

APPLICATION OF ENA TO INVESTIGATE THE EFFECT OF PARTIAL SUBSTITUTION OF Zn BY Al IN EPOXY COATINGS ON DELAMINATION KINETICS OF UNDERLYING STEEL

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Abstract

The possible effects on the protective performance of zinc-rich paints (ZRP) modified by combination of Zn dust with Al paste were investigated using electrochemical noise analysis (ENA). The role of two different Zn contents was tested for two different ZRP formulations prepared with the same vol. % Zn:Al ratio as well as with the same binder and hardener types applied. The possible losses of protective performance of both ZRP were evaluated by means of EN measurements performed for tested coatings on steel substrate specimens during 168 hrs immersion test in 0.05 mole NaCl. Due to supposed changes of cathodic nature of steel surface with immersion time ENA was used to provide information about possible delaminated corroding area time development for tested coating/steel systems.

Keywords: Zinc-rich paints, electrochemical noise analysis, ration Zn:Al

1. INTRODUCTION

Combination of Zn dust with aluminium paste in modified zinc-rich paints (ZRP) has been tested recently from the point of view possible effects on the protection performance of an epoxy based ZRP. At the same time it was demonstrated that Electrochemical Noise Analysis (ENA) used in immersion tests of these modified ZRP can be useful tool for study of these effects. After longer immersion time (168 hrs) in 0.05 mole NaCl it was found for this type of ZRP the barrier protection is dominant mechanism of protection. As convenient parameter for interpretation of ENA results was chosen low frequency noise impedance spectrum modulus of impedance ($Z_{0.08\text{Hz}}$) considered being a good indicator of residual barrier properties of tested ZRP after exposure in 0.05 mole NaCl. In fact, noise impedance spectrum characteristics (MEM curves) for this type of ZRP can be considered as not only providing information on loss of protective properties of tested ZRP but also on possible start of the underlying steel corrosion process. Similarity of MEM Noise Impedance Spectrum characteristics with simulated electrochemical impedance spectrum for which impedance analog for coated steel surface is accepted has recently provided an alternative interpretation of above mentioned characteristics. As with penetration of electrolyte into coating, a double layer forms at the disbonded region of the coating/steel interface and corrosion begins double-layer capacitance C_d value increases as delaminated corroding area A_d increases. It should be noted the possibility of using C_d variation for estimation of A_d variation at given time of exposure was already tested for different ZRP with Al additions.

In present work we wanted to verify this approach for providing information on delamination kinetics of the underlying steel if similar type of ZRP is applied on steel substrate with aim to protect against corrosion during exposure in 0.05 mole NaCl. At the same time we wanted to demonstrate the possibility of using this approach for the study of the role Al particles in ZRP with different Zn content, in which during exposure to the corrosive electrolyte different time development of A_d is expected. Apart of EN measurements more advanced microscopic method were used for metallographic analysis of tested coatings after immersion tests. EDX mapping and structure (SEM - SE image) of cross-sections were chosen for this purpose.

2. EXPERIMENTAL

Two types of ZRP were prepared using Zn and Al pigments (see **Table 1**) with the different overall pigment volume concentration (OPVC) and the same vol. % Zn:Al ration.

Table 1 Characteristics of tested ZRP with Al additions

sample	OPVC (vol%)	Zn:Al ratio (vol%)	Filler	Binder	Hardener
AKAI 110	55	94:6	Alum.Stapa 2NL	Epikote 1001	Epicure 3115
AKAI 111	60	94:6	Alum.Stapa 2NL	Epikote 1001	Epicure 3115

Zinc dust used for preparation of coatings was 4P16 (supplied by UMICORE Zinc Alloys and Chemicals Co.). In combinations with Zn dust aluminium paste Aluminium Stapa 2NL (supplied by ECKART GmbH) and the same type of binder and hardener (supplied by Momentive Co.) were used.

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

Immersion tests using ENA for tested coatings on steel substrate specimens were performed with use of the same experimental set-up as described earlier [2]. 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. Data treatment in frequency domain (MEM Noise Impedance Spectrum characteristics providing C_d values) was used for estimation of instantaneous A_d values at given times of exposure in 0.05 mole NaCl. For this purpose $A_d(t)$ can be estimated from C_d values measured at given time t (μF) by means of empirical equation $A_d = C_d(t)/20$ if 20 is the typical value of the bare steel double-layer capacitance adopted to estimate the underlying metallic active surface ($\mu\text{F}\cdot\text{cm}^{-2}$) [3].

3. RESULTS AND DISCUSSIONS

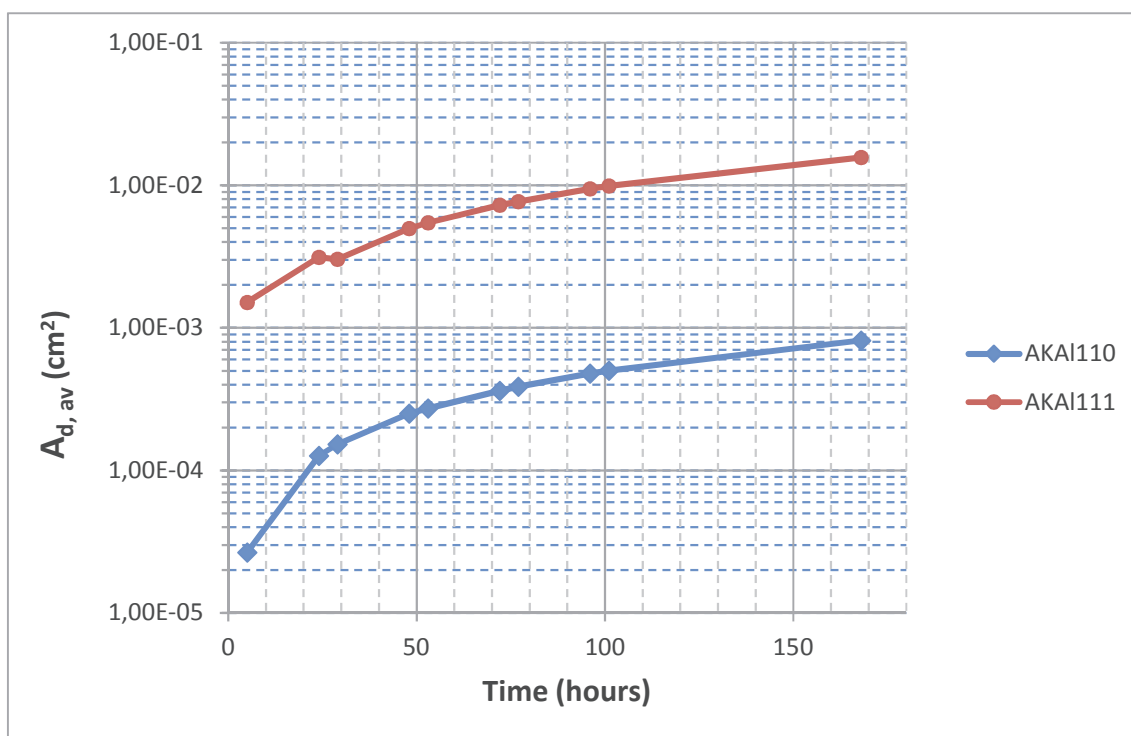
11 measurements were performed on type specimen AKAI110 as well as on type specimen AKAI 111 during uninterrupted immersion tests performed on steel panels coated by tested ZRP. **Table 2** lists the parameters obtained by mentioned approach to analysis of 11 sets of ENA data for AKAI 110 and AKAI 111. These parameters included instantaneous C_d and A_d values estimated for given immersion times.

Due to very dynamic changes of cathodic nature of steel surface with immersion time, the average delaminated corroding area ($A_{d,av}$) time development in 168 hrs exposure of tested ZRP to 0.05 mole NaCl was chosen for evaluation of delamination kinetics of the underlying steel. $A_{d,av}$ development with immersion time in immersion tests using ENA and performed on tested steel/paint systems can be seen in **Figure 1**.

From **Figure 1** can be seen the relative performance of systems AKAI 110 and AKAI 111 in contact with test electrolyte is very different. As for AKAI 110 it is shown trough rather slow corrosion process observed after 48 hrs of immersion higher resistance to water and corrosive species permeation is expected for this type of ZRP. This is probably associated with slow zinc self-corrosion which occurs at very low rates and over rather small delaminated area ($A_{d,av} \approx 2.50 \cdot 10^{-4} \text{ cm}^2$) of the active zinc particles. In spite of the fact, this parameter started to show small degree of progressive deterioration for the system AKAI 110. In the end of the test average delaminated corroding area for AKAI 110 was almost 20 times smaller than in the case of system AKAI 111. It is obvious that in the opposite to AKAI 110 higher degree of progressive deterioration observed for AKAI 111 can be probably associated with significant degree of coating film blistering and massive amounts of voluminous zinc corrosion products precipitation inside of coating. It can be these products which provide a mechanical driver for adhesion loss enhancing delamination.

Table 2 Instantaneous C_d and A_d values for AKAI 110 and AKAI 111 after different immersion time

Immersion time t (hrs)	AKAI110		AKAI 111	
	C_d (F)	A_d (cm ²)	C_d (F)	A_d (cm ²)
0-0.17	$2.90 \cdot 10^{-8}$	$1.45 \cdot 10^{-3}$	$4.37 \cdot 10^{-8}$	$2.18 \cdot 10^{-3}$
5	$3.00 \cdot 10^{-8}$	$1.50 \cdot 10^{-3}$	$2.86 \cdot 10^{-8}$	$1.43 \cdot 10^{-3}$
24	$4.94 \cdot 10^{-8}$	$2.47 \cdot 10^{-3}$	$2.03 \cdot 10^{-7}$	$1.01 \cdot 10^{-2}$
29	$9.80 \cdot 10^{-8}$	$4.90 \cdot 10^{-3}$	$3.08 \cdot 10^{-7}$	$1.50 \cdot 10^{-2}$
48	$7.73 \cdot 10^{-8}$	$3.90 \cdot 10^{-3}$	$1.08 \cdot 10^{-5}$	$5.40 \cdot 10^{-1}$
53	$1.60 \cdot 10^{-8}$	$8.00 \cdot 10^{-4}$	$4.88 \cdot 10^{-8}$	$2.40 \cdot 10^{-3}$
72	$1.94 \cdot 10^{-7}$	$9.70 \cdot 10^{-3}$	$3.06 \cdot 10^{-6}$	$1.53 \cdot 10^{-1}$
77	$5.19 \cdot 10^{-7}$	$2.60 \cdot 10^{-2}$	$1.28 \cdot 10^{-7}$	$6.37 \cdot 10^{-3}$
96	$4.66 \cdot 10^{-8}$	$2.33 \cdot 10^{-3}$	$5.05 \cdot 10^{-6}$	$2.52 \cdot 10^{-1}$
101	$3.55 \cdot 10^{-7}$	$1.77 \cdot 10^{-2}$	$2.27 \cdot 10^{-8}$	$1.13 \cdot 10^{-3}$
168	$9.84 \cdot 10^{-7}$	$4.90 \cdot 10^{-2}$	$5.10 \cdot 10^{-6}$	$2.55 \cdot 10^{-1}$


Figure 1 Time development of $A_{d,av}$ values in 168 hrs exposure

At the same time can be supposed this high degree of system deterioration can be associated with localized anodic reactions on steel which can drive oxygen reduction adjacent to the attack leading to cathodic degradation of the adhesive bond due to generation of OH^- at steel surface. It should be noticed that for AKAI 110 cathodic degradation of the adhesive bond can be decreased in the presence of Al particles just only through the decrease of the rate of the oxygen diffusion into the coating/steel interface [4]. In this case Al particles work as active pigment according to Eq. (1):



According to it, it seems in the case of AKAI 110 that Al particles can work as active pigment only in the case of lower Zn content (i.e. slow zinc self-corrosion associated with high resistance to water and corrosive species permeation). By this way, low susceptibility of AKAI 110 to delamination (when compared to AKAI 111) can probably be explained. In accordance with it, neither blistering, nor distribution of localized regions of electrolyte penetration and certain “hot spots” existence (where Cl⁻ ions penetrate the coating to its base) can be observed for AKAI 110 when compared with AKAI 111 if metallographic analysis has been performed after the test (see **Figure 2** and **Figure 3**).

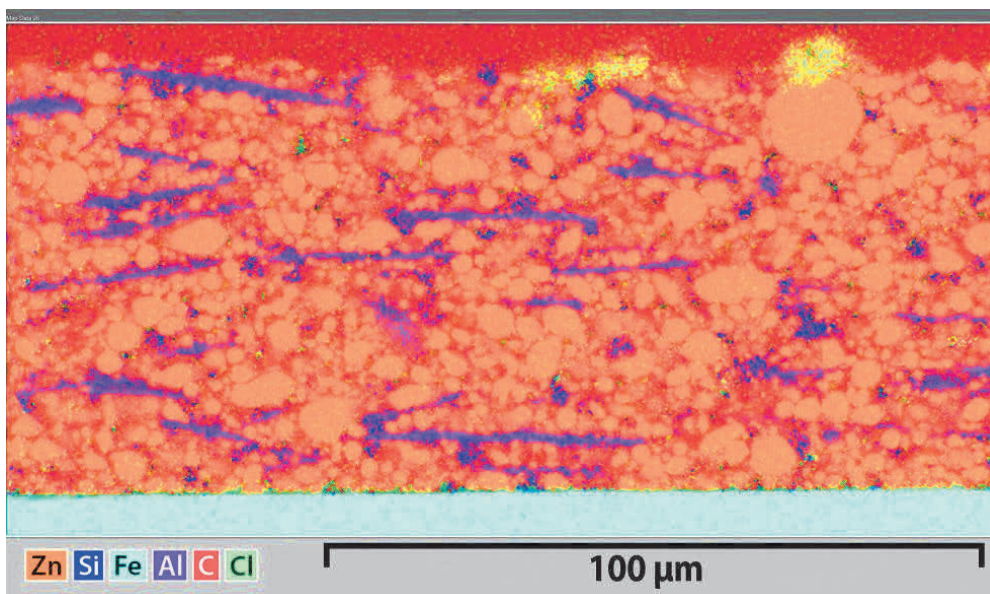


Figure 2 EDX mapping and structure (SEM-SE image) of cross sections for AKAI 110 after 168 hrs of exposure in 0.05 mole NaCl

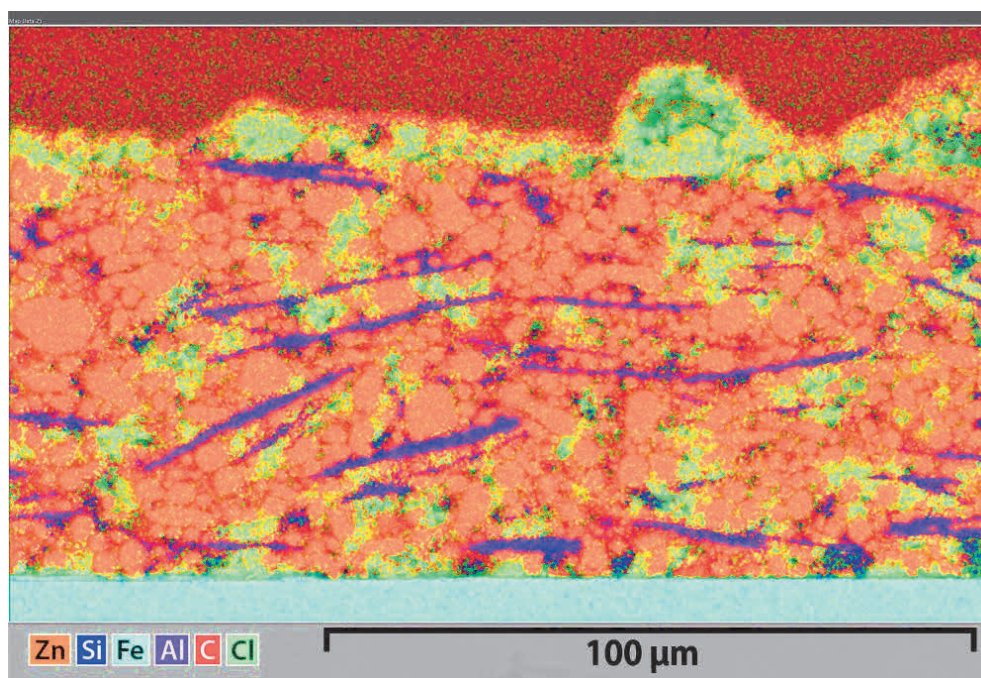


Figure 3 EDX mapping and structure (SEM-SE image) of cross sections for AKAI 111 after 168 hrs of exposure in 0.05 mole NaCl

At the same time reasonable good correlation with mentioned above conclusions was found when MEM Noise Impedance Spectrum characteristics of tested coating (MEM curves) estimated in the end of test were compared (see **Figures 4** and **5**).

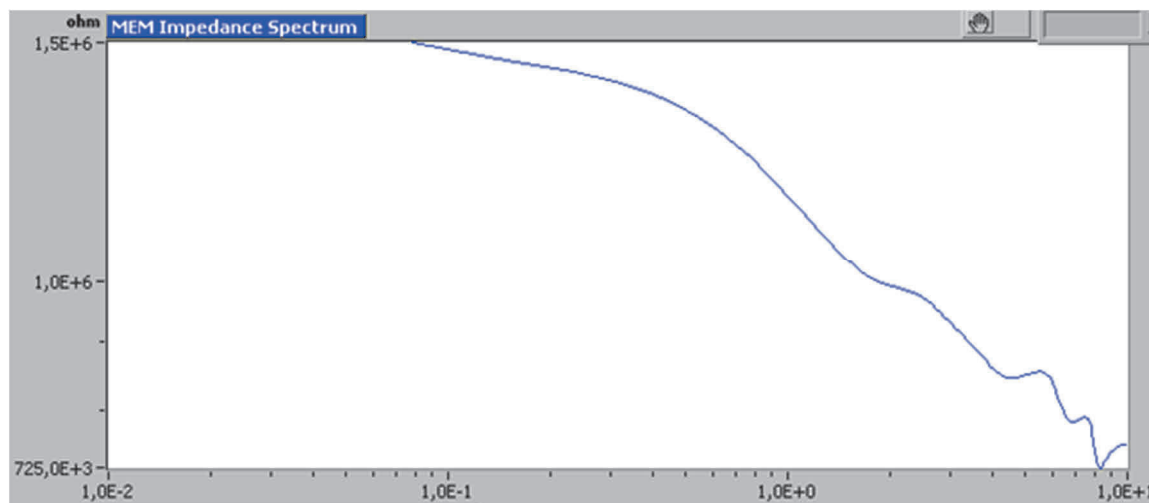


Figure 4 Noise impedance spectrum (MEM curve) for AKAI 110 after 168 hrs of exposure

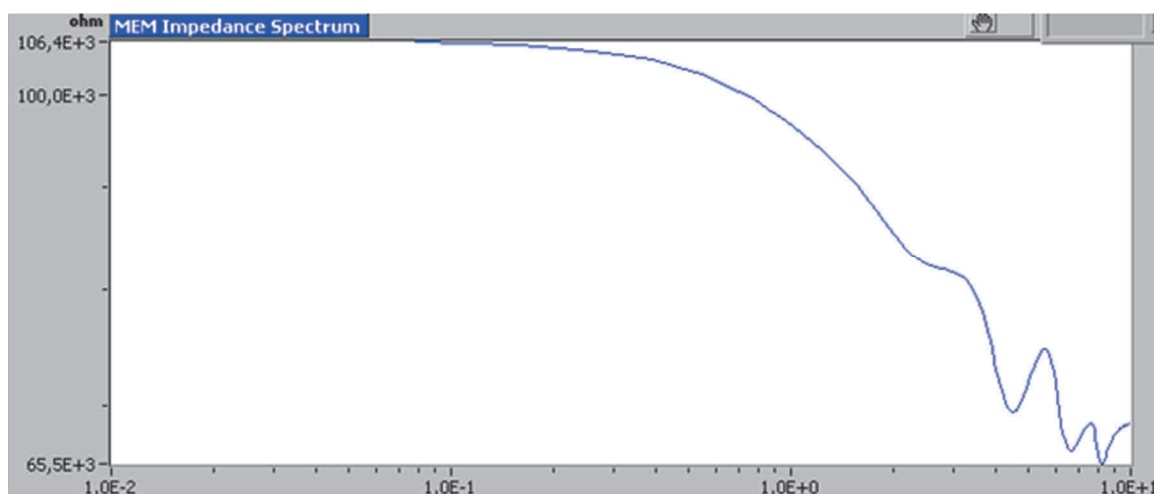


Figure 5 Noise impedance spectrum (MEM curve) for AKAI 111 after 168 hrs of exposure

It is obvious that for AKAI 110 high $Z_{0.08\text{Hz}}$ value can be attributed to low susceptibility of this system to delamination whereas for AKAI 111 much lower $Z_{0.08\text{Hz}}$ can correspond to rather significant degree of blistering and delamination mentioned above. These observed differences can be also caused by formulation of AKAI 111 in which overall pigment concentration (OPVC) is probably over overall critical pigment volume concentration (OCPVC).

4. CONCLUSION

For two different ZRP modified by Al additions the role of Al particles in ZRP with different Zn content on delamination kinetics of underlying steel was explained using modified approach to analysis EN data obtained during immersion tests in 0.05 mole NaCl. The results obtained can be applied to elucidate differences in blistering process and extent of delamination expected for different formulation of this type of ZRP.

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