The uneven corrosion of deep drawn coil-coatings investigated by EIS

A.C. Bastos a,∗, M.G.S. Ferreira a, b, A.M.P. Simões b

 a DECV/CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal
 b DEQB/ICEMS, Instituto Superior Técnico, UTL, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

1. Introduction

Problems related to mechanical deformation are issues of major concern in the coil coating industry due to residual stresses that lead to loss of adhesion and cracking of the paint film. These issues have been studied by several authors. An interesting investigation, based on mechanical methods, was carried out with galvanised steel pre-painted with polyester/melamine systems [1–3]: free paint films were characterized by rheological measurements and tensile testing and their properties correlated with the integrity of the same films on coil-coatings after bending and deep-drawing. Scratches and cracks were found to be the most common defects introduced on the paint film during the deep-drawing process [4]. Other studies have focused on the anticorrosive performance of formed coil-coatings using mainly electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM). The effect of bending (mandrel test) and drawing (cupping test) on polyester systems applied to steel sheet coated with hot dip zinc (pure or alloyed with 1–2% aluminium) has been analysed [5]. The bending and the uniaxial forming of silicon polyester coated galvanised steel were investigated [6] as well as the influence of uniaxial deformation on the corrosion performance of pre-coated packaging steel [7]. Combination of thermal ageing with mechanical deformation was studied using the Erichsen cupping test [8,9]. The present authors studied a coil-coating system submitted to uniaxial, biaxial, plain strain and deep-drawing [10–12]. All studies put in evidence the adverse influence of mechanical deformation on the protective properties of coil-coatings by affecting both the barrier properties and the adhesion to the substrate. Cracks were observed in the paint layer and sometimes in the zinc layer. Electrochemically, the degradation was associated to an increase in the paint film capacitance, a drop in the paint film resistance and the appearance of metallic corrosion underneath the organic coating, being the evolution of these parameters faster for samples with higher deformation.

The corrosion of deep-drawn cups is not uniform and the most severe degradation takes place in the regions of highest deformation [12]. These results led us to further investigate the corrosion of formed cups, characterizing and comparing the response of each distinct region. With this purpose, electrochemical cells were designed in order to restrict the measurements to chosen areas, the corrosion of samples being assessed by EIS and SEM.

2. Experimental

2.1. Materials and samples

The coil-coating under test was steel sheet 800 μm thick with an electrodeposited zinc layer of 7 μm of nominal thickness. The surface was pre-treated by an industrial process consisting of phosphatation followed by chromate rinse. The applied organic coating consisted of a 5 μm polyester primer plus a 15 μm polyurethane midcoat, without topcoat. 85 mm diameter coil-coating sheets were formed by rectangular deep drawing to cups of 42 × 42 × 56 mm3 – Fig. 1(a). The drawing force was 3 × 107 N, the holding force was 3.6 × 106 N and the tool was slightly oiled.

* Corresponding author.
E-mail address: achastos@ua.pt (A.C. Bastos).

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2.2. Electrochemical impedance spectroscopy

2.2.1. Electrochemical cells

The formed sample was assumed to consist of five distinct regions – Fig. 1(b):

- Top, region T, corresponding to about 16% of the global area;
- Corners, regions C, 4 × (∼2.5%) of global area;
- Horizontal edges, regions H, 4 × (∼4%) of global area;
- Vertical edges, regions V, 4 × (∼6%) of global area;
- Sides, regions S, 4 × (∼8.5%) of global area.

The global area of the samples was ∼44 cm². Plastic moulds were designed to delimit each particular region and electrochemical cells were made by fixing the moulds to the surface with epoxy glue (Araldite® rapid) – Fig. 1(c). The overall sample response was measured by delimiting the global area with insulating tape and immersing the sample in the testing solution – Fig. 1(d).

2.2.2. Experimental conditions

A three-electrode arrangement was used, with a saturated calomel electrode as reference, a platinum counter electrode and the exposed area acting as working electrode. The cells were filled with 5 wt% (0.86 M) NaCl aqueous solution made with p.a. grade reagent and distilled water and were connected to a Gamry FAS1 Femtostat coupled to a PC4 controller board. All measurements were performed at room temperature, in a Faraday cage, with the solution quiescent and exposed to air. Impedance measurements were made at open circuit potential, with a sinusoidal signal of 10 mV RMS, in the frequency range 50 kHz to 1 mHz with 7 points per decade, logarithmically distributed. A minimum of 3 samples was tested for each region. Fitting of the spectra was made using ZView 2.70 software from Scribner Associates.

2.3. Scanning electron microscopy

A Hitachi S-2400 scanning microscope (15–25 kV) was used to perform the microscopic inspection.

3. Results and discussion

3.1. Electrochemical response

Fig. 2 depicts impedance spectra acquired on the whole cup and on the regions of the formed cup after 1 day, 1 week and 1 month of immersion. The responses are different for every region, ranging from impedance on the top close to 10¹¹ Ω cm² down to 10⁸ Ω cm² on the corners. The top is the only region that shows a capacitive behaviour at all tested frequencies while the capacitive response of the paint film is practically absent at the corners. All other regions have a capacitive response at high frequencies followed by a resistive response. Corrosion is already present in most of the regions after 1 day of immersion, detected as a second time constant at lower frequencies. The overall sample response lies in the middle of the local responses. With time, the impedance measured at all regions decreases but the top still shows high values and no signs of corrosion. For the remaining regions, the impedance response becomes closer to the overall sample response.

Quantitative comparison of the different regions was made using impedance parameters obtained by numerical fitting of the spectra. The equivalent electrical circuits (EEC) commonly used for painted metals [13,14] were applied to our data – Fig. 3. In a first stage the spectrum was dominated by the paint film capacitance (Cf) and the paint film resistance (Rf). Corrosion of the substrate was detected when a low frequency process appeared, with a double layer capacitance (Cdl) and a charge transfer resistance (Rct). Circuit (a) was used to model the spectra obtained in region T, whereas circuit (b) was applied to regions V and S. In these, Rct is the solution resistance and the true capacitances were replaced by constant phase elements, Q, whose impedance is given by $Z_Q = 1/(Y_0(j\omega)^n)$ where $j$ is the square root of $-1$, $\omega$ is the angular frequency (in radians), $Y_0$ is the frequency independent admittance of $Q$ and $n$ is the power of $Q$. For the sake of comparison, $Y_0$ was taken as a measure of the capacitance. Circuit (c) was used to fit the impedance response of regions C and H, since a third time constant appeared at intermediate frequencies, between those where paint and the corrosive process respond. This time constant was attributed to the role of corrosion products [15], eventually in the form of a barrier layer, and two elements were added to account for their resistive and capacitive responses, $R_{cp}$ and $Q_{cp}$.

The measured values of the top, with high resistance \((10^{-9}–10^{-10})\) the substrate, and is proportional to the “wet” area, where paint is delaminated from the paint film, by the corners and horizontal edges. From the parameters related to the evolution; and a third region, with the lowest resistance, composed of deformation. The effect of immersion can also be observed in the micrographs of Fig. 6. The top region remained unaffected while the other regions showed many round-shaped holes with approximately 1–5 \(\mu\)m that appear to be originated by the loss of pigments close to the surface. This was also observed and discussed before the ingress of water swells the polymer matrix and creates internal stresses that work on the expulsion of pigments close to the surface. In addition, water can interfere with the polymer–pigment interface, weakening the bonds and facilitating pigment loss. These

**Fig. 2.** Impedance spectra obtained on the cup and on the local regions after 1 day, 1 week and 1 month of immersion.

**Fig. 3.** Equivalent electrical circuits (EEC) used to fit the impedance obtained in each region.

**3.2. Morphology of the degradation**

The order of protective performance found by EIS is corroborated by the inspection of the samples after immersion. No signs of degradation were detected on the top region (Fig. 5(a)), while on the horizontal edges and corners several round andprotobuferant blisters were observed (Fig. 5(b)). The highest concentration of blisters occurred on the corner which is the region with highest strain. Only a few round blisters appeared on the sides (Fig. 5(c)) whereas on the vertical edges the blisters were elliptical and aligned with the direction of the major strain (Fig. 5(d)). Microscopic inspection shows the existence of a number of pinhole defects on the organic coating even before immersion (Fig. 6). The shape and number of defects varied according to the region of the sample and is dependent on the type and degree of deformation. The effect of immersion can also be observed in the micrographs of Fig. 6. The top region remained unaffected while the other regions showed many round-shaped holes with approximately 1–5 \(\mu\)m that appear to be originated by the loss of pigments close to the surface. This was also observed and discussed before the ingress of water swells the polymer matrix and creates internal stresses that work on the expulsion of pigments close to the surface. In addition, water can interfere with the polymer–pigment interface, weakening the bonds and facilitating pigment loss. These
defects can also propagate towards the bulk of the paint film, opening the path for water, oxygen and ions. More defects mean lower film resistance, weaker barrier properties and faster corrosion.

An additional factor for the degradation is the cracking of the phosphate layer in regions with higher strain. In the cracked points the paint film loses adhesion and the phosphate layer no longer protects the underlying zinc. Another aspect to consider is the reduction of the paint thickness. The observed paint thickness reduction is not large enough to be the main cause of the drop in $R_f$. It seems to be a minor factor compared to the micro-defects and the phosphate cracking.

An interesting feature is the wrinkles observed by SEM in the vertical edges after immersion. Wrinkles with the same shape were observed by Ueda et al. [1] in samples formed by cylindrical deep drawing and were explained by the residual stresses in the polymer. At the vertical edges, the cup suffers elongation along the major strain direction and compression in the orthogonal direction. The mechanical work deforms the metal plastically whereas the paint layer is deformed mainly elastically. The paint remains under stress after the forming process due to its bonding to the substrate and to the polymer crosslinking that prevent its relaxation. Supplementary stress due to swelling by water absorption causes the appearance of the wrinkles.

3.3. Determination of the overall cup response from the local response of constitutive regions

The EIS data presented so far was obtained from a number of similar samples. The results to be presented in this section were performed with the same sample. First, the overall response was monitored by EIS during 21 days of immersion. After that time, the sample was removed from solution and plastic moulds delimited 5 regions for EIS measurements. Fig. 9 gives the overall response of the cup after 21 days of immersion and the impedance of five of its regions obtained in the same day with the same testing protocol. The regions presented the following fraction areas: T (0.161), C (0.103), H (0.160), V (0.229), S (0.347) for a total area of 43.6 cm$^2$. It is again possible to divide the response of the formed sample in three groups: the high impedance top, with little contribution to the overall response, regions V and S with intermediate performance and regions C and H, the most degraded.

Using the local impedance responses, obtained in the same conditions and within an interval of a few hours, an attempt was made to reproduce the overall response from the local ones. This was made in two different ways: (i) calculation using the experimental data and (ii) simulation using the fit results for each constitutive region.

3.3.1. Calculation using the experimental data

Each experimental file consisted of an array of points $(f, Z', Z'')$ where $f$ is the frequency, $Z'$ is the real part of the impedance and $Z''$ is the imaginary part of the impedance. By using the spectra obtained in each region, for the same immersion time and using the same experimental procedure and frequencies, it is possible to obtain a new set of $(f, Z', Z'')$ for the overall response, taking into consideration the area fraction of each region.

Fig. 4. Evolution of the electrochemical parameters obtained by numerical fitting of EIS data.

Fig. 5. Macroscopic morphology of the various regions of the cup at the end of exposure.
As the impedances of all regions are arranged in parallel, the overall impedance, $Z$, is given by:

$$\frac{1}{Z} = \sum_{i=1}^{n} \frac{1}{Z_i}$$

(1)

where $Z_i$ is the absolute impedance measured in each partial region $i$ for a total of $n$ regions. The experimental files were generated with the impedance normalized for unitary area. Normalized impedance ($Z^0$, in $\Omega$ cm$^2$) and absolute impedance ($Z$, in $\Omega$) are related by

$$Z^0 = Z A$$

(2)

**Fig. 6.** Micrographs of the coating surface before ($t=0$) and after immersion ($t=21$ days).

**Fig. 7.** Phosphate layer of (a) an unstrained panel and (b) a 23% elongated panel.
where $A$ is the area of the working electrode under analysis. The normalized area, $\theta_i$, of each region $i$ is given by:

$$\theta_i = \frac{A_i}{A}\quad(3)$$

Consequently, Eq. (1) can be re-written,

$$\frac{1}{Z_0} = \sum_{i=1}^{n} \frac{\theta_i}{Z_0^i}\quad(4)$$

As

$$Z_0^i = Z_0^i' + jZ_0^i''\quad(5)$$

Eq. (4) becomes:

$$\frac{1}{Z_0} = \sum_{i=1}^{n} \frac{\theta_i}{Z_0^i + jZ_0^i''}\quad(6)$$

Re-arranging in order to separate the real and imaginary parts,

$$\frac{1}{Z_0} = \sum_{i=1}^{n} \frac{Z_0^i}{(Z_0^i')^2 + (Z_0^i'')^2}\cdot \theta_i - j\sum_{i=1}^{n} \frac{Z_0^i}{(Z_0^i')^2 + (Z_0^i'')^2}\cdot \theta_i\quad(7)$$

Since the admittance, $Y$, is the reciprocal of impedance,

$$\frac{1}{Z_0} = Y_0' - jY_0'' = Y_0''\quad(8)$$

with

$$Y_0' = \sum_{i=1}^{n} \frac{Z_0'^i}{(Z_0'^i)^2 + (Z_0''^i)^2}\cdot \theta_i\quad\text{and}\quad Y_0'' = \sum_{i=1}^{n} \frac{Z_0''^i}{(Z_0'^i)^2 + (Z_0''^i)^2}\cdot \theta_i\quad(9)$$

Eq. (8) also gives,

$$Z_0' = \frac{1}{Y_0' - jY_0''} = \frac{Y_0''}{(Y_0''')^2 + (Y_0'')^2} + \frac{Y_0'''}{(Y_0''')^2 + (Y_0'')^2}\quad(10)$$

Finally,

$$Z_0' = \frac{Y_0''}{(Y_0'')^2 + (Y_0''')^2}\quad(11a)$$

$$Z_0'' = \frac{Y_0'''}{(Y_0'')^2 + (Y_0''')^2}\quad(11b)$$
Fig. 10. Equivalent circuit used for simulating the overall impedance of the cup.

By using Eqs. (9) and (11) a new array of \((f, Z'_0, Z''_0)\) is obtained for the global area, calculated from the values of \(Z'\) and \(Z''\) measured in each region, at selected frequencies and considering the respective area fractions. The calculation can be performed using a simple spreadsheet. The success of this procedure depends on using:

- The same experimental protocol in the data acquisition, especially the same frequencies;
- the same testing conditions, particularly the same time of immersion;
- representativeness of the selected regions for measurement, since for regions C, H, V and S, only one of the four available regions was used;
- accurate estimation of the fraction area of each region.

3.3.2. Numerical simulation using the fit results of local spectra

A second approach to compute the overall response from local results was the simulation using an EEC that aggregated the response of the five partial regions. The experimental local spectra were numerically fitted using equivalent circuits from Fig. 3 and the values obtained were applied in parallel in a global circuit to simulate the overall response (Fig. 10). The values used in the simulation for each region were normalized by dividing the resistances and multiplying the capacitances by the fractional area occupied by each region, \(\theta\), and are presented in Table 1.

3.3.3. Validation of the approaches used to reconstruct the overall response from the local spectra

Fig. 11 shows the experimental overall response, together with the spectrum reconstructed according to the formalism presented in Section 3.3.1 and the spectrum simulated as described in Section 3.3.2. The two approaches are similar and close to the experimental curve, in spite of discrepancies in the phase angle at lower frequencies. It is important to emphasize that the reconstruction was based on the response of five regions out of 17. There are four C, H, S and V regions and only one of each was measured and its response assumed to be representative of the other similar regions. The variation in response of similar regions is the main reason for the reconstruction not to be closer to the real

Table 1

<table>
<thead>
<tr>
<th>Region</th>
<th>T</th>
<th>V</th>
<th>S</th>
<th>C</th>
<th>H</th>
</tr>
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<tr>
<td>(Y_{01}) (F cm(^{-2}) s(^{-1}))</td>
<td>(8.1 \times 10^{-11})</td>
<td>(5.1 \times 10^{-10})</td>
<td>(6.2 \times 10^{-10})</td>
<td>(1.8 \times 10^{-10})</td>
<td>(3.5 \times 10^{-10})</td>
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<tr>
<td>(n_l)</td>
<td>0.92</td>
<td>0.86</td>
<td>0.88</td>
<td>0.91</td>
<td>0.89</td>
</tr>
<tr>
<td>(R_l) ((\Omega) cm(^{-2}))</td>
<td>(1.8 \times 10^9)</td>
<td>(2.6 \times 10^9)</td>
<td>(4.5 \times 10^4)</td>
<td>(1.9 \times 10^4)</td>
<td>(2.8 \times 10^4)</td>
</tr>
<tr>
<td>(Y_{0cp}) (F cm(^{-2}) s(^{-1}))</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>(3.8 \times 10^{-7})</td>
<td>(7.7 \times 10^{-7})</td>
</tr>
<tr>
<td>(n_{cp})</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.64</td>
<td>0.5</td>
</tr>
<tr>
<td>(R_a) ((\Omega) cm(^{-2}))</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>(4.0 \times 10^4)</td>
<td>(3.1 \times 10^4)</td>
</tr>
<tr>
<td>(Y_{0al}) (F cm(^{-2}) s(^{-1}))</td>
<td>–</td>
<td>(3.9 \times 10^{-6})</td>
<td>(7.0 \times 10^{-6})</td>
<td>(1.2 \times 10^{-6})</td>
<td>(6.2 \times 10^{-6})</td>
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<tr>
<td>(n_{al})</td>
<td>–</td>
<td>0.75</td>
<td>0.55</td>
<td>0.73</td>
<td>0.87</td>
</tr>
<tr>
<td>(R_e) ((\Omega) cm(^{-2}))</td>
<td>(1.3 \times 10^7)</td>
<td>(8.7 \times 10^5)</td>
<td>(1.6 \times 10^6)</td>
<td>(1.4 \times 10^6)</td>
<td></td>
</tr>
<tr>
<td>(\theta)</td>
<td>0.161</td>
<td>0.229</td>
<td>0.347</td>
<td>0.103</td>
<td>0.160</td>
</tr>
</tbody>
</table>

Fig. 11. (a) Bode plot of the overall cup impedance acquired experimentally after 21 days of immersion (○○○) and spectrum computed from the local regions either by calculation (♦♦♦) or by numeric simulation using the fitted results of the local spectra (——).
response. It must be noted, additionally, that the strain distribution along the sample is more complex than the assumed here, of five distinct regions with constant strain and well-defined limits. The strain is distributed along the surface following continuous variations, but such a model is very hard to work with, since the impedance point-to-point variations cannot be determined experimentally.

4. Conclusions

The impedance response of a sample with a complex geometry was investigated by designing electrochemical cells that allowed the measurement of particular areas with approximately homogeneous properties. The electrochemical and morphological data coincided in the comparison of the different regions of the sample. Higher degradation was observed in the most strained areas (corners and edges). Micro-defects were found in the paint film in the vicinity of pigments. The number and size of defects increased with strain and with time of immersion. It was possible to approximately reconstruct the overall impedance response from the local impedances. Two different and independent approaches were tested with nearly the same results: calculation using the local experimental data and numerical simulation after fitting the local spectra.

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References