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The effect of heat treatment of TiO_2 coatings obtained by the sol-gel method on the corrosion resistance of chromium steel

EWA SZAŁKOWSKA[1*], JAN MASALSKI[2], BARBARA KUCHARSKA[3], JÓZEF GŁUSZEK[2]

[1]Department of Chemistry, Częstochowa University of Technology,
al. Armii Krajowej 19, 42-200 Częstochowa, Poland

[2]Institute of Inorganic Technology and Mineral Fertilizers, Wrocław University of Technology,
Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

[3]Institute of Materials Engineering, Częstochowa University of Technology,
al. Armii Krajowej 19, 42-200 Częstochowa, Poland

The corrosion resistance of chromium steel without coating and with a four-layer one-component TiO_2 coating has been examined in acidic sulphatic solution at pH 3.0 and the temperature of 25±0.2 °C. TiO_2 coatings were obtained by the sol-gel method. $Ti(C_3H_7O)_4$ (tetraisopropyl orthotitanate) was used as the titanium precursor. Chromium steel was coated with the dip coating method. The structure and phase composition of the TiO_2 coatings were determined from X-ray diffraction data. The topography of TiO_2 coatings before and after corrosion tests was examined by scanning electron microscopy. The protective effect of one-component coatings was evaluated based on polarization curves. The heat-treating of the coatings influences their protective properties. In the solution examined, the best protective properties exhibited TiO_2 coating (4 layers) heat-treated at 500 °C for 10 minutes.

Key words: *sol-gel method; potentiodynamic curves; X-ray diffraction;* TiO_2*; stainless steel*

1. Introduction

TiO_2 is a ceramic material that can be deposited in layers on different metallic substrates. TiO_2 layers are hard and chemically resistant and also possess a high dielectric constant and a high index of refraction. Thus, they are widely applied in electronics and optics [1–4]. They are also used in the form of coatings as corrosion protection and wear-resistant materials. The most common methods of TiO_2 deposition are CVD and PVD [5-7]. The sol-gel method, however, is also used to obtain TiO_2 layers [8–12].

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[*] Corresponding author, e-mail: ewas@mim.pcz.czest.pl.

Grain boundaries have crucial influence on the final properties of ceramic systems, regardless of the method by which they are obtained. Grain boundary properties are in turn defined by the porosity and segregation of impurities. The structure and composition of grain boundaries have great influence on surface properties. This is directly connected to surface functional properties such as corrosion and wear resistance. Porosity as well as pores size depend on many mutually dependent factors, i.e. the precursor used, the pH of the solution, the catalyst used, the solvent, time and temperature, reactor type, and finally component concentration in solution. One of the ways to achieve smaller pore size is to mix reactants by means of ultrasounds [13]. The pore volume (porosity) of coatings obtained by the sol-gel method may vary between 0 and 65%, pores size between 0.4 and 5 nm, and the specific surface between 1 and 250 m^2/g [14, 15]. The sol-gel method enables precise control of the microstructure of the deposited layer, i.e. the control over pore size and volume as well as specific surface.

Research conducted to date by the authors [16–19] has shown that a considerable improvement of the corrosion resistance of chromium steel can be achieved by using a protective oxide coating produced by the sol-gel method.

2. Experimental

One of the steps of the sol-gel method is high-temperature treatment of oxide coatings. The steel substrate might show a phase transition during this operation if iron steel is used. To avoid it, chromium steel (a modification of AISI 403) was chosen. The additional elements – molibdenium and vanadium (absent in AISI 403) – stabilize the precipitated carbides, making the steel more temperature-resistant. The chemical composition is given in Table 1. Samples were in the form of discs 12.0 mm in diameter and 1.0 mm thick. Before coating, the surfaces were ground with emery paper #1000, rinsed with distilled water, and degreased with tetrachloromethane in an ultrasonic washer.

Table 1. Chemical composition of the stainless steel used (% w/w)

C	Mn	Si	P	S	Cr	Ni	Mo	V	W	Cu
0.12	0.51	0.35	0.026	0.029	12.4	0.43	0.11	0.04	0.13	0.12

To obtain the TiO_2 sol, a solution containing 6.0 cm^3 of tetraisopropyl orthotitanate $Ti(C_3H_7O)_4$ and 45.0 cm^3 of anhydrous ethanol was used, to which a solution containing 6.0 cm^3 30% (m/m) of hydrous acetic acid and 45.0 cm^3 of anhydrous ethanol was added during stirring. The solution obtained was left in a closed vessel to age. After 3 to 5 hours, the solution became turbid, yielding 2.0% (m/m) of TiO_2 sol. The hydrolysis of tetraisopropyl orthotitanate proceeds as follows:

$$Ti(C_3H_7O)_4 + (2 + n)\ H_2O \rightarrow TiO_2{\cdot}nH_2O + 4C_3H_7OH \qquad (1)$$

The viscosity of the solution at 20 °C was 3.4–3.5 cP, as measured with a Hoppler viscosimeter.

Films were deposited on the samples by dip coating. First, the sol was homogenized for 45 minutes in an ultrasonic washer, then the samples were dipped in the sol for 2 minutes in order to establish the equilibrium at the boundary of the substrate/solution phases. The dipping and withdrawing of samples was performed at a constant rate of 1.0 mm/s. The samples were then kept at t = 25 °C for 24 hours and heat-treated in an electric furnace, heated to a maximum temperature of 300 °C, 400 °C, 500 °C, or 750 °C at a rate of 2.0 °C/min and kept at that temperature for 10 minutes. The process was repeated 4 times. Each following layer was deposited on a previous one heat-treated at the same temperature. For comparison, uncoated steel was examined in the same conditions.

X-ray diffraction of TiO_2 coatings was performed with MRD-Philips equipment (Materials Research Diffractometer), with a parallel $Cu_{K\alpha}$ beam falling on the layer at a constant angle (Θ = 4°). The intensity of the diffracted beam was measured within the angle range 2Θ = 20–100°. In the analysis of the experimental data, the PC-Identify program was used. The program was linked to the crystallographic database "Database – PDF1". Phase identification was done by comparing the 2Θ diffraction angle values and the reflex intensity (I) provided by the X-ray diagrams with the table data included in the „PC-Identify" program.

Electrochemical examinations were also performed. Polarization curves were measured in a conventional three-electrode thermostated system at 25±0.2 °C. In the potentiodynamic tests, a platinum electrode was used as an auxiliary one and a saturated calomel electrode (SCE) as a reference one. An analysis of the dependence of current density on the potential applied in acidic sulphate solution (pH 3.0) was performed by means of an automated measuring system consisting of an EP-20 potentiostat, an EC 20B generator, a 5D logarithmic amplifier (ELPAN, Poland), and a system for signal recording (AMBEX, Poland) connected to a PC. The potential was changed from cathodic to anodic values with respect to SCE at a small rate (1.0 mV/s), since the passivation process is typically slow.

For the polarization curves of uncoated and untreated chromium steel, 10 repetition scans were carried out, while 3 repetitions were performed for uncoated and heat-treated as well as for coated and heat-treated chromium steel. Differences between repetitions for the same type of samples did not exceed 5%. In some cases, when differences were bigger, additional repetitions were carried out.

The surface topographies of coatings deposited on chromium steel were obtained using a JEOL JSM-5400 scanning microscope before and after the experiment.

3. Results and discussion

The main objective of the X-ray analysis was to determine the structure and phase composition of TiO_2 coatings. X-ray diagrams are shown in Fig. 1. Significant reflexes are visible. Those due to the steel substrate are marked with asterisks and those caused by the TiO_2 layer with arrows.

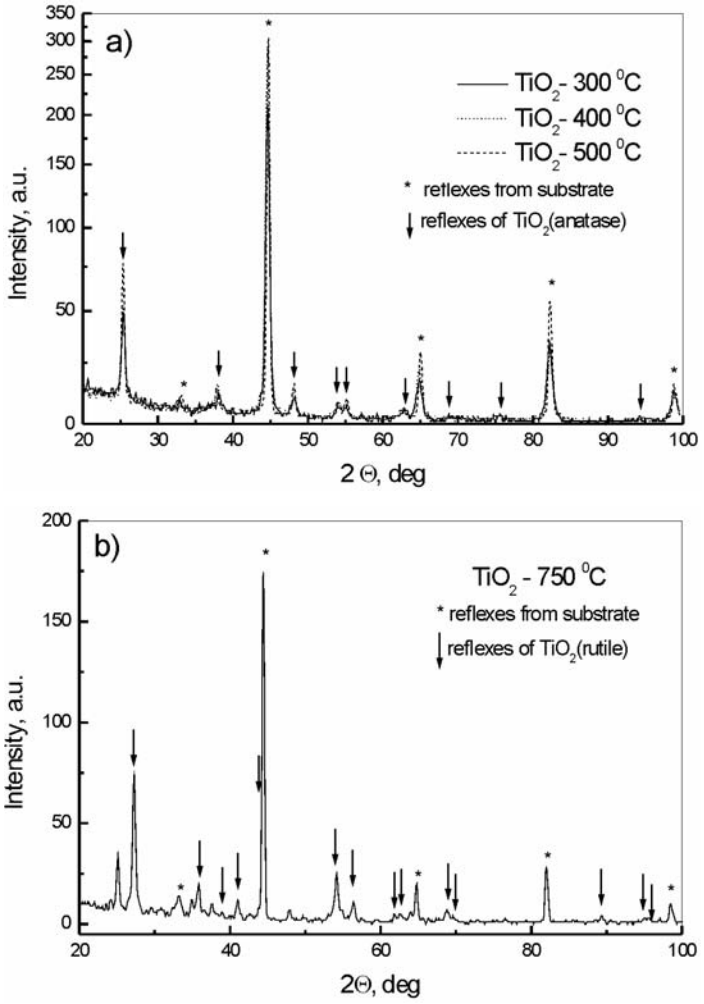

Fig. 1. X-ray diffraction of TiO_2 coatings on chromium steel coatings heat-treated at: 300 °C, 400 °C, and 500 °C a coating heat-treated at 750 °C

As far as the the phase structure is concerned, the coatings heat-treated at 300 °C, 400 °C, and 500 °C (Fig. 1a) are identical, i.e. they all possess the crystallographic structure of anatase (ASTM identification card 21-1272). As the heat-treatment temperature rises, however, an increase of the reflex intensities can be observed (Fig. 1a). The TiO_2 coating heat-treated at 750 °C (Fig. 1b) exhibits the crystallographic structure of rutile (ASTM identification card 21-1276) as well as weak reflexes originating from another phase, which cannot be identified due to their low intensity.

In order to determine the anticorrosion effectiveness of coatings, potentiodynamic polarization curves in an acidic sulphatic solution with pH 3.0 were measured (Figs. 2–5).

The analysis of the curves for uncoated steel indicates that the cathodic oxygen reduction takes place at a slower rate on heat-treated than untreated steel. During the

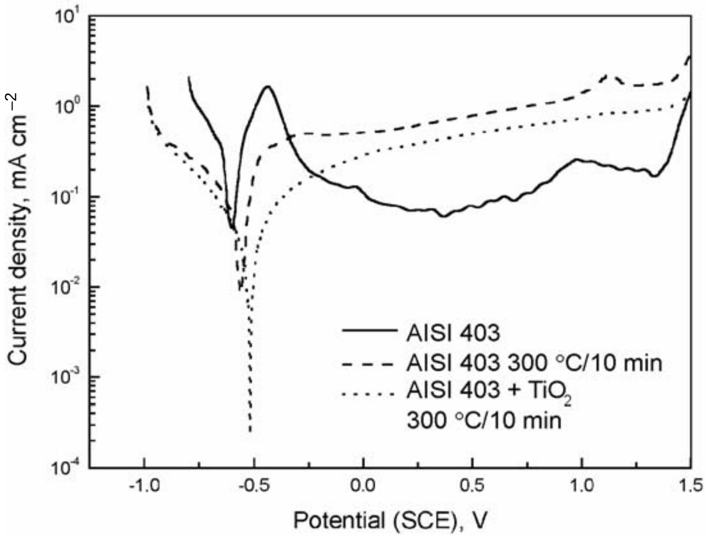

Fig. 2. Polarization curves recorded for chromium steel (uncoated and untreated, uncoated and heat-treated at 300 °C, TiO_2-coated and heat-treated at 300 °C) in a sulphatic solution with pH 3.0

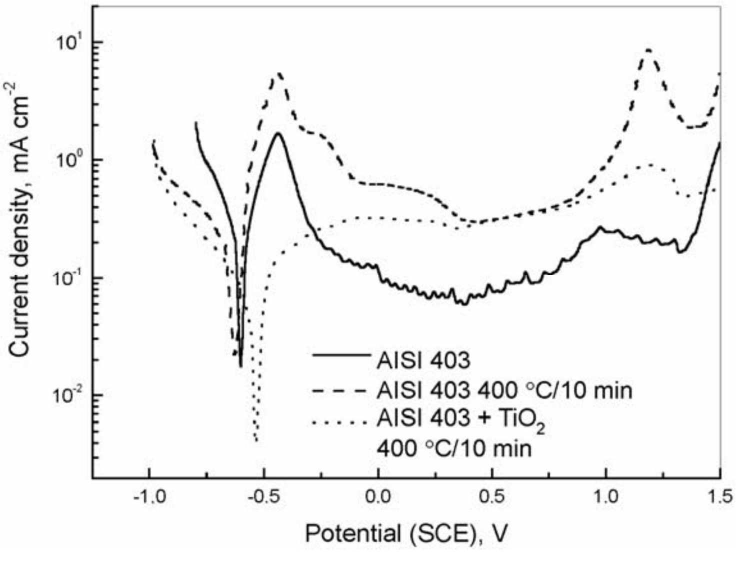

Fig. 3. Polarization curves recorded for chromium steel (uncoated and untreated, uncoated and heat-treated at 400 °C, TiO_2-coated and heat-treated at 400 °C) in a sulphatic solution with pH 3.0

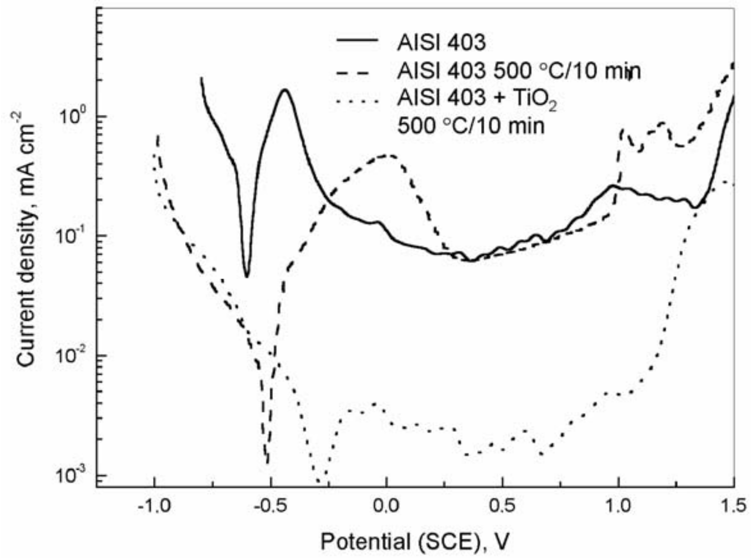

Fig. 4. Polarization curves recorded for chromium steel (uncoated and untreated, uncoated and heat-treated at 500 °C, TiO_2-coated and heat-treated at 500 °C) in a sulphatic solution with pH 3.0

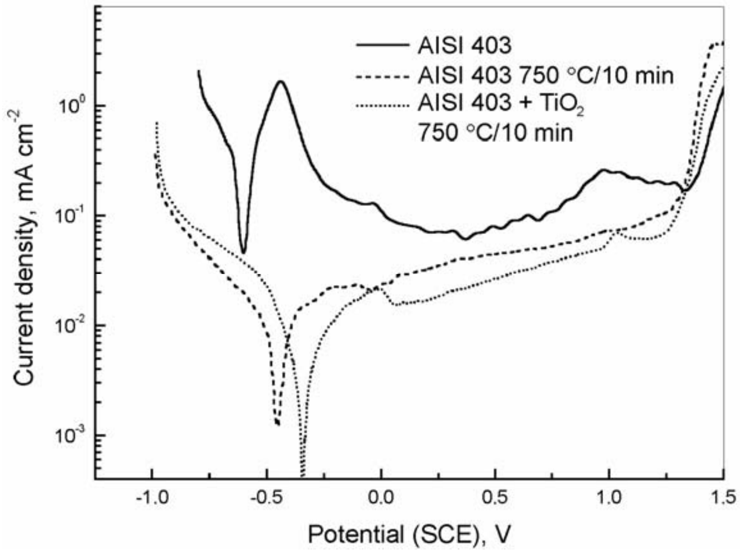

Fig. 5. Polarization curves recorded for chromium steel (uncoated and untreated, uncoated and heat-treated at 750 °C, TiO_2-coated and heat-treated at 750 °C) in a sulphatic solution with pH 3.0

steel heat-treatment in air, chromium spinel appears on its surface. Its general formula is $FeFe_{2-x}Cr_xO_4$, where x represents values close to 2 [20]. It is therefore highly probable that the chromium–iron spinel on the steel surface slows down cathodic reduction. Heat-treatment temperature has an influence on steel behaviour in the corrosion solution. A decrease in the cathodic and anodic current density is observed when the steel is heat-treated at 500 °C or 750 °C. The best corrosion resistance was shown by steel heat-treated at 750 °C and the worst by steel heat-treated at 400 °C. As can be seen in Figures 2–5, TiO_2 coatings also slow down the cathodic processes, the most effective being observed for the layer heat-treated at 500 °C. For coatings heat-treated at 300 °C or 400 °C (Figs. 2 and 3), deterioration in the passive state properties is observed. On the other hand, a considerable decrease in both cathodic and anodic current density could be achieved for coatings heat-treated at 500 °C or 750 °C, and the speed of the anodic process decreased by a factor two at the cathodic-anodic transition potential as compared to the steel substrate.

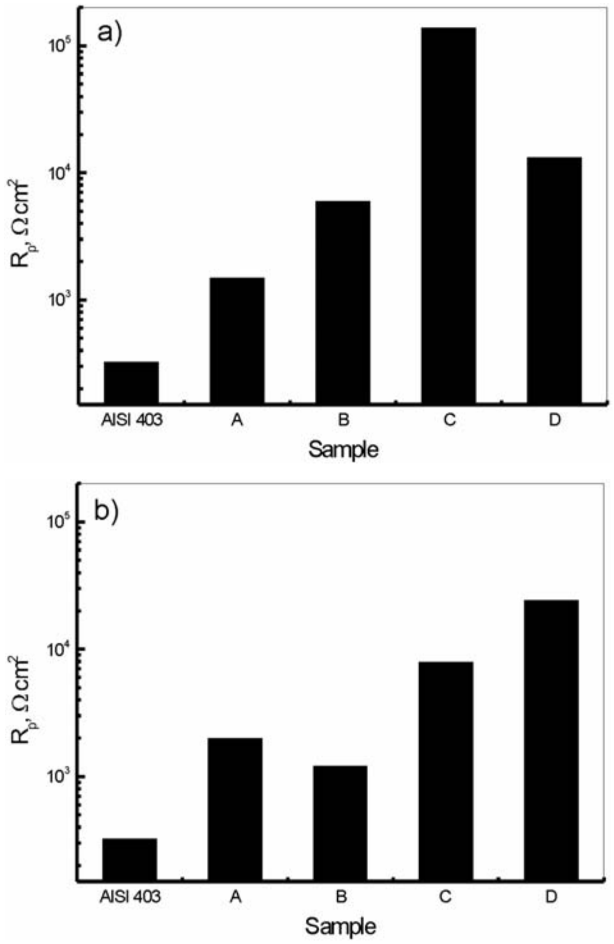

Fig. 6. Comparison of the polarization resistance R_p of a) coated and uncoated AISI 403: A) coating heat-treated at 300 °C, B) coating heat-treated at 400 °C, C) coating heat-treated at 500 °C, D) coating heat-treated at 750 °C; b) treated and untreated AISI 403 steel: A) steel heat-treated at 300 °C, B) steel heat-treated at 400 °C, C) steel heat-treated at 500 °C, D) steel heat-treated at 750 °C

A larger decrease in TiO_2 coating corrosion speed when heat-treated at 750 °C is difficult to obtain since the coatings are porous. When higher heat-treatment temperatures are applied, an increase in the Cr_2O_3 crystalline layer on the border of steel/coating phases was observed, increasing the number of cracks produced at lower temperatures.

To evaluate the quality of the coatings, the polarization resistance R_p was determined. Experimental points close to the cathodic-anodic transition potential were used. In an E–i plot, they form a straight line, whose slope is directly connected to the polarization resistance. Values of R_p were determined using linear regression (Fig. 6). A change in the heat-treatment temperature of the coatings causes alterations in the polarization resistance of AISI 403 steel with coatings. From Fig. 6 it can be concluded that the heat-treatment temperature of TiO_2 coating influences its protective properties. This is due to the removal of H_2O and ROH, as well as to the densification of the gel structure. The best protective properties were shown by coatings heat-treated at 500 °C and the worst by coatings heat-treated at 300 °C.

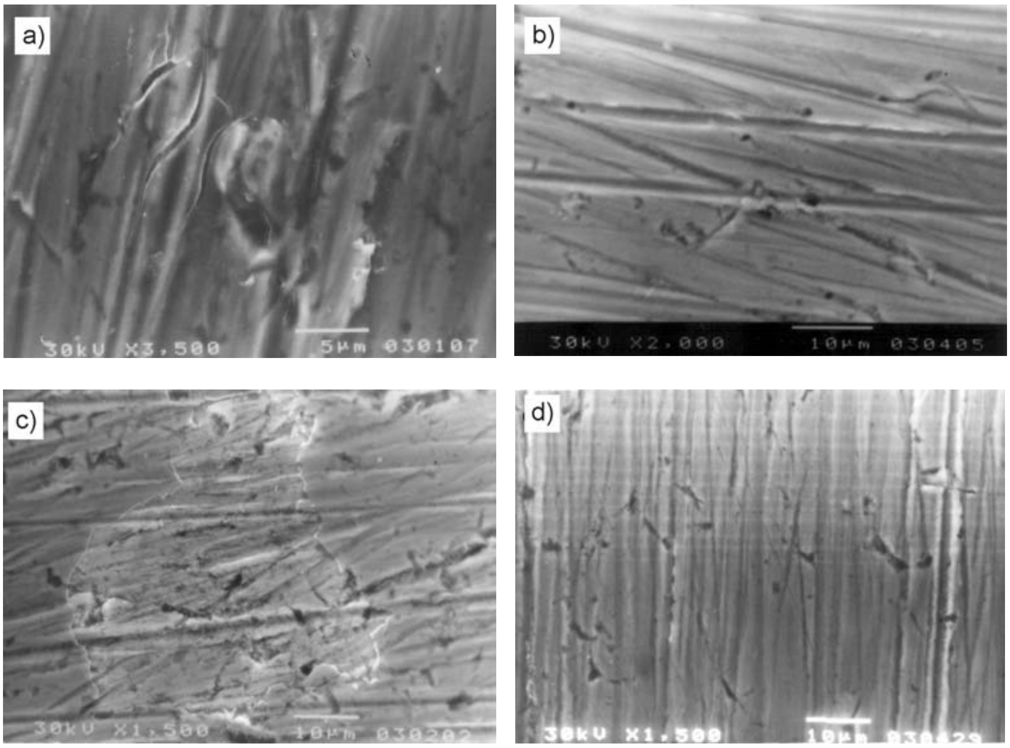

Fig. 7. The microstructure of TiO_2 coating on chromium steel: a) heat-treated at 300 °C, b) heat-treated at 500 °C, c) heat-treated at 300 °C after corrosion tests in a sulphatic solution with pH 3.0, d) heat-treated at 500 °C after corrosion tests in a sulphatic solution with pH 3.0

Coatings heat-treated at 300 °C or 500 °C were subject to microscopic examination before and after corrosion tests. Due to their relatively small thickness, the coatings reflect irregularities and scratches on the substrate resulting from the use of sandpaper (Figures 7a and b). The coating heat-treated at 500 °C showed the same thickness on the entire substrate surface (Fig. 7b). After the corrosion test performed in a sulphatic solution with pH 3.0, the coating partially dissolved but preserved its continuity. The coating heat-treated at 300 °C shows local discontinuities (cracks) (Fig. 7a), which may be due to the heat-treatment process. After the corrosion tests, considerable losses were observed (Fig. 7c) due to a fast dissolution of the coating at the cracks. The coated substrate heat-treated at 300 °C shows a significantly higher level of corrosion than that heat-treated at 500 °C (Figs. 7c and d).

It is therefore necessary to improve or to modify the sol-gel method used to obtain TiO_2 coatings. Such coatings are porous and do not protect the metallic substrate from water and oxygen penetration, although thermal treatment leads to a certain decrease in porosity.

4. Conclusion

TiO_2 coatings have been deposited on chromium steel by means of the sol-gel method. These coatings improve the corrosion resistance of steel in acidic sulphatic solution with pH 3.0, but the protective properties of the coatings depend on the heat-treatment temperature. This is due to the vaporization of H_2O and ROH and to the densification of the gel structure. The best protective properties were shown by a four-layer TiO_2 coating heat-treated at 500 °C for 10 minutes. The temperature of heat-treatment of steel also influences its behaviour in the corrosion solution. The best corrosion resistance was found for AISI 403 steel heat-treated at 750 °C for 10 minutes. On the basis of X-ray diffraction, the structures and phase compositions of the investigated oxide coatings were obtained. TiO_2 coating produced at 750 °C exhibits a rutile crystallographic structure. Coatings heat-treated at lower temperatures, on the other hand, show an anatase crystallographic structure.

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