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# DEGRADATION ANALYSIS OF FIBRE-METAL LAMINATES UNDER SERVICE CONDITIONS TO PREDICT THEIR DURABILITY

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*Fibre-Metal Laminate (FML) is an advanced material expected to possess improved mechanical properties than its sole constituents. Yet, only few studies focus on its durability. Thus, the aim of this study is to analyse the corrosion behaviour of FMLs based on carbon fibre composite (CFRP) and stainless steel (SST) in a sodium chloride solution. To fulfil this purpose, potentiodynamic polarisation and electrochemical impedance spectroscopy (EIS) were utilized. It has been observed that, as FML, the carbon composite and the stainless steel would effectively form a galvanic cell that facilitates the composite acting as a cathode and the stainless steel as an anode. Moreover, galvanic corrosion is accompanied by pitting corrosion of the stainless steel electrode. Also the impedance data recorded can quantify the polarisation resistance of the materials, whereas the polarisation technique is more appropriate to measure the galvanic couple current density and the couple potential of a CFRP/stainless-steel-hybrid laminate. Accordingly, carrying out both electrochemical methods is a powerful approach to predict the galvanic corrosion behaviour of FMLs under service.*

**Keywords**: Fibre-metal laminates, CFRP, stainless steel, electrochemical methods, potentiodynamic polarisation, impedance spectroscopy.

## 1. Introduction

In the nineteen fifties, research focused on the crack growth properties of structural materials used in aircrafts. At this time, metal bonding was developed in order to create a laminated structure (several sheets of material united by the means of an adhesive) which appeared to show good resistance to fatigue crack growth. Indeed, the crack opening of the fatigue crack in the outer layer is slowed

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down because the other layers are intact and hence bridge the crack [1]. This concept has then been improved with the addition of fibres to the adhesive. This resulted in a so-called Fibre-Metal Laminate (FML): the lamination of metal foils with sheets of fibre reinforced polymer. FMLs are advanced materials expected to judiciously combine the mechanical properties of fibre reinforced resin and metal to achieve lighter components than the traditional monolithic materials, whilst displaying similar or even higher specific strength and stiffness. In the present investigation, the FML under focus is based on carbon-fibre reinforced plastic (CFRP) plies and stainless steel (SST) foils in order to combine materials with similar mechanical properties.

Yet, while humidity is an environmental parameter, most polymeric matrices tend to absorb water as a result of their polarity [2]. For FMLs, even though the carbon composite layers are protected by outer steel sheets, moisture and/or solvents absorption is an issue to consider since they can be absorbed by the composites' resin at the FML edges, through cracks in the steel foil or voids in the composite.

However, only little research is carried out on the corrosion behaviour of FMLs based on carbon composites. Yet, Sinmazçelik et al. [3] point out that there is a "problem of galvanic corrosion between the carbon fibres and aluminium in moisture environment", which demands more research. This is also the conclusion made by Bieniás et al. [4] who investigate the corrosion behaviour of four FMLs (CFRP/aluminium, CFRP/titanium, GFRP/aluminium, GFRP/titanium) and demonstrate that the CFRP/aluminium-hybrid is susceptible to corrosion because of the electrical conductivity of embedded carbon fibres. In addition, in the study of Peng and Nie [5], where the galvanic corrosion behaviour of three hybrid systems combining a carbon fibre fabric with steel, aluminium and titanium in a 3.5% sodium chloride (NaCl) solution is investigated. The authors show that steel (ASTM A1018) is severely corroded exhibiting an even higher corrosion current than uncoated aluminium A356 at the beginning of the test.

FMLs based on carbon fibres and metal alloys are prone to experience degradation over time. Nonetheless, aircraft structures are intensively used in several service conditions and expected to last about 30 years [6]. Therefore, it is crucial to study the FMLs' corrosion behaviour. Once it is known, it will be possible to find specific technical solutions to prevent it. The present study hence offers a method to investigate the electrochemical reactions occurring in CFRP/stainless steel-hybrid laminates under service conditions.

An appropriate testing is selected based on the study's purpose, the materials chosen, the service conditions and the possible corrosion forms to occur.

The aim of this study is to analyse the corrosion process at an interface, which is not in direct contact with the environment. Thus, the plane surface of the steel layer is not exposed to any corrosive milieu in any test and general corrosion can be put aside. Thus, only localized corrosion can be undergone at the CFRP/steel interface. Since localized corrosion is inherently concentrated on discrete areas of the metal surface, conventional methods based on physical changes are hardly feasible. In contrast, electrochemical techniques are more appropriate because they are based on measuring the electron flow produced by electrochemical reactions. A review of the methods already applied to CFRPs allows restraining to two electrochemical tests commonly employed for steel and CFRP: potentiodynamic polarisation and Electrochemical Impedance Spectroscopy.

## 2. Materials and experimental methods

The present study focuses on FMLs composed of carbon-fibre reinforced plastic (HexPly® 8552 stacked as $[0°,90°]_s$) [7], and an austenitic stainless steel AISI 301 (also X10CrNi18-8). Its composition is given in Table 1.

*Table 1*

**Chemical composition of the steel alloy X10CrNi18-8 [8]**

| C | Si | Mn | P | S | N | Cr | Mo | Ni |
|---|---|---|---|---|---|---|---|---|
| 0.05-0.15 | ≤ 2.00 | ≤ 2.00 | 0.045 | ≤ 0.015 | ≤ 0.11 | 16.0-19.0 | ≤ 0.80 | 6.0-9.5 |

The potentiodynamic polarisation consists of varying the system's potential at a specific rate (usually in mV/s) and constantly measuring the corresponding current between the working and the reference electrodes. Given the sample's geometry, the current density can be calculated. Then the polarisation curve is plotted with the current density versus the electrode potential (E). The advantage of this technique is that the polarisation curves of SST and CFRP are recorded separately but it permits to have an insight into the galvanic corrosion behaviour of the heterogeneous system through the overlapping of the polarisation curves. Furthermore, pre-tests have shown that the composite electrode acts as a noble electrode and will be the cathode in the electrochemical cell, whereas the stainless steel will behave as the anode. So the present investigation is done by cathodic polarisation of the composite electrode and anodic polarisation of the stainless steel.

Electrochemical Impedance Spectroscopy (EIS) is a non-destructive technique and has emerged as a powerful technique currently available for identifying corrosion reaction mechanisms, and methods that are developed to extract kinetic parameters (rate constants, transfer coefficients) [9]. This method consists of the measurement of the electrode current response to low amplitude sinusoidal potential modulation. It allows characterising electrochemical processes taking place in the vicinity of the electrode through the determination of an equivalent electrical circuit [9]. This electrical circuit is constituted of classic electrical components (resistor, capacitor, inductor…) and enables to quantify the electrolyte resistance (R1), the double layer capacitance (C2) and the material polarisation resistance (R2) by matching the simulated impedance with the experimental data. In addition, EIS may be coupled with mechanical testing.

The two electrochemical techniques require the same experimental configuration: a three-electrode electrochemical cell. The probe under study is the working electrode. The samples are partly immersed into the solution with an immersed section of 30.0 mm x 50.0 mm. The reference electrode is a Radiometer Analytical Ag/AgCl electrode. It has an offset of +230 mV versus a Standard Hydrogen Electrode (SHE). All potentials are referred to this electrode. The counter electrode is a Pt/C-foil. The service conditions are here simulated by the samples' immersion into a 1 M NaCl solution, at room temperature.

For the CFRP probes, the electrical contact is improved by applying a silver lacquer. The samples are cleaned with acetone, then rinsed in deionised water and air dried. Prior to each measurement the working electrode is weighed and its area is calculated in order to have access to current densities.

The electrochemical experiments are all carried out using a Vertex potentiostat from Ivium Technologies. The steady state is checked by measuring the open circuit potential for 4 hours for CFRP (290 mV vs. Ag/AgCl), 60 hours for SST (-96 mV vs. Ag/AgCl).

The potentiodynamic polarisation tests are carried out at a scan rate of 0.1 mV/s in order to obtain steady-state. The CFRP samples are polarised by cathodic polarisation starting from a potential above the open-circuit potential ($E_{OCP}$ + 50 mV) until −200 mV vs. Ag/AgCl; and the SST probes by anodic polarisation from a potential below the open-circuit potential ($E_{OCP}$ - 50 mV) until +400 mV vs. Ag/AgCl.
The impedance spectra are obtained at open-circuit potential ($E_{OCP}$) with an amplitude of 10 mV, which is considered sufficient to get a linear system response, a prerequisite for EIS. Single sine wave measurements are performed with 10 points per decade, at frequencies between 10 mHz and 1 MHz for the CFRP electrodes; between 0.5 mHz and 100 kHz for the stainless steel electrodes.

Data acquisition and analysis are performed with computer assistance and the corrosion parameters obtained by polarisation are determined by “$R_p$ fit” using the EC-lab software. For the $R_p$ fit, a linear fit is carried out on the I-E curve in the potential range surrounding the galvanic couple potential (10 mV/s on both sides). The inverse of the slope corresponds to the polarisation resistance. $E_{corr}$ is determined at the minimum of the current density and $I_{corr}$ is calculated based on the Stern-Geary equation (see Equation 1). $I_{corr}$ can be properly determined only if the anodic reaction’s Tafel constant ($\beta_a$, in V/decade) and cathodic Tafel constant ($\beta_c$, in V/decade) are provided. Thus, a Tafel plot is required to calculate $I_{corr}$ by the $R_p$ fit. For the impedance spectroscopy data, the fitting of experimental data is made by the Simplex and Randomize method with more than 10 000 iterations, minimising considerably the bias.

$$R_p = \frac{\beta_a \beta_c}{2.3 I_{corr}(\beta_a + \beta_c)} \tag{1}$$

## 3. Results and discussion

The potentiodynamic polarisation curves of CFRP and SST are presented in semilogarithmic form in Figure 1. The results are presented in Table 2.

*Table 2*

**Corrosion parameters for optimized polarisation conditions**

| | $I_{corr}$ (μA) | $E_{corr}$ (mV) vs Ag/AgCl | $\beta_a$ (mV) | $\beta_c$ (mV) | $R_p$ (Ω) |
|---|---|---|---|---|---|
| SS301 | 2.02 | -78.53 | 83.80 | 63.20 | 7,000.0 |
| CFRP [0°,90°]$_s$ | 30.47 | 318.51 | 21.20 | 540.40 | 290.0 |

It can be observed that CFRP forms a galvanic corrosion cell with stainless steel. The corrosion potentials correspond to the respective open-circuit potentials in the ideal case. Yet, they are different in practice as in the present case. Besides, the carbon composite material possesses a more positive corrosion potential (about 319 mV) than the stainless steel electrode (-79 mV) so CFRP is the cathode of the heterogeneous system, SST the anode. In addition, the system displays a critical potential difference of 398 mV between both materials.

Furthermore, by overlapping the polarisation curves, the galvanic corrosion parameters (the couple current $I_{couple}$ and the couple potential $E_{couple}$) are quantified for a CFRP/steel-configuration (cf. Figure 1). Thus, the system’s couple potential is 50 mV, which is closer to the corrosion potential of stainless steel. Therefore, it is predictable that the dominating reaction will be the anodic reaction. One can conclude that if CFRP and stainless steel react together, the metal part would oxidise.

The system's galvanic couple current density ($j_{couple}$) has a value of 23.1 µA/cm² and it constitutes the corrosion rate of the hybrid material. Finally, the polarisation resistance (also called corrosion resistance) of the stainless steel electrode is higher than the one of the CFRP sample (7,000 Ω versus 390 Ω). This may be the consequence of the stainless steel's passivation. Yet, at sufficient anodic potential, the passive oxide film of the stainless steel fails and pits appear locally as seen in Figure 2. This indicates that the corrosion form at stake is pitting corrosion.

All in all, the measurements realized show promising results and can be extended to assess the impact of further material parameters.

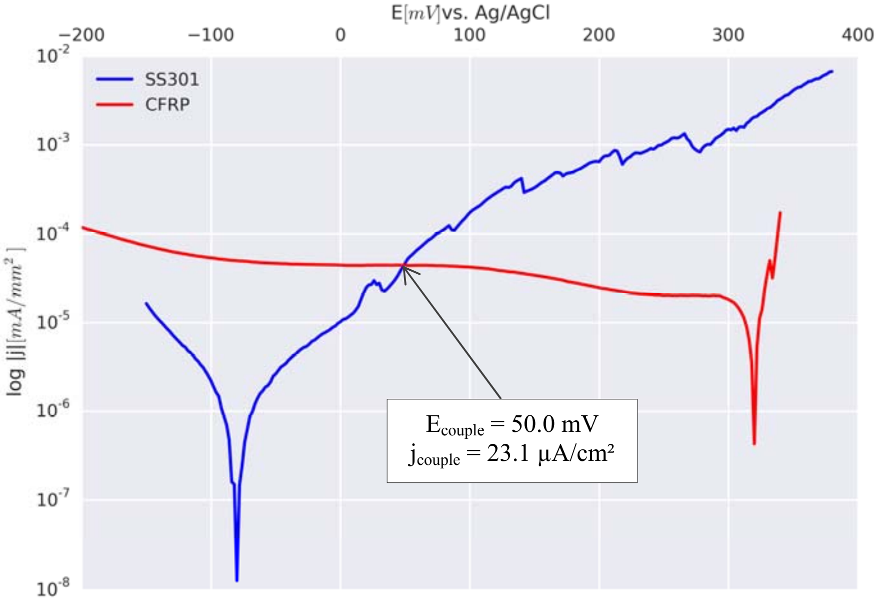

Fig. 1: Polarisation curves for determining corrosion parameters

Fig. 2: Specimen SS301 after anodic polarisation showing pits

Figure 3 shows the experimental and theoretical Nyquist plots made from the impedance data for the carbon composite electrode (CFRP [0°,90°]$_s$) at $E_{OCP}$. In this case, the electrolyte resistance (R1) is 1.2 Ω and the composite's polarisation resistance 352.7 Ω (cf. Table 3). Due to the proximity of the reference electrode to the working electrode, the ohmic drop negligence is proved to be consistent. One can notice that at lower frequencies, the experimental curve becomes linear with an angle of approximately 45°. However, the emphasis is made on the semi-circles in order to determine the resistances.

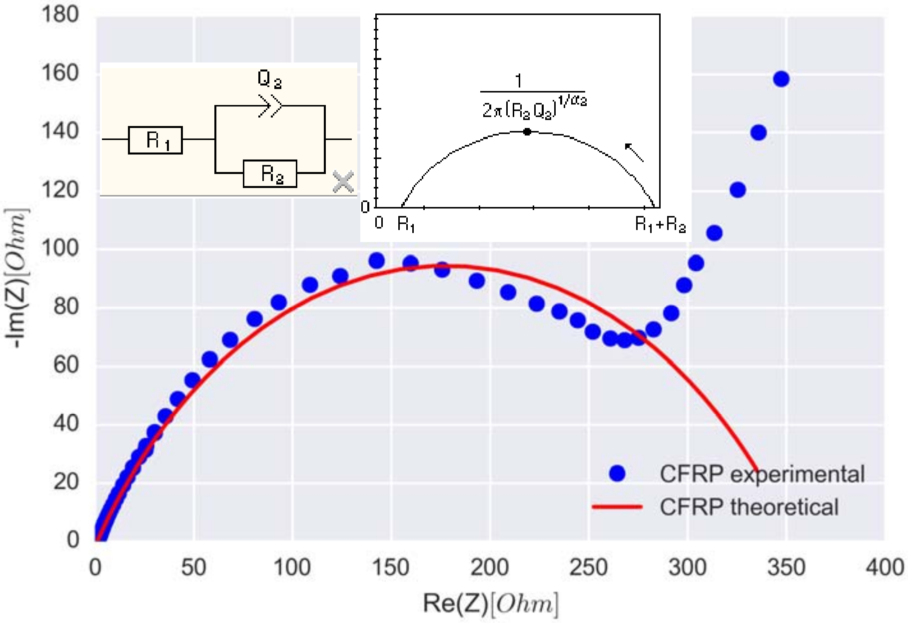

Fig. 3: Experimental and simulated Nyquist plot for CFRP [0°,90°]$_s$ at $E_{OCP}$

The Nyquist plot for the stainless steel electrode is shown in Figure 4. It can be observed that the semi-circle is not completed and an extrapolation is needed to obtain the polarisation resistance value ($R_p$). In fact, this phenomenon implies that the corrosion of stainless steel is slow, which complies with the steel's high corrosion resistance determined before, and that it cannot be observed in the frequency range used.

All the results are presented on Table 3. Considering all the probes, the values of the electrolyte's resistance are very low and indicate that the setup is correctly configured.

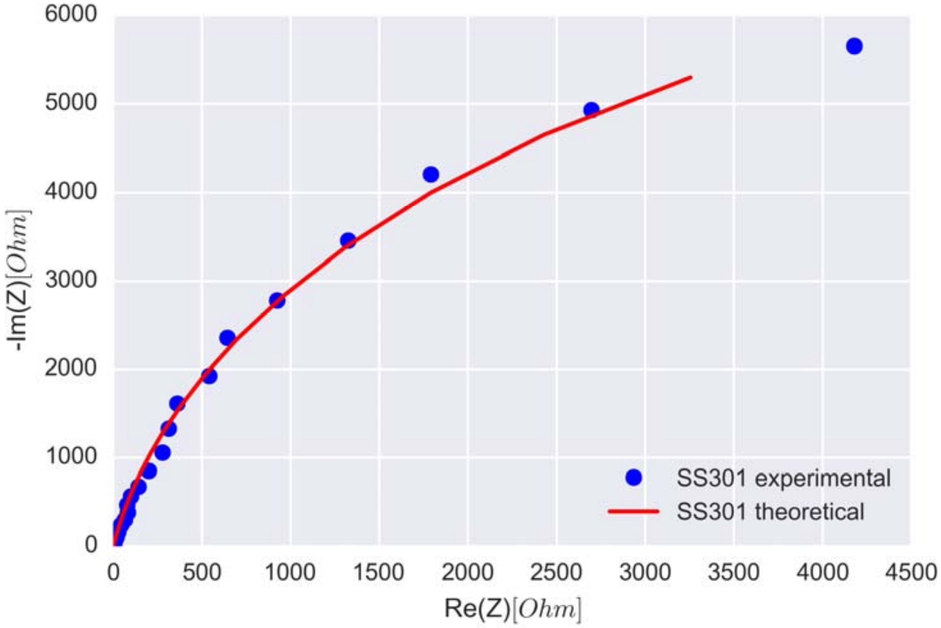

Fig. 4: Experimental and simulated Nyquist plot for SS301 at $E_{OCP}$ (after 60h of immersion)

*Table 3*

**EIS corrosion parameters**

| | $R_1$ (Ω) | $R_p$ (Ω) | $C_2$ (µF/cm²) |
|---|---|---|---|
| SS301 | 0.7 | 15,030.0 | 43.7 |
| CFRP [0°,90°]$_s$ | 1.2 | 352.7 | 3.5 |

Furthermore, the results obtained with EIS are in agreement with those obtained by potentiodynamic polarisation. Indeed, the polarisation resistance determined by both methods are of the same order of magnitude. Nevertheless, considering that EIS dissociates the polarisation resistance from the ohmic drop, impedance spectroscopy permits best to define the materials' polarisation resistance.

The stainless steel hence presents a corrosion resistance of 15 kΩ and the CFRP of about 353 Ω. Thus, the polarisation resistance of the stainless steel electrode is two magnitudes higher than the one of the composite electrode, which confirms the global passive behaviour of the stainless steel AISI 301. Yet, its oxide layer still breaks down locally and some pits form at specific locations, as observed visually after the test.

## 4. Conclusions

Potentiodynamic polarisation has been used as a first approach to study the electrochemical behaviour of a highly heterogeneous system by testing its constituents separately. The electrochemical behaviour of SST and the one of CFRP have hence been monitored, which permitted a first insight into interactions between SST and CFRP. It has been concluded that their combination is susceptible to galvanic corrosion, where stainless steel would locally oxidise.

Thus, three essential parameters have been measured to characterise this corrosion phenomenon: the galvanic couple current density, the galvanic couple potential and the polarisation resistance. The potentiodynamic polarisation method affords determining all of these corrosion parameters but it is limited by graphical interpretation. Indeed, the main source of error is found for the corrosion current, which is calculated by means of the Tafel branches' slopes. Thus, EIS was found to be a more suitable method for measuring the polarisation resistance. Thereby, the correct potential has to be applied, the steady state must be reached and an equivalent circuit must be known to properly employ impedance spectroscopy.

Nevertheless, the study is not finished and some points needs to be clarified:

- the measured corrosion densities will have to be compared to calculations based on Faraday's law, which indicate how much SST can be removed in one year for 1 µA/cm² corrosion current density. Hence the practical corrosion rate will be known.
- the materials' impedance behaviour should be given closer consideration at lower frequencies by means of a Bode plot.
- EIS should be given more attention for explaining the corrosion phenomena at stake and developing an adequate model of a CFRP/stainless-steel-FML.
- the possible coupling of EIS and mechanical testing should be tested.

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