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Effect of curing on the corrosion protective properties of thin organosilane films on aluminium

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Abstract

Film properties and corrosion protection given by thin organosilane films (bis-1,2-(triethoxysilyl)ethane: BTSE) on aluminium were investigated as a function of curing. The thickness was determined using spectroscopic ellipsometry (SE). Impedance spectra, modelled by an electrical equivalent circuit, show three time constants. The variation of the elements in these three time constants as a function of the immersion time in a NaCl solution indicate the structure of the film after curing. It can be concluded that the barrier properties of the organosilane films are influenced more by the curing temperature than by the curing time.

1. Introduction

A thin film of organosilane molecules is an interesting alternative system for the toxic hexavalent chromium conversion pre-treatments used for corrosion protection of metals [1, 2]. The adhesion of organosilane molecules to the metallic substrate by an oxane (Me–O–Si) bond has been confirmed [3]. This oxane bond is a result from the interaction of silanol groups (Si–OH) with hydroxyl groups on the metal surface. The formation of this chemical bond between the silane layer and the metal distinguishes this coating system from the chemical conversion systems, where a redox reaction between the metal and the reactive ions in the solution is responsible for the conversion of the surface. For chromium conversion layers, corrosion protection to the underlying substrate is provided by a self-healing effect orchestrated by the hexavalent chromium ions present in the layer, reforming the film in case of local defects. For silane coatings, the corrosion protective properties depend on the barrier effect against corrosive attack. All the parameters improving the barrier properties of the silane layers must be investigated.

Previous results [4] have shown that the film thickness increases linearly with bath concentration for BTSE (bis-1,2-(triethoxysilyl)ethane). The deposited film is, however, very porous in the uncured condition, and does not protect the substrate. Curing is necessary to create barrier properties [5].

The combination of electrochemical impedance spectroscopy (EIS) and spectroscopic ellipsometry (SE) is very useful for determining the variation of the silane film thickness, composition, morphology and barrier properties as a function of the curing conditions.

Spectroscopic ellipsometry is particularly suited to determine the thickness and the optical properties of thin layers using visual spectroscopic ellipsometry (Vis-SE), and for the chemical composition using infrared spectroscopic ellipsometry (IRSE).

In previous work [5], the authors have shown that curing of the organosilane film introduces significant modification in the impedance diagrams. Uncoated or covered with an uncured silane film, the impedance of the substrate only has one relaxation time constant, typical for the aluminium oxide layer; the uncured film is too permeable to modify the impedance spectra. With cured films the classical spectra for organic coatings with two relaxation time constants are observed. However, under certain curing conditions a third time constant appears in the medium frequency range. Special attention has been given to the presence and behaviour of this phenomenon. This third relaxation has been attributed to the formation of highly cross-linked and dense polymer regions in the film, or alternatively, to the presence of an interfacial layer at the surface of the metal substrate, which is more reticulated than the bulk of the film [2, 5].

In the present work, the barrier properties of BTSE silane films on aluminium in 0.5 M NaCl are investigated as a function of curing temperature (100 and 200 °C) and time (0–24 h).

2. Experimental

2.1. *Materials and treatments*

All experiments were carried out on electropolished aluminium (AA1050) plate. The electropolishing conditions have been reported in previous work [5]. Samples were ultrasonically degreased in hexane, methanol and acetone. Before organosilane deposition, substrates were alkaline-cleaned at 65 °C with AC 1055TM from Brent Europe (pH 10) and rinsed in de-ionized water.

A 10 vol. % BTSE solution was prepared following the procedure described in Ref. [5]. Less concentrated solutions (2, 4, 6 and 8 vol. % BTSE) were obtained by dilution of the hydrolysed 10 vol.% BTSE solution with methanol.

The silane film was applied by dipping the aluminium substrate for 100 s in the BTSE solution and blow drying with compressed air (for the fresh, uncured film) or curing. Films were cured at 100 and 200 °C, for a time necessary to reach a constant film thickness.

2.2. *Spectroscopy ellipsometry (SE)*

Spectroscopic ellipsometry was performed with a J.A. Woollam Co VASE (Variable-Angle Spectroscopic Ellipsometer) in the UV–visible and near infrared spectral range (300–1700 nm) with a resolution of 10 nm. Three angles of incidence were used; 65, 75 and 85°. At these angles the analysed area is, respectively, 0.273, 0.407 and 0.811 cm^2.

The optical model used in this paper has been described earlier [5] and consists of stratified layers with flat and parallel interfaces, each layer described by its thickness and optical constants. The optical behaviour of the electropolished and treated aluminium substrate is expressed in terms of pseudo optical constants (taking into account the superficial oxide layer). The organosilane film (of which the optical constants are not known) is modelled with a Cauchy dispersion relation [6]. To improve the quality of the simulation, two corrections were made: an extra parameter to characterize the non-uniformity of the film thickness and the Bruggeman effective medium approximation (EMA) [7] to take into account the roughness of the film/substrate interface.

2.3. *Electrochemical impedance spectroscopy (EIS)*

Electrochemical impedance spectroscopy was performed with an Autolab FRA100. The electrochemical cell was a classical three electrodes arrangement: an aluminium plate with a surface of 3.8 cm^2 as working electrode, a saturated calomel electrode (SCE) as reference electrode and a large platinum grid as counter electrode. In order to improve the quality of the impedance measurements in the very high frequency range (higher than 10^5 Hz), a platinum wire in series with a capacitor was placed in parallel with the reference electrode. This set-up was proposed by Mansfeld to reduce the phase shift induced by the reference electrode at high frequency [8]. The measurements were performed at the open circuit potential in a frequency range between 1 and 10 mHz, with a signal amplitude of 10 mV. The solution was 0.5 M NaCl at room temperature and open to the air.

3. Results and discussion

3.1. *Characteristics of the organosilane film after curing*

The characteristics of the organosilane films were determined before immersion with SE, and after 24 h immersion in 0.5 M NaCl with EIS. An immersion time of 24 h prior to EIS analysis was selected for two reasons: stabilization of the film in the electrolyte, and limitation of film degradation.

3.1.1. *Influence of curing time*

Figures 1 and 2 show the variation of the relative thickness of the organosilane layers as a function of curing time for a 5 and a 10 vol. % BTSE film cured at 100 and 200 °C. The relative thickness was calculated with reference to the thickness of the fresh uncured film. The film thickness decreases with curing time and temperature. The influence of the curing temperature is, however, less pronounced for a film obtained from a 10 vol.% BTSE solution. In this case the uncured film is less porous and already more reticulated (confirmed by EIS results). The variation of the thickness is in agreement with previous results and is attributed to drying and reticulation of the BTSE molecules during curing [5].

Figure 3 presents the evolution of the EIS spectra as a function of curing time at 100 °C for a 207 nm fresh film

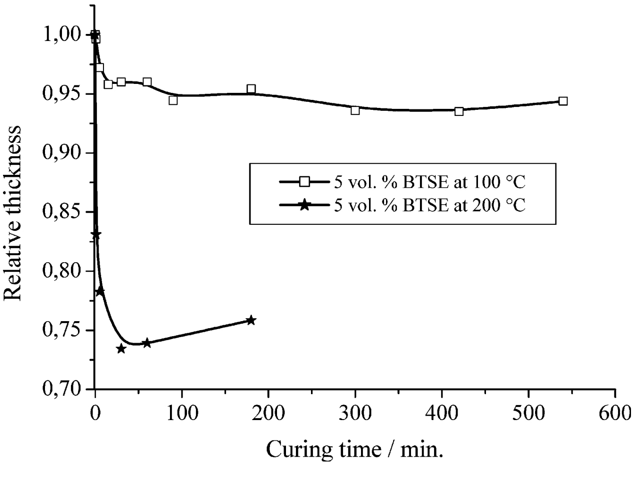

Fig. 1. SE variation of the relative thickness as a function of curing time for a 5 vol. % BTSE cured at 100 and 200 °C.

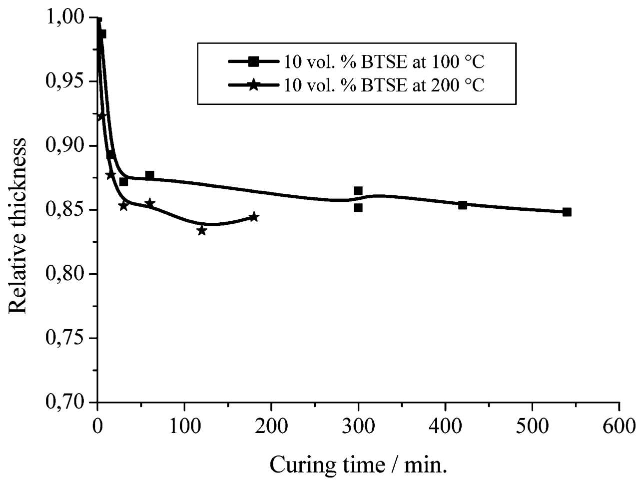

Fig. 2. SE variation of the relative thickness as a function of curing time for a 10 vol. % BTSE cured at 100 and 200 °C.

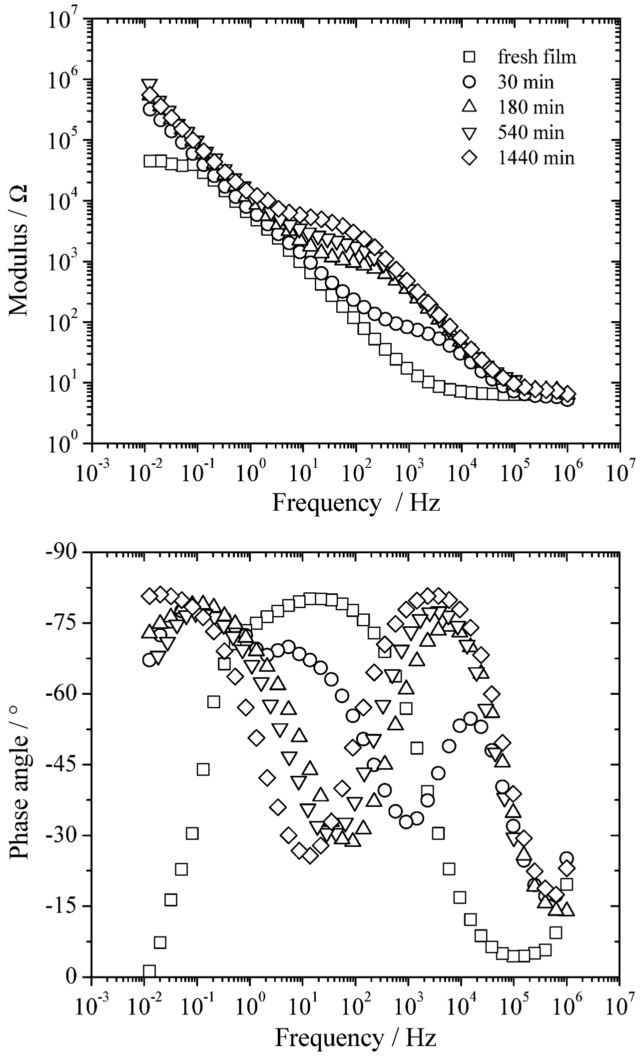

Fig. 3. EIS spectra as a function of curing time at 100 °C for a 5 vol. % BTSE after 24 h immersion in 0.5 M NaCl.

(5 vol.% BTSE) on aluminium (AA 1050) after 24 h of immersion in 0.5 M NaCl solution. The same evolution is observed for an organosilane film obtained from a 10 vol. % BTSE solution, where the average thickness is about 420 nm. The fresh uncured organosilane film is not detected with EIS; the impedance spectra are the same as for the uncoated substrate. This implies that uncured films are porous and have no barrier effect. Already after 5 min of curing, however, three relaxation time constants are observed. One at high frequencies (10^5–100 Hz), a second at intermediate frequencies (100–1 Hz) and the third at low frequencies (below 1 Hz). Figure 4 clearly shows these three relaxation phenomena (phase angle plot) after 30 min of curing. When curing time increases several modifications of the impedance spectra are observed. First, the relaxation at high frequency shifts towards lower frequencies and the amplitude and phase angle increase. Second, due to the shift of the relaxation at intermediate frequencies also to lower frequencies, the third time constant is observed after 60 min of curing at 100 °C. This means that this third relaxation is then shifted to frequencies below 10^{-2} Hz.

To interpret these data, the equivalent circuit presented in Figure 5 can be used. This circuit is composed

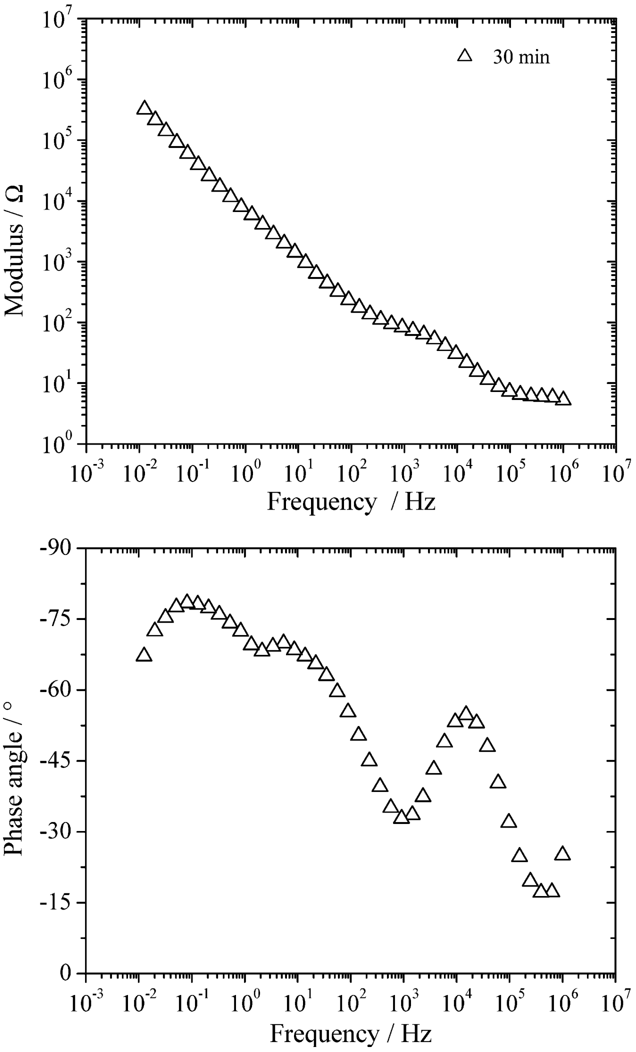

Fig. 4. EIS spectrum after 30 min curing at 100 °C for a 5 vol. % BTSE after 24 h immersion in 0.5 M NaCl.

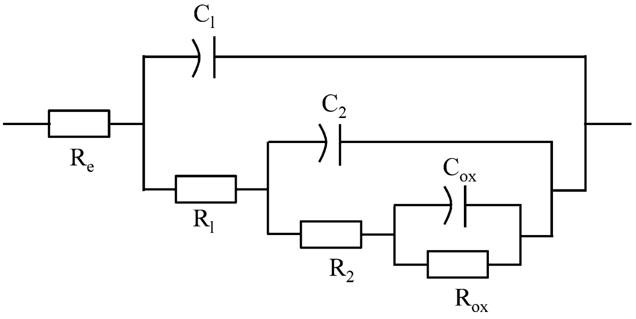

Fig. 5. Equivalent circuit used for EIS data modelling.

of three RC components where the capacitances are replaced by constant phase elements (CPE) to improve the quality of the fit. The impedance of such an element is written as follows:

$$Z_{\mathrm{CPE}} = \frac{1}{(j\omega)^n Q}$$

The fitting of EIS data is done on data obtained between 10^5 and 10^{-2} Hz. The first time constant (R_1Q_1) in the high frequency range (10^5–100 Hz) can be attributed to the organosilane film and the third one (R_3Q_3) in the frequency range lower than 1 Hz to the behaviour of the oxide layer on the aluminium substrate.

Due to the fact that the second or intermediate relaxation time (R_2Q_2) is observed simultaneously with the one at high frequency (R_1Q_1) after a short curing time, it is suggested that this second relaxation time can also be attributed to the silane film. This indicates that the cured film is not a homogenous layer. This heterogeneity may be the result of the existence of high and low cross-linked phases inside the bulk of the layer, or, of the presence of a stronger reticulated interfacial region between the aluminium oxide and the bulk of the film. Thermal analysis (DSC) cannot confirm the presence of two phases [9].

Figure 6 presents the variation of the parameters of the equivalent circuit after fitting.

The resistance R_1, attributed to the resistance of electrolyte inside the pores of the organosilane film, increases significantly at the beginning of curing (for about 30 min) and then remains constant. The maximum of R_1 and the time necessary to reach this maximum can be used to characterize the barrier properties of the film after curing. During the same time Q_1 decreases and also reaches a constant value. The increase of R_1 can be explained by a decrease of the porosity of the layer due to cross-linking of the BTSE molecules. The decrease of Q_1 can be explained by a

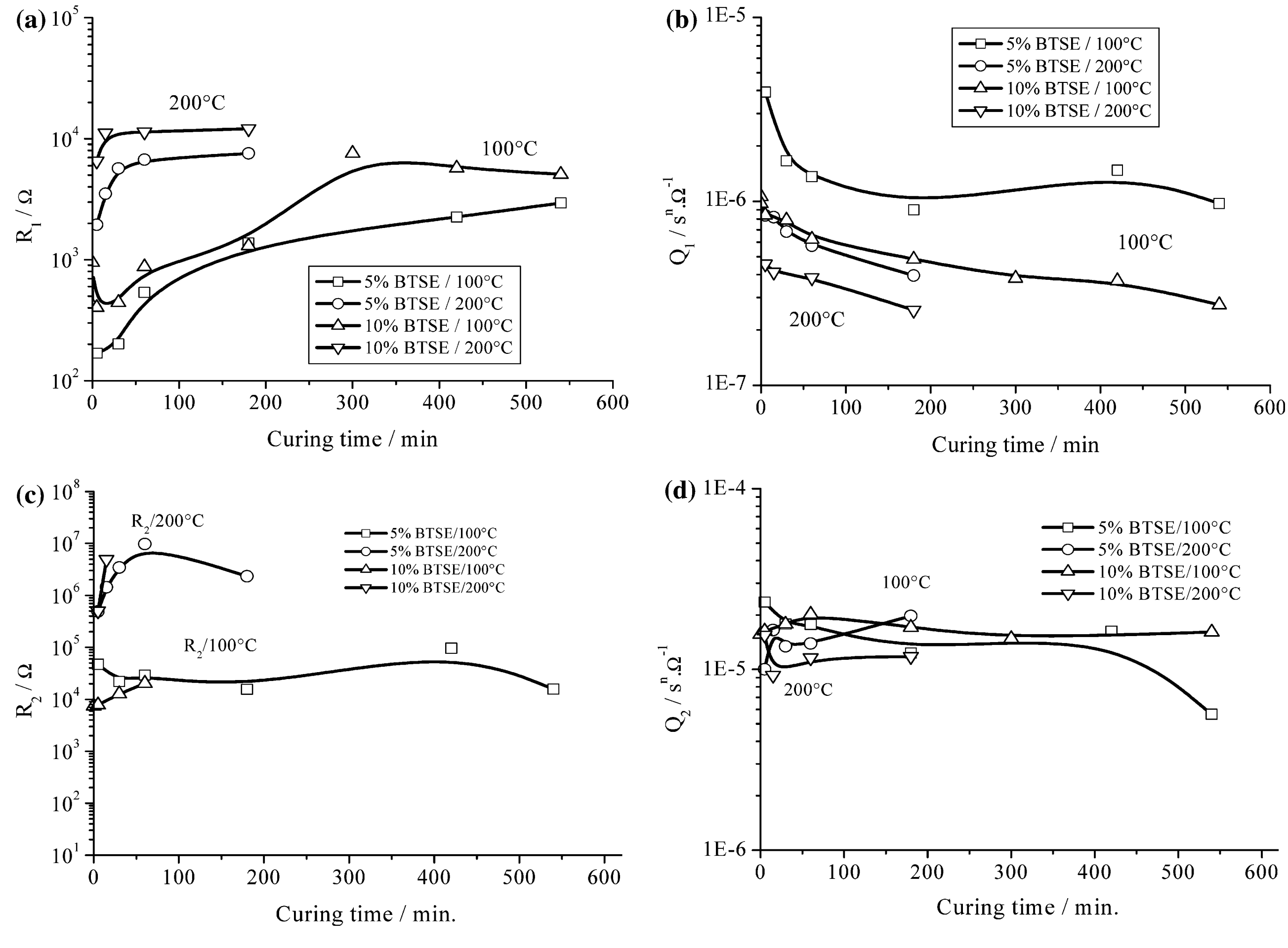

Fig. 6. Variation of the parameters of the equivalent circuit as a function of the curing time for 5 and 10 vol. % BTSE cured at 100 and 200 °C: a, R_1; b, Q_1; c, R_2; d, Q_2.

decrease of the polarizability of the film and/or by a more difficult penetration of water.

R_2 and Q_2 appear after a few minutes and remain constant; R_2 is higher than R_1, Q_2 higher than Q_1. It is suggested that this second phase is an interfacial layer on the aluminium substrate, with a high cross-link density (high resistance) but very thin (Q is inversely proportional to the thickness of the film).

R_3 and Q_3 cannot be calculated because the third relaxation constant is shifted towards frequencies below 10 mHz. At these frequencies the validation conditions of impedance measurements are not fulfilled (stationary behaviour and linearity).

So, it must be emphasized that the two RQ relaxations, which can be determined by EIS in the investigated frequency range, characterize the film and not an electrochemical (corrosion) reaction of the substrate (aluminium oxide layer). As a consequence, the amplitude of the impedance at minimum frequency must be carefully interpreted.

3.1.2. *Influence of curing temperature*

As mentioned before, the minimum value of the film thickness is reached more rapidly when the curing temperature increases (Figures 1 and 2).

On the other hand (Figure 6), the maximum of R_1 is higher at higher curing temperature and the minimum of Q_1 is lower. The final values of these two parameters are reached more rapidly at 200 °C than at 100 °C.

R_2 increases with curing temperature and Q_2 remains constant.

The influence of the curing temperature is thus more pronounced on the bulk of the silane film than on the interfacial layer. The thickness of this interfacial layer remains nearly constant (Q_2) and the reticulation is greater at higher temperature (increase of R_2). The increase in R_1 and decrease in Q_1 show clearly that the cross-linking of the bulk of the film is not complete at 100 °C even after long curing times, and can further evolve at higher temperatures.

The variation of these parameters show that the temperature is an essential parameter in the curing kinetics. The fact that even after a very long curing at 100 °C, the film cannot reach the same reticulation degree as at 200 °C, confirms this statement.

3.1.3. *Influence of bath concentration (thickness of the fresh uncured film)*

A significant increase of film thickness with bath concentration can be observed in the SE spectra [5]. This is confirmed by higher values of R_1 and lower values of Q_1, while R_2 and Q_2 do not vary significantly.

3.2. *Corrosion protective properties of the organosilane films*

The corrosion protection provided by organosilane films has been assessed by examining the variation of the equivalent circuit components as a function of the immersion time in 0.5 M NaCl solution. The EIS spectra in 0.5 M NaCl confirm the results obtained in Na_2SO_4; a fresh uncured film does not protect the aluminium substrate [5].

Figure 7 shows the spectra of a 5 vol.% BTSE film cured for 30 min at 200 °C as a function of the immersion time in 0.5 M NaCl.

At the beginning (clearly visible after 24 h) three relaxation times can be observed. After about 100 h in the aggressive solution, the third relaxation has shifted towards frequencies lower than 10 mHz and cannot be detected anymore.

As a function of the immersion time, R_1 decreases slightly (Figure 8) and Q_1 increases, due to the ingress of the solution inside the silane film. It is obvious, however, that the longer the curing time, the better the barrier properties of the bulk of the film. R_2 and Q_2 are relatively constant as a function of the immersion time and are not so influenced by the curing conditions. The most important conclusion is that R_2 is always higher

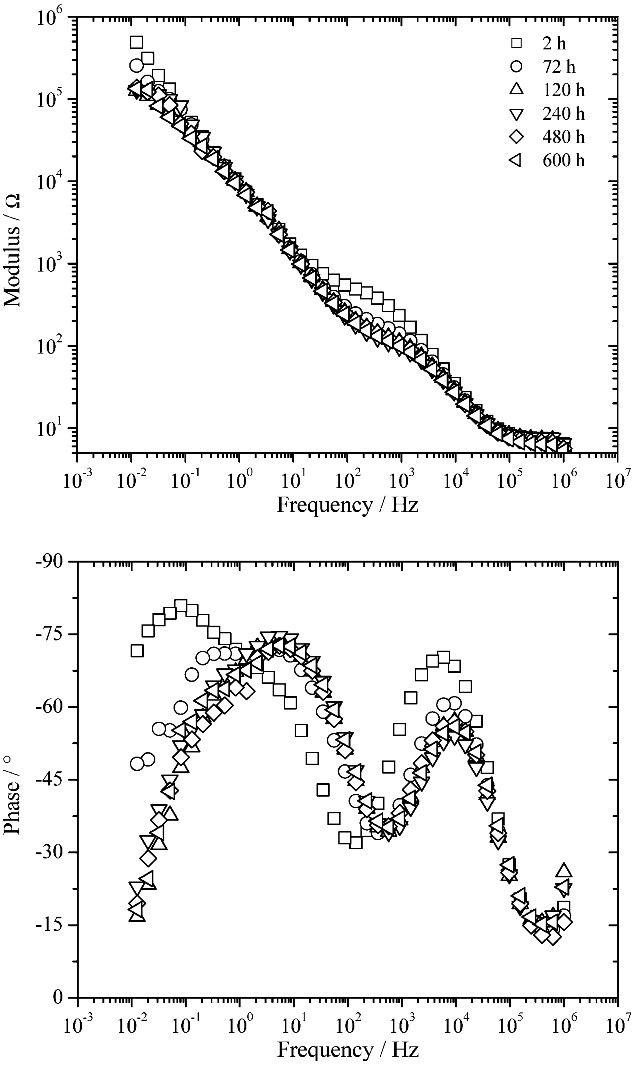

Fig. 7. EIS spectra of a 5 vol. % BTSE cured 30 min at 200 °C as a function of the immersion time in 0.5 M NaCl.

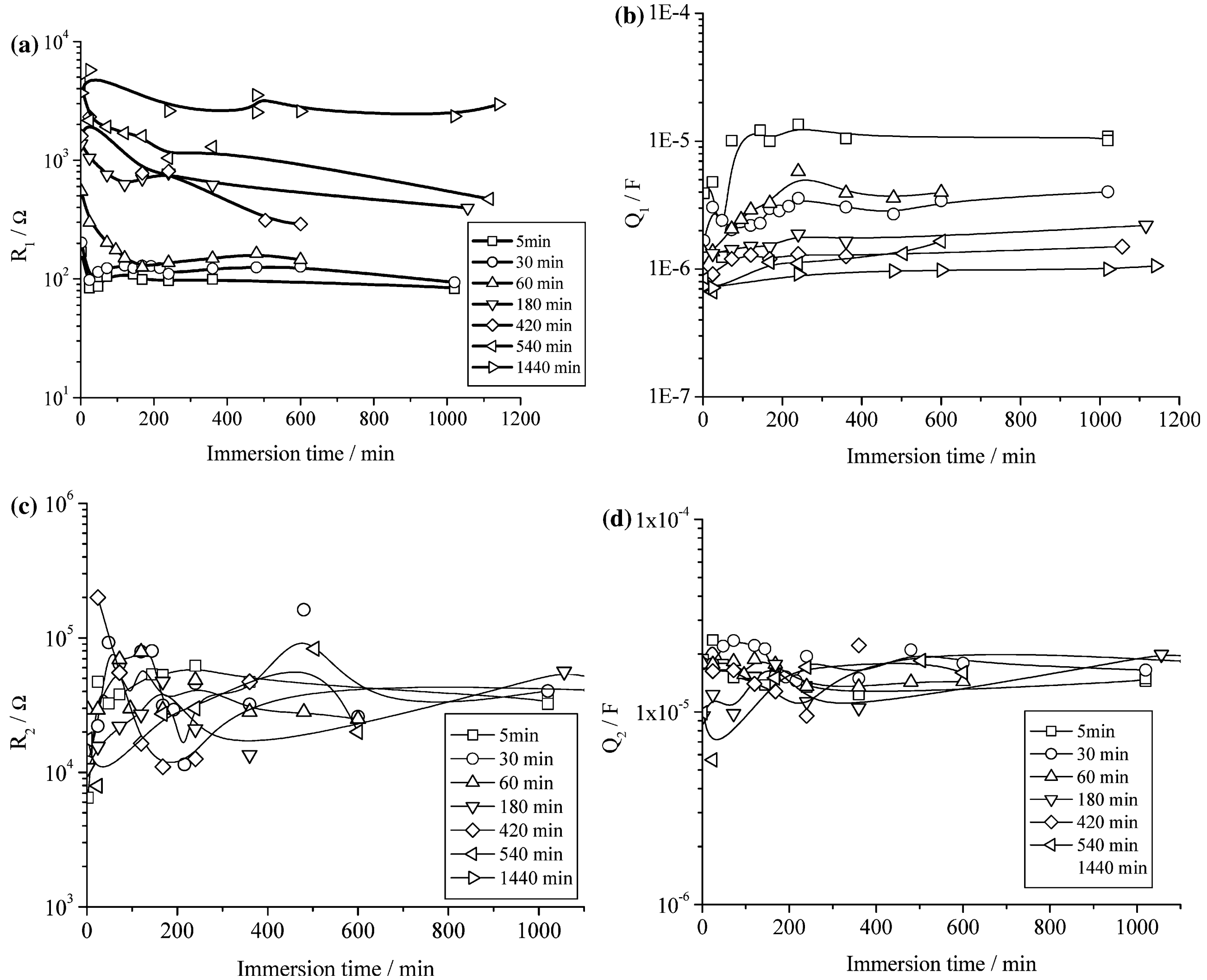

Fig. 8. Variation of the parameters of the equivalent circuit as a function of the immersion time for a 5 vol. % BTSE cured during different times at 100 °C: a, R_1; b, Q_1; c, R_2; d, Q_2.

than R_1; the barrier resistance of the interface layer is higher than that of the bulk of the silane film and does not decrease as a function of the immersion time. R_3Q_3 can only be calculated for very short immersion times due to the high impedance of the coating. The third relaxation time is shifted towards frequencies lower than 10 mHz where the validation conditions of EIS are no longer fulfilled. This means, as mentioned before, that it is not possible in these conditions to characterize an electrochemical (corrosion) reaction at the interface between the coating and the substrate.

3.3. *Observation of the samples with SEM*

Since EIS does not provide us with information on the corrosion behaviour of the coated metal, Scanning Electron Microscopy (SEM) was employed. Figure 9 presents the SEM pictures of a fresh film and a cured film (180 min/100 °C) after 30 days of immersion in 0.5 M NaCl. On the cured silane coated samples no pitting is observed, in contrast to the uncoated aluminium substrate or the fresh film.

4. Conclusions

A fresh uncured film of BTSE cannot protect an aluminium substrate. Curing modifies the structure of the organosilane layer resulting in increased barrier properties and corrosion protection. During curing reticulation of the film occurs, characterized by a decrease in the thickness and an increase in the refractive index of the film. However, the cured film structure is not homogenous and two *RQ* circuits are necessary to model the impedance measurements, attributed to two types of structure present in the film. The bulk of the layer is modelled by R_1Q_1. The curing kinetics play a very important role and are dominated by the influence of the temperature. R_1 reaches a maximum and Q_1 a minimum value, which depend on the curing temperature used: the higher the temperature, the higher the

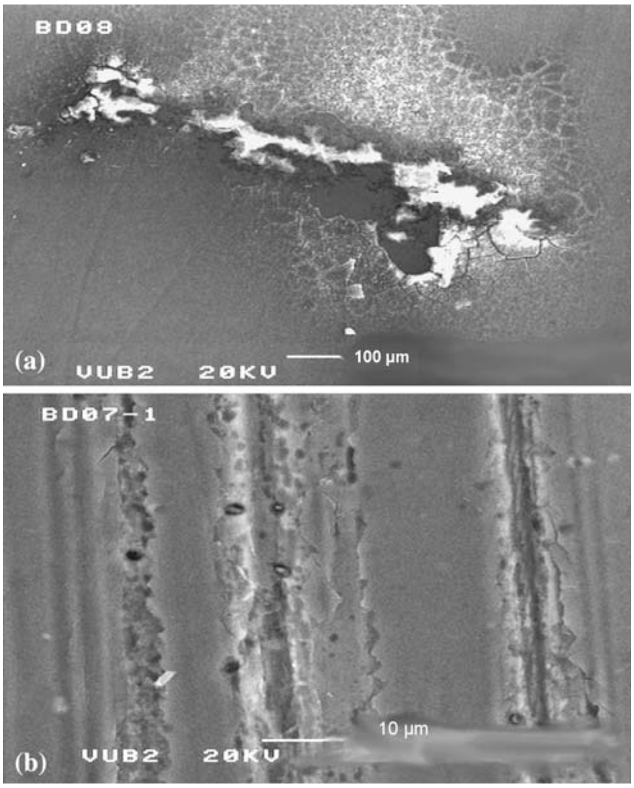

Fig. 9. SEM picture after 30 days of immersion in 0.5 M NaCl (a) 5 vol. % BTSE fresh film; (b) 5 vol. % BTSE cured 180 min/100 °C.

maximum value of R_1 and the lower the minimum of Q_1. Once reached however, these values remain constant throughout further curing, indicating that the structure of the bulk of the film remains unchanged.

A second phase, characterized by R_2Q_2, appears very rapidly during curing. R_2 is higher than R_1 (this phase is more reticulated than the bulk of the film) and Q_2 is higher (due to the very low value of the thickness of this layer) than Q_1. They remain constant as a function of curing time. When the film is fully cured, both *RQ* circuits remain constant. It can be concluded that a very thin interfacial layer plays a determining role as barrier in an aggressive environment.

R_3Q_3 can not be detected in the investigated frequency range. This means that it is impossible to assess the corrosion rate of the substrate based on R_3. However, with the SEM observations it can be concluded that no pitting corrosion is detected under the cured layer.

These results show that a careful interpretation of the modulus of the impedance at the minimum frequency is necessary to assess the corrosion rate of a coated metal.

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