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Corrosion Protection and Delamination Mechanism of Epoxy/Carbon Black Nanocomposite Coating on AA2024-T3

A. Foyet, T. H. Wu, A. Kodentsov, L. G. J. van der Ven, G. de With, and R. A. T. M. van Benthem

Department of Chemical Engineering and Chemistry, Laboratory of Materials and Interface Chemistry, Eindhoven University of Technology, 5600 MB Eindhoven, the Netherlands

The barrier property of a nanocomposite epoxy coating containing 1 or 1.25 vol% of carbon black (CB) applied on AA2024-T3 was investigated by using electrochemical impedance spectroscopy. Micro-electrochemical impedance spectroscopy and optical microscopy were also used to investigate the delamination of the nanocomposite coating containing 1.25 vol% carbon black (CB). A defect of about 500 μm in diameter was created in the composite coating as well as in the unfilled reference sample. The polarization resistance of the unfilled coating decreases 10 times faster than that of the composite. The blister size of the nanocomposite coating is also smaller after 200 h of immersion. It was concluded that the composite delaminates by a factor of ten slower compared to a similar unfilled coating. A protective mechanism was proposed in order to explain this observation. The presence of CB conductive pathways in the composite and the electrical contact between the coating and the substrate is helpful to delocalize electrons generated from the metallic part. After oxidation, electrons do not remain localized at the interface as they have the possibility to migrate into the coating through the CB percolation pathway. This reduces the rate of interfacial oxygen reduction and thus the rate of coating delamination.

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Numerous studies have been done concerning the application of organic coatings on the corrosion protection of metallic substrates. It is commonly agreed that control of corrosion based on organic coatings is mainly provided by the use of three options: electrochemical inhibitors, sacrificial filler (active protection) and barrier coatings (passive). Inhibitive pigments like chromates are commonly used on aluminum alloys while sacrificial coatings such as zinc-rich primers offer cathodic protection on steel substrates. In this last case, electrical attachment of a less passive anode (the sacrificial filler) prevents discharge of current from the metal to the electrolyte. The exact mechanism by which barrier coatings protect metals from corrosion is still unclear. Some authors say that the passive protection offered by barrier coatings is due to their high electrical resistance above the interface thus preventing external flow of ionic currents between anodic and cathodic areas. Various studies exist about the use of conducting polymers in corrosion protection. A number of protective mechanisms have been proposed in this case but the most acceptable is the combination between electrochemical inhibition and cathodic protection.

Recently, the addition of few percent of conducting polymer to a non-conducting polymeric matrix has drawn particular attention. It was shown that the modification of a paint formulation by adding 0.2 to 0.6 wt% of conducting polymers (such as polyaniline, polypyrole or other conducting polymers) increases significantly the protective properties of the coatings on steel substrates. The role of the conducting polymer is its ability to intercept electrons at the metal surface and to transport them into the coating. Oxygen reduction and / or further oxidation (in the case of polyaniline) prevents discharge of current from the metal to the electrolyte. The exact mechanism by which barrier coatings protect metals from corrosion is still unclear. Some authors say that the passive protection offered by barrier coatings is due to their high electrical resistance above the interface thus preventing external flow of ionic currents between anodic and cathodic areas. Various studies exist about the use of conducting polymers in corrosion protection. A number of protective mechanisms have been proposed in this case but the most acceptable is the combination between electrochemical inhibition and cathodic protection.

On the other hand, only a few reports exist on the corrosion protection of metal using carbon-black (CB) nanocomposite coatings. Zhang et al. studied the corrosion resistance of steel coated with a nanometer CB composite in 3 wt% NaCl and showed that adding CB nanoparticles in the coating is effective in improving the corrosion resistance of the steel. The composite coating provided the best corrosion protection to the steel in a NaCl solution with a CB content of 1 wt%. Because of the large specific surface area of CB and its high activity, there is a strong interface connection between coating and CB nanoparticles. In addition, during the initial stage of curing CB nanoparticles can move easily in the coating and fill the micropores of the coating so that the packing density of the composite is improved. Such nanocomposite coatings provide a much better barrier against corrosive ions such as chloride. Wei et al. evaluated the corrosion (in 3% NaCl) of mild steel protected with carbon black filled fusion-bonded epoxy coatings and found a positive change of the corrosion performance when the carbon black weight fraction was above the percolation threshold. Above the percolation threshold, the low electric resistance resulting from the CB conducting network in the coating dominated most of the current responses to the sinusoidal potential excitation. It was shown that only a small amount of electrolyte penetrates into the composite coating to alter the dielectric properties of the system during an immersion period of about 400 days.

It appears that the nanocomposite coating containing CB particles is very promising as material for corrosion protection of steel. To the best of our knowledge, epoxy coatings containing CB particles were not tested on aluminum alloy and no delamination study was done on such composite coating from a small and controllable defect area. Some coatings may have good barrier properties but delaminate rapidly after damage. The aim of this work is to study the delamination of epoxy nanocomposite coating on bare AA2024 alloy. Micro-electrochemical impedance spectroscopy (EIS) is combined with optical and confocal microscope visualization of the substrate to study the delamination from a local defect. Results are compared with a reference unfilled coating in order to appreciate the role of the conducting particles on the delamination. A protection mechanism provided by the CB conductive pathway is proposed.

Experimental

The coating used in this work is a two-component solvent free system comprising Epikote 828 (Resolution Nederland BV) epoxy and Jeffamine D230 (Huntsman BV, Belgium) as curing agent. In all formulations, the epoxy-to-amine mole ratio was 1.2/1. The nanocomposite was prepared by adding carbon black powder into the epoxy and stirring by using a high speed shear mixer with a double impeller disk. Ultrasonic treatment was employed after the dispersion in order to break down the carbon aggregates and achieve a fine dispersion of the nanoparticles. The curing agent was added in the final step of the mixing process and the composite was applied on AA2024-T3 panels by using a square applicator. The surface of the AA2024-T3 alloy was sanded with an abrasive pad, rinsed with water and degreased in acetone before coating application. This pretreatment reduces the thickness of the oxide layer on AA2024-T3 and exposes the intermetallic compounds on the surface of the substrate. This substrate
will be denoted as AA2024 in the text. The electrical conductivity of composite containing different CB fractions was measured and the percolation threshold was obtained with 1.1 vol%. The composites used for corrosion test contain 1 and 1.25 vol% of carbon black; these volume fractions are below and above the percolation threshold, respectively. In order to evaluate the performance of the nanocomposite, an unfilled epoxy coating (without carbon black) of similar chemical structure and composition was applied on AA2024. All coatings were cured at room temperature for 4 days followed by a post-cure at 100 °C for 4 hours; the thickness was about 60 μm in all cases. Nanocomposite coatings were microtomed and the microstructure was studied by using an FEI Sphera transmission electron microscope.

Electrochemical impedance spectroscopy (EIS) was employed to monitor the barrier properties of coatings after immersion in a 0.5 M NaCl solution. A commercial corrosion cell was used. All data were recorded at room temperature using a Potentiostat / Galvanostat (EG&G, Model 283) coupled with a frequency response detector (EG&G, Model 1025). The impedance of the composite applied on AA2024 was also measured in the dry state in order to check the electrical contact between the substrate and the composite. The surface of the nanocomposite film (applied on AA2024) was coated with silver paint to form a parallel plate capacitor in which the dielectric material is the nanocomposite. All EIS tests were performed in a Faraday cage.

Delamination was studied by drilling a hole with a flat slightly conical tip with a diameter of about 500 μm in the coatings. For this purpose, a small electrical drill was mounted on a device which allows depth control of the defect. As shown in Figure 1, a home-made micro-electrode was placed on the hole in order to record the EIS signal during the corrosion process. This system forms a three electrode micro-electrochemical cell consisting of an AA2024 working electrode, a small platinum wire counter electrode and a small commercial Ag/AgCl, KCl sat electrode from EG&G. The flow rate of the 0.5 M NaCl solution from the electrode was so small that the diameter of the drop at the point of contact with the sample surface was always close to 4 mm during the experiment. The surface wetted by the drop was considered as the working electrode area. The cell was placed in a chamber to avoid air motion around the drop and to reduce its evaporation rate. This chamber was introduced in a Faraday cage in order to minimize external interference on the EIS signal. Micro-EIS data were recorded at several time intervals in the frequency ranging from 100 kHz to 10 mHz by using a 5 mV AC voltage amplitude. Experiments were performed at room temperature using a Potentiostat/Galvanostat (EG&G 283) coupled with a frequency response detector (EG&G 1025).

For the unfilled transparent coating, the EIS signal and optical images of the coating were recorded from the same hole at several time intervals in order to correlate the change in the EIS signal to the visual corrosion product. The nanocomposite coating is non-transparent, so confocal microscopy was employed to visualize the delamination frontier since this technique is capable of detecting small height changes. N-methyl pyrolidone (NMP) was also used to dissolve and remove the composite coating at the end of EIS test and the trace of corrosion was monitored on the substrate with an optical microscope.

Results and Discussion

Microstructure and AC response of the composite.— The electrical properties of composite materials are related to the distribution of the filler particles in the matrix. Carbon black particles tend to agglomerate when mixed with a polymer. Figure 2 displays a transmission electron micrograph (Fig. 2a) and the ac response (Fig. 2b) of an epoxy amine nanocomposite coating containing 1.25 vol% CB. The image shows a random distribution of the CB clusters and particles in the polymer matrix. This nice distribution was achieved by the combination of shear mixing and ultrasonication. One objective of this work is to establish electrical contact between CB clusters and the AA2024 substrate. The presence of aluminum oxide on the alloy
may have a negative influence (Ohmic drop) on the electrical contact between the nanocomposite and the substrate.

The impedance of the nanocomposite (with 1.25 vol% of CB) applied on AA2024 was measured in dry state in order to test the electrical contact between the substrate and the composite. This measurement is helpful to avoid any misinterpretation of the EIS data when conductive coatings are immersed in 0.5 M NaCl. Figure 2b shows the electrical response of a dry composite coating. The Bode plot of the composite is characteristic of electrode processes under charge transfer control. This reveals the existence of CB conductive pathway in the nanocomposite. The AC conductivity of a free standing composite film (not shown in this document) also confirms the existence of a CB conductive pathway in the coating. The intercept of the impedance magnitude with the y-axis at low frequency gives a charge transfer resistance in the range of $10^5$ $\Omega \cdot$cm$^{-2}$. Since the electrical AC conductivity of a free standing nanocomposite film at 10 mHz is $3.4 \times 10^{-6}$ S$\cdot$cm$^{-1}$ this reveals a low interfacial Ohmic drop. The result confirms not only the presence of CB percolation pathways in the composite but also the existence of electrical contact between the AA2024 substrate and the composite coating.

**Barrier properties of clear and nanocomposite coatings with CB conducting pathways.**— Organic and composite coatings are permeable to water, oxygen and other agents which may affect the adhesion. Accordingly, some coatings may have acceptable adhesion while dry and fail badly when tested under high humidity or after immersion in water for several hours.15 In the present work, unfilled coatings as well as the nanocomposite adhere on AA2024 both in their dry and wet states with the adhesion pull-off strength value close to 8 MPa. The presence of carbon black in the composite did not result in a dramatic change of the adhesion of this material on the AA2024 substrate. The barrier property of coatings was studied in NaCl solution by using impedance spectroscopy. Figure 3 displays the EIS results of the unfilled coating and the nanocomposite coating in which the carbon black concentration is below or above the percolation level. Below the percolation threshold (Fig. 3a and 3b), the impedance magnitude appears in all cases as a straight line with a negative slope while the phase angle is very close to 90° over the whole frequency range. The sample thus behaves like an ideal capacitor having a phase shift of 90° in the same frequency range. This reveals the absence of electrochemical process in both systems. Both samples have a very good barrier property which is stable up to 140 days of immersion in 0.5 M NaCl solution.

Above the percolation threshold (Figure 3c), the impedance behavior is characteristic of a polarizable electrode. But the charge transfer process observed in this case should be interpreted carefully since it is not due to corrosion. It is important to notice the overlapping (or a very small shifting at intercept with |Z| axis) of all data recorded after 150 days of immersion in 0.5 M NaCl. Corrosion reactions and ions transport would have led to a decreasing coating resistance with the immersion time. The overlapping curves account for the good barrier properties of the nanocomposite coating. The shape of the EIS curve is similar to that of Figure 2b. The end frequency of Figure 2b is $10^7$ Hz instead of $10^5$ Hz as in Figure 3c, thus the presence of two peaks on the phase angle of the dry system. The electrical conductivity of the composite dominates the impedance spectra of the immersed sample.

**Corrosion induced delamination of clear coating and composite with CB conductive pathways.**— Defect morphology.— Sample preparation is a crucial step during the investigation of coating delamination from a local defect area. The instrument used to generate the hole or the scratch should not induce additional stress in the coating around the defect center. Otherwise in some cases, partial delamination of the coating may occur around the hole. This would probably lead to an erroneous interpretation of the final test results. In the present case, a small electrical drill was mounted on a stage to allow the depth profile control. Before the test, samples were examined with confocal and optical microscopes in order to check the shape of the defect as well as eventual failure. Figure 4 displays the confocal micrographs of the nanocomposite and the unfilled coating sample. From these images it appears that the boundary of all holes is smooth and that no major delamination was induced during the drilling process. The profile confirms the conical shape of holes with a base diameter of about 500 $\mu$m and a depth of about 160 $\mu$m. It also confirms the reproducibility of the drilling device. The coating thickness is close to 60 $\mu$m; the depth profile indicates how the AA2024 substrate was partially removed during drilling. It is important to expose the coating/AA2024 interface to the NaCl solution since the delamination process will start from this region.

**Micro-EIS investigation of the delamination process.**— EIS data of the unfilled and the nanocomposite undamaged coatings were previously recorded (Figure 3) at the open circuit potential (ocp) by using the macro-scale commercial electrochemical cell. The home-made micro-electrode was utilized to record EIS data (at the ocp) on a small portion of the undamaged coatings. After normalization by the area (0.126 cm$^2$), all data were in agreement with the results obtained by using the commercial cell. A similar test with an uncoated AA2024 substrate gives comparable results. This confirms the reliability of the micro-electrode. The micro-electrode was placed on top of the defect in such a way that the NaCl solution completely wetted the surface around the hole. The advantage of this micro set-up in comparison to a large size EIS set-up is that only a very small area of the sample is exposed to the electrolyte and it allows a local study of the corrosion process. The diameter of the drop (0.5 M NaCl) on the substrate is about 4 $\mu$m, large as compared to the size of the defect but small if compared with the macro-EIS. Although micro impedance spectroscopy can give valuable information about the corrosion rate of nanocomposite and clear coatings, one should be careful about the origin of the signal recorded on a
defective system as shown in this case. Two different corrosion propagation mechanisms can be responsible for the EIS signal. The first is the enhancement of corrosion reaction on the metallic part, i.e. pitting corrosion in the \( z \)-direction at the bottom of the defects which can give a similar EIS signal. The second is the combination of both uniform interfacial corrosion propagation (filliform-type) and the pitting corrosion at the bottom of the defect.

Figure 5 displays the micro-EIS data of the unfilled epoxy and the nanocomposite defective coatings. All data were normalized with electrode area (0.126 cm\(^2\)) which corresponds to the surface covered by the NaCl drop. Holes where flushed carefully (without wetting the whole panel) with water every 48 h in order to remove the corrosion products and avoid blocking of the defect center. For the unfilled coating (Fig. 5a) at the early stage of immersion \((t \leq 5\) h\), \(|Z|\) appears
as a straight line with negative slope at frequencies above 1 Hz and
as a horizontal plateau at lower frequencies. The phase angle shows
a single large plateau at a value close to 80 degree at intermediate
frequencies. Although charge transfer exists at the defect center, the
capacitive behavior of the coating dominates the initial impedance
plots. After 5 h of immersion, a small deflection appears at about
200 Hz on the |Z| vs frequency plot; the intercept of the Bode mag-
nitude with the |Z| intercept decreases gradually with immersion time
and the phase shift shows two clear peaks. This accounts for the pre-

cence of two time constants in the system; the high frequency time
constant is related to the coating properties while the low frequency
time constant is due to the combined electrical double layer of the
hole and the metal coating interface. As expected, the EIS data of the
unfilled coating is characteristic of a defective coating. The change
in the |Z| intercept value (at low frequency) with time (from $2 \times 10^6$
to $10^4 \Omega \cdot \text{cm}^2$) accounts for the decreasing polarization resistance
of the system with the immersion. This shows the progress of corrosion
reactions and the coating delamination or pitting corrosion on the
exposed base material.

Impedance spectra of the nanocomposite coating (Fig. 5b) are
similar to those of the unfilled sample. It is important to notice the
presence of three peaks in some phase angle plots of the composite.
This originates from the additional carbon-black conducting phase in
this system. On the other hand, all |Z| curves tend to overlap at high
frequency while the low frequency intercept of the magnitude with
|Z|-axis decreases from about $9 \times 10^4$ to about $10^6 \Omega \cdot \text{cm}^2$ after 213
h of immersion. The change in the polarization resistance is less pro-
nounced in this case as compared to the unfilled coating. This suggests
that the pitting corrosion and/or the delamination processes are slower
for the composite coating. In order to check the reproducibility, EIS
measurements were repeated three times on samples prepared from
different batches but with similar composition and microstructure.

The results were comparable with the above mentioned data.

Both coatings were deposited on similar substrate (from one batch)
and the same area of the base material was exposed to the electrolyte.
Therefore, enhancement of pitting corrosion in the z-direction of the
exposed metal cannot be the main mechanism responsible for the EIS
signal. Both coatings should have the same micro-EIS response if that
was the main phenomenon. It can be concluded that delamination of
the coating from the defect area dominates the response. In such case,
the system behaves almost like a defective coating with natural micro-

pores or micro-cracks and can be fitted with a modified electrical
model of defective coating systems.

The equivalent circuit shown in Figure 6 is proposed to fit the
micro-EIS data of the defective nanocomposite coating. In this model,
$R_s$ is the solution resistance, $R_m$ and $R_p$ are the pore and the polar-
ization resistance, respectively. Two constant phase elements (CPE),
$Q_p$ and $Q_{dl}$ were used to account for the non-ideal behavior of the
coating capacitance and the double layer capacitance, respectively.
The combination of two CPE also takes into account the presence of
a carbon black conductive pathway in the coating. As shown in
Figure 6, the model fits the experimental data rather well; replacing
the capacitor by CPE decreased the fitting error. A similar model was
used to analyze the EIS data of unfilled coatings but all constant phase
elements were replaced by real capacitors in this case.

Several authors study the delamination of organic coatings on
metallic substrates by using EIS. Mansfeld16 reported on the relation
between the delaminated area $A_d$ and the polarization resistance or the
double layer capacitance:

$$\frac{C_{dl}}{C_{dl}} = C_{dl}^0 A_d \quad R_p^0 = R_p^0 / A_d \quad [1]$$

In these relations $C_{dl}$ and $R_p^0$ represent, respectively, the double layer
capacitance and the polarization resistance of the coated system at
time $t$ while $C_{dl}^0$ and $R_p^0$ correspond to the double layer capacitance
and the polarization resistance of the same but uncoated substrate
immersed in the same electrolyte. From the above equations, it is clear
that the polarization resistance of a coating system will decrease with
the increasing debonded area. Based on those relations, Armstrong
et al.17,18 studied the delamination of organic coatings on steel and
discussed the possible existence of pores and defects through which
ions flow and induce interfacial delamination of the coatings. On the
other hand, it is not very clear whether data obtained in bulk solutions
for bare metals ($R_p^0$, $C_{dl}^0$) are in agreement with corresponding data
for the metal/coating interface.16 The equations 1 need to be adjusted
before applying to the present system because there is an artificial
defect initially in the sample. It was shown from the confocal images
that part of the AA2024 substrate is removed below the coating. Exper-
imental results show that the delamination of coatings around the
defect is the dominant process which generates changes of EIS sig-
nal. For each system, the ratio between initial polarization resistance

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Figure 4. Confocal microscope micrographs and the depth
profile of defects before the corrosion test.
Figure 5. Bode representation of the impedance data of defective unfilled epoxy coating (a) and nanocomposite coating with 1.25 vol% CB (b). All data were recorded in 0.5 M NaCl with the micro-electrode and normalized with the contact area of the drop with the surface 0.126 cm². The defect diameter was 500 μm in all cases.

(directly after immersion) and its value at time t will be proportional to the delaminated ratio and thus

\[
\frac{R_p(t = 0)}{R_p(t)} \propto A_d \tag{2}
\]

Figure 7 compares the ratio between the polarization resistance of the nanocomposite (with conductive pathway) and the unfilled coatings. For the composite coatings the ratios of the polarization resistance are below 20 after 220 h of immersion in 0.5 M NaCl. The results of three tests carried out on different composite samples with similar composition are all in agreement. In contrast, the resistance ratios are

Figure 6. Fitting example (a) and equivalent model (b) of defective nanocomposite coating on AA 2024.
Figure 7. Ratio between the polarization resistances of nanocomposite with conductive pathway vs unfilled coating. The resistances were obtained by fitting micro-EIS data with the electrical model of Figure 6 or its modified version.

quite high for the unfilled coating after the same period of immersion in NaCl. This reveals the fast delamination of this system.

Micro-EIS analysis shows a clear difference between the behavior of unfilled and the nanocomposite coatings. A corrosion mechanism involving interfacial coating delamination is suggested to explain the observation. This mechanism can be confirmed by using different analytical tool. Direct observation of the corrosion product or the debonded area with an optical or a confocal microscope can give additional information.

Optical and confocal microscope investigation of the delamination process.— In the case of the unfilled transparent coating, electrochemical impedance data and the optical picture of the coating around the defects were recorded simultaneously on the same sample. EIS experiments were stopped at several time intervals; the sample was flushed with water in order to remove some crystallized salts and subsequently submitted to optical microscopy analysis. Figure 8 displays the optical texture of a sample after different immersion times.

From zero to 24 h of immersion, no real coating delamination is observed but corrosion reactions probably occur at the bottom of the defect. At longer immersion times, corrosion products appear at the interface between the coating and the substrate as indicated by discoloration. The delamination starts from the defect and propagates at the interface. Note that the end of the discolored region around the hole cannot be assigned to the delamination frontier but corresponds to the interfacial corrosion product because delamination can be more extended than the observed frontier. Also note that the corrosion initiation is not symmetrical around the cylindrical hole. The reactions start from some specific point and seem to propagate faster in certain directions. This effect can be due to the presence (or the absence) of favorable intermetallic inclusions around the point where corrosion started or to the rolling direction in the AA2024 substrate.

Because nanocomposite coatings are non-transparent; it is not possible to obtain the time dependent optical visualization of the delamination process. Instead, confocal microscopy was used to analyze the composite coating at the end of EIS test. Alternatively in some cases (Fig. 9b) the coating was removed by using the NMP and the corrosion products were imaged with the optical microscope.

In order to be sure that NMP will not clean the interfacial corrosion product, traces of the corrosion product were monitored on a transparent (unfilled) coating before and after removal of the coating. Both pictures were compared and shown to be in agreement with experimental error. Figure 9 shows the blister size of a nanocomposite coating around the defect. A blister of about 1 mm in diameter can be seen on the confocal image of the composite after 250 h of immersion. The optical image of Fig. 9b shows a similar trace of corrosion after coating removal. Both experiments were carried out on samples of similar composition and microstructure but prepared from different batches. This shows the reproducibility of the test. Note that the scale bar (200 μm) is smaller in the case of the composite coating as compared to the unfilled sample (Fig. 8) indicating that the delaminated area is smaller for the nanocomposite. As in the unfilled coating, corrosion starts from a specific part of the defect and seems to have a directional preference.

It is clear from the optical images that the delamination rate is slow for the nanocomposite as compared to unfilled coating. The observation is in agreement with the EIS results. This confirms that the decreasing polarization resistance of the coating (as shown in the EIS signal) with the immersion time is related to the interfacial corrosion and to the coating delamination. Concluding, the nanocomposite coating in which the carbon black form a conductive pathway provides better corrosion protection of AA2024 compared to the unmodified coatings. Although the exact mechanism by which the nanocomposite coating works better is unclear explanation based on the propagation of charge carriers through the coating may account for this observation.

Figure 8. Optical micrographs of defective unfilled (transparent) coating on AA2024 after several time of immersion in 0.5 M NaCl.
Protection mechanism of nanocomposite coating with CB pathways on AA2024.— The electronic properties of the substrate surface have a strong influence on the delamination mechanism of organic coatings on metallic substrates. For a substrate covered by semiconducting oxide such as steel and zinc, the exchange current resulting from a change in the oxidation state of the interfacial oxide (i.e. $\text{Fe}^{2+}$ to $\text{Fe}^{3+}$) can be measured at the intact coating interface. The cathodic reaction (oxygen reduction) is the driving force for the delamination of non-conducting organic coatings on such a substrate. The process is known as the cathodic delamination mechanism. In the case of Al and aluminum alloys, which are mostly covered by a non-conducting oxide, the oxidation of the substrate below the coating is responsible for the corrosion evolution. A non-conducting coating delaminates from a small defect according to the anodic undermining mechanism. Differences between the corrosion mechanisms of those substrates are due to the possibility of interfacial electron conduction for the case of steel or zinc and its absence for aluminum.

When nanocomposite coating with CB conducting pathways are used, electrical contacts can be established between the steel surface and the composite or between the intermetallic compound on AA2024 substrate and the composite. Consequently, electrons generated at any defective region will not be localized at the coating-metal interfaces as in the case of insulating coatings. Localization of electrons at the interface favors interfacial oxygen reduction and thus coating delamination. In that case, debonding will be accelerated by the $\text{OH}^-$ resulting from the reduction of oxygen. Figure 10 shows the delamination mechanism of a defective nanocomposite coating on AA2024. The multiple percolation and interconnection between particles in the composite or the electrical contact between the composite and the intermetallic will increase the region where electrons transfer is allowed. Electrons generated at the defect will migrate both into the coating and to the interface. This spreading of electrons into the coating will decrease the rate of oxygen reduction at the metal-coating interface and thereby reduce the coating delamination. This might be the reason why the delamination rate is slow when a composite coating with CB conducting pathways is applied on AA2024. The protection provided by nanocomposite containing CB could be enhanced if one applies a top-coating on this composite layer in order to avoid the enhancement of pitting corrosion due to the large cathodic area of conductive composite exposed to air. In this case, a new interface could be defined and oxygen reduction may shift from the metal-composite to the composite-top coating interface.

The use of CB as conducting fillers is advantageous over the application of conducting polymer additives. Conducting polymers
may easily oxidize, reduce or generate some radicals after water uptake. The redox species and radicals may destabilize the coating matrix and increase the ion transport through the film. In contrast, CB particles are chemically inert and electrochemically inactive allowing only electron transport. Therefore, the life time and the barrier properties of the polymeric matrix will not be significantly affected.

**Conclusions**

Unfilled epoxy coating and a nanocomposite epoxy coating containing CB conducting pathways were applied on AA2024 alloy. The delamination of the coatings was studied by creating a defect of about 500 μm in diameter and by using optical microscope and micro-electrochemical impedance spectroscopy to monitor the corrosion evolution.

Large delaminated areas with underfilm corrosion products were found when the substrate with the unfilled coating was analyzed by using optical microscopy. In case of nanocomposite, the size of the blister was smaller. This result is in agreement with the change of the polarization resistance obtained from micro EIS; all confirms that the corrosion rate is higher for the unfilled coating as compared to the nanocomposite. A corrosion protection mechanism based on the spreading of electrons from the defect center into the composite coating was proposed to explain the efficiency of this system. Electrons generated from the substrate can migrate through the conductive pathways into the coating. This will reduce the rate of oxygen reduction at the coating substrate interface and decrease the delamination rate.

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