

# Characterisation of Reinforced BTSE Films Deposited on Anodized Aluminium Substrate

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*This paper discusses the improvements achieved in the anticorrosive properties of some silane films by pretreating the metallic substrate prior to films deposition and by reinforcement with some reinforcement agents. One has compared the behaviour of silane films, deposited on aluminium substrate, and the reinforced silane films deposited on anodised aluminium substrate. The use of scanning electron microscopy highlighted the modifications of substrate surface characteristics prior and after the anodisation process, while electrochemical techniques such as open circuit potential, electrochemical impedance spectroscopy and potentiodynamic polarization were employed in order to characterize the deposited films from the corrosion behaviour point of view.*

**Keywords:** silane films, anodized aluminium, electrochemical impedance spectroscopy, composite materials, corrosion

Silane films have been used as intermediate layers for a long period of time and are still considered as a viable alternative to chromate coatings, as their anticorrosive properties and their ability to form condensed films on different substrates improve the final properties of the product without the drawback of the associated environmental issues [1,2]. The improvements in the protective performance of the silane films are usually achieved using various additions of substances with corrosion inhibiting properties such as silica, titanium and titanium dioxide nanoparticles, cerium, lanthanum and zirconium compounds or silicon carbide [1-10].

In order to obtain the desired properties of the silane films, one should take into account some important aspects related to the deposition process, such as the substrates pre-treatment, deposition time and the corresponding curing treatment. These steps are of a paramount importance for the final properties of the silane films, as reported in [11-16]. Our previous research was focused on the curing treatment and on the determination of the optimum deposition time for the silane films, in order to obtain films with improved anticorrosive protection properties resistance. Aluminium was used as substrate and octyltriethoxysilane (OTES), vinyltriethoxysilane (VTES), bis-1,2-(triethoxysilyl)ethane (BTSE), bis(3-triethoxysilylpropyl)tetrasulfidesilane (BTESPT), and tetraethylorthosilicate (TEOS) were the deposited silanes [4, 17].

As previously reported in several studies, the anticorrosive properties of aluminium may be enhanced by anodisation, as the oxide layer formed through this process enables a higher bonding between the silane film and the aluminium substrate. The most commonly used electrolyte solutions are consisting of sulphuric acid containing molybdate, permanganate species, tartaric acid, alkaline borax solution or oxalic acid [18-26].

The anticorrosive properties of the silane films were evaluated by means of electrochemical impedance spectroscopy and potentiodynamic polarisation as these electrochemical techniques have been previously used for this purpose [4,17,27,28].

This paper focuses on the combined effect of anodisation of the substrate and reinforcement of the silane film using titanium and titanium dioxide. *The aim of paper is to*

*emphasize the effects of anodisation and reinforcement on the anticorrosive protection properties of 5% BTSE silane films deposited on aluminium substrate.*

## Experimental part

### Materials

The metallic substrate was polished with coarse (600) and fine emery paper (2000), and cleaned with a 15% sodium carbonate solution, rinsed with distilled water and ethylic alcohol and then rinsed again with distilled water. The cleaned substrate was dried and subjected to anodisation.

The electrochemical cell used for the anodisation of the metallic substrate consists of the aluminium substrate used as anode (2cm<sup>2</sup>), a lead electrode used as cathode (6cm<sup>2</sup>) to provide an uniform current distribution, and an electrolyte solution of 1 M H<sub>2</sub>SO<sub>4</sub>. There were several parameters which were varied during the anodisation process, namely the current density and time of exposure. The current density series used for anodisation was 0.3, 0.35 and 0.4 A/cm<sup>2</sup>, and the exposure time was 6, 8 and 10 min.

In order to visualize the surface of the pre-treated substrate, the anodised samples were subjected to optical microscopy. This step was performed with an Intel QX3 microscope, the images were recorded at a 60x magnification. One has also used the associated software for generating (starting from the recorded images) emulated images corresponding to IR filtration.

Bis-1,2-(triethoxysilyl)ethane (BTSE), purchased from Fluorochem Ltd, Hadfield, U.K, was the silane used as a protective coating. A 5% BTSE solution was prepared by adding the silane in a 50:50 (v:v) mixture of ethanol (Merck) and distilled water and then was deposited on the anodised aluminium substrate at the optimum hydrolysis time of the silane solution, determined in a previous study [11]. The above mentioned films were cured at room temperature for 24 h.

In order to further increase the anticorrosive properties of the silane films, one reinforced the silane films with titanium and titanium oxide particles, the corresponding suspension load being 1g/L. The suspension solutions were kept in equilibrium using a 40KHz Condel 3106 ultrasound bath to avoid the naturally occurring sedimentation, for the

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whole duration of reinforced silane films deposition (10 min). The obtained composites were cured at room temperature ( $25\pm 2^\circ\text{C}$ ) for 24 h.

### Methods

The scanning electron microscopy was performed using a Carl Zeiss Merlin Gemini II microscope with an Oxford Instruments X-Max EDS detector.

Before the SEM analysis, the samples were cleaned with ethanol. The parameters for this analysis were: current on sample,  $I_{\text{probe}}$ , 1nA, energy of the electron beam 5-15kV and the working distance between the sample and column varied between 8.2 and 8.7mm. The analysis time was about 2 minutes.

The electrochemical tests were performed in a three electrode electrochemical cell consisting of a saturated Ag/AgCl reference electrode (Radiometer Analytical), a platinum mesh counterelectrode ( $5\text{ cm}^2$ , Radiometer Analytical) and a coated aluminium working electrode. The electrolyte solution was 3.5% NaCl (Sigma Aldrich).

The stability in time of the coated films was monitored by open circuit potential, for 10 min, with a recording rate of 12 measurements/min.

The electrochemical impedance spectroscopy was conducted by applying a 10 mV sinusoidal potential perturbation for a scanning frequency range between 100 kHz and 100 mHz with a recording rate of 10 measurements/decade.

The potentiodynamic polarisation tests were performed by scanning the potential between -1 and 0.5V, with a scan rate of 10 mV/minute.

### Results and discussions

#### Optical microscopy

The effect of the anodisation process on the metallic substrate was investigated by optical and SEM microscopy. The pores shape and size could be controlled during the

anodisation process, by modifying parameters such as current density and exposure time.

In figures 1a and 1b, one may see the influence of the working parameters on the number of pores, namely an increase in the pores density while increasing the current density and exposure time.

At low current density and low exposure time, one may see the effect of the surface treatment prior to anodisation, by remaining traces of the cleaning process with emery paper that were still noticeable (fig. 1c).

#### Scanning electron microscopy

The size of the reinforcement agents was established by scanning electron microscopy.

In figure 2a, one may see the array of the Ti particles and in figure 2.b. the size of the particles may be seen. The Ti particles have sizes in the range of micrometers.

In figure 3a, one may see the array of the  $\text{TiO}_2$  and in figure 3b the size of the particles may be seen. The medium size of the  $\text{TiO}_2$  particles is in the range of nanometers ( $95.04\times 80.25\text{ nm}$ ).

The investigation of the reinforced silane films and that of the metallic substrate was performed by scanning electron microscopy. The size and placement of the pores were easily observed through SEM, so that one may notice shallow and large indentation, together with regular large pores which were formed at small exposure times and low current densities ( $i=0.3\text{ A/cm}^2$  and  $t=6\text{ min}$ ), while deep, small indentations and also small pores were formed at high current densities and high exposure time.

For example, at the same exposure time (6 min) but different current density, one may see some differences in the sizes of pores, so at higher current density ( $0.4\text{ A/cm}^2$ ), the pores are displayed relatively uniform, with small sizes and high depth (fig. 4a), while at low current density ( $0.3\text{ A/cm}^2$ ), the pores have small depth, are big sized, superficial and randomly displayed (fig. 4b).

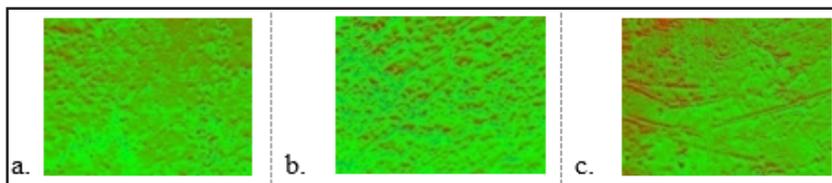


Fig. 1. The IR emulated images obtained with the optical microscope at 60x magnification for the Ti particles reinforced 5% BTSE films deposited on an anodised substrate at  $i=0.3\text{ A/cm}^2$  and  $t=8\text{ min}$  (a),  $i=0.4\text{ A/cm}^2$  and  $t=10\text{ min}$  (b) and at  $i=0.3\text{ A/cm}^2$  and  $t=6\text{ min}$  (c)

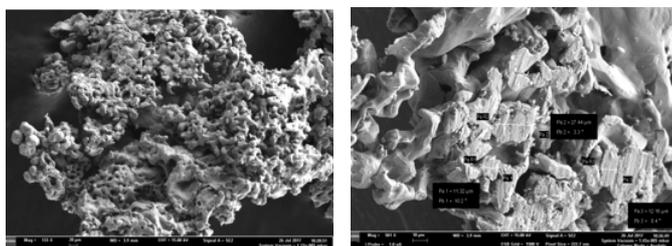


Fig. 2. SEM images of the Ti particles at 133 (a) and 501 (b) magnification

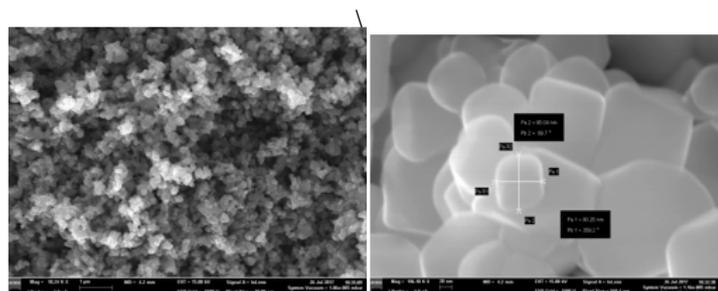


Fig. 3. SEM images of the  $\text{TiO}_2$  particles at 10.24 K (a) and 196.18 k (b) magnification

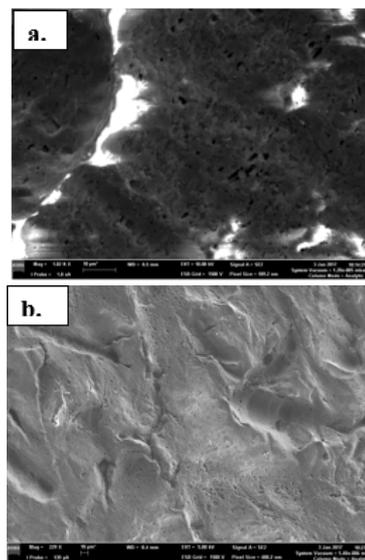


Fig.4. SEM images of the metallic substrate anodised for 6 min at a current density of  $0.4\text{ A/cm}^2$  (a) and  $0.3\text{ A/cm}^2$  (b)

### Energy dispersive X-ray spectrometry

The composition of the reinforced silane films and that of the metallic substrate were given by the energy dispersive X-ray spectrometry (EDS). The results showed that the metallic substrate used for deposition is an alloy of aluminium with carbon (81.83% Al, 15.24% C) [17].

After the anodisation step, the composition of the aluminium substrate surface was modified. In table 1, one may see the composition of the substrate after the anodisation and deposition of a 5% BTSE film. The presence of the silane film was confirmed by the presence of Si in the composition of the layer (3.61%, table 1).

Element	Wt, %
C	5.24
O	47.89
Al	39.02
Si	3.61
S	4.23

**Table 1**  
THE COMPOSITION OF THE ANODISED METALLIC SUBSTRATE COATED WITH A 5% BTSE FILM

The reinforcement agents were detected in small quantities, the titanium was present as an homogenous particulate dispersion embedded into the silane films, while titanium dioxide was dispersed relatively uniform through the film.

### Open circuit potential

Open circuit potential (OCP) was recorded in order to establish the stability in time of the tested silane films. In figure 5, is represented the variation of the open circuit potential in time for the films deposited on the anodised

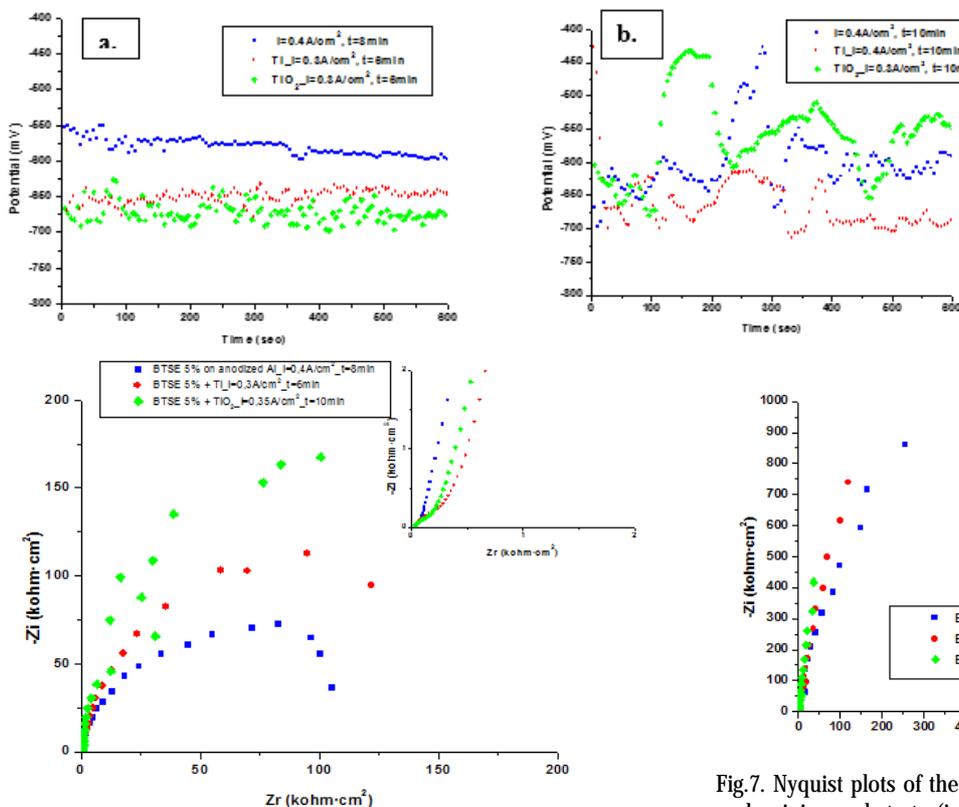


Fig.6. Nyquist plots of the 5% BTSE films deposited on anodised aluminium substrate ( $i=0.4A/cm^2$ ,  $t=8min$ ), 5% BTSE Ti films deposited on anodised aluminium substrate ( $i=0.3A/cm^2$ ,  $t=6min$ ) and 5% BTSE  $TiO_2$  reinforced film deposited on anodised substrate ( $i=0.35A/cm^2$ ,  $t=10min$ ) that show low values of the polarisation resistance

metallic substrate. An example for each type of film (not reinforced, reinforced with Ti and with  $TiO_2$ ) is given in order to highlight their stability in time for them. In figure 5.a., one may see a variation of the OCP in a small range of values, hence a high stability of the deposited films in time, while in figure 5b, the OCP varies in a large domain of values showing a low stability in time of those films. The other investigated films showed a variation closer to the ones represented in figure 4.a., indicating a good enough stability in time.

### Electrochemical impedance spectroscopy

The EIS results of the investigated films are presented in tables 2-4. One may see an improvement in the values of the polarisation resistance after the anodisation of the metallic substrate surface and after the reinforcement of the films. Compared with the value of the polarisation resistance,  $196.1 kohm\cdot cm^2$  [17], obtained for the 5% BTSE film deposited on a metallic substrate that was not submitted to the anodisation step, the values obtained after the anodisation of the substrate are higher. One exception was recorded for the anodised substrate at  $i=0.4A/cm^2$  for 8 minutes, due to some cracks and crevices into the silane films, which may act as preferential ways for the corrosion attack. The higher values of the polarisation resistance are due to some improvements of the adhesion of the metallic substrate by anodisation.

The pre-treatment of the substrate also has a great influence upon the values of the capacitance, the substrate that was not anodised showing a capacitance of  $1282nF/cm^2$  [17], while the anodisation process led to lower values. Low values of the capacitance are an indicator of the compactness of the film caused by a better bonding of the film with the aluminium substrate.

In figure 6 and 7, one may see the Nyquist plots for the 5% BTSE films deposited on anodised aluminium substrate

Fig. 5. The variation of the open circuit potential in time in a 3.5% NaCl electrolyte for 5% BTSE films deposited on anodised metallic substrate with high stability (a) and low stability (b)

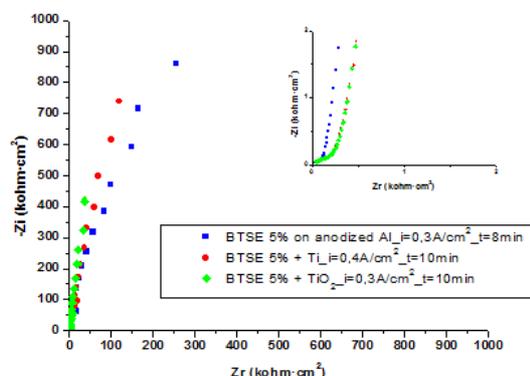


Fig.7. Nyquist plots of the 5% BTSE films deposited on anodised aluminium substrate ( $i=0.3A/cm^2$ ,  $t=8min$ ), 5% BTSE Ti films deposited on anodised aluminium substrate ( $i=0.4A/cm^2$ ,  $t=10min$ ) and 5% BTSE  $TiO_2$  reinforced film deposited on anodised substrate ( $i=0.3A/cm^2$ ,  $t=10min$ ) that show high values of the polarisation resistance

Anodisation parameters		$k_{pr}$ for 5% BTSE films deposited on anodised aluminium substrate		
$i$ , A/cm <sup>2</sup>	Time, min.	Anodised substrate	Reinforced with Ti	Reinforced with TiO <sub>2</sub>
0.3	6	1.4	1.2	2.7
	8	23.4	38.3	5.3
	10	4.1	46.7	21.1
0.35	6	3.6	4.4	3.8
	8	19.9	18.1	7.5
	10	15.8	17.1	1.7
0.4	6	20.9	27.4	18.9
	8	0.8	20.7	4.5
	10	3.3	73.2	3.9

**Table 2**  
THE VALUES OF THE PROTECTION COEFFICIENT OBTAINED FOR THE 5% BTSE FILMS

that showed extreme values for the polarisation resistance, the other films having values contained in the interval bordered by the two extreme cases.

In order to highlight whether or not this anodisation and reinforcement treatments brought any improvements, one has calculated a dimensionless protection coefficient ( $k_{pr}$ ) as the ratio between the value of the polarisation resistance of the anodised substrate/reinforced films deposited on anodised aluminium and the value of the polarisation resistance of the film deposited on aluminium (eq. 1). This coefficient shows in a better way the magnitude of the improvements brought in by the substrate pre-treatment and by the reinforcement, being equal to:

$$k_{pr} = \frac{R_{2,i}}{R_{2,0}} \quad (1)$$

where  $R_{2,i}$  is the polarisation resistance of the anodised substrate/reinforced films deposited on anodised aluminium;

$R_{2,0}$  is the polarisation resistance of the film deposited on aluminium (196.1kohm·cm<sup>2</sup>).

The values of the protection coefficient obtained for the 5% BTSE reinforced films deposited on anodised aluminium substrate are presented in table 5. As far as the reinforcement is concerned, one may see that the best results are obtained for the films reinforced with Ti. This may be explained that in comparison with the results obtained for the films reinforced with TiO<sub>2</sub>, that has a certain degree of solubility in the silane solution, the reinforcement with Ti will confer the composite material structure better properties compared to the films reinforced with TiO<sub>2</sub>.

#### Potentiodynamic polarisation

The potentiodynamic polarisation (PDP) was a useful technique in investigating the corrosion rate of the 5% BTSE films in NaCl 3.5% solution. The marginal differences in the polarization resistance results obtained from the EIS spectra in comparison with those from the potentiodynamic polarisation may be attributed to the fact that EIS is a non-destructive technique, while the potentiodynamic polarisation is a destructive one, hence the reason of considering the corrosion rate from the PDP technique instead of  $R_p$ . In practical applications, a low corrosion rate is the parameter of interest in characterizing the corrosion resistance of the investigated coatings. It is useful to take

advantage of the possibility to extract also other parameters of interest from the PDP technique such as the corrosion potential and the corrosion current density ( $i_{cor}$ ). The lower the corrosion rate and corrosion current density are, the better the anticorrosive properties of these films are. If these coatings do not meet some of the requirements for anticorrosion protection, they have a limited area of applications, especially since these films applications require enough strength to avoid perforation or exfoliation.

Pretreating the substrate by anodisation and the reinforcement of the silane film with particles, one has obtained improved anticorrosive properties confirmed by the low values of the corrosion rate obtained experimentally. In figure 8 and 9 are presented the Tafel plots of the investigated silane films (deposited on anodized aluminium substrate, deposited on aluminium substrate and reinforced with Ti and deposited on aluminium substrate and reinforced with TiO<sub>2</sub>), that show extreme values (highest and lowest) for the corrosion rate. All the other investigated samples have values contained in the interval bordered by the two extreme cases.

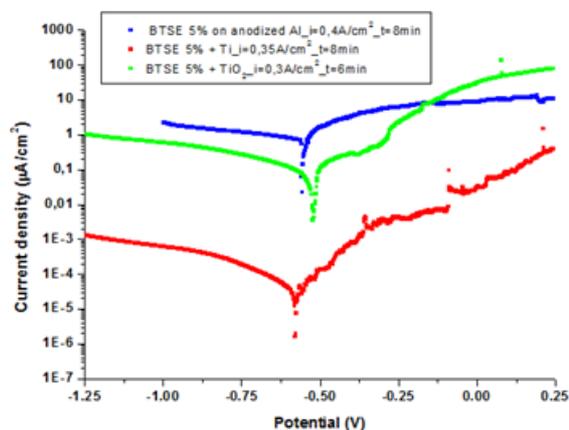


Fig.8. The Tafel representations for the 5% BTSE films deposited on anodised aluminium in a 3.5% NaCl that show high values for the corrosion rate

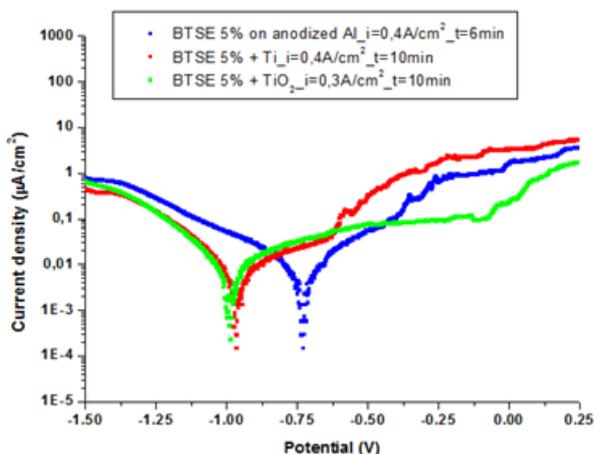


Fig.9. The Tafel representations for the 5% BTSE films deposited on anodised aluminium in a 3.5% NaCl that show low values of the corrosion rate

## Conclusions

This paper showed the improvements in the anticorrosive protection properties of 5% BTSE films deposited on a pre-treated aluminium substrate by anodisation and the ones obtained by reinforcement of the films using Ti and TiO<sub>2</sub> particles.

One compared the behaviour of the 5% BTSE films deposited on aluminium substrate, the silane films deposited on anodised aluminium substrate and the reinforced films. Scanning electron microscopy and optical microscopy highlighted the differences in the surface characteristics of the substrate prior and after the anodisation process.

The investigated films were characterized by complementary electrochemical techniques such as open circuit potential for establishing the stability in time of the deposited films, the electrochemical impedance spectroscopy for the corrosion resistance of the films and potentiodynamic polarisation for the corrosion behaviour determined by the corrosion rate.

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