Volume 6 Paper C024

Mechanisms of Diffusion of Reactive Species in the Cathodic Delamination of Polyester Coated Steel

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Abstract

A very important mechanism of organic coating deterioration is the cathodic delamination.

The basic knowledge about the diffusion mechanism of ions, oxygen and water through the coatings and through the defects in the coatings is not yet complete.

In this study a double electrochemical cell has been used in order to keep separated the solution in contact with an artificial defect (inner solution) and the solution in contact with the rest of the intact organic coating (outer solution). In this way it is possible to polarise the sample in the cathodic region and to control the environment (ions and concentration, oxygen, water activity) in the defect and around the defect. Moreover it is possible to measure electrochemical parameters in the two different areas of the coating.

Samples of polyester coated phosphatised steel were studied using this cell.

The cathodic delamination was measured, in different solutions, by measuring the distance of delamination from the artificial defect after different times of exposure under cathodic polarisation. The coating properties has been evaluated also by analysing Electrochemical Impedance data obtained during polarisation in the two parts of the cell; the data were compared with the dalaminated area.

The behaviour of different cations has been compared and it was found a different diffusion mechanism for the couple Li and Na and the ions couple K and Ce. The second couple, because of the smaller dimesion of the hydrated shell can diffuse through the coating, while Na and Li diffuse mainly through the defect.

Introduction

The cathodic delamination is one of the more important processes promoting the degradation of a protective organic coating [1]. It can occur both in the case of coating on cathodically protected structures and also in the case of organic coated steel at the free corrosion potential.

Many studies have been dedicated to this subject [2-6], (in particular those of Leidheiser and coworkers [7-13], van Ooij and coworkers [14,15], Dickie and coworkers [16,17], and more recently Stratmann and coworkers [18,19,20] and Steinsmo and colleagues [21,22,23]) regarding the mechanisms of cathodic delamination of organic coatings on steel. It is, however, important to increase the scientific knowledge in this field for being able to develop new protective systems more resistant to cathodic disbonding of the coating from the substrate caused by the local alkaline environment due to the reaction of oxygen reduction producing OH- anions.

The process proceeds under coatings due to continuous migration of water and oxygen [7,18] (necessary for the cathodic reaction) and positive ions (cations), necessary in order to locally balance the electric charge, while the anions would not be expected to influence the process, even if in some cases an influence [9,12] has been observed. The water is important also because it is essential for the diffusion of the hydrated ions, it can nucleate the delamination process and, in some cases, it has been found that it is the rate determining step of the process [24].

The diffusion process (or migration) of ions, water and oxygen, which in some cases can be described by the Fick's law, while in other

situations it is not-Fickian, is therefore fundamental to the kinetics of the delamination process and it can occur essentially in two ways:

1) through the defect in the coating promoting the corrosion process and the delamination as well as through the delaminated interface

2) through the intact coating (figure 1).

In the case of cation diffusion through the coating, the mobility measured depends on the dimensions of the hydrated ion [8,9] and in order to study the behaviour of the ions in the coating, radioactive isotopes have been used [12]. It is important to remember also the fundamental importance that the metal surface plays in the kinetics of cathodic delamination, because the cathodic reaction rate can be reduced by the presence of chemical conversion layers (chromates, phosphates, etc.) and because the pretreatments can improve the adhesion and, therefore, reduce the delamination rate.

With regard to the loss of adhesion mechanisms documented in the literature, caused by the alkaline pH (estimated between 10 and 14 in the delamination front [7,18]) these mechanisms can be divided in three groups:

1) oxide reduction;

2) alkaline hydrolysis of the polymer

3) weakening of the interface (interfacial fracture).

Every steel surface is covered by a thin surface oxide [8]. The reduction of the iron from Fe^{3+} to Fe^{2+} leads to the production of oxides partially soluble in the local alkaline environment causing the detachment of the coating. Such mechanism has been reported in the case of epoxy coatings on cathodically protected structures [5]. In the case of alkaline hydrolysis of the polymer there is a chemical degradation of the polymer matrix of the coating because of very elevated pH (saponification reaction [2]) It is supposed that the locus of failure is in the polymer in the immediate vicinity of the surface (a thin layer of polymer remains adhered to the metal). Such mechanism has been

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observed in the case of polybutadiene [2]. This mechanism is rarely the only one acting in the system, but it is frequently observed in connection with reactions of interfacial weakening [5]. This last mechanism, for instance, is typical of the cathodically protecting polyethylene coatings [24].

The aim of this work was to obtain more information on the cathodic delamination mechanism, in order to improve the cathodic delamination resistance of organic coatings, in particular by improving the knowledge of cation diffusion.

Experimental procedure

This study, as previously mentioned, concentrated on the transport mechanisms through polyester coatings on phosphatised steel during processes of cathodic delamination. For this purpose it was necessary to have organic coating systems that showed delamination rate neither too fast (difficult to follow) nor too slow (causing very long testing time). After a series of preliminary analyses using various coatings (waterborne paints, epoxy, polyurethane, polyester, etc) and various substrates (low-carbon steel, stainless steel), we chose for this study polyester powder coating (with coating thickness around 70 μm) on low-carbon steel. Before the coating deposition the substrates were degreased and phosphatised. The samples were produced in an industrial plant for powder coating deposition.

The cathodic delamination tests were carried out by polarising the samples with an artificial defect (diameter of the defect was about 3.2 mm) at the cathodic potential of -1 V (± 0.05 V) vs Ag/AgCl ($+207$ mV SHE). At this potential, maintained by a potentiostat with a graphite counter electrode, the anodic reaction is negligible and the cathodic reaction is the oxygen reduction in presence of water producing OH$^-$ ions. The aim is to increase the cathodic delamination rate occurring at the free corrosion potential by polarising the samples, without modifying the reaction mechanism (for example, promoting cathodic reactions which are not present at the free corrosion potential).

The EIS measurements were obtained using the classic three electrodes setup with 10 mV of signal amplitude and frequency range 10^5–10^{-3} Hz.

The tests were carried out at room temperature using different electrolytes (distilled water, NaCl, KCl, LiCl and CeCl) and concentrations (0.6 and 0.06M).

The most important aspect of the test was the cell which cell was developed in order to separate the environment in contact with the defect and the environment in contact with the intact coating and it is shown in figure 2. A polymeric funnel is placed just around the defect and it is filled with the inner solution (in contact with the defect). The diameter of the funnel in contact with the coating is slightly greater than that of the defect (about 4 mm) and, therefore, the defect is completely inside the funnel. The thickness of the funnel wall is less than 1 mm. Around the funnel is placed a cylindrical cell and between this cell and the funnel is placed the outer solution. In this way we can control the ions concentration both in the inner and outer solutions. We call this cell *double cell* and it is similar to cells used by other authors [8,22,25]. With this cell we were also in the condition to obtain EIS data related to the intact coating (external part which has an area of about 15 cm^2) and related to the delaminated area through the defect (internal part).

Results and discussion

The reliability of the experimental set-up (double cell) was demonstrated in a previous work, showing that the cell does not influence in a significant way the delamination process [26].

An example of delamination rate is in figure 3. We noted that plotting the delaminated area as a function of time, the trend is approximately linear. The approximation to a linear trend is sufficiently good, except sometimes for the initial step of delamination, we obtained worse correlation using other types of function (parabolic, exponential, etc),

and for this reason we decided to fit all the data in this way. The linear trend was also found by other investigators [5,7,19].

This result is in agreement with a delamination process under diffusion control and following the laws of Fick (diffusion front a function of the root of the time). The area is a quadratic function of the delamination front (diameter of the delamination circle) and, therefore, the delaminated area evolution with time is linear.

By fitting the experimental data to a straight line it is possible to obtain two parameters: the induction time, interception of the straight line with the X axis, which physically represents the time necessary in order to start the process of delamination and the slope of the curve that represents the delamination rate. The accuracy of this last parameter in many cases is very low because of the data scatter, and the discussion of the induction time results can be considered only qualitative.

For every diagram also the correlation coefficient (c.c.) is calculated that represents the correspondence of the experimental data with the interpolating straight line. The correlation coefficient is sufficiently close to one, considering also the fact that every point in the diagram originates from a different sample and this can contribute to the data scatter.

The first type of comparison, shown in figure 4, deals with the influence of cations diffusion. We measured the delamination processes using system with the same saline solution (NaCl or KCl) in the internal and external parts of the new cell, and systems where the external solution was distilled water. The different delamination rates are obvious in figure 4.

All the tests with solutions containing KCl have a delamination rate that is clearly higher than the delamination rate in NaCl solution, evidencing a clear influence of cation mobility on the delamination rate.

Moreover an interesting result can be noted in figure 4. In the case of NaCl solution, the absence of ions in the external solution (between

the cylinder and the funnel) does not reduce the delamination rate suggesting Na+ ions diffusion exclusively through the defect. On the contrary, in the case of the KCl solutions the delamination rate is strongly reduced in absence of KCl in the external solution, demonstrating that K+ cations diffuse both through the defect as well as through the coating.

The different mobility of the cations is probably due to the different hydrated cations dimensions. Actually, despite the fact that the atomic number of potassium is greater than the atomic number of sodium, the hydrated Na+ ion is larger than K+ ion (Table 1).

Assuming, in the case of potassium, the delamination rate is a function of two different contributions: the cations diffusion through the coating (K_c) and the cation diffusion through the defect (K_d), and measuring a delamination rate in the case of KCl in the outer solution of 8.29 mm²/h and a delamination rate of 5.46 mm²/h in the case of distilled water as outer solution, it is possible to write:

$$\frac{5.46}{8.29} = 0.66 = \frac{K_d}{K_d + K_c} = 0.66$$

(1)

We can conclude, as a rough estimation, that a third of the cations diffuse through the coating and two thirds through the defects.

In order to further investigate this aspect, figure 5 shows the trends obtained with the cell with solutions with different concentrations of NaCl: 0.6M, 0.06M and without NaCl. Without NaCl (distilled water) the delamination is almost non- measurable, showing that the concentration reduction causes a reduction of the cathodic delamination rate. The diffusion of the cations is, therefore, for our system, the rate determining step in the cathodic delamination.

In figure 5 it is moreover possible to see the differences in the induction time: diminishing the salt content, the induction time is reduced. This fact, already seen in figure 4, can be explained by the hypothesis that the induction time is determined by the diffusion of

water through the coating. In fact only when water is present under the coating, the delamination process can begin. The presence of ions in solution reduces the activity of water and, therefore, its diffusion in the coating (in Table 2 is reported the water activity for different electrolytes and concentrations).

It is possible, therefore, to conclude regarding the water diffusion through the coating that a lower salt concentration favours the water transport phenomena which control the induction times.

In order to better understand the ions transport mechanism through the coating and the defect we performed some EIS measurements in the two different part of the cell using four different cations: Li^+, Na^+, K^+ and Ce^+., with the same concentration (0,6M) in the two parts of the cell.

The measurements obtained in the external part of the cell (intact coating) were modelled by using a very simple equivalent electrical circuit consisting in a resistance (the coating resistance Rp) in parallel with a capacitance (the coating capacitance Cc). The most important parameter is the coating resistance Rp because it is a direct measure of the ion transport through the coating. The trend of Rp as a function of the delaminated area (obtained on different sample after 200 hours of polarisation) is shown in figure 6 in the case of the KCl solution. The correlation between delaminated area and coating resistance is clear: increasing the delaminated area, increases the cations diffusion through the coating balancing the charge. For large delamination (370 mm^2), the Rp value drops reaching a value close to 10^7 ohm.

In figure 7 it is shown the same trend for samples in contact with NaCl solution. In this case, even in the case of large delamination, the Rp values are still high (higher than 10^8 ohm), but a correlation between Rp and delaminated area is in any case present. It is possible to conclude that also the EIS measurement confirm that in the case of Na+ cations the diffusion is mainly through the defect, but a measurable diffusion through the coating is present.

In the case of samples in contact with LiCl solution the coating resistance is always very high (in the order of 10^9 ohm), the

delamination area was always very small and therefore it was impossible to find any correlation.

Figure 8 shown the correlation between delaminated area and Rp in the case of CeCl solution. The delaminated area for this solution was often very large. The data shown a large Ce+ diffusion through the defect.

The EIS data obtained in the inner part of the cell were more difficult to interpret. We modelled the EIS data adding to the previous model in series with the coating resistance the charge transfer resistance Rct in parallel with the double layer capacitance Cdl (typical circuit for defective coatings). However a clear correlation of the measured parameters with the delaminated area was not found, probably because the electrochemical behaviour inside the defect is quite complex and it is influenced by the oxygen diffusion. In figure 9 the evolution of the charge transfer resistance Rct as a function of the immersion time is reported. The evolution is almost the same for all the cation with the exception of Ce + containing solution. Only when the delamination is very large, the Rct values are able to discriminate samples with different delamination areas.

Conclusions

The cathodic delamination behaviour of a polyester coating on mild steel has been investigated by controlling the solution in contact with the defect and the solution in contact with the intact coating.

Concerning the species diffusion Li+ and Na$^+$ ions migrate mainly through the defect, while K$^+$ and Ce+ ions diffuse both through the defect and through the coating. The reason for the different behaviours is the different dimensions of the hydrated cations and therefore it seems that the studied polyester coating has a critical ions dimension which is about 2.5 Å.

The water diffusion in the coating controls the induction time for delamination and the kinetics of water diffusion is determined by the activity of the water in the solution.

Acknowledgements

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