# A Comparative Study of the Corrosion Behaviour of PVD Al-Based Coatings on Mild Steel by EIS and (AC)DC/AC Electrochemical Evaluation Techniques

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## ABSTRACT

Three different corrosion test techniques were used to evaluate the behaviour of an Al-based PVD metallic coating. These were the salt spray test (SST), electrochemical impedance spectroscopy (EIS) and a more recently developed (AC)DC/AC cyclic test. The (AC)DC/AC cyclic test method is used for the first time to evaluate the corrosion behaviour of PVD Al-based coatings. It requires very short test times compared to the SST and EIS tests. The substrate metal was mild steel and the coating was PVD AlCr(N). The aim was to establish and optimise evaluation methods that can give meaningful data in a shorter period of time. The results show that SST (with coated samples periodically removed for evaluation) and EIS (with equivalent periodic coating evaluation after simple immersion in neutral salt solution) offer a similar ranking of corrosion degradation which progresses with exposure time from 0 to 384 h. The new (AC)DC/AC technique provides rapid evaluation of corrosion degradation behaviour (in around 24 h), also with a similar progression of coating degradation observed.

## INTRODUCTION

Coating providers generally need to evaluate wear and/or corrosion performance of new coating materials before they are used in different applications. In practice it is highly desirable to apply a rapid assessment method which can evaluate the corrosion behaviour of coatings in a shorter time than conventional corrosion test techniques, designed to evaluate long exposure periods (and therefore being very expensive to run and slow to generate the required information) [1, 2]. Aluminium and its alloys are widely used in industry, since they provide versatile properties such as low weight and high strength, good corrosion resistance (in neutral pH) and wear resistance that, although poor for pure aluminium, can be significantly improved by the addition of suitable alloying elements. For these reasons, the corrosion behaviour of aluminium and its alloys in aggressive media has been extensively studied [3]. Al-based coatings can be used both as a physical corrosion barrier and as a sacrificial anode (together with alloying element additions such as zinc, tin and indium) to a steel substrate [4, 5]. However, the mechanical properties of such materials (and hence their tribological properties) are commonly also rather poor [6, 7]. Al-based nanostructured metallic coatings with modified and improved corrosion resistance and (importantly) better wear performance can now be deposited using advanced techniques such as plasma-assisted Electron Beam (EB) Physical Vapour Deposition (PVD). This deposition method is employed to enhance the mechanical properties, thermal stability and corrosion protection (both physical barrier and galvanic behaviour) of metal surfaces; for example, PVD ceramic coatings are now widely used to increase the in-service lifetime (and performance and/or product quality) of tools and engineering components in a wide range of industrial sectors [6, 7, 8]. As the metallic coatings sector continues to grow and develop (and new advanced deposition techniques are developed to substitute for, or replace, 'problem' coatings such as electroplated cadmium or hard chrome), it is becoming increasingly necessary to find rapid test procedures to evaluate effectively the corrosion behaviour of new coating system candidates. Conventionally methods such as salt spray (SST) and immersion tests coupled with (increasingly used) electrochemical impedance spectroscopy (EIS) techniques are very popular, but can be time-consuming in their execution (SST) and/or interpretation (EIS), for evaluating the corrosion behaviour of coatings prior to their use in serial production. Salt spray testing offers many well-established benefits, such as a standardised protocol for conducting the test, evaluating the results and a basic simplicity of test procedure; however, the method has been criticized for its inability to provide quantitative performance evaluation and for often being unrepresentative of the results seen in the non-idealised, commercial conditions of practical use [9].

The surface degradation mechanisms of PVD coatings on steel in aqueous media have previously been monitored using EIS methods [8, 10, 11, 12, 13, 14] – and the technique has been shown to be useful in studying the localised corrosion of coatings [8, 10, 12]. It also offers many benefits, such as the determination of numerical values for coating corrosion

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*http://dx.doi.org/10.14332/svc14.proc.1888*

57th Annual Technical Conference Proceedings, Chicago, IL May 3–8, 2014 ISSN 0737-5921

damage, investigating the mechanisms of electrochemical reactions in the corrosion process and measuring changes in dielectric media and charge transfer characteristics of various coating systems to explore the distribution of coating defects (and their evolution with time) [9, 15]. Although the test itself is rapid, long-term exposure between periodic EIS measurements (for comparison with temporal data gathered from other techniques such as SST) can take weeks (and sometimes months) to obtain satisfactory results. Therefore, there remains a strong incentive to obtain representative results in shorter times and provide a more rapid indication of likely long-term corrosion behaviour of coated metal surfaces.

Hollaender et al. [16, 17] developed a rapid (AC)DC/AC cyclic electrochemical test that combines AC (EIS) and DC (cathodic polarisation) measurements, initially for the testing of coated metal surfaces in food packaging applications. Suay and co-workers [2, 17, 18] subsequently adapted the test for paints on steel surfaces, with considerable success. However, relatively few other studies have been performed to reveal the evolution of the EIS response after application of repetitive cathodic DC polarisation which aims to degrade the coating and coating/metal substrate interface by producing $H_2$ gas and $OH^-$ ions (that promote pore formation and coating disbondment) [19, 20, 21, 22, 23]. Furthermore, the applicability of such cyclic testing to metallic, electrically-conducting films has until now not been systematically investigated. Figure 1 shows a schematic diagram of the (AC)DC/AC cycle test procedure that was proposed by Garcia and Suay [24].

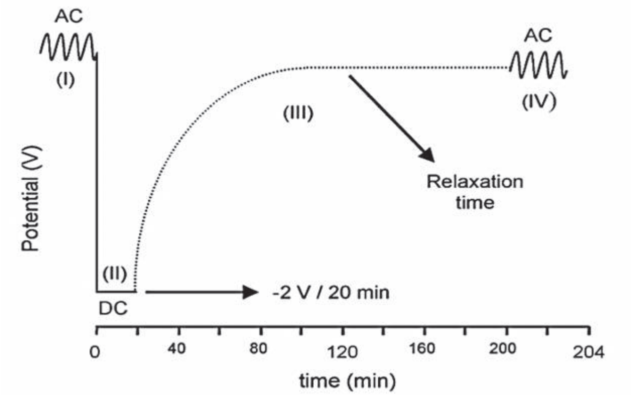

*Figure 1: Schematic diagram of (AC)DC/AC test procedures.*

A possible way to detect the existence of $H_2$ gas and $OH^-$ ions produced from cathodic reactions is to study the relaxation of (open circuit) potential that follows each cathodic polarisation cycle, to verify the system re-stabilisation before subjecting it to a further EIS step [18, 25]. Allahar et al. [20, 21, 26, 27] conducted a series of studies on dielectric coating relaxation to a stable Open Circuit Potential (OCP) after the application of cathodic DC polarisation. Furthermore, the magnitude of the constant polarisation voltage applied during the DC step was varied, depending on the type of coating assessed. The authors stated that the post-polarisation relaxation time reveals details of coating breakdown. Studying the evolution of OCP after cathodic DC polarisation (during post-polarisation relaxation) can be used to provide more detailed information about the coating performance and integrity. Sukiman et al. [25] showed that a coated metal system can relax according to two possible trends involving single or double time constants (α and/or β), depending primarily on the type and extent of cathodic reactions occurring (Figure 2).

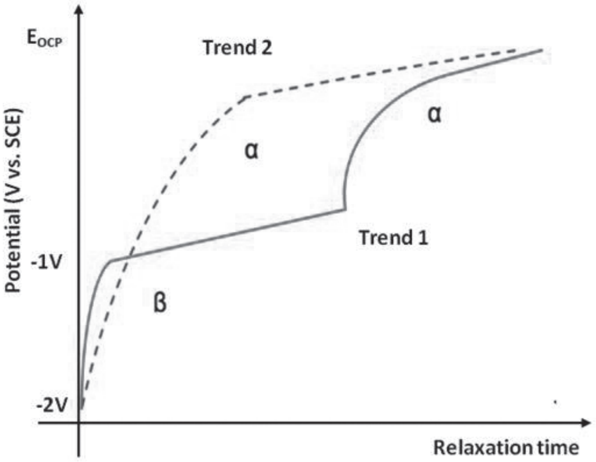

*Figure 2: Trends of potential transients during relaxation stage following the cathodic DC polarisation.*

The (AC)DC/AC cyclic test procedure is repeated several times depending on the type and quality of the coating. The number of cycles can be increased or decreased until the coating is significantly damaged. Nevertheless, the cumulative test time per sample is typically no more than 24h, which is much shorter than for conventional SST and EIS tests, which require much longer periods of time to obtain satisfactory results [25, 28].

This work focuses on a comparative study of the evolution of the corrosion behaviour of metallic, Al-based PVD coatings under three different corrosion testing regimes; i.e. salt spray test, EIS-coupled immersion test, and a 'new' (for this type of coating system) cyclic (AC)DC/AC method. The techniques were applied on PVD AlCr(N) coated mild steel samples to investigate the corrosion degradation characteristics and structural changes during both long-term and short-term exposure, in an attempt to obtain meaningful results from cyclic repetition of high DC cathodic polarisation over a relatively short time period (around 24 h or less).

## EXPERIMENTAL PROCEDURE

### Materials

Mild steel substrate coupons 50mm x 25mm x 1mm were ground and polished, ultrasonically cleaned in acetone and dried. AlCr(N) metallic films were deposited at 300° C on mild steel substrates by electron beam plasma assisted PVD using a twin-EB PAPVD machine. The chemical composition of the PVD AlCr(N) coatings used in this study and the deposition conditions are given in Table 1.

*Table 1: Summary of chemical composition and deposition conditions of PVD AlCr(N) coatings.*

| | |
|---|---|
| Process Temperature (°C) | 300° C |
| Targeted Al/Cr atomic ratio | ~ 3:1 |
| Actual Al at. % | 66.5±0.3 |
| Actual Cr at. % | 19.2±0.1 |
| Actual N at. % | 14.3±0.3 |
| Coating Thickness | 7.8 µm |

**Corrosion evaluation tests**

*Salt Spray Test (SST)*

To evaluate the performance of the PVD AlCr(N) coatings on mild steel, salt spray corrosion tests were performed according to ASTM B117 [29] by which the samples were exposed to salt spray fog produced with a 5wt % NaCl solution at 35°C. Additionally, samples were periodically removed after different periods of time from (24 to 384 h) washed under running water, dried and examined – visually, by SEM and by EDX spectroscopy.

*Electrochemical Impedance Spectroscopy (EIS)*

The EIS tests were carried out periodically on as-deposited coatings immersed into 3.5wt % NaCl solution for exposure times up to 384 h (and corresponding to the exposure times applied also in SST). A conventional three-electrode electrochemical cell was used, comprising the coated sample (with 0.738 cm$^2$ exposed area) as the working electrode, a platinum bar used as a counter electrode and saturated calomel electrode ($Hg/Hg_2/KCl$ sat.) as reference electrode. A Solatron SI 1286 Electrochemical Interface and SI 1260 Impedance/Gain Phase Analyser were used to perform the tests. A 10mV AC signal was applied over a range of frequencies from $10^2$ to $10^5$ Hz [24, 30]. Obtained EIS data were presented in terms of Bode plots (log of |Z| and phase angle as functions of log frequency *f*). The impedance spectra were analysed using Z-view software (Scribner Associates) and modelled using the equivalent circuit shown in Figure 3.

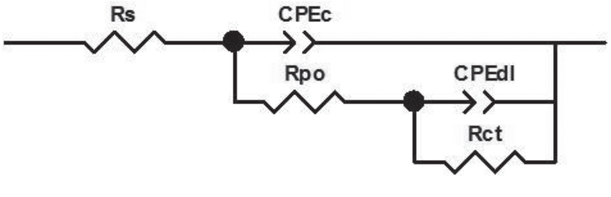

*Figure 3: Equivalent circuit used to model EIS and (AC)DC/AC tests.*

*(AC)DC/AC cyclic test*

The (AC)DC/AC test procedure consisted of a sequential combination of high DC cathodic polarisation and AC impedance spectroscopic measurement, applied over a number of cycles on PVD AlCr(N) coated mild steel samples, until the coating was significantly damaged. In this study the (AC)DC/AC test procedure was carried out in the following steps [1, 2]:

- Initial (AC) step. A small amplitude (10 mV) AC signal is applied over a frequency range from $10^{-2}$ to $10^5$ Hz for 15 min, to gather information on the current state of the coating system before applying DC cathodic polarisation.
- DC step. A constant high cathodic potential (-2V *vs*. SCE) is applied for 20 min.
- OCP step. Following the application of DC polarisation, the coating is left to relax at resting potential for 3h, to reach a steady state.
- AC step. The same initial AC step is repeated to obtain information on the new steady state OCP condition of the coating.

In this work the DC/AC sequence was repeated six times (for around 24 h in total) to trace the degradation path of the coating, using impedance spectra obtained after each DC polarisation/relaxation cycle. As with the abovementioned EIS immersion testing, the AC evaluation step was carried out using a Solatron SI 1286 electrochemical interface and SI 1260 Impedance/Gain Phase Analyser and the resulting impedance spectra were again modelled using the equivalent circuit shown in Figure 3.

*Equivalent circuit interpretation*

Generally, EIS data analysis requires an appropriate Equivalent Circuit (EC) which, in principle, comprises basic electrical elements (such as resistors and capacitors), attributable to the physical and electrochemical properties of the studied system. The EC shown in Figure 3 comprises the following elements: solution resistance $R_s$, pore resistance $R_{po}$, charge transfer resistance $R_{ct}$, constant phase element $CPE_c$ (representing the coating capacitance) and constant phase element $CPE_{dl}$ (representing the double layer capacitance).

CPEs in the equivalent circuit describe the distribution of relaxation times, due to inhomogeneities present at the solid/liquid interface [31]. This non-ideal behaviour may arise from coating heterogeneities such as surface roughness and local changes in composition or structure. In such a case the coating cannot be simply described by discrete resistive or capacitive electrical elements and CPEs thus provide better circuit fitting results. The impedance of a CPE ($Z_{CPE}$) is defined by:

$$Z_{CPE} = \frac{1}{C\,(j\omega)^n} \tag{1}$$

Where $C$ is the capacitance and $n$ is the exponent that relates to the extent of heterogeneity; the latter is also assumed to adopt different values in the range ($1 \leq n \leq 0.5$). When the value of $n$ approaches unity, the CPE is equivalent to a pure capacitor, while $n$ values closer to 0.5 are indicative of diffusion processes and, consequently, the CPE indicates a Warburg diffusion component [11, 28, 31].

$R_{po}$ and CPE$_c$ are related to the coating characteristics [1, 11, 22]; $R_{po}$ representing the resistance to current flow through the pores, which can provide a measure of coating porosity and deterioration:

$$R_{\mathrm{po}} = \frac{\rho d}{A} \qquad (2)$$

Where ρ is the electrical resistivity of the electrolyte in the pores, $d$ is the coating thickness and $A$ is the total surface occupied by the pores. $R_{po}$ thus tends to decrease with immersion time, as the electrolyte penetrates through the pores and/or columnar structure of the coating and reaches the coating/metal substrate interface (increasing the effective surface area in contact with the electrolyte). The decrease in pore resistance value can also be related to an increase in area $A$ which relates to an increase in the number of pores (or in their size) if the coating is damaged. However, $R_{po}$ can also be seen to increase with immersion time under certain circumstances – probably due to the deposition of corrosion products that can block the pores [11, 28].

The coating capacitance $C_c$ is a measure of coating integrity and can be determined by the composition and structure of the coating material:

$$C_{\mathrm{c}} = \frac{\varepsilon \varepsilon_{\mathrm{o}} A}{d} \qquad (3)$$

Here, $\varepsilon_o$ is the permittivity of free space ($8.854 \times 10^{-12}$ F/m); $\varepsilon$ is the dielectric constant of the coating material, $A$ and $d$ are the coating surface area and the thickness, respectively [1, 10, 11, 22, 32]. Typical literature values of dielectric constant for aluminium oxide films range from 8 to 12 [33, 34, 35].

The charge transfer resistance $R_{ct}$ and double layer capacitance $C_{dl}$ represent the corrosion process and coating disbondment at the coating/metal interface. $R_{ct}$ is associated with charge transfer behaviour of the metal substrate. The double layer capacitance $C_{dl}$ is effectively a measure of coating disbondment area and can only be determined precisely at the advanced stages of coating deterioration [28].

**Coating characterisation**

The surface morphology and corrosion products of PVD AlCr(N) coatings after different exposure times in salt spray were characterized by scanning electron microscopy (SEM) using a JEOL-JSM 6400 at 20 kV accelerating voltage. Furthermore, the elemental composition was determined by EDX line scans across the coated surfaces, before and after exposure to SST. This can show the progression of corrosion damage on (and within) the coating with increasing exposure time.

## RESULTS AND DISCUSSION

### Corrosion behaviour of PVD AlCr(N) coatings

*Morphology analysis of corroded areas after SST exposure*

Figure 4 shows a cross-sectional micrograph of the as-deposited (i.e. not exposed to SST) sample with coating thickness 7.8 µm. Two different layers were found in the coating, one comprised mainly Al and Cr that were combined to form an AlCr intermetallic layer and the other was a thin layer of Cr (deposited to improve coating adhesion), close to the substrate interface. The cross-sectional SEM micrographs, with EDX line scans across the PVD AlCr(N) coatings exposed to SST for 48 h and 123 h, are depicted in Figures 5 and 6. The coatings were deemed to have failed the corrosion test after 48 h since coating damage and corrosion products were clearly visible at this point. A combination of coating components (Al and Cr) and corrosion products composed of oxides (of Fe, Al and Cr) are revealed in the surface layer. The cross-sectional SEM micrographs with EDX line scans revealed that the coating exposed to SST for 123 h is significantly more damaged when compared to that exposed for 48 h. It was a clear that, after 123 h exposure to SST, the coating/substrate system experienced severe corrosion, as both deep pits and wide crevices were detected.

*EIS data and analysis*

EIS data obtained after different immersion times in 3.5wt % NaCl solution are presented in Complex and Bode plots shown in Figure 7 (a - c). The impedance modulus at low frequencies can be considered as an indication of the corrosion resistance of the coating system. Consequently, it is convenient to simplify the EIS data interpretation to consider basic parameters, such as the total resistance of the coating system (represented by the low frequency impedance modulus, $|Z|_{0.01\mathrm{Hz}} \sim R_s+R_{po}+R_{ct}$) and coating capacitance (represented by the high frequency impedance modulus $|Z|_{1000\ \mathrm{Hz}} = 1/\omega C$) [22, 35, 36]. It can be clearly observed that the resistance of the PVD coated mild steel is very high ($10^5$ Ωcm$^2$) just after immersion but, with increasing immersion time to 2 h, the impedance $|Z|$ decreased to $10^4$ Ωcm$^2$, indicative of the dissolution of a surface oxide film. However, with further passage of time (24 h), the electrolyte penetrated through defects in the coating (i.e. pores and columnar structure), resulting in a further reduction of the impedance response to $10^3$ Ωcm$^2$, indicating progressive coating deterioration. As the PVD coated mild steel system undergoes continuous degradation

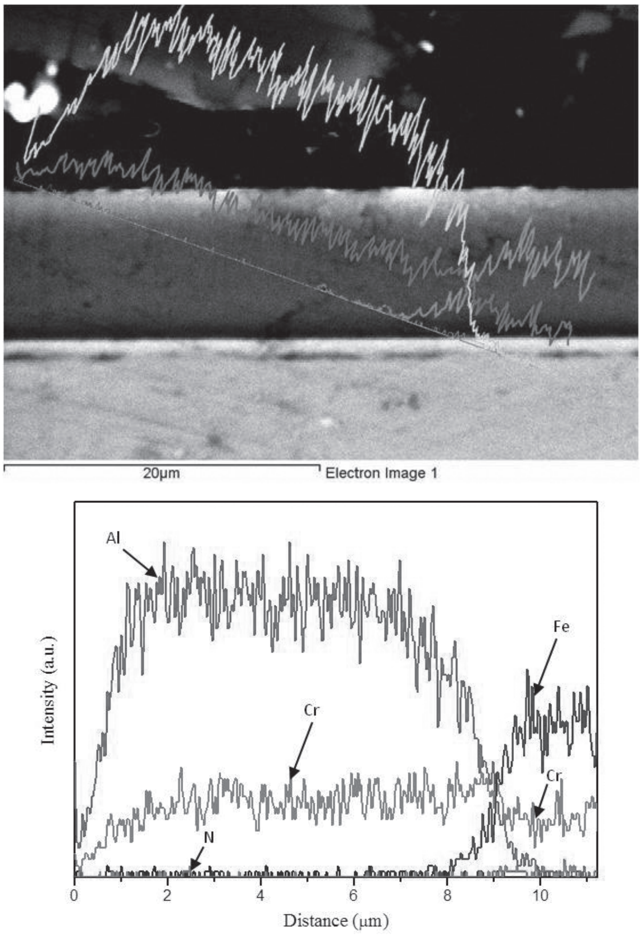

*Figure 4: Cross sectional SEM image as deposited PVD AlCr(N) coating and corresponding EDX line scan (at 70° angle to the normal to the surface, to improve the spatial resolution).*

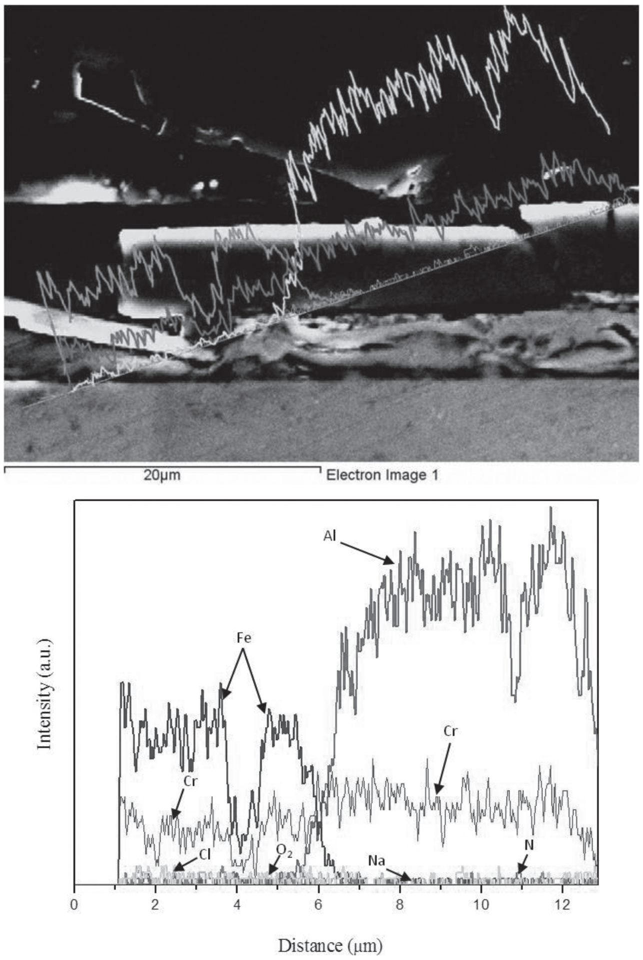

*Figure 5: Cross sectional SEM image of PVD AlCr(N) coating and corresponding EDX line scan after 48h time exposure to SST (at 70° angle to the normal to the surface, to improve the spatial resolution).*

with increasing immersion time (123, 216 and 384 h) the penetration of the electrolyte through the coating provides direct paths to the coating/substrate interface.

The evolution of pore resistance $R_{po}$ and charge transfer resistance $R_{ct}$ with EIS exposure time describes the coating corrosion degradation behaviour, as shown in Figure 7d. $R_{po}$ was found to decrease systematically with increasing EIS exposure time, as the electrolyte penetrated more extensively through the coating, eventually reaching the coating/substrate interface. The pore resistance $R_{po}$ provides an indication of porosity development in the coating layers and thus the overall level of deterioration. The observed decrease in $R_{po}$ can be correlated to higher porosity levels in the coating and thereby to increasing coating damage. Charge transfer resistance $R_{ct}$, which is primarily associated with interfacial charge transfer processes, decreases with exposure time as the electrolyte gains more access to the coating/substrate interface [1, 2]. Also, the evolution of coating capacitance $C_c$ and double layer capacitance $C_{dl}$ *vs* EIS exposure time (shown in Figure 7e) can be linked to the corrosion behaviour of the coating with increasing immersion time. The behaviour of the coating capacitance $C_c$ can be related to a reduction in the effective thickness of the coating, due to the passing of the electrolyte into the coating pores and/or columnar microstructure. The value of $C_{dl}$ provides a measure of the exposed area of the coating/substrate interface. The value of $C_{dl}$ increases as the electrolyte spreads across (and disbondment area extends at) this interface; however, it can only be calculated with reasonable precision at the advanced stages of deterioration (and is strongly associated to coating disbondment, with consequent corrosion of the exposed metallic substrate surface) [1, 2].

*Evolution of the (AC)DC/AC cyclic test*

The evolution of impedance spectra with increasing number of DC cycles applied to the PVD AlCr(N) coated mild steel is presented in Complex and Bode plots shown in Figure 8 (a - c). The corrosion resistance of PVD AlCr(N) coated steel was determined from the value of impedance $|Z|_{0.01\text{ Hz}}$ as function of the number of the DC cycles. It can be clearly

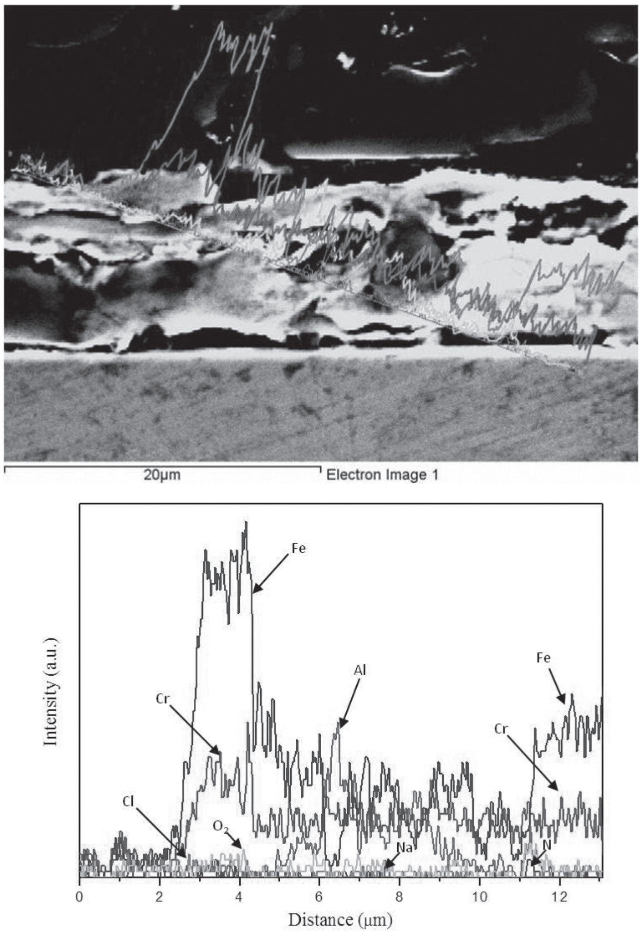

*Figure 6: Cross sectional SEM image as deposited PVD AlCr(N) coating and corresponding EDX line scan after 123h time exposure to SST (at 70° angle to the normal to the surface, to improve the spatial resolution).*

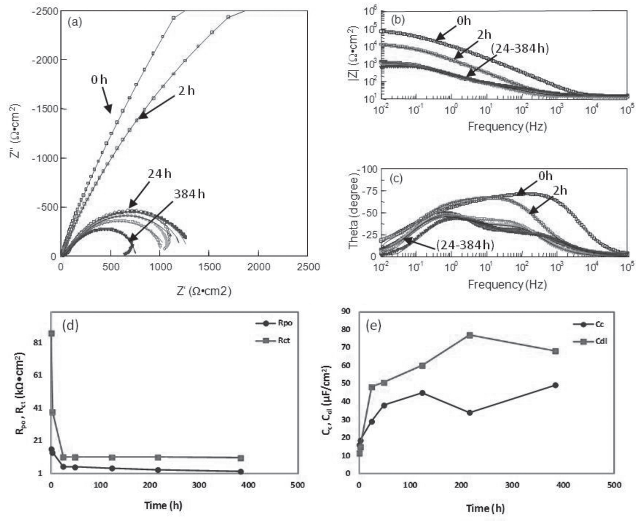

*Figure 7: Complex (a) and Bode plots (b & c) of PVD AlCr(N) coated mild steel after (0 -384 h) immersion times in 3.5wt. % NaCl solution with evolution of (d) pore resistance $R_{po}$ and charge transfer resistance $R_{ct}$, (e) coating capacitance $C_c$ and double layer capacitance $C_{dl}$ vs. exposure time to EIS.*

observed that the resistance of the PVD coated mild steel system is very high ($10^5$ Ωcm²) at the initial stage of EIS examination. The impedance after application of the first cathodic DC polarisation cycle decreased to $10^4$ Ωcm², which is indicative of nascent surface oxide film dissolution. The same value of impedance ($10^4$ Ωcm²) was obtained after the second DC cycle but the impedance decreased to $10^3$ Ωcm² after the third cycle, indicating cathodic reactions taking place at the coating surface (and possibly at the interface with the substrate, via coating porosity) due to generation of $H_2$ gas and $OH^-$ ions, which also contribute to coating degradation [19, 37, 38].

$$2H_2O\ (l) + 2e^- \rightarrow H_2\ (g) + 2OH^- \qquad (4)$$

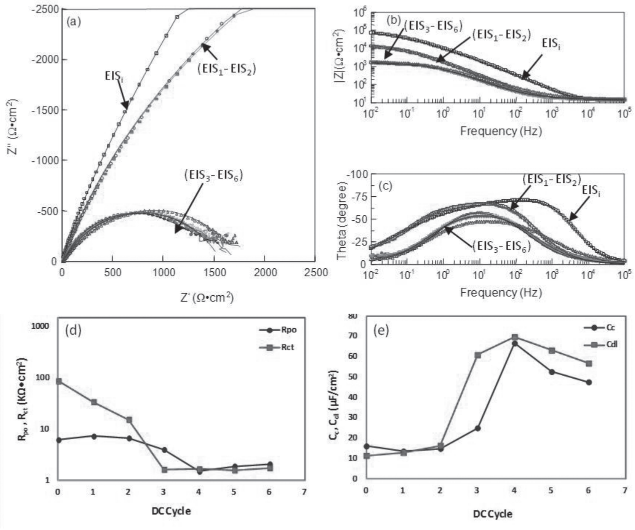

*Figure 8: Complex (a) and Bode plots (b & c) of PVD AlCr(N) coated mild steel after (AC)DC/AC cycle test immersion in 3.5wt. % NaCl solution with the evolution of (d) pore resistance $R_{po}$ and charge transfer resistance $R_{ct}$, (e) coating capacitance $C_c$ and double layer capacitance $C_{dl}$ vs. DC cycles.*

Further coating degradation was observed after application of 4, 5 and 6 DC cycles, until the coating was virtually destroyed.

Figure 8d shows the evolution of pore resistance $R_{po}$ and charge transfer resistance $R_{ct}$ with increasing number of DC cycles. The equivalent circuit shown in Figure 3 was employed to analyse EIS data after application of six DC cycles to the coating. The pore resistance $R_{po}$ decreases with increasing number of applied DC cycles as the electrolyte penetrates more extensively through the coating. The charge transfer resistance $R_{ct}$ decreases with increasing number of applied DC cycles as the substrate becomes more exposed to corrosion attack from the electrolyte. Also, evolution of the coating capacitance $C_c$ and double layer capacitance $C_{dl}$ with increasing number of DC cycles (shown in Figure 8e) can be linked to the progressive corrosion degradation of the coating. The value of $C_c$ increases with increasing the number of cycles as the passage of electrolyte into the coating causes damage. The value of $C_{dl}$ increases as the electrolyte spreads (and areas of coating disbondment extend) across the coating/substrate interface.

When impedance spectra obtained periodically during EIS immersion (Figure 7) are compared to those produced from the DC/AC cathodic polarisation test cycles (Figure 8), it can clearly be seen (Figure 9) that the EIS results after 48 h immersion in 3.5wt % NaCl solution are very similar to those results obtained after application of the third DC cycle. This indicates an opportunity to evaluate the corrosion behaviour of the coating in much shorter times through (AC)DC/AC testing, to achieve a similar degree of corrosion damage to that obtained from (longer-term) SST exposure and comparable, numerical, values to those obtained by conventional EIS measurements from electrolyte immersion.

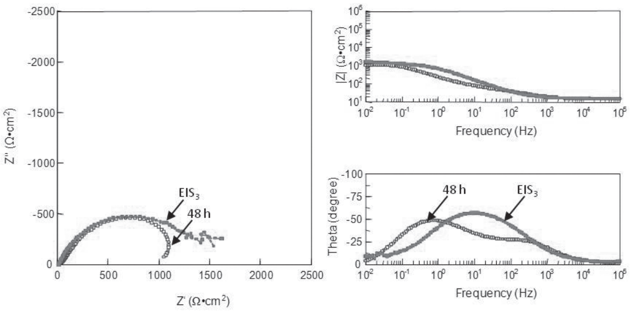

*Figure 9: Comparative Complex and Bode plots of PVD AlCr(N) coating measured by EIS after 48 h immersion in 3.5wt % NaCl solution and (EIS3) after applied third DC cycle.*

## CONCLUSIONS

A comparative study between the results of three evaluation techniques: namely SST, EIS-coupled immersion and cyclic (AC)DC/AC cathodic polarisation, demonstrates a similar corrosion ranking in each for the AlCr(N) PVD coated mild steel examined in this work, indicating good correlation of observed physical phenomena among these techniques. SST and EIS offer a similar ranking of corrosion degradation at comparable immersion times; regardless of the qualitative nature of results obtained from SST (i.e. no numerical information regarding the underlying corrosion processes occurring).

On the one hand, this shows the limited applicability of SST (over and above simple salt solution immersion) for assessing the degradation of PVD metallic coatings on steel; on the other, it illustrates that periodic EIS evaluation of such coatings subjected to simple bath immersion can provide useful, numerical information to characterise (and quantify) likely degradation susceptibility in use. However, after applying six cycles of cathodic DC polarisation to the AlCr(N) coating our preliminary results appear to indicate that meaningful EIS data can be obtained in a much shorter cumulative time period (24 h or less), compared to traditional SST and EIS immersion tests; the quantitative results from cyclic DC polarisation correlate well with the conventional EIS data (collected periodically over 384 h).

The (AC)DC/AC test technique is shown therefore to be a promising route for rapid, yet meaningful, evaluation of PVD metallic coating corrosion degradation susceptibility on metal substrates – with the potential to permit more rapid optimisation of PVD coating properties to suit specific applications.

## ACKNOWLEDGMENTS

The authors wish to thank Sarah Banfield and Jonathan Housden (Wallwork Cambridge, UK) for PVD coating provision, Chris Bennett (NMB-Minebea UK) for access to salt spray test facilities, the UK EPSRC for PVD coating development support under research grant code TS/H000658/1, the Libyan Government for sponsorship of Fahima Indeir (PhD funding support) under grant No. 8648 and the SVC Foundation for sponsorship of Fahima Indeir in attending the 57th SVC TechCon 2014, Chicago, USA.

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