ANALYSIS OF EN IMPEDANCE SPECTRA FOR DETERMINATION OF CORROSION-RELATED DIFFUSION EFFECT ON BARRIER PROPERTIES OF Zn AND Al PIGMENTED EPOXY COATINGS

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Abstract

The effect of different vol. % Zn:Al ratio in Zn and Al pigmented epoxy coatings with the same OPVC (40 vol. %) has been investigated by means of EN measurements performed in 0.05 M NaCl for 168 hrs. Analysis of EN data in frequency domain permits to evaluate changes of the noise impedance spectra due to possible contributions from charge transfer and mass transport reactions occurring in pores filled with corrosion products and at the delaminated areas of tested coatings. The interpretation of EN noise impedance spectra for determination of water penetration and the loss of adhesion in combination with the single frequency (1 kHz) impedance test results for tested coatings has also been discussed.

Keywords: Painting system, Zn pigment, Al pigment, electrochemical noise analysis, delamination of coating

1. INTRODUCTION

Opposite with epoxy zinc rich coatings (ZRP) the modified type of ZRP with partial substitution of Zn by Al have not yet been widely studied. For some exceptions can be considered recently published articles on the use of ENA for characterization of these types' coatings regarding to delamination kinetics of underlaying steel. In all of them for noise impedance spectrum interpretation similarity of those characteristics with simulated electrochemical impedance spectrum (EIS) for coated steel is accepted [1] and it was used to provide information about disbonded region of the coating/steel interface.

This approach to electrochemical characterisation of tested coating systems protective performance can be supplemented by analysis of EN data with implementation of a modified noise resistance R_n^* and noise resistance R_n values [5]. According to Bierwagen et al [2] the value of the difference between these noise resistance values may give an estimation of the degree of imperfections in a coating. For Zn and Al pigmented epoxy coatings with low OPVC (40 vol. %) and different vol. % ratio Zn:Al the relation of parameter R_n^*- R_n to oxygen reduction reaction (ORR) occurring on Zn particles in the coating can be important for understanding of a barrier mechanism and optimising coating formulation. Implementation of this parameter into the noise impedance spectrum interpretation as well as parameters related to changes in the resistive properties seems to be necessary for better understanding of key factors affecting protective performance of the mentioned above type of coatings. Considering possible similarity of MEM impedance spectrum obtained by use of ENA with simulated EIS plots for ZRP the work of Vilche et al [6] offers some possibilities of application for given purpose. It should be noticed these authors successfully simulated EIS plots for ZRP by the transfer function which involves the constant phase element CPE = $[C(i\omega)^{\alpha}]^{-1}$ with a parameter α = 0.4 – 0.6. In addition to it a finite diffusion impedance was considered to account for the transport process through the coating together with the charge transfer resistance of the Zn dissolution process occurring in parallel with ORR. In this case parameter R_n^* - R_n can possibly be used in terms including the charge transfer resistance R_A of this process in the coating according to Vilche et al model.

The main aims of this study were so checking of this possibility and verifying how accurately a new approach to noise impedance spectrum interpretation can help to distinguish differences in the protective performance of tested coating systems. Apart from electrochemical measurements more advanced microscopic method was used for metallographic analysis of tested coating systems after immersion tests. EDX mapping and structure (SEM – SE image) of cross-sections were chosen for this purpose.

2. EXPERIMENTAL

2.1. Materials

Two types of modified Zn pigmented epoxy coatings were prepared using Zn and Al pigments (see **Table 1**) with the same value of OPVC = 40 vol. % and different vol. % of Zn:Al ratio.

Table 1 Characteristic of ZRP modified with Al additions

Sample	OPVC (vol%)	Zn:Al ratio (vol%)	Filler	Binder	Hardener
AKAl 112	40	88:12	Alum.Stapa 2NL	Epicote 1010	Epicure 3115
AKAl 107	40	94:6	Alum.Stapa 2NL	Epicote 1010	Epicure 3115

Zn dust for preparation of coatings was 4P16 (supplied by UMICORE Zinc Alloys and Chemicals Co.). In combination with Zn dust aluminum paste Alum.Stapa 2NL (supplied by ECKART GmbH) and also the same type of binder and hardener (supplied by Momentive Co.) were used. In order to avoid the particle sedimentation and for better dispersion ion-exchangeable inorganic pigment Syloid 244 based on synthetic amorphous silica was used in both types of tested coatings.

Both tested coatings were applied by a spreader bar to steel C4Q panels previously polished and degreased. The average thickness of dry film was 55 μm for tested coatings.

2.2. Method

Immersion tests using ENA for tested coatings on steel substrate specimens were performed with use of the same experimental set-up as described earlier [4]. The potential and current noise (ENP and ENC) values (for given data set measured for given immersion time) were collected for measurement periods of 600 s with sampling rate of 20 Hz (12 000 points for period) using GAMRY ESA 410 software in the end of 168 hrs exposure test in 0.05 M NaCl. These data were used to obtain MEM Noise Impedance Spectrum characteristics as well as R_n^*- R_n values for both tested coating systems.

In addition to it changes in the resistive properties of tested coating systems were estimated when immediately after EN measurements single frequency (1 kHz) impedance test was performed with the use of HIOKI LCR HITESTER.

3. RESULTS AND DISSCUSIONS

Due to the fact that both tested coating systems after 168 hrs of exposure to 0.05 M NaCl can be considered for rather stationary systems with barrier mechanism (with high noise impedance $Z_{n,f\to 0}$ values) only MEM curves presented here were checked because of providing a smoother version of impedance spectrum as compared to FFT curves. As can be seen from **Figures 1–2** MEM impedance spectrum is for every of tested coatings different confirming by this way quite different barrier properties of tested coatings.

This fact corresponds also to quite different degree of barrier effect development because water and/or solution penetration within coating through pores and ionic pathways can be delayed and dependent on contributions from charge transfer and mass transport reactions different in tested coatings.

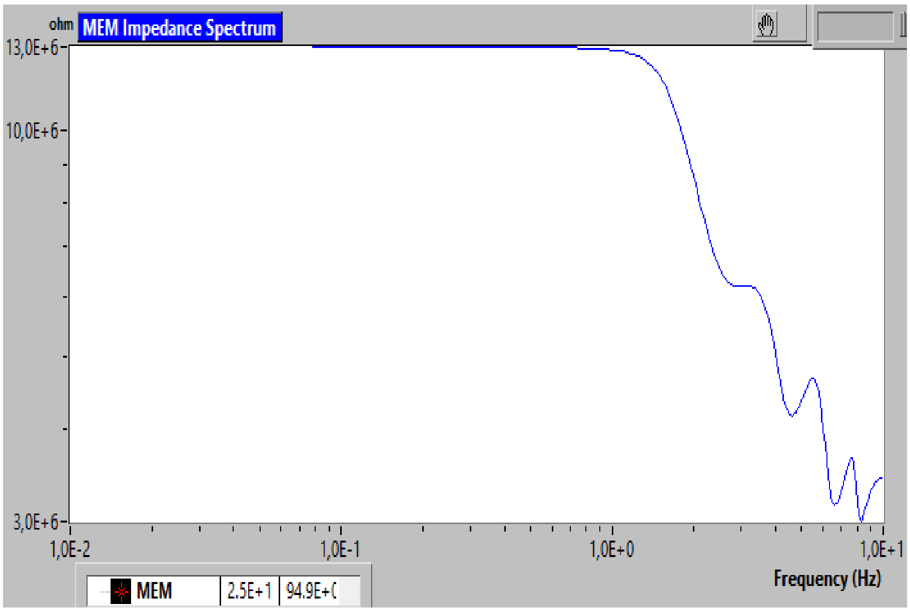

Figure 1 Noise impedance spectrum (MEM curve) for AKAl 112 after 168 hrs exposure

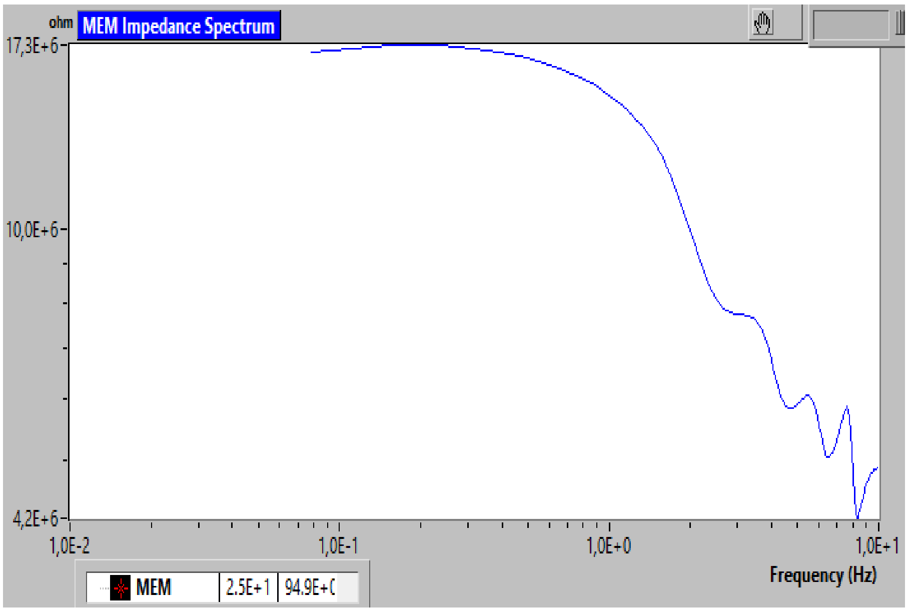

Figure 2 Noise impedance spectrum (MEM curve) for AKAl 107 after 168 hrs exposure

Considering possible interpretation of presented MEM curves according Vilche et al [6] it should be remembered the Warburg impedance Z_w for a diffusion process in a layer of finite thickness is given by the expression

$$Z_w(\omega) = R_{DO}(i\omega\delta^2/D)^{-0,5}\tanh(i\omega\delta^2/D)^{0,5} \qquad (1)$$

where R_{DO} denotes the $\omega \rightarrow 0$ limit of $Z_w(\omega)$, δ is the thickness of the diffusion layer and D is the diffusion coefficient.

Eq (1) assumes that a.c. diffusion layer thickness (i.e. the distance travelled by diffusion species in the low frequency oscillating perturbations) is very much less than the d.c. Nernstian diffusion layer thickness [8]. In the fact if the frequency-dependent diffusion length is defined as $\delta = \sqrt{D/\omega}$ and $s = (\delta/L)^2$ where L is the coating thickness then values of Z estimated by the single frequency (1 kHz) impedance test can be used to substitute values of $Z_{w\infty}$ when the tanh term approaches unity and $Z_w = R_{DO}\sqrt{is}$. The same test can also provide values of R_c involved in Vilche et al model.

Considering these suggestions is possible to check how accurately MEM impedance spectrum can be reproduced according to the following expressions

$$[Z(\omega)]^{-1} = Y_0\sqrt{i\omega} + \frac{R_c + R_{DO}\left(\delta/_L\right)\sqrt{i\omega}\tanh\left(\delta/_L\right)\sqrt{i\omega} + (R_n^* - R_n)}{\left[R_c + R_{DO}\left(\delta/_L\right)\sqrt{i\omega}\tanh\left(\delta/_L\right)\sqrt{i\omega}\right](R_n^* - R_n)} \tag{2}$$

where
$$Y_0 = \frac{1}{\sigma\sqrt{2}} \tag{3}$$

whereas
$$\sigma = \frac{RT}{n^2F^2A\sqrt{2}}\left(\frac{1}{D_{O2}^{0.5}c_{O2}}\right) \tag{4}$$

where n = number of electrons in ORR, A = delaminated area, D_{O2} = diffusion coefficient of oxygen in the polymeric coating and c_{O2} = solubility of oxygen inside the polymer at temperature T.

For practical use of Eq. (2) should be remembered that implementation of R_n^* - R_n value means possibility of development situation when $R_n^* - R_n < 0$. In this case the defect developed locally at the coating/steel interface is not galvanically protected by sufficient amount of Zn particles around the defect. Opposite to it when still sufficient amount of Zn particles remains at the coating/steel interface available for local galvanic protection of a defect developed locally, then $|R_n^* - R_n|$ value instead of $(R_n^* - R_n)$ value should be used in Eq. (2).

It should be noted the relative values of R_{DO} and σ determine whether the system is under charge-transfer control for $R_{DO}/\sigma > 10$ or under diffusion control if $R_{DO}/\sigma < 0.1$ [9]. For tested coating systems in the end of 168 hrs exposure in 0.05 M NaCl values of D_{O2} = 1.18E-10 cm^2s^{-1} and c_{O2} = 4.02E-8 mol/cm^3 were found [10]. As compared with D_{O2} and c_{O2} values reported before for non-pigmented polymeric coating in 0.5 M NaCl [11] these values are much smaller due to suggested better barrier properties of tested coatings. By this way for known values of D_{O2} and c_{O2} delaminated area size for given type of coating in the end of the test can be calculated using fitting parameter Y_0 values estimated for MEM curves in **Figures 1–2**. In **Table 2** are values of parameters involved in Vilche et al model (with the use of R_n^*- R_n in terms including R_A) for tested coating systems.

Table 2 Summary of parameters involved in Vilche et al model estimated for tested coating systems in the end of 168 hrs exposure

Sample	δ (cm)	R_{DO} (Ω)	R_c (Ω)	R_n^* - R_n (Ω)	Y_0 ($s^{0,5}$/Ω)	A (cm^2)
AKAl 112	1.062E-03	13.0E+06	18.227E+06	12.812E+06	4.646E-08	5.753E-05
AKAl 107	7.610E-04	17.3E+06	13.149E+06	-5.305E+06	6.847E-08	2.597E-04

As the loss of adhesion is directly linked to the reduction of oxygen at the steel/coating interface this approach can be used for determination of delaminated area size. Considering of 168 hrs exposure to 0.05M NaCl in relation to the formulation and the structure of tested coatings **(see Figure 3 and 4)** it is clear the Al particles in combination with inorganic pigment Syloid can reduce cathodic delamination to minimum by preventing the transport of oxygen and water through coating. The tortuous detours provided by flake shaped Al pigment particles seems to increase the diffusion path and decrease the cross-section area through which diffusion occurs. It should be noticed the high number of Al particles in the coating AKAl 112 can improve coating delamination resistance also due to possible decrease of chemical activity of Zn in the coating/steel interface. For this region in the end of experiment a considerable reservoir of burried Zn remains available for local galvanic protection should a defect developed locally to expose an isolated Zn particle **(see Figure 3).**

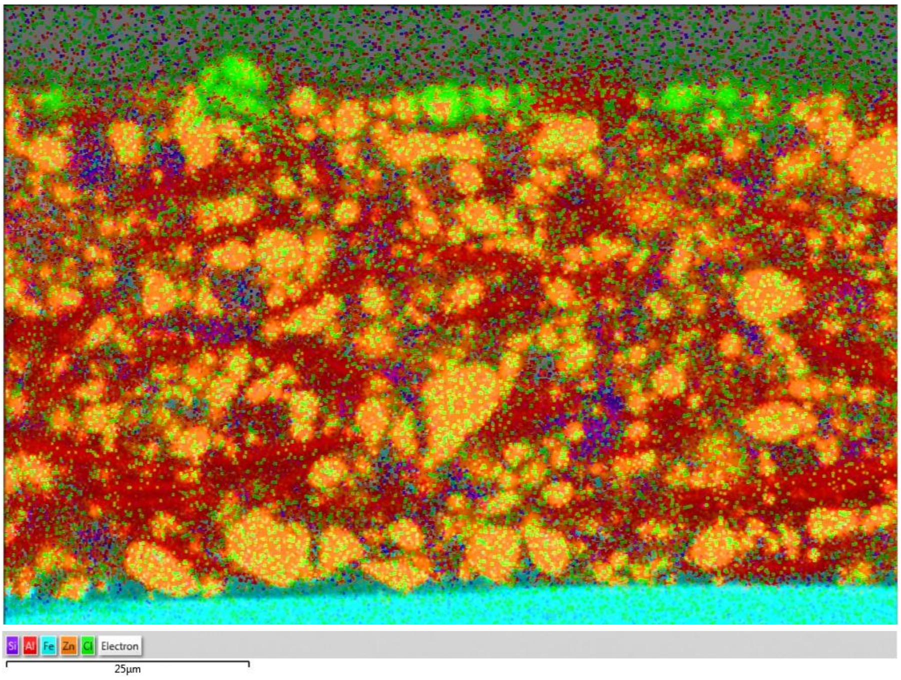

Figure 3 EDX mapping and structure (SEM-SE image) of cross-section for AKAl 112

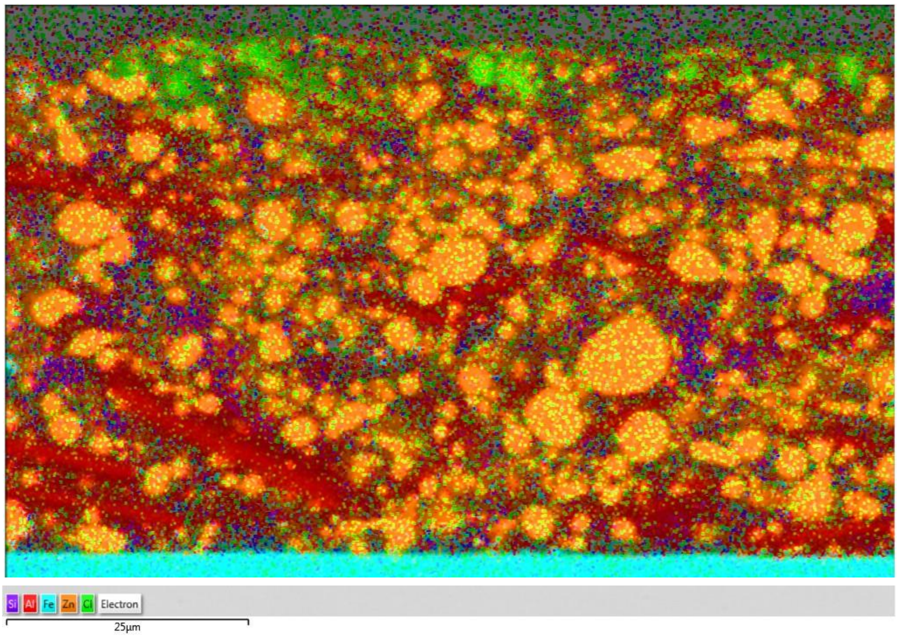

Figure 4 EDX mapping and structure (SEM-SE image) of cross-section for AKAl 107

4. CONCLUSIONS

A new approach for the use of ENA in combination with the single frequency (1 kHz) impedance test measurements has been proposed and utilized for the noise impedance spectrum interpretation. Through this new approach the role of various parameters on the delaminated area size has been investigated to achieve better understanding of barrier mechanism and help optimizing coating formulation to be ensuring resistance to cathodic delamination.

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