

Electrochemical study of different ageing tests for the evaluation of a cathaphoretic epoxy primer on aluminium

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Abstract

Different ageing tests (salt spray of intact and scratched samples, immersion) were used for the evaluation of the corrosion resistance of a lead-free epoxy primer used in the automotive industry and cathaphoretically deposited on pre-treated aluminium 6016. The evaluation of the degree of degradation was carried out by electrochemical impedance spectroscopy. These tests were compared to accelerated degradation obtained by means of a test combining ac and dc polarizations.

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1. Introduction

Owing to their barrier properties against corrosive species, organic coatings are often used to protect metals against corrosion. In the automotive industry, cathodic electrocoating is widely used in the corrosion protection system as a primary layer coating. This deposition method has several advantages including high throw power, superior corrosion protection, high coating utilization (>95%), low level of pollution (aqueous system) and is easy to automate. Corrosion protection is guaranteed only if good adhesion properties are attained between the metal and the coating. Enhanced adhesion can be achieved by the use of an appropriate surface preparation prior to coating (etching, polishing, etc.) or with a good pre-treatment which can also provide additional corrosion protection.

Short-term test methods are required to evaluate the corrosion resistance of paint/metal systems and decide among coatings designed for long-term durability. The principle of accelerated testing is the application of specific stresses (temperature, humidity, salts, UV lights) at higher levels than in

natural exposure to produce accelerated ageing or deterioration of the system [1,2]. A prime objective of an accelerated test is to cause the coating to degrade or fail in a shorter time period than under natural conditions without changing the failure mechanisms. So far a direct correlation between natural degradation and the weathering device currently being used is not clear, therefore accelerated tests are generally only used for comparative purposes.

Many ways of degradation are accessible for a primer coating such as immersion in electrolyte, continuous salt fog or SO₂ exposure. Cyclic corrosion tests combining different exposures (humidity, salt fog) and drying steps are also increasingly used. These methods are based on the idea that electrolyte and oxygen are needed for corrosion at a metal surface and that increasing temperature accelerates the transport of oxygen and electrolyte through paint films and accelerates the corrosion reactions [3]. For some accelerated tests, use is made of scribed panels to emulate coating damage. This type of acceleration is essentially related to the damage-protective properties of the coating/pre-treatment/metal system and not to the barrier properties of the coating. In recent years, the protective properties of coating systems have been improved and the exposure ageing tests necessitate increasingly longer

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times before visual observation of the initiation of degradation.

Recently an electrochemical test combining dc and ac measurements (ac/dc/ac procedure) was developed allowing an assessment of the anti-corrosive properties of a coating in a very short time [4–6]. After a first ac measurement at the open-circuit potential, the test sample is treated for a short time by a constant cathodic current (dc). After a stabilization period, the sample undergoes another ac measurement. These steps are repeated by means of programmed cycles until the loss of the coating protective properties is observed in the ac spectrum. The evolution of the impedance spectrum is generally attributed to both coating degradation due to pore formation and to a delamination process, which is accelerated by the OH⁻ production at the metal surface during cathodic polarization.

The evaluation of degradation can be visual, mechanical, electrochemical, etc. The use of electrochemical techniques combined with accelerated tests has resulted in new information concerning the degradation mechanisms of coatings in corrosive environments [7–9]. In particular, electrochemical impedance spectroscopy (EIS) has been shown to be a very useful technique for the study of the performance of anti-corrosive primers [10–12].

The aim of the present work was to investigate the protective properties of an experimental epoxy coating cathodetically deposited on a 6016 aluminium alloy (typically used in the automotive industry). Up to now, poor attention has been paid to the effect of the pre-treatment on the variation of adhesion strengths of the electrocoat to metal surfaces. Conversion coating processes such as chromate treatment use health hazardous materials, which are under severe Environmental Protection Agency regulatory restrictions. In the automotive industry, phosphatation is also used on aluminium alloys but generates high sludge amounts in the treatment bath. One of our motivations is to evaluate environmentally friendly processes for aluminium alloys, which could possibly replace the current treatment to achieve similar or better adhesion performances. For this purpose, we studied the improvement of adhesion of the coating to the metal by comparing non-pre-treated panels to samples pre-treated with a commercial Zr/Ti conversion coating. Different accelerated degradation tests were compared: salt fog exposure of intact and scratched samples and immersion of intact samples in NaCl 0.5 M at different temperatures. The evolution of the sample degradation was evaluated by EIS after different exposure times. The results of these evaluation procedures were then compared to a cyclic ac/dc/ac test.

2. Experimental

2.1. Materials

The composition of the 6016 aluminium alloy is given in Table 1. All the test panels (100 mm × 50 mm × 1 mm) were

Table 1
Chemical composition (weight %) of the AA 6016 aluminium alloy

	Weight %
Al	97.900
Si	1.184
Mg	0.318
Fe	0.300
Mn	0.126
Cu	0.118
...	0.054

degreased with acetone and immersed for 10 min in a commercial acid etching bath. The samples were then rinsed with deionised water. The studied pre-treatment is a commercial Zr/Ti conversion treatment. The samples were immersed for 2 min in the commercial bath at 25 °C followed by rinsing with deionised water and air-dried at 60 °C for 3 min.

The paint under study is an experimental lead-free cathaphoretic epoxy coating. The cationic bath conditions were: a distance between the anode and cathode of 5 cm, an anode/cathode ratio of 1:4 and a bath temperature of 30 °C. The voltage and application time were adapted as a function of the desired coating thickness as shown in Table 2. When the painted samples were removed from the cationic bath they were rinsed with deionised water and cured for 25 min at 175 °C. The dry film thickness was measured with a “Minitest 3001” coating thickness gauge using standards of known thickness as references. The T_g value measured by a differential scanning calorimeter is 95 °C. The Zr/Ti pre-treated samples are named ZT and the samples without pre-treatment NP.

2.2. Testing methods and equipment

A conventional three-electrode cell was used for the electrochemical tests. The working electrode was the investigated sample (exposed area of 4.9 cm²). The counter electrode was a platinum plate and all potentials were measured with respect to an Ag/AgCl reference electrode. The cell was filled with the electrolyte solution and placed in a Faraday cage in order to minimize external interference on the system.

2.2.1. EIS

The impedance spectra were obtained at the rest potential using a frequency response detector EG&G 1025 coupled

Table 2
Electrocoating conditions of the different tested samples

Pre-treatment	Voltage (V)	time (min)	Thickness (μm)
None	100	1	6.8 ± 0.5
	200	3	15.8 ± 0.6
	250	3	20.2 ± 0.6
Zr/Ti pre-treated samples	70	1	7.2 ± 0.4
	200	3	15.7 ± 0.5
	250	3	19.9 ± 0.5

with an EG&G 283 potentiostat. Both devices were computer controlled using Powersuite[®] software. The impedance measurements were carried out over frequencies ranging from 100 kHz to 10 mHz (or 100 mHz depending on the measurement type) using a 20 mV rms amplitude signal voltage for intact coatings and 5 mV rms for scratched samples. The impedance data were fitted with electrical equivalent circuit models by using ZsimpWin[®] software.

2.2.2. The ac/dc/ac procedure

The ac/dc/ac procedure consists of a combination of cathodic polarization (dc) and EIS measurements (ac) [4]:

- i. ac measurement following the procedure described above in the EIS section;
- ii. dc: the test sample was cathodically polarized at $-3 \text{ V}/_{\text{Ag}/_{\text{AgCl}}}$ during 2 h followed by a 3 h relaxation time until it recovered a new steady state;
- iii. ac measurement carried out to determine the new state.

This test procedure was applied at least three times and was fully automated with the EG&G 1025/Powersuite[®] equipment.

2.2.3. Accelerated tests

Immersion tests were made with intact samples immersed in aerated NaCl 0.5 M at different temperatures (25, 45 and 60 °C). Salt fog exposure was used for intact and scratched samples and consisted in samples exposition to neutral salt fog chamber in accordance with ASTM B117. For both tests the coating thickness was 20 μm .

For the study of intact coatings, the samples were transferred to an electrochemical cell containing NaCl 0.5 M after different exposure periods in the salt fog chamber. After an EIS measurement the samples were immediately returned to the salt fog chamber so that the time spent out of the chamber was as short as possible (maximum 1 h).

Scratched samples were also exposed to salt fog. The artificial defect was obtained by scratching the coating with a cutter reaching the metallic substrate. The linear defect produced was $2 \pm 0.02 \text{ cm}$ long. The width determined with the help of an optical microscope (Nikon) was around 40–60 μm . The scratches were always performed in the orthogonal direction with respect to the rolling marks. After different exposure times to salt fog, the samples were analysed by EIS in 0.1 M Na₂SO₄ acidified at pH 1 by H₂SO₄ in order to dissolve the corrosion products which developed during exposure to salt fog. For this reason, each sample was examined only once and a new sample was used for each exposure time.

Each measurement was repeated at least three times with a different sample in order to verify the reproducibility of the test.

2.2.4. Equivalent circuit interpretation

The equivalent circuit model generally used to interpret the EIS data of coating degradation is given in Fig. 1 [13]. This

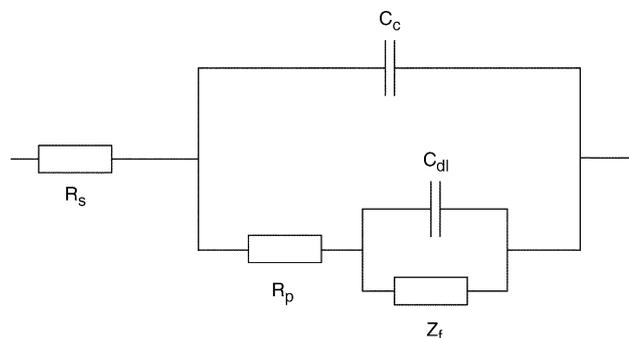


Fig. 1. Electrical equivalent circuit for corroding coated metals.

circuit consists in the uncompensated electrolyte solution resistance between the reference and the working electrode R_s , the coating capacitance C_c , the coating pore resistance R_p , the electrical double layer capacitance C_{dl} and an electrical element related to the electrochemical reactions at the metal/electrolyte interface Z_f . For reactions controlled by charge transfer, Z_f can be replaced by the charge transfer resistance R_{ct} .

The pore resistance is a measurement of the porosity and of the loss of barrier properties of the film. R_p values are related to the number of pores or capillary channels perpendicular to the substrate through which the electrolyte reaches the interface. The pore resistance decreases with immersion time, except in the case where some pore or defect blockage by corrosion products occurs. The coating capacitance C_c is generally assumed to be a measurement of water absorption by the coating. The coating capacitance is defined by:

$$C_c = \frac{\varepsilon \varepsilon_0 A}{d} \quad (1)$$

where ε is the dielectric constant of the coating, ε_0 , the permittivity of the vacuum, A , the area of the coating and d its thickness. The dielectric constant of water is about 20 times greater than that of a typical coating, so the penetration of water through the coating is generally accompanied by an increase of C_c . The amount of water absorbed by the coating can be estimated from the capacitance data by using the empirical formula derived by Brasher and Kingsbury [14]:

$$X_v = \frac{\log(C_c/C_0)}{\log 80} \quad (2)$$

where X_v is the volume fraction of water absorbed by the coating, C_0 , the coating capacitance at the beginning of exposure (dry film capacitance) and 80 is the dielectric constant of water.

The electrical double layer capacitance C_{dl} and the charge transfer resistance R_{ct} are parameters related to the delamination or disbonding of the coating. C_{dl} increases as the area over which the coating has disbonded increases. However, the accumulation of corrosion products at the interface reduces the electroactive area, so that C_{dl} is more a measurement of the electroactive area than the delaminated area. The active

metal area, noted A_w , can be calculated from:

$$A_w = \frac{C_{dl}}{C_{dl}^0} = \frac{R_{ct}^0}{R_{ct}}$$

where C_{dl}^0 is the area-specific double layer capacitance of the uncoated metal and R_{ct}^0 is the area-specific charge transfer resistance of the uncoated metal. R_{ct} and C_{dl} values can only be determined when at least two time constants are clearly observed in the impedance spectra.

All the capacitances were mathematically modelled using constant phase elements ($Q = C(i\omega)^{-n}$) in order to consider non-ideal behaviour. The fitting of the experimental spectra provided the electrical circuit elements with a χ^2 fit parameter below 0.01.

3. Results and discussion

3.1. Intact coatings

Fig. 2a and b show the evolution as a function of the immersion time in the NaCl solution of the modulus versus frequency of coated samples (Bode-modulus plots). Different stages can be distinguished: capacitive (C), mixed capacitive and resistive (CR) and resistive (R) behaviours. In the early times of immersion, the coating acts as a barrier against water and electrolyte (stage C). Therefore, the coating behaves as a dielectric and the resulting impedance modulus logarithm varies linearly as a function of the frequency logarithm. The loss of barrier properties corresponds to the penetration of water and electrolyte through the pores and defects of the coating up to the metal. At this stage (CR), the low-frequency modulus progressively decreases reflecting the decrease of the pore resistance (R_p). The time at which the low-frequency modulus starts to decrease varies slightly with the surface preparation prior to coating: an average of 40 days for non-pre-treated samples (Fig. 2a) and 50 days for Zr/Ti pre-treated samples (Fig. 2b). For both surface preparations, a rapid decrease of the low-frequency modulus is observed from the moment the coating loses its barrier properties. Once the metal beneath the coating is in contact with the electrolyte, corrosion of the metal starts at the base of the pores. Corrosion may significantly affect the adhesion of the coating by the increase of pH accompanying the oxygen reduction or by the presence of corrosion products. The loss of adhesion causes an increase of the active metal surface area so that a second time constant (R_{ct} C_{dl}) appears in the Bode-diagrams. The second time constant starts to be visible after 47 days and 62 days for NP and ZT samples, respectively.

For intact samples exposed to salt fog, the three stages of degradation are also observed by EIS. There is a good correlation between the results obtained with both tests. Actually, the EIS spectra obtained as a function of immersion time or salt fog exposure show that the Zr/Ti pre-treatment enhances the corrosion resistance of the coating. Moreover for ZT sam-

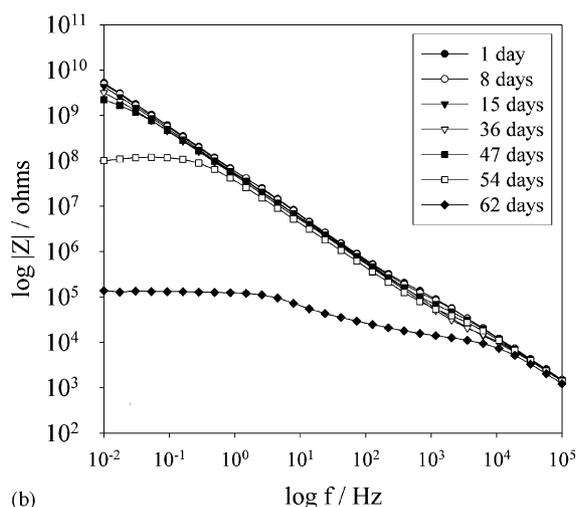
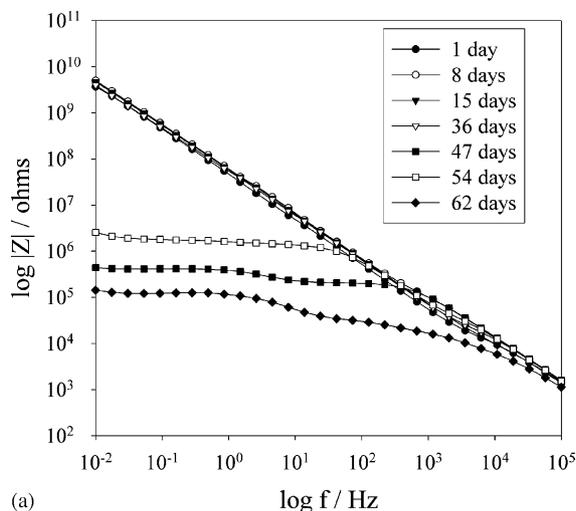


Fig. 2. Bode-modulus plots for different immersion times in NaCl 0.5 M of electrocoated aluminium samples without pre-treatment (a) and with a Zr/Ti pre-treatment (b).

ples, after 40 days of exposure to salt fog the total impedance is still high as for the immersion test after the same testing period. The time at which non-pre-treated samples lose their barrier properties is somewhat shorter for salt fog exposure than for the immersion test. This difference can be accounted for by the higher exposure temperature and the higher oxygen concentration at the coating surface in the case of salt fog exposure. At the end of both tests, no visible signs of deterioration were detected while significant changes in the EIS response occurred.

Parameters R_p and C_c were determined by fitting the impedance diagrams with the electrical equivalent circuit model shown in Fig. 1. The resulting values are illustrated for both tests as a function of exposure time in Figs. 3 and 4. In agreement with the observed decrease of the low-frequency impedance modulus, R_p shows an important decrease with exposure (Fig. 3), especially for samples NP, which give R_p values below 10^7 ohms cm^2 after 40 days of exposure. The pore resistance is higher for ZT samples than for NP samples

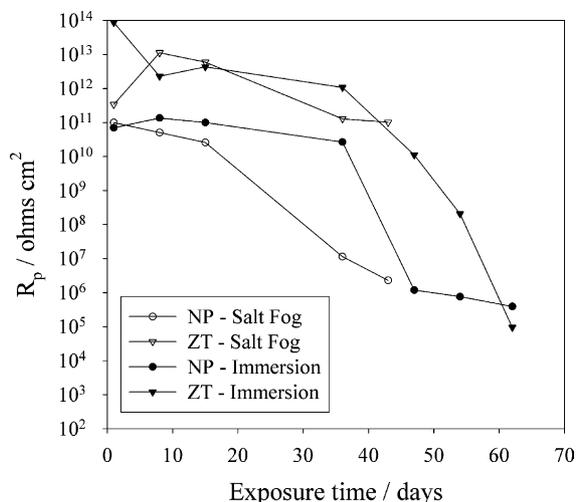


Fig. 3. Pore resistance as a function of exposure time to salt fog or to an immersion test for NP and ZT samples.

suggesting that the pre-treatment could also have a beneficial role on the barrier properties of the coating.

The coating capacitance values reflect water and electrolyte ingress in the coating. The C_c values are almost constant as a function of exposure time for samples NP and ZT exposed to both tests (Fig. 4), meaning that during the period from 1 to 60 days there is probably no significant water absorption by the coating. Cathodically deposited coatings are known to be rather impermeable to water so that there is only a slight absorption of water by the coating at the early moments of contact as illustrated by the inset in Fig. 4. The volume fraction of water absorbed by the coating can be estimated from Brasher and Kingsbury (Eq. (2)) and is about 0.06 which is very low.

The coating degradation can be accelerated by an increase in temperature as illustrated in Fig. 5 where values of the pore resistance are given as a function of the immersion time in

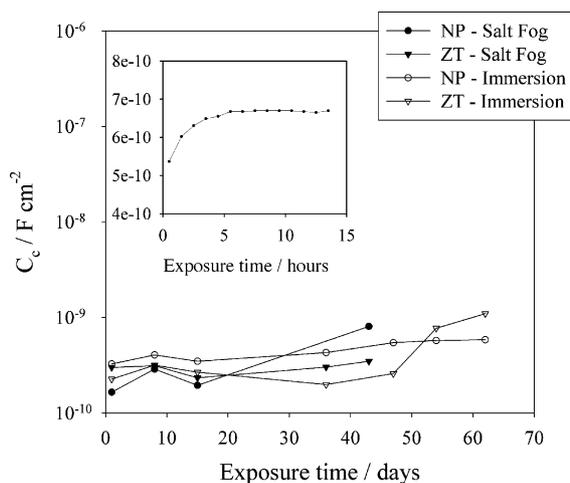


Fig. 4. Coating capacitance as a function of exposure time to salt fog or to an immersion test for NP and ZT samples; inset: coating capacitance for a ZT sample in the first hours of immersion in NaCl 0.5 M.

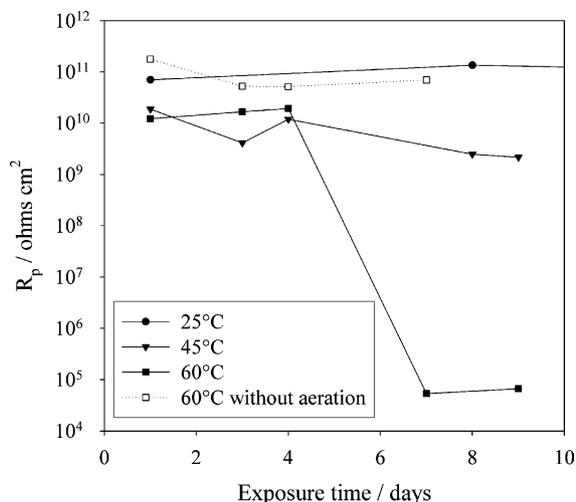


Fig. 5. Pore resistance as a function of the exposure time for NP samples immersed in aerated NaCl 0.5 M at different temperatures.

aerated 0.5 M NaCl at different temperatures. Increasing the temperature will cause a faster loss of the barrier properties after 7 days for an immersion temperature of 60 °C for example. This important decrease cannot be accounted for by a softening of the coating and the subsequent increase of the number of pores since the glass transition temperature of the electrocoating (95 °C) is higher than the highest experimental temperature. On the other hand increasing the temperature facilitates water and electrolyte penetration through pores and accelerates oxygen diffusion and the corrosion reactions at the exposed metal/electrolyte interface. The role of oxygen is primordial in the coating degradation as it causes metal corrosion and the subsequent delamination of the coating. To illustrate the importance of the presence of oxygen, immersions have been carried out in a non-aerated solution at a temperature of 60 °C. After 7 days no degradation was observed in the impedance spectra while the immersion in the same but aerated solution resulted in values of pore resistance below 10^5 ohms cm^2 .

3.2. Coatings with an artificial defect

Intact coatings are generally used to evaluate the barrier properties and water permeation by the coating. Adhesion evaluation needs long exposure times since the related electrical parameters can only be accurately determined when the corresponding time constant is clearly visible in the impedance spectra. Moreover, the presence of corrosion products may affect the estimation of A_w from the calculated C_{dl} and R_{ct} values.

As is the case with normalized tests, the adhesion properties of a coating to a metal are generally determined by scratching the coating and measuring the delaminated area after a determined exposure time. Some authors used EIS to follow the degradation of scratched coatings and to calculate the delaminated area around the scratch [15,16]. This task is

Table 3
Visual observations of scratched samples degradation during exposure to salt fog

Exposure time to salt fog (days)	Without pre-treatment	Zr/Ti pre-treatment
3	1 filament/cm; length < 1/2 mm	No degradation
10	2–3 filaments/cm; length: 2–3 mm	Initiation of some filaments; length < 1/2 mm
17	3–4 filaments/cm; length: 3 mm	<1 filament/cm; length < 1 mm
33	>10 filaments/cm; length: 5–6 mm	<1 filament/cm; length: 1–1 1/2 mm

generally delicate since the presence of corrosion products inside the defect and under the coating considerably affects the determination of the delaminated area. The choice of an appropriate electrolyte is in this case crucial. The electrolyte should allow the dissolution of the corrosion products formed during exposure and not cause the formation of new corrosion products during the contact before the impedance measurement. According to a previous work [17] and to a study performed by Fedrizzi et al. [18,19], acidified Na_2SO_4 0.1 M seems to be the most appropriate choice for measuring the impedance spectra of scratched coated aluminium alloys.

Samples NP and ZT covered with a 20 μm thickness coating were scratched and exposed for maximum 33 days to salt fog. The exposure resulted in an important development of filiform corrosion for non-pre-treated samples. The initiation of filiform corrosion was already visually observed after 3 days of exposure. On the other hand, Zr/Ti pre-treated samples show the presence of small filaments only after 17 days of exposure to salt fog. These observations, resumed in Table 3, show the beneficial influence of the Zr/Ti pre-treatment on the adhesion of the coating to the 6016 aluminium alloy.

EIS was performed on samples exposed for maximum 10 days to salt fog. After exposure, the scratched samples were assembled in a three-electrode electrochemical cell filled with Na_2SO_4 0.1 M at pH 1. The impedance measurements were carried out after 1 h, time necessary to reach stationary conditions (stable corrosion potential). The resulting impedance spectra show only one time constant corresponding to the second time constant in the electrical circuit shown in Fig. 1. The time constant related to the coating is shifted towards frequencies higher than 100 kHz. This shift can be explained by the presence of a macroscopic defect and to the subsequent lowering of R_p to a value close to the electrolyte solution resistance.

C_{dl} values were determined by fitting the impedance spectra with a one time constant electrical model describing the electrochemical reactions at the exposed metal surface. The C_{dl} values were then divided by the double layer capacitance of the bare metal to give the evolution of the active metal area as a function of exposure (Fig. 6). Higher double layer capacitance values are observed for NP samples explained by the poor adhesion of the coating when samples are not pre-treated before being painted. Moreover non-pre-treated samples show a significative increase of the double layer capacitance as a function of the exposure time to salt fog and thus an increase of the delaminated area. For the Zr/Ti pre-treated samples, the values are constant during the first 10 days of exposure to salt fog. Accordingly, the tendency

observed for C_{dl} values of both samples fully agrees with the visual observation of a development of filiform corrosion on non-pre-treated samples while Zr/Ti pre-treated samples were not degraded after 10 days of exposure to salt fog.

After 10 days of exposure, the solubilization of the corrosion products formed on non-pre-treated samples becomes harder. As a consequence, a rather accurate estimation of the extent of filiform corrosion can only be obtained for short exposure times. However in the present case 10 days of exposure is long enough to distinguish the behaviour of the two types of samples (NP and ZT) and to observe the increase of the delaminated area on non-pre-treated samples.

Consequently, combining exposure to salt fog of intact and scratched samples and following their degradation by EIS allows the evaluation of the influence of the pre-treatment on the loss of barrier properties and on the adhesion of the coating to the substrate.

3.3. AC/DC/AC

The ac/dc/ac test was performed with coatings of 7, 16 and 20 μm of average thickness. Since the cycles are repeated on the same sample and the resulting degradation is rather severe, the lowest frequency for the EIS measurements was 0.1 Hz. An example of the resulting impedance spectra is presented in Fig. 7 for a Zr/Ti pre-treated sample with a 16 μm coating thickness. The low-frequency impedance modulus

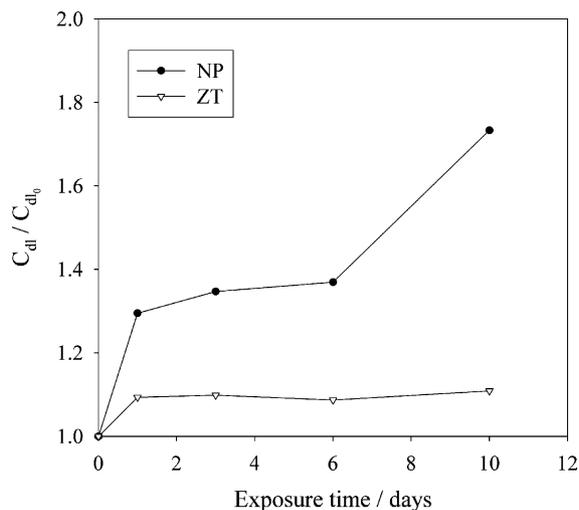


Fig. 6. Values of the double layer capacitance C_{dl} divided by the bare metal double layer capacitance C_{dl0} as a function of exposure to salt fog of scratched NP and ZT samples.

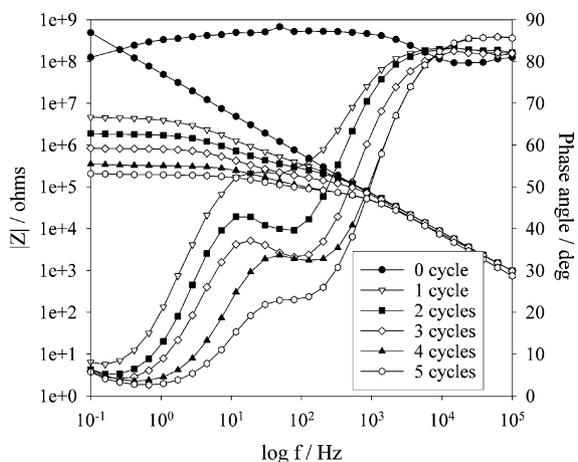


Fig. 7. Bode plots after different ac/dc/ac cycles for a ZT sample with a 16 μm thickness coating.

rapidly decreases with time demonstrating an important loss of the barrier properties. In addition, the presence of a second time constant becomes visible after the first or second ac/dc/ac cycle. The degradation is also optically noticeable from the presence of blisters on the surface at the end of the test as illustrated in Fig. 8 for a 7 μm coating thickness.

Electrical parameters were obtained by fitting the impedance spectra with the equivalent electrical circuit of Fig. 1. As for the salt spray and immersion tests, the coating capacitance values are almost constant during the test and seem not to be influenced by the cathodic stress. The pore resistance values show an important decrease after one cycle, afterwards the values continue to decrease gradually as a function of the number of cycles as observed for the evolution of the low-frequency impedance modulus. An increasing electrochemical activity at the metal/electrolyte interface also results from the application of ac/dc/ac cycles since the C_{dl} values show a rather important increase (Fig. 9a) while R_{ct} decreases with the number of cycles (Fig. 9b).

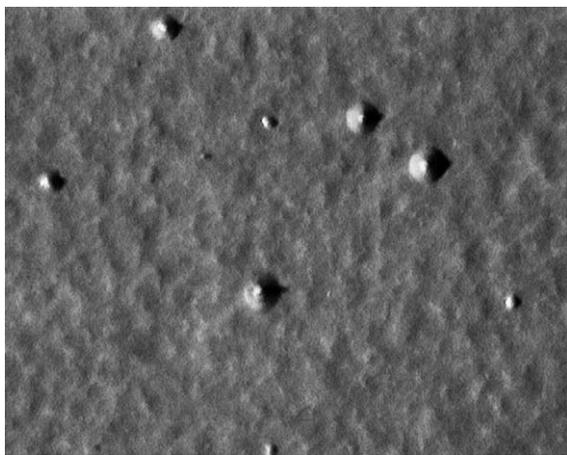
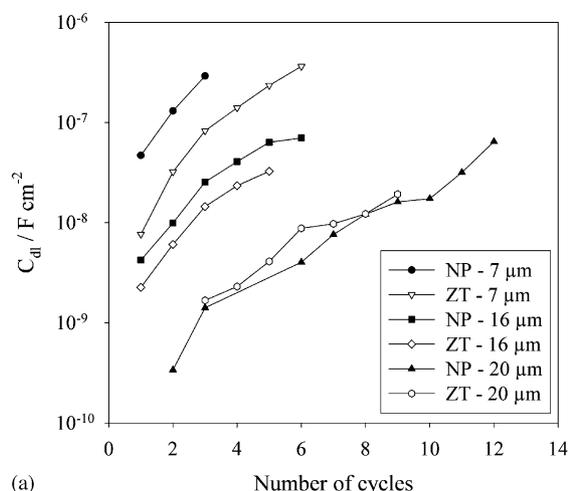
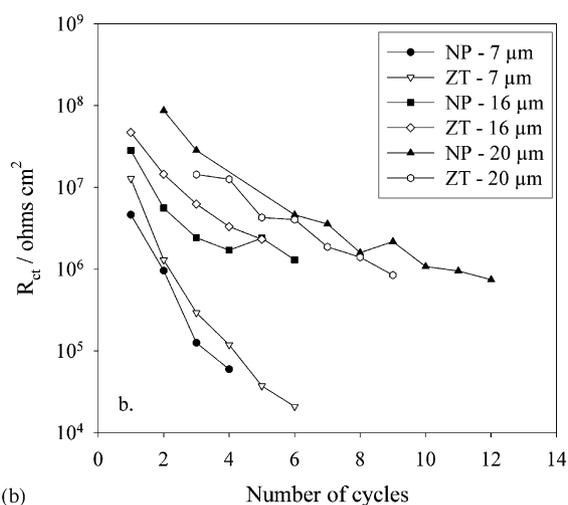


Fig. 8. Stereo-microscopy (magnifying power: 100 \times) of a NP sample with a 7 μm coating thickness after exposure to three ac/dc/ac cycles.



(a)



(b)

Fig. 9. Double layer capacitance (a) and charge transfer resistance (b) as a function of the number of ac/dc/ac cycles for NP and ZT samples with different coating thicknesses.

The imposed cathodic stress is responsible for rapid degradation of the coating which can be explained by: (1) an increase of the number of pores caused by the penetration of chloride ions balancing the concentration of cations (H^+ or Na^+) because of the high negative electrical field [20]; (2) the production of OH^- during the cathodic reaction at the metal/electrolyte interface resulting in a delamination process. The important decrease of R_p after one cycle can probably be explained by a high initial porosity of the coating. Applying a cathodic polarization will result in fast penetration of the electrolyte through the total thickness of the coating. Delamination occurs in the pore regions and results in the formation of blisters as observed in Fig. 8.

Decreasing the coating thickness probably results in a higher pore density, which causes faster degradation of the coating as confirmed by the evolution of the electrical parameters. In addition, the Zr/Ti pre-treatment gives rise to higher pore resistance than for non-pre-treated samples (NP). The effect of the pre-treatment is also detected in the C_{dl} values which are smaller for ZT samples in agreement with a slighter

delamination. This effect is however mainly observed for the lowest thickness (7 μm) for which the time necessary for the electrolyte to reach the metal is shorter. Smaller thicknesses consequently result in a rapid start of the corrosion process and in the consequent adhesion loss of the coating from the substrate. The use of thinner coatings therefore reveals after a very short test period the beneficial contribution of the pre-treatment on the coating adhesion.

4. Conclusions

Different ageing tests were used to characterize the barrier and adhesion properties of a cathodic coating electrodeposited on a 6016 aluminium substrate. Intact and scratched samples were investigated and their degradation was followed by EIS. The corrosion resistance of intact samples was evaluated by a salt fog exposure test and by immersion in an aerated NaCl 0.5 M solution. A rather good correlation was observed between both tests. We further observed an increasing degradation rate when the test temperature was higher in the case of the immersion test. This test essentially pointed out the fundamental role of oxygen in the coating degradation.

The EIS investigation of scratched samples provided a very fast evaluation of the adhesion of the coating to the substrate. The difficulty arises in the choice of the appropriate test conditions (electrolyte, pH, contact time, etc.). The electrolyte has to be able to dissolve the corrosion products formed during the sample exposure in order to allow the interpretation of the impedance spectra by simple electrical models which provide the estimation of the delaminated area. An acidified 0.1 M sodium sulphate solution was selected to perform these tests. The analysis of the resulting impedance spectra confirmed that the application of a Zr/Ti pre-treatment before coating considerably enhances the adhesion of the coating to the substrate. The most accurate results were obtained for short exposure times (up to 10 days) to salt fog. For longer exposures it was difficult to dissolve the entirety of the corrosion products formed under the coating and consequently to fit the EIS spectra with a simple model.

Furthermore, the ac/dc/ac procedure has shown the advantage of offering a very rapid evaluation of the quality of a coating/pre-treatment/metal interface. Results obtained after some cycles with thin coatings correlate well with the classical tests. Moreover, this method allows the loss of barrier properties to be followed as well as the loss of adhesion without having to scratch the sample. This avoids the difficulty of the choice of the test conditions cited above. However, since the imposed stress (cathodic polarization) is far from the nat-

ural exposure of such coatings, this kind of test method is to be discussed with precaution.

The short time investigation of intact and scratched samples by different testing methods shows that impedance spectroscopy is particularly appropriate to get a rapid evaluation of the quality of a substrate/coating system since we could observe after a very short exposure time the influence of the Zr/Ti pre-treatment on both barrier properties and on the adhesion of the coating to the substrate.

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