

Exploring the Truth About Aluminum Flakes as Barrier Pigments in Corrosion Protective Coatings

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ABSTRACT

For corrosion protective coatings to be successful, they rely, to a great extent, on having a satisfactory barrier property, signifying the coating's inherent ability to withstand the permeation of seawater and oxygen. Aluminum flakes have for several decades been used to enhance this barrier property in coating formulation work, albeit with a lack of evidence. In the present work, we have thus explored the truth about aluminum flakes in protective coatings by investigating a series of coatings, in which the aluminum concentration has varied from 0 to 9 wt%. This has been tackled by a combination of traditional testing, including salt spray and cyclic ageing, as well as more advanced methods such as EIS. The results from all testing demonstrate no correlation between the aluminum flake concentration used and the coatings' protective performance. Moreover, by extracting the coating capacitance from EIS measurements, we find minimal to no differences in the barrier property as a result of changes in the aluminum concentration. This is also demonstrated in the calculated water diffusivity coefficients, which increase in the order; $6 \rightarrow 9 \rightarrow 0 \rightarrow 3$ % with values varying from 3.0 to $3.7 \text{ cm}^2 \text{ s}^{-1}$ for the entire range. Interestingly, a linear correlation between aluminum concentration and the coatings' dielectric constants is demonstrated, with values ranging from 4.5 to 18.4 for fully saturated coatings upon going from 0 to 9 wt% aluminum.

Key words: Barrier property, Aluminum flakes, Salt spray, Cyclic ageing, EIS, Coating performance

INTRODUCTION

The success of corrosion protective coating systems relies, to a great extent, on the coatings' inherent barrier properties. This barrier property signifies the coating's ability to withstand the permeation of sea water and oxygen, thus minimizing corrosion of the underlying metal. While various additives or pigments can promote the barrier property of coatings, one of the most common pigments is aluminum flakes [1-4]. The idea behind their use is simple, and essentially relies on having the aluminum flakes in the coating oriented parallel to the underlying substrate. With them in place, the pathways for sea water and oxygen effectively increase, thus preventing the progression of corrosion. However, while having been employed in numerous coating formulations for many years, the evidence for the success of aluminum flakes as barrier pigments is still lacking.

We believe one of the reasons for this lies in the fact that most studies only carry out traditional testing and evaluation. Such testing relies primarily on assessing performance based on corrosion creep and pull-off adhesion after some type of laboratory exposure test, e.g., neutral salt spray as per ISO 9227 [5] or ASTM B117 [6]. The problem with this is that neither corrosion creep nor pull-off adhesion is a suitable barrier property indicator. This will then often result in inconclusive test results that also will depend on a myriad of other factors than just the coating's inherent barrier property.

To circumvent these shortcomings, we employ electrochemical impedance spectroscopy (EIS) measurements, which is a well-known method to characterize a coating's barrier property [7-9]. In addition, EIS allows us to simultaneously detect corrosion and other interfacial phenomena taking place underneath the coating itself, all while keeping the coating intact. EIS is thus the perfect tool to investigate changes in formulations and their impact on the resulting barrier properties, thus enabling us once and for all to uncover the truth about aluminum flakes in corrosion protective coatings.

To tackle this, we investigate a total of four tailor-made coating systems, where the aluminum flake concentration has been systematically varied from 0 to 9 wt%. These coatings are then investigated by both traditional exposure tests and EIS measurements.

EIS BACKGROUND AND THEORY

Although EIS as a technique has been around for decades, it is still not well established as a method in the coatings industry. Some additional background and theory will therefore be given here as a foundation for the results and discussion. For a more in-

depth background, the reader is urged to read elsewhere, e.g., recent review paper by Margarit-Mattos [9].

EIS measures the AC impedance of a coated metal immersed in a saline solution, e.g., 5 wt% NaCl. The resulting impedance from such a measurement will depend on the state of the coating, as well as the duration of immersion. In most cases, the data can be curve-fitted to either one of the two equivalent circuits shown in Figure 1.

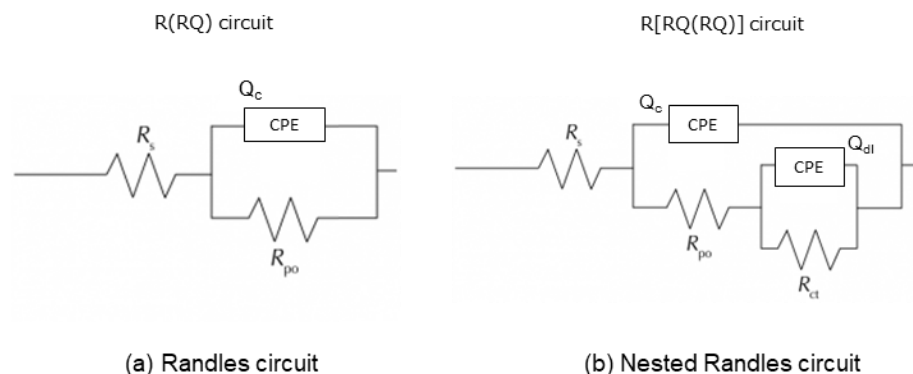


Figure 1: Equivalent circuits typically used to fit EIS data.

R_s , R_{po} and R_{CT} represent the resistance for the solution (electrolyte), the pore resistance, and the charge transfer resistance, respectively. Q_c and Q_{dl} refer to constant phase elements for the coating and double layer, respectively. These two equivalent circuits represent typical conditions of a coating, with (a) being an intact coating, while (b) represents a “defective” coating, where corrosion is taking place at the steel interface underneath the coating. For the majority of work on EIS characterizations of coatings, a simple Randles circuit, as depicted in (a), is sufficient.

The various parameters obtained from equivalent circuit modeling represent different physical and chemical characteristics of the coating during the measurement. While Q_c provides information about the coating's dielectric properties, R_{po} signifies a direct measure of the barrier property. R_{CT} and Q_{dl} are on the other hand parameters associated with reactions occurring at the metal substrate interface, e.g., corrosion.

For this paper, we will only focus on R_{po} and Q_c , as these are specific parameters related to the barrier property of coatings. R_{po} is most widely used out of the two because its magnitude depends directly on the density and size of available sea water pathways in a coating. Such pathways arise naturally in a coating, and a lower value of R_{po} signifies a higher permeation of sea water. As coatings degrade over time, be it due to long term service in a corrosive environment or otherwise, more, and larger conductive pathways will form, thus lowering the value of R_{po} . In terms of specific

values, a common critical threshold used extensively in the literature is that R_{po} should never be below $10^6 \Omega \text{ cm}^2$ [10-13]. Coatings with values lower than $10^6 \Omega \text{ cm}^2$ are considered to offer little to no barrier protection of the underlying metal substrate.

Q_C is a constant phase element, or CPE for short, used to replace a pure capacitor in the curve-fit to ensure a better overall fit of the data. This is a common substitution, and the use of CPE's reflects the inhomogeneity of coatings, where the local concentration and distribution of its constituents will vary to some extent in all spatial dimensions. This will in effect mean that the coating itself will act as a series of different capacitors, each with its own individual time constants. A CPE offers a solution to this, reflecting a non-ideal capacitor behavior one typically finds when measuring coated metals. The impedance of a CPE is given by:

$$Z_{CPE} = \left(\frac{1}{Q_0} \right) (i\omega)^{-n} \quad (1)$$

Here Q_0 is a pseudo-capacitance, while n is an integer between 0 and 1. ω is the angular frequency while i is defined as $\sqrt{-1}$. The integer, n , indicates how “capacitor-like” the response is, and coated metals will often have CPE elements with values ranging between 0.7 and 1.0. The actual capacitance of a CPE element in an (RQ) subcircuit can be calculated using the following formula:

$$C_{CPE} = \frac{(RQ_0)^{\frac{1}{n}}}{R} \quad (2)$$

For Q_C , the coating capacitance, C_C , is calculated by:

$$C_C = \frac{(R_{po}Q_{C,0})^{\frac{1}{n_C}}}{R_{po}} \quad (3)$$

By assuming that a coating can be represented as a parallel plate capacitor, we can further relate C_C to the following equation:

$$C_C = \frac{\epsilon_r \epsilon_0 A}{d} \quad (4)$$

In this equation, ϵ_0 is the permittivity of vacuum ($8.854 \times 10^{-14} \text{ F cm}^{-1}$) and ϵ_r is the relative dielectric constant of the coating. A and d represent the measurement area and thickness of the coating, respectively. (4) is important because it shows that the change in capacitance is directly proportional to a change in the coating's dielectric constant. When exposing a coating to an aqueous medium, its capacitance will change, and this change can be attributed to an effective increase in its dielectric constant. The reason for this is that a dry coating tends to have ϵ_r -values between 2-8 [12, 14, 15], whereas the dielectric constant of water is significantly higher; 79.0 at 23 °C [16]. This difference

in magnitude means that C_c can be directly linked to the water uptake of the coating through the famous Brasher-Kingsbury equation [17]:

$$\Phi = \frac{\log (C_c(t)/C_c(0))}{\log \varepsilon_W} \quad (5)$$

where Φ denotes the volume fraction of water in the coating, while $C_c(0)$ and $C_c(t)$ are the coating capacitances initially, i.e., $t = 0$, and the corresponding coating capacitance at any given time, t , respectively. ε_W represents the dielectric constant for water. The changes in capacitance may also be related to water diffusivity through the coating [12]:

$$\frac{2\sqrt{D}}{d\sqrt{\pi}}\sqrt{t} = \frac{\ln C_c(t) - \ln C_c(0)}{\ln C_c(\infty) - \ln C_c(0)} \quad (6)$$

where D is the diffusion coefficient for water and $C_c(\infty)$ represents the coating capacitance at saturation, i.e., where the coating capacitance does not vary significantly with respect to time. The other parameters have been described before. Thus, by measuring the coating capacitance as a function of time when immersed in an aqueous solution, one can determine the coating's water uptake as well as the rate at which the water takes to diffuse into the coating.

EXPERIMENTAL PROCEDURE

Coating formulations and sample preparation

Four separate two-component polyamine cured epoxy coatings were prepared, wherein the aluminum flake concentration varied from 0 to 9 wt% in increments of 3%. The coatings were formulated with the same pigment volume concentration (PVC) to ensure that any change in coating performance could be attributed to the aluminum pigment concentration directly. For simplicity, the coatings will be hereafter consistently referred to as 0Al, 3Al, 6Al, and 9Al.

For testing, dry abrasive blasted (Sa 3 [18]) carbon steel panels (EN 10025-2 S355 [19]) with medium roughness ($R_z = 70-90 \mu\text{m}$) as per ISO 8503-1 and ISO 8503-5 [20, 21] and dimensions 150 x 75 x 3 mm were consistently used.

All panels were coated with 2 x 125 μm of each of the four coatings described above, i.e., a total nominal dry film thickness (DFT) of 250 μm , by standard airless spray. The first coat was cured for approximately 24h at room temperature before the next coat was applied. The average DFT of the tested panels varied between 250-300 μm in compliance with the requirements of ISO 19840 [22] and ISO 12944-6 [23].