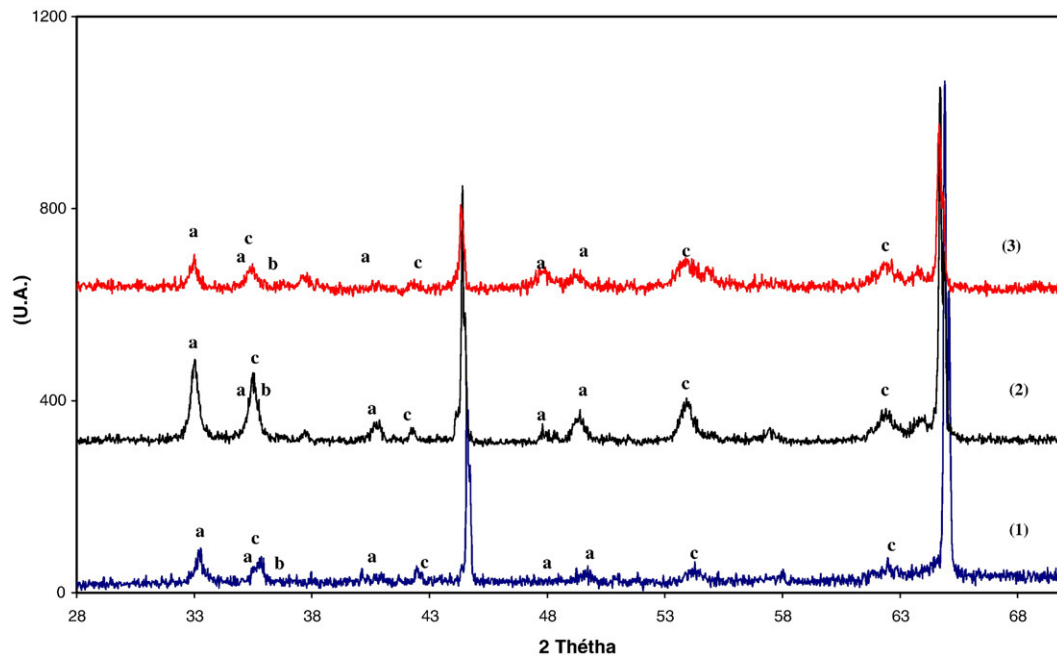

Fig. 5. Micrographs (SEM) of the conversion layer after immersion in pure water during 720 h in darkness.

Fig. 6. X-ray diffraction patterns of initial conversion layer (1), after immersion in NaCl 3% (2) and in pure water during 30 days in the dark (3), a. Fe_2O_3, b. Fe_3O_4, c. $FeCr_2O_4$.

SIMS analysis allowed a precise evaluation of the surface state of the final layers: the coating consists of two layers, a TiO_2 outer layer and an inner layer containing iron chromium oxides. The specific surface area measured by the B.E.T. method was approx. 580 m^2/m^2 and X-ray diffraction showed that the anatase (more efficient form for photo-catalysis) was the main crystalline form of TiO_2. Since the stainless steel plates with conversion layer and TiO_2 deposit were prepared for their use as new supported photocatalysts for water treatment, they may be exposed to potentially corrosive environments (polluted aqueous systems), and they were therefore tested for their corrosion resistance.

3.2. Tests of corrosion resistance of conversion layer/TiO₂ deposit on F17 stainless steel

To evaluate the corrosion resistance of the duplex TiO_2/conversion layer on stainless steel, we used different tests. Some are soft, as the test in pure water or in 3% NaCl solution. others are more severe, as the test under wet atmosphere or the salt spray test.

In a first step, we have tested the corrosion resistance of the stainless steel used in this work without coating in pure water and in 3% NaCl, during 720 h in darkness. The results show a transgranular type failure. Micrographs revealed a faceted structure with individual separated grains. Both in pure water and in 3% NaCl, SEM examination revealed that the majority of the cracks observed exhibited a branched, transgranular morphology typical of Chloride Stress Cracking (CSC), while the unbranched, transgranular nature of some cracks suggested that they were initiated by fatigue. Moreover, for NaCl 3%, we also observed by SEM other types of corrosion such as uniform defects, pitted surfaces, Crevice Corrosion.

When the stainless steel was protected by the conversion layer, no effect on the morphology was observed after immersion in pure water during 720 h (as shown in Fig. 5), and there was no modification of the coating composition. The X-ray diffraction analysis showed that the main crystallised compound of the coating was Fe–Cr oxide (Fig. 6).

In the case of the stainless steel plates coated with a conversion layer, the test in 3% NaCl resulted in the formation of a rust colored precipitate on the surface and inside the pores of the conversion layer, as shown by SEM micrographs (Fig. 7). An important loss of mass equivalent to 30% was observed.

In contrast, after 720 h in ultra pure water in darkness, the TiO_2 deposit on the conversion layer did not show any damage, water
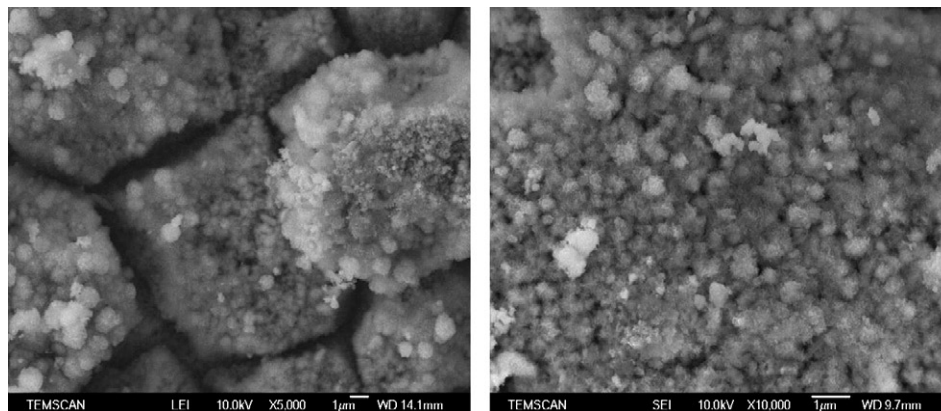
Fig. 7. SEM micrographs of the conversion layer after immersion in 3%NaCl during 720 h in darkness.
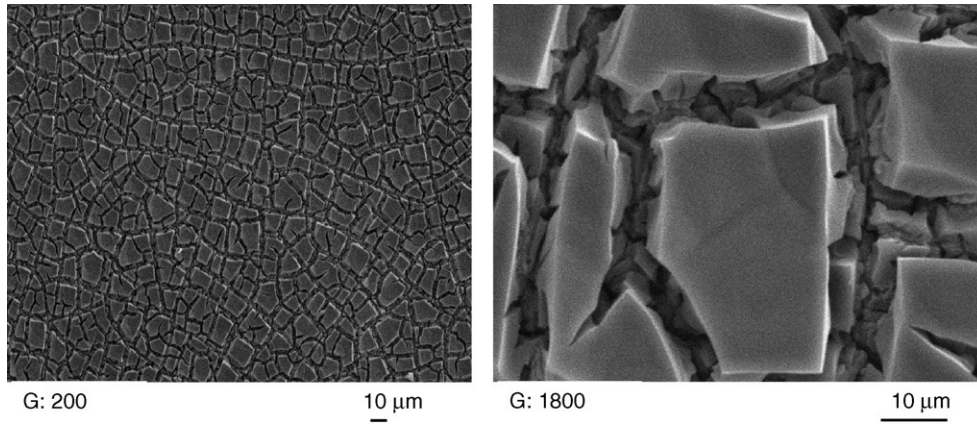
Fig. 8. SEM micrographs of the conversion layer/TiO$_2$ coating after immersion in pure water during 720 h in darkness.
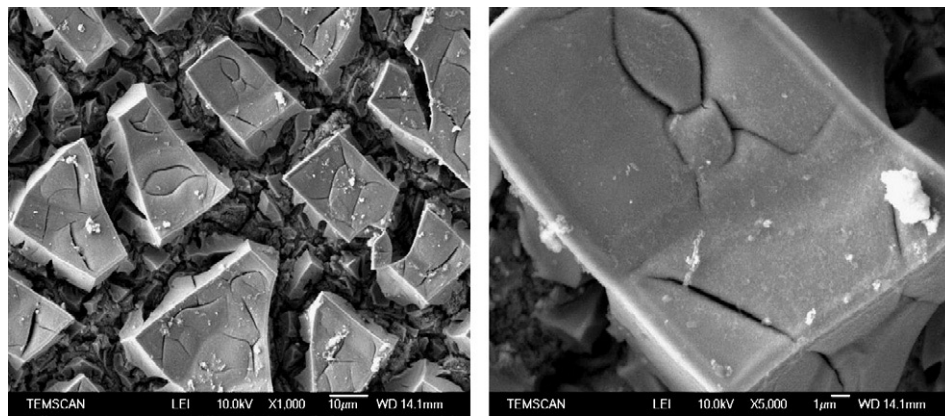

Fig. 9. SEM micrographs of conversion layer/TiO$_2$ system after immersion in 3%NaCl during 720 h in darkness.

remained clean and transparent. The structural analyses by XRD (X-ray diffraction), as well as the microstructural analysis by SEM (Fig. 8), show the conservation of the morphology and the composition of the deposit.

In the salt solution, the micrographs obtained by SEM-FEG (Fig. 9) show the formation of a very small quantity of white NaCl crystals on the enriched-TiO$_2$ parts of the sample. These crystals are usually obtained after such corrosion tests because they are very difficult to eliminate even after rinsing due to the roughness of the samples. No

loss of mass was observed and the salted solution was clear and transparent.

Therefore, we can conclude that the protection against corrosion provided by the conversion layer combined with TiO$_2$ coating on stainless steel in pure water and salted solution was quite good. More drastic tests were used in a second step. The samples were submitted to the soft test under wet atmosphere followed by the severe one. The variation of the sample mass according to the number of cycles is represented in Fig. 10. The results show the very good performance of the deposit that was not affected under the conditions of these tests, since there was no mass modification.

In the last step, the most severe test (the salt spray test) was performed. After 192 h, the samples pre-functionalized by a conversion layer were deteriorated, with formation of red rust accompanied by an important increase of the weight of the conversion coating ($\Delta m = 0.83$ g, Table 4). However, the samples covered by the duplex deposit, conversion layer/TiO$_2$ coating, showed a very good resistance, without any form of corrosion and no mass variation. This test has been continued for 500 h in the case of the duplex deposit, and the result was the same : no corrosion and no mass change.
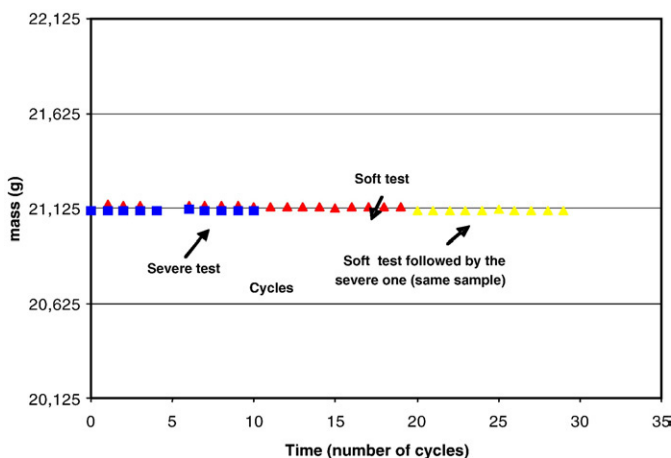

Fig. 10. Variation of the sample mass according to the number of test cycles.

Table 4
Salt spray test: Mass variation versus time (number of cycles)

	$t = 168$ h	$t = 500$ h
Steel	+1.5 g	+5 g
Conversion layer	+ 0.83 g	No measurement (too high)
Duplex coating (CC/TiO$_2$)	−0.01 g	−0.03 g

4. Conclusion

In this study, a new supported photocatalyst for water depollution was prepared by TiO_2 deposition using a sol–gel process, after formation of the conversion layer on the stainless steel surface. The samples covered by the duplex deposit, conversion layer/TiO_2 coating, were tested by standard corrosion tests carried out at three stages (steel plate, conversion layer and duplex). Although the ferritic stainless steels are well-known for their corrosion resistance, an important deterioration of steel was observed in ultra pure water as well as in salted solutions. The conversion layer alone was not sufficient to protect steel. In contrast, the association "conversion layer/TiO_2 deposit" exhibited total protection in the short and long-range, even under severe conditions. Therefore, this duplex layer represents a good alternative to existing means to protect ferritic stainless steels against corrosion in aqueous medium, and opens new prospects in the field of surface treatment and protection of this material. Moreover, TiO_2 being a good photocatalyst for the degradation of organic pollutants in water, the stainless steel treated samples could be used as new supported photocatalyst for water treatment, as the material shows excellent characteristics for this purpose due to its resistant in aggressive media and structural characteristics of the surface.

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