



# Evaluation of Coated Al Alloy Using the Breakpoint Frequency Method



Zhicao Feng\*, G.S. Frankel

Fontana Corrosion Center, The Ohio State University, Columbus, Ohio 43210-1185, USA

## ARTICLE INFO

### Article history:

Received 15 September 2015  
 Received in revised form 20 November 2015  
 Accepted 22 November 2015  
 Available online 2 December 2015

### Keywords:

Al Alloys  
 Organic Coatings  
 Electrochemical Impedance Spectroscopy  
 Breakpoint Frequency

## ABSTRACT

Electrochemical Impedance Spectroscopy (EIS) was used to study coated Al alloys during long-term exposure in 5 wt% NaCl solution. The breakpoint frequency extracted from Bode plots allows the determination of the electrochemically active area of the sample. It shifts from low to high frequency with increasing exposure time due to the enlargement of the active area. The appearance of a high breakpoint frequency  $f_b$ , usually in the range of  $10^2$  to  $10^3$  Hz, occurred after a certain exposure time associated with a sharp drop of open circuit potential and low frequency impedance, and was accompanied by the visual initiation of corrosion under the coating. The incubation time before  $f_b$  appears can be used as a criterion to evaluate the performance of chromate primer combined with different surface pretreatments. Optical profilometry analysis was conducted to determine the corroded area of coated sample after long-term exposure. The corroded area of one coating system was very close to, but that of another coating system was much higher than, the electrochemically active area estimated by the breakpoint frequency method, due to the different extent of attack. This indicates that the breakpoint frequency may be only valid for the determination of defect area during the initiation of attack, but probably not for the propagation to large regions of attack.

© 2015 Elsevier Ltd. All rights reserved.

## 1. Introduction

High strength aluminum alloys are widely used in structural aircraft applications because of the combination of good mechanical properties and light weight. However, during exposure to corrosive environments, Al alloys are prone to localized corrosion such as pitting, intergranular and crevice corrosion [1–4]. Therefore, Al alloys for aircraft applications are usually protected from the environment using multi-layered organic coating systems [5,6]. The most aggressive environments for coated metals involve either immersion in an aqueous environment or exposure to wet conditions such as humid air, deposited aerosol droplets, and condensation. Unfortunately, no organic coating can behave as a perfect barrier to completely block water transport through them, due to their free volume and defects offering possible paths for water penetration where corrosion attack occurs [7,8]. The active area of coatings can be used to indicate the coating quality and extent of degradation.

A good coating providing a large ohmic potential drop makes the metal substrate nonpolarizable, so that DC electrochemical methods like linear polarization are unable to evaluate the

corrosion rate of coated metals [9]. Electrochemical impedance spectroscopy (EIS) is a technique capable of characterizing the electrochemical interface of coated metals and assessing corrosion resistant properties of coatings [10–13]. Fitting of EIS data to an equivalent circuit has been widely used to analyze EIS results for coated metals, providing important parameters such as coating capacitance, pore resistance in the coating, and metal/interface capacitance and resistance [14–20]. The metal/electrolyte interfacial capacitance measurement is one possible metric to quantify the electrochemically active area in the coating, under the assumption that the specific capacitance (capacitance per unit area) of the metal/electrolyte interface is a constant. In typical aqueous environments, metal/electrolyte interfacial specific capacitance is usually about 15 to 30  $\mu\text{F}/\text{cm}^2$  [21,22]. The electrochemically active area is equal to the measured metal/electrolyte interfacial capacitance divided by the specific capacitance [12]. Additionally, the change of pore resistance in the coating has been used by Haruyama *et al.* [23] to determine the electrochemically active area via the following expression:

$$R_{po} = \rho d / A_d \quad (1)$$

where  $R_{po}$  is the pore resistance in the coating.  $A_d$  is the electrochemically active area.  $\rho$  and  $d$  are the specific bulk resistivity and coating thickness, respectively. The above approaches require computer modeling of the measured EIS spectra. Haruyama *et al.* proposed another method, the breakpoint

\* Corresponding author.

E-mail addresses: [feng.212@buckeyemail.osu.edu](mailto:feng.212@buckeyemail.osu.edu), [fengzhicao@gmail.com](mailto:fengzhicao@gmail.com) (Z. Feng).

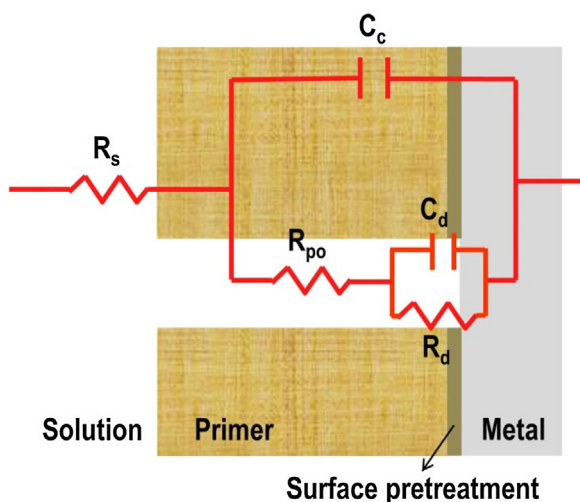
frequency method, to determine electrochemically active area of the coating without modeling [23]. Based on that, Scully *et al.* proposed the low breakpoint frequency theory, which allows determination of the electrochemically active area ratio as small as 0.01% [11,12]. More detailed information about breakpoint frequency is provided below.

The breakpoint frequency method has been utilized to evaluate the performance of organic coatings on steels [12–16,19,23,24]. However, even though the corrosion performance of coated Al alloys is commonly assessed by EIS [25–27], the breakpoint frequency approach has rarely been used. Huang *et al.* [28] confirmed the excellent corrosion resistance of anodized Al alloy 6061 by noting that the breakpoint frequency was almost constant with exposure time. Instead of qualitatively confirming corrosion resistance, however, the breakpoint frequency method has potential beyond the qualitative confirmation of corrosion resistance as it is a powerful technique that can quantitatively calculate the active area of Al under coatings; monitor the early stage of coating degradation, and rank coating performance.

The purpose of this work is to evaluate the use of breakpoint frequencies to monitor the coating defect area with time for different coating systems on an Al alloy substrate. The appearance of a high breakpoint frequency is shown to be the time when the visually localized corrosion occurred. The defect areas estimated by the breakpoint frequency method are compared with that measured by optical profilometry after a long-term EIS test. The breakpoint frequency and low frequency impedance values are also used to rank the performance of different surface pretreatments under a chromate-containing primer.

## 2. The Breakpoint Frequency Method

The nested equivalent circuit shown in Fig. 1 is often used to model the response of coated metals. Scully [10,12] utilized it to determine the correlation between the defect area ratio and breakpoint frequency based on the theory of Haruyama *et al.* [23]. The intact coating covering most of a metal can be considered to be a capacitor of magnitude  $C_c$ . Small defects in the coating such as pores are modeled by a resistor  $R_{po}$ . Faradaic processes occurring at the electrolyte/metal interface at the end of the pores are modeled using a capacitor  $C_d$  in parallel with a resistor  $R_d$  representing the defect capacitance and polarization resistance, respectively. The



**Fig. 1.** Nested simplified Randles circuit of a coated Al alloy with a defect.  $R_s$  is the solution resistance,  $C_c$  is coating capacitance and  $R_{po}$  is pore resistance.  $C_d$  and  $R_d$  represent defect capacitance and resistance associated with reactions at the pore bottom.

synthesized Bode magnitude and phase plots shown in Fig. 2 were obtained using the nested simplified Randles circuit for a sample of area  $10 \text{ cm}^2$  and varying the defect area percentage from 0.00001% to 0.1%. These curves were adapted from Scully's work [10,12]. Table 1 shows the defect area ratios and the corresponding values of each component assumed for the curves in Fig. 2. The solution resistance,  $R_s$ , was assumed to be  $1 \Omega$  and  $r_{po}$  was assumed to be  $1 \Omega \text{ cm}^2$  because of the low resistivity of the solution in the coating pores [12]. Here, lower case letters represent area normalized values of each component.  $c_c$  is typically on the order of 1 to  $10 \text{ nF/cm}^2$  [14], and was assigned here as  $1 \text{ nF/cm}^2$ .  $r_d$  was assumed to be  $10^3 \Omega \text{ cm}^2$  based on the charge transfer resistance of bare Al measured using EIS [29–31]. The double-layer capacitance per unit area is usually considered similar to that for mercury, 15 to  $30 \text{ uF/cm}^2$  [21,22]. A linear relationship was found between double layer capacitance and corroded area for scratched and CPC-coated AA 2024-T3, exhibiting a double layer capacitance on the order of  $10^{-4} \text{ F/cm}^2$  [32]. This was assigned to be the value of  $C_d$  in Table 1. The overlapped Bode magnitude curves in the high frequency range of Fig. 2 for all three defect area ratios reflect the constant values of  $R_s$  and  $C_c$ . The two resistance plateaus and the capacitive region in between shift downward with increasing defect area ratio, which lowers  $R_{po}$  and  $R_d$  (in  $\Omega$ ) and increases  $C_d$  (in F).

Breakpoint frequencies in the Bode magnitude plot are defined as a boundary where a capacitive region first transitions to a resistive region when the frequency shifts from high to low values [10,12]. At the transition, the impedance of the capacitance is equal to the plateau resistance and the phase angle is about  $45^\circ$ . So the breakpoint frequency can also be determined in the Bode phase plot where, following the curve from higher to lower frequency, the phase angle first shifts below  $45^\circ$  [10,12]. High and low breakpoint frequency were defined based on the feature of the Bode plots as follows [12]:

$$f_h = \frac{1}{2\pi\epsilon\epsilon_0\rho A} \frac{A_d}{A} \quad (2)$$

$$f_l = \frac{d}{2\pi\epsilon\epsilon_0r_d A} \frac{A_d}{A} \quad (3)$$

where  $f_h$  and  $f_l$  are high and low breakpoint frequency, respectively,  $A$  and  $A_d$  are the total exposed coating area and defect area, respectively,  $\rho$  is the resistivity in pores,  $d$  is the coating thickness,  $r_d$  is the unit area defect resistance, and  $\epsilon$  and  $\epsilon_0$  are the dielectric constant for the coating saturated with water and permittivity of free space, respectively. The relationship between  $f_h$  and the defect area ratio is independent of the substrate. However,  $f_l$  is dependent on the area normalized polarization resistance at the metal/electrolyte interface, indicating that the relationship between  $f_l$  and the defect area ratio depends on the material. In this work, the substrate is always Al alloy. So,  $f_l$  can still be used to evaluate coatings qualitatively. This area dependence of  $f_l$  can only be observed for good coatings with a very small defect area.

The benefit of the breakpoint frequency method is its ability to monitor the defect area as a function of time only using the high frequency range of Bode magnitude plots, with no need for analyzing the complicated behavior in the low frequency range. Moreover, the double layer capacitance and charge transfer resistance of a specific bare metal are not needed when using the high breakpoint frequency method.

## 3. Experimental

The surfaces of the AA7075-T6 (UNS A97075) panel substrates were treated five different ways: chromate conversion coating

Download English Version:

<https://daneshyari.com/en/article/183308>

Download Persian Version:

<https://daneshyari.com/article/183308>

[Daneshyari.com](https://daneshyari.com)