ANYAGVIZSGÁLÓK LAPJA
MINŐSÉGBIZTOSÍTÁS * ÁLLAPOTELLENŐRZÉS
Elektronikus folyóirat
2012/4

A KOLLOIDOLDAT-GÉL MÓDSZERREL ELŐÁLLÍTOTT SiO2 AND TiO2 VÉKONY RÉTEGEK VÉDŐ ÉS MECHANIKAI TULAJDONSÁGAINAK MEGHATÁROZÁSA
DETERMINATION OF CHOSEN PROTECTIVE AND MECHANICAL PROPERTIES OF THE SiO2 AND TiO2 THIN COATINGS OBTAINED BY SOL – GEL METHOD

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***Kulcsszavak**: kolloidoldat-gél módszer, vékony rétegek, titándioxid, szilíciumdioxid, elektrokémiai vizsgálatok, tapadás*
***Keywords:** sol-gel method, thin coatings, titanium dioxide, silicon dioxide, electrochemical studies, adhesion*

Absztrakt

A kolloidoldat-gél módszerrel fémes alapra (316L) felvitt SiO_2 és TiO_2 vékony rétegek védő és mechanikai tulajdonságait határozták meg. A rétegek folytonosságát pásztázó elektron mikroszkóppal (SEM) vizsgálták. A korróziós vizsgálatokat (elektrokémia méréseket) 1, 3 és 5 rétegű SiO_2 és TiO_2 rétegeken hajtották végre. Az elektrokémiai mérések igazolták a bevonatok korrózióvédő hatását. A mechanikai vizsgálatokhoz hidraulikus szakítógépet (MTS 810) használtak a 100kN-ig terjedő tartományban. A statikus szakító és fárasztó vizsgálatokat 1 és 3 rétegű SiO_2 és TiO_2 rétegeken hajtották végre. A szakító vizsgálatok előtt és után elvégzett SEM eredmények és a röntgen spektroszkópia azt mutatták, hogy a réteg tapadása az alapanyaghoz a szakítás során nem változott

Abstract

Protective and mechanical properties of SiO_2 and TiO_2 thin coatings obtained by sol-gel method onto metallic substrates (316L) were determined. Continuity of the coatings was examined by Scanning Electron Microscope (SEM). Corrosion tests (electrochemical studies) were performed for single, triple and five layered SiO_2 and TiO_2 coatings. Electrochemical studies have confirmed that the coatings behave as a corrosion barrier. The mechanical tests were conducted on a hydraulic testing machine MTS 810 with a range to 100 kN. Static tensile tests and fatigue strength tests were conducted for single layer and triple layer SiO_2 and TiO_2 coatings. The SEM observations and Energy Dispersive X-ray Spectroscopy (EDS) analyzes, after tensile tests have confirmed that adhesion of the coatings to the substrates between the samples before and after tensile test did not changed.

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1. INTRODUCTION

SiO_2 and TiO_2 coatings were obtained to improve surface properties of the metallic substrates. Metallic materials with required mechanical properties, covered by ceramic or glass coatings have better resistance to oxidation, corrosion, erosion and wear [1]. That composition should find possible application in chemical or medical industry.

To obtain ceramic coatings onto metallic surfaces several methods are used: physical vapour deposition, chemical vapour deposition, plasma spraying, laser cladding, chemical plating or sol-gel process [2]. The sol-gel method is the most promising. The method is easy, cost effective and is one of the low temperature methods of obtaining thin coatings [3]. Moreover sol-gel method allows to coat irregular shapes.

The sol-gel method is based on hydrolysis and condensation of liquid precursors. We can distinguish three main sol-gel techniques: dip-coating, spin coating and meniscus coating. Dip-coating method is based on immersing the substrate into hydrolizate and detaining substrates into hydroliate for specified time. After that substrates are pulled out and dried. Spin coating method is based on putting drops of hydrolyzate on rotating, with constant speed, substrates. Whereas meniscus coating method is based on depositing the sol onto a substrate using a porous cylinder coated with sol. The cylinder moves very close above the surface of the substrate, so sol forms a meniscus.

The main advantage of sol-gel method is the possibility of obtaining thin ceramic and glass coatings at low temperatures (even room temperatures). This property allows to place into or onto coatings many substances, for example metallic nanoparticles, drugs and even chosen bacteria [4]. The multiply choice of additions makes it possible to obtain coatings with broad spectrum of properties, for example: anti – reflective, scratch-resistant or antiseptic properties [**Hiba! A könyvjelző nem**

létezik., [5]. With the properties mentioned above, the sol-gel products may be used to create different kind of sensors [**Hiba! A könyvjelző nem létezik.**], self-cleaning or antireflective coatings and coatings for medical implants [6]. Coatings like SiO_2, TiO_2, SiO_2-TiO_2, SiO_2-TiO_2-ZrO_2, SiO_2-Al_2O_3-ZrO_2-P_2O_5, protect the implant from corrosion and are biotolerant. In addition, glasses and ceramic coatings increase the wear resistance and decrease the friction [7]. This is an important issue because products of corrosion and friction cause inflammation in the body or damage of the tissues and organs.

For anti-corrosion coating functionality, sol-gel coatings should be coherent to the substrate, should maintain continuity and have appropriate roughness.

In our research we have obtained coatings by dip-coating method. Raman spectroscopy studies have shown, that obtained coatings were crystalline TiO_2 and amorphous SiO_2 [8], which means that obtained coating were consistent with the expectations. SEM observations have confirmed that coatings were continuous. The exampleS of continuous and not continuous coating are shown in Fig.1.

2. EXPERIMENTAL

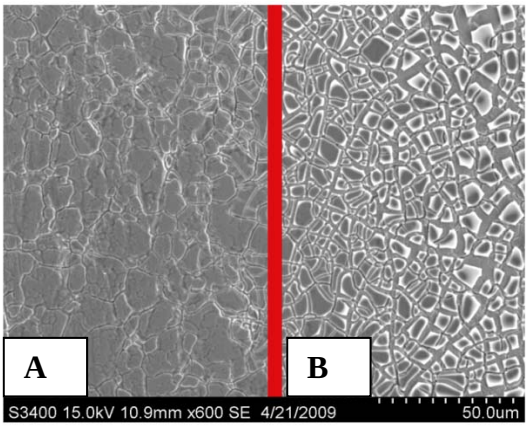

Fig. 1. SEM images of single layer TiO_2 coating obtained by sol-gel method: A) continuous coating, B) not continuous coating

2.1 PREPARATION OF THE SiO_2 AND TiO_2 COATINGS

The sol-gel precursors used for silicon dioxide (SiO_2) coatings were tetraethyl orthosilicate (TEOS - [Si(OC2H5)4]) and tetraethyl orthosilicate (TIPO - [TiCOC3H7)4]) for titanium dioxide (TiO_2) coatings. The reagents used were etanol (EtOH - [C2H5OH]) and hydrochloric acid (HCl) for SiO_2 coatings and isopropanol (izoPrOH - [C3H7OH]), acetylacetone (AcAc - [C5H8O2]) for TiO_2 coatings. All materials were purchased from Sigma Aldrich and used without further purification.

Dip coating technique is based on dipping the substrate into the hydrolizate. The substrates were immersed in the hydrolizate at a speed of 34.26 [mm/min]. The retention time (time after immersion of the substrate and before the start of extraction) is depending on the number of superimposed layers.

Creating the first layer, substrates were kept in the hydrolyzate for 60 seconds. While applying the second and third layer on the same substrate, the retention time was respectively accordingly: 30 seconds and 15 seconds. For the fifth layer, the retention time was also 15 seconds. The retention time was reduced to minimize the dissolution of already formed layers in the hydrolyzate. After the imposition of each layer the samples were dried in the air for 24 hours. The last step of obtaining coatings was annealing at 500°C for 1h. In case of triple SiO_2 and TiO_2, coatings were also soaked after imposition of each layer.

The substrates used in the research were made from stainless steel (316L). Before the research, substrates were purified in ultrasonic cleaner with acetone for 15 min. Than substrates were rinsed with distilled water and after that with ethanol and left to dry.

2.2. THE TEST METHODS

The surface morphology, microstructure and elemental composition of the SiO_2 and TiO_2 thin coatings were characterized by Scanning Electron Microscope HITACHI S-3400 (SEM).

SEM observations and Energy Dispersive X-Ray Spectroscopy (EDS) research were carried out to examine the continuity of the obtained coatings

The electrochemical study consisted of recording polarization curves in a three-electrode cell. Referenced electrode was a saturated calomel electrode (NEK), while the auxiliary electrode was a platinum electrode. The measuring system consisted of a measurement vessel, SI1286 potentiostat and a computer. The survey was conducted in an artificial physiological fluid (SBF) in which the samples were immersed for 10 minutes before the test. The samples were polarized in the direction of the anode at a rate of 1mV/s, starting from the potential (- 1000mV). The study was conducted to determine the effect of SiO_2 and TiO_2 coatings on the corrosion resistance of 316L steel.

The tensile tests were conducted on MTS 810 machine with the tensile stress range from 0 to 100 kN. The study consisted of static tensile tests and

fatigue strength tests. The testing samples were substrates covered by single and triple SiO_2 and TiO_2 coatings.

Static tensile tests were performed in accordance to the polish norm PN-EN ISO 6892-1:2010 [9]. The extension speed was 0.3 mm/min in elastic range and was increased to 3 mm/min after crossing the yield strength. The stress-strain graph for the sample covered by single SiO_2 coating is shown in Fig. 2. For all the samples graphs were almost the same.

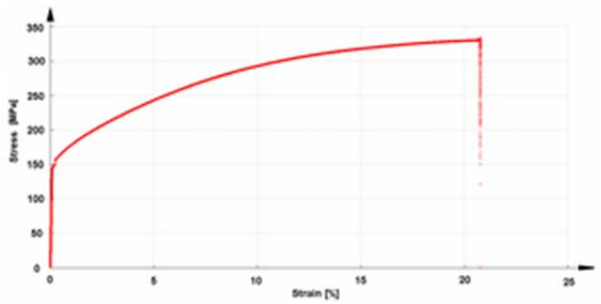

Fig. 2. Stress-strain graph for the sample covered with SiO_2 coating

FATIGUE STRENGTH TESTS.

Analysis of the graphs, obtained for the samples tested in the static tensile test and increasing cyclic test (Fig. 3), were performed to select appropriate values for the load and the frequency for test. Analysis of these data allowed choosing the appropriate test parameters: cyclic load was 4.5 kN/1.5 kN and frequency was 10 Hz.

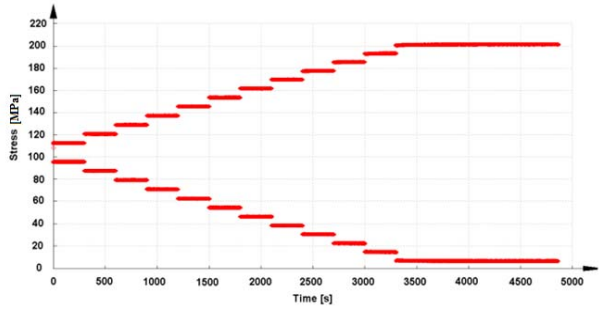

Fig. 3. Graph of increasing cyclic test.

SEM analysis of the samples was conducted after tensile tests to verify continuity of the coatings and adhesion of the coatings to the substrates. The burst area was the area of interest.

3. RESULTS

3.1. CORROSION TESTS

The electrochemical measurements consisted of potential measurements and polarisation curves. The effect of the heat treatment on electrochemical parameters of substrates was noticed (Fig. 4). In this case, the electrochemical parameters obtained from 316L steel after heat treatment, were the research base.

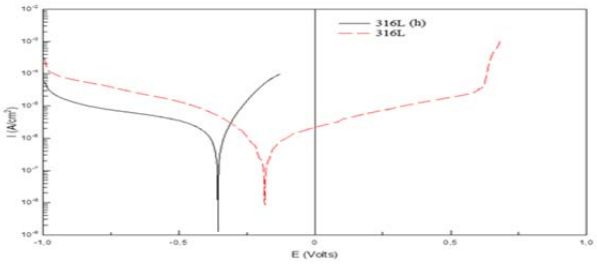

Fig. 4. Polarization curve for: 316L - sample without coating before heat treatment and for 316L (h) - sample without coating after heat treatment.

The researched samples were substrates covered by single, triple and with five layer SiO_2 and TiO_2 coatings. Samples were soaked after imposition of all layers. Additionally triple layer SiO_2 and triple layer TiO_2 coatings were soaked after imposition of each layer. All samples with the results of the research are presented in Table 1.

The Figure 5 clearly shows that the corrosion resistance of the samples with SiO_2 coatings are enhanced with the number of applied layers for samples with the heat treatment after imposition of all layers.

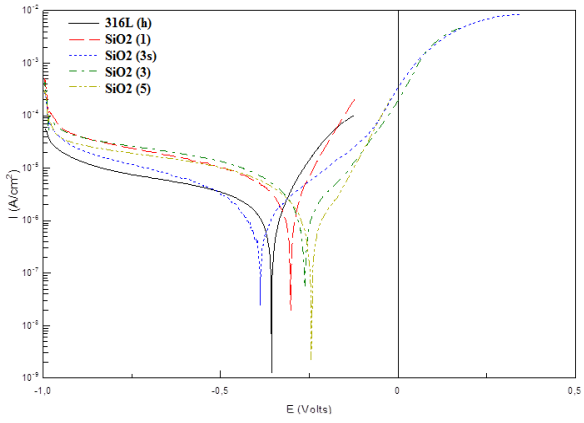

Fig. 5 Polarization curve for: 316L (h) - sample without coating after heat treatment; SiO_2 (1) - sample with single layer SiO_2 coating; SiO_2 (3s) - sample with triple layer SiO_2 which was soaked after imposition of each layer; SiO_2 (3) – sample with triple layer SiO_2 coating; SiO_2 (5) - sample with five layer SiO_2 coating.

Table 1 Corrosion currents (iKOR), corrosion potentials (ECORR) and polarization resistance (Rp) obtained

Lp.	Sample	R_p [Ωcm^2]	i_{KOR}[A/cm^2]	E_{KOR}[V]
1	316L without coating before heat treatment	67614	1,19*10^{-6}	- 0,18456
2	316L without coating after heat treatment	24646	3,27*10^{-6}	- 0,35733
3	316L with single layer SiO_2 coating	12720	2,05*10^{-6}	- 0,30398
4	316L with triple layer SiO_2 coating	17433	1,49*10^{-6}	- 0,26373
5	316L with triple layers SiO_2 coating, which were soaked after imposition of each layer	28610	2,82*10^{-6}	- 0,38945
6	316L with five layers SiO_2 coating	30112	0,86*10^{-6}	- 0,24480
7	316L with single layer TiO_2 coating	164940	0,16*10^{-6}	- 0,11795
8	316L with triple layer TiO_2 coating	22230	1,17*10^{-6}	- 0,23340
9	316L with triple layer TiO_2 coating, which were soaked after imposition of each layer	13709	1,90*10^{-6}	- 0,25106
10	316L with five layer SiO_2 coating	13058	1,99*10^{-6}	- 0,24863

The analysis of electrochemical parameters obtained for TiO_2 coatings on steel 316L (Fig. 6) has shown the electrochemical corrosion resistance did not depend on the number of layers (thickness). However the polarization resistance for single layer TiO_2 coating in relation to the soaked substrate without coating, has increased more than 6 times.

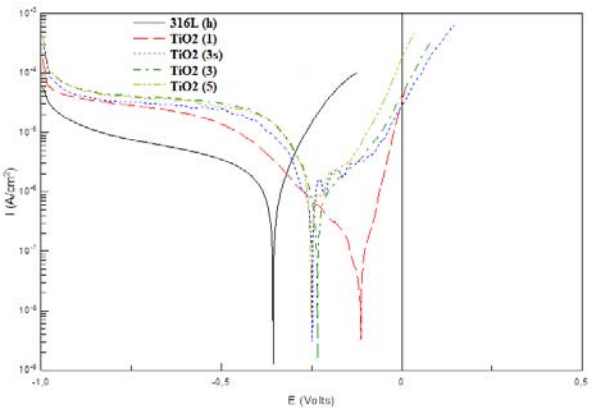

Fig. 6 Polarization curve for: 316L (h) - sample without coating after heat treatment; TiO_2 (1) - sample with single layer TiO_2 coating; TiO_2 (3s) - sample with triple TiO_2 which was soaked after imposition of each layer; TiO_2 (3) – sample with triple layers TiO_2 coating; TiO_2 (5) - sample with five layers TiO_2 coating.

The polarization curves of SiO_2 and TiO_2 coatings on 316L confirmed that the coatings behave as corrosion barriers, showing the positive shift of the corrosion potential *E*corr (*Fig. 5 and Fig. 6*).

3.2. TENSILE TESTS

The detailed SEM images and EDS analysis of the coatings after tensile tests were presented in our earlier work [8] and have shown that coatings maintain continuity. In this work, we focused on maintaining the adhesion of the coatings to the substrates after performing fatigue tensile tests in the burst area.

The examples of SEM images of the surfaces of the coatings after fatigue strength tests are shown in the Figures 7 to 10. The SEM images show that the coatings have good adhesion to the substrates and have maintained continuity after tensile tests.

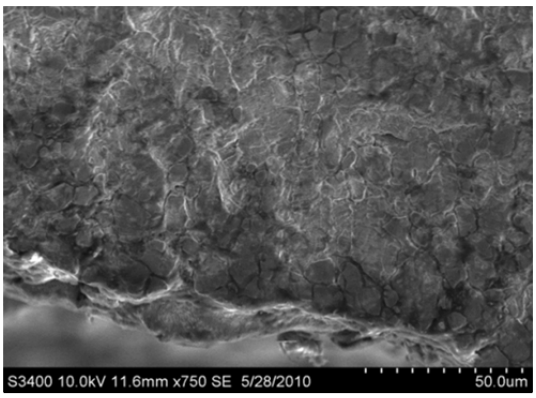

Fig. 7 SEM image showing single layer SiO_2 coating obtained by dip coating technique onto 316L substrate after fatigue strength tests

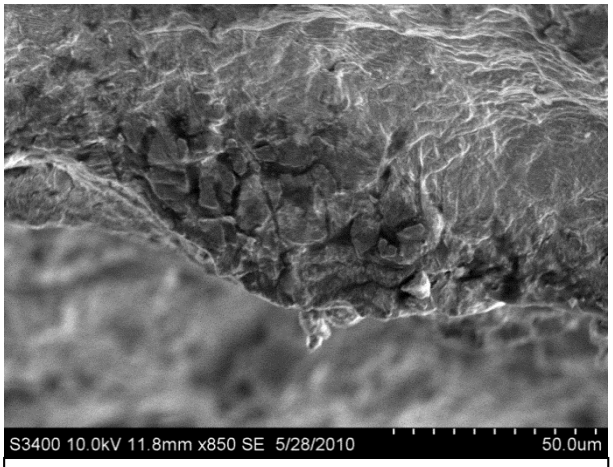

Fig. 8 SEM image showing triple layer SiO_2 coating obtained by dip coating technique onto 316L substrate after fatigue strength tests

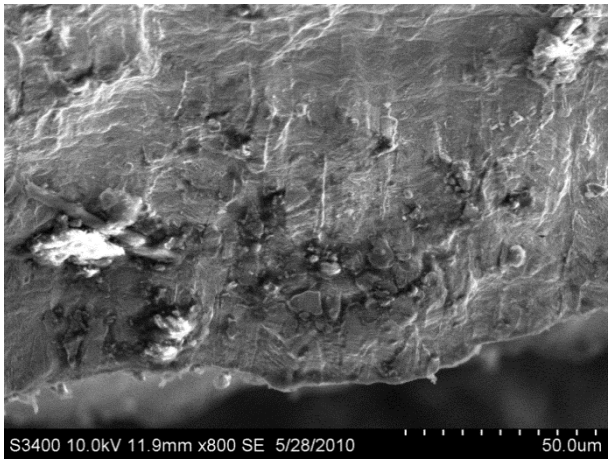

Fig. 9 SEM image showing single layer TiO_2 coating obtained by dip coating technique onto 316L substrate after fatigue strength tests

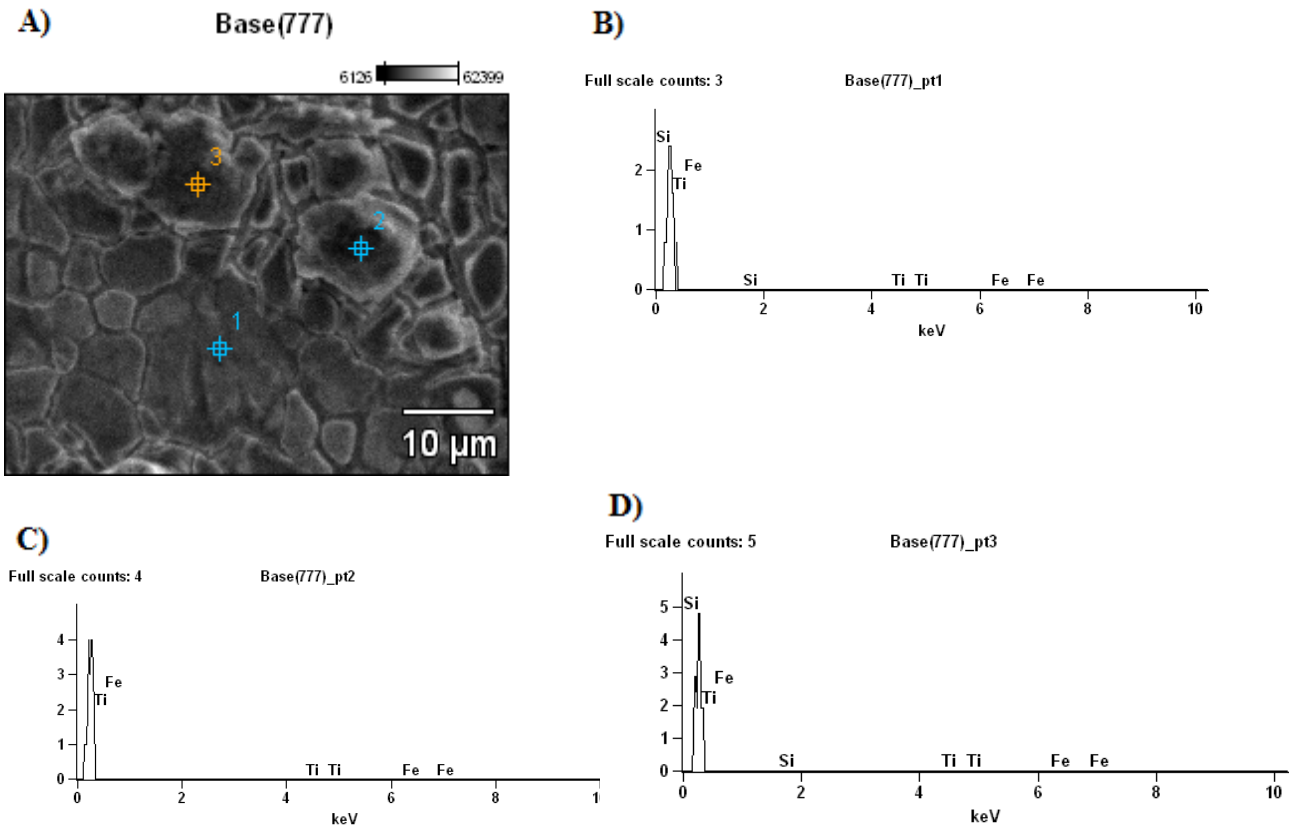

Fig. 10 A) SEM image showing triple layer TiO_2 coating obtained by dip coating technique onto 316L substrate after fatigue strength tests with SEM - EDS analysis of the: **B)** point 1; **C)** point 2; **D)** point 3.

However, for triple TiO_2 coatings we have conducted detailed analyses EDS, because of occurring furrows. The EDS analyses (Fig. 10) confirmed continuity of triple TiO_2 coatings. We have detected titanium in all the surveyed points were.

The research has confirmed, that there were no differences in the adhesion of coatings to the substrates between the samples before and after tensile test. The interruptions of the coatings took

place, where the fracture of the samples took place.

The coatings were not damaged or destroyed outside of the fracture of the metallic substrate, what testifies their strong adhesion to the substrate. Furthermore, the lack of flaking of the coatings after a tensile test indicates that the plasticity obtained by sol-gel materials is similar to the plasticity of the metallic substrate. This may be related with a small thickness of the coating (~ 300 nm). Coatings behave similar to the glass fibres.

4. Conclusions

SiO_2 and TiO_2 thin sol-gel coatings were obtained onto stainless steel substrates (316L) by dip coating technique. An annealing step was performed. Preliminary research has confirmed that the SiO_2 and TiO_2 coatings obtained by sol-gel method have mechanical and protective properties, adequate to use them as protective coatings. The electrochemical studies have confirmed that obtained SiO_2 and TiO_2 coatings behave as a corrosion barrier. Moreover, SEM observations after the tensile tests have shown that the coatings were at least as flexible as substrates and their adhesion to the substrates remains unchanged after tensile tests.

5. References

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