EN APPLICATION FOR EVALUATION OF INHIBITION EFFICIENCY OF SOME INHIBITING ADDITIONS ON THE SYSTEM´S CORROSIVITY FOR ALUMINIZED CARBON STEEL - OXYGEN FREE WATER AT 60 °C

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Abstract

For cooling tubes manufactured of aluminized carbon steel with inner surface welded longitudinally the question arises if the anticorrosion quality of Al coating produced on external surface can be influenced by the presence of the weld area on internal surface. In fact this quality is related to Al coating ability to prevent or at least to inhibit the corrosion process occurring during penetration of coating by water environment to the steel-coating interface. Electrochemical noise (EN) measurements provide a set of parameters which can be used to obtain useful information relating to possible impacts of time development of expected active-passive transitions in Al coating on kinetics of the underlying steel corrosion process.

Keywords: Aluminized carbon steel, localized corrosion, electrochemical noise

1. INTRODUCTION

In the present paper, we demonstrate preliminary conditions of passivity breakdown for aluminized tubes made from carbon steel longitudinally welded squared tubes. As the anticorrosion quality of Al coating produced on external surface can be influenced by the presence of the weld area on internal surface (not exposed to water environment), demonstration of coating ability to prevent the corrosion process should be necessary for this case. The presented work covers the effect of possible modelling of localized corrosion events in Al coating as well as at Al coating-steel interface during 99 h exposure tests in oxygen free water at 60 °C for critical pH value. According MacDonald et al. [1] at 60 °C and in the range of pH = 3.04 - 8.23 existence of stable oxide $Al_2O_3 \cdot 3H_2O$ forming a coherent film on the surface of aluminium can be supposed in initial stages of exposure even to oxygen free water. In this case if critical pH value 8.23 for reaction $Al_2O_3 \cdot 3H_2O = 2\ AlO_2^- + 2H^+ + 2H_2O$ is considered, pH of water can be stabilized on value 8.2 due to K_2HPO_4 and $Na_2B_4O_7$ additions to demonstrate initial conditions of passivity for aluminized tubes of steel. In these initial stages of exposure a film of oxide with barrier type of protection can so be supposed for underlying steel. In fact this barrier type of protection quality is related to Al coating ability to produce passivity in all parts of aluminized layer without possible occurrence of localized corrosion at the coating-steel interface. If Al coating produced on external surface of underlying steel can be influenced by the presence of weld area on internal surface, part of aluminized layer close to coating-steel interface tends to be cracked and tendency to localized corrosion is expected to increase. Electrochemical noise (EN) measurements provide a set of parameters which can be used to confirm these considerations.

2. EXPERIMENTAL

Test specimens used in this work were small segments of squared tubes made from aluminized carbon steel welded longitudinally (made in PRC). Aluminized layer was produced on external surface of squared tubes of carbon steel by hot dipping process with the following characteristics: thickness 25 µm, composition tabulated for aluminium Alloy 3003. For study of active-passive transitions in Al coating during 99 h of exposure to deaerated water solution with K_2HPO_4 and $Na_2B_4O_7$ (pH = 8.2) additions at 60 °C electrochemical noise (EN) measurements were used. Two identical specimens were used as working electrodes for these measurements performed on samples with (a) exposed area of coating over the weld area on internal surface and (b) exposed area of coating over no weld area on internal surface.

All measurements were performed in a special cell manufactured for EN measurements in SVUOM Ltd. This cell consisted of two cylindrical parts partially machined at intersection parts to get free intersection space between them for the electrolyte used for measurements. At the same time two openings were machined at the bottoms of both parts of this cell to make possible the installations of working electrodes. This arrangement enabled installation of a stirrer and heater element in order to attain the preset temperature in both parts of this cell as well as installation of a silver/silver chloride (reference) electrode. The working electrodes were fixed in the same positions (pressed against a rubber O-rings onto openings made at the bottoms of both parts of this cell). Tested solution was used in sufficient quantity to provide a volume-to-metal surface area ratio larger than 100 $ml \cdot cm^{-2}$ (including both corroding electrodes exposed area). Oxygen free conditions for tested solution were ensured by purging of nitrogen into tested solution during each of experiments.

Due to uninterrupted immersion test under conditions as indicated above EN signals were recorded on corroding electrodes using zero-resistance ammetry in open circuit, a procedure developed to monitor localized corrosion using noise methods. EN signals for given data set measured at different exposure times (1, 23, 27, 47, 51, 71, 75, 95 and 99 hours) were collected in measurement periods of 600 s with sampling frequency of 20 Hz using GAMRY potenciostat with ESA 410 software. All the data presented here are only in the form current noise data analysis in the time domain (more suitable for application of shot noise theory [2] to EN). If this theory is applied to EN for given bandwidth of measurement (b) only parameters including the mean current (I) and the standard deviation of the current fluctuations (σ_I) can be used for calculations of shot noise parameter q (the average charge in each event) without considering of Stern-Geary constant B. In this case (for the low power spectral density PSD of potential and current, e.i. for ψ_I and ψ_E) $\sqrt{\psi_I}$ and $\sqrt{\psi_E}$ can be replaced by $\frac{\sigma_I}{\sqrt{b}}$ and $\frac{\sigma_E}{\sqrt{b}}$ so that q can be represented by equation [3]:

$$q = \frac{\sigma_I^{\,2}}{2Ib} \tag{1}$$

This shot noise parameter can be considered as giving successful results when applied to discriminate between corrosion mechanisms [4]. Time change of this parameter estimated during the exposure of Al coating under conditions mentioned above was therefore used to discriminate between different degree of localized attack of Al coating on specimens of type (a) and (b).

3. RESULTS AND DISCUSSION

Nine measurements were performed on (a) type specimen as well as (b) type specimen during uninterrupted immersion tests under experimental conditions mentioned above. **Table 1** lists the parameters obtained by statistical analysis of these nine sets of current noise data for (a) type of specimen as well as for (b) type of specimen. These parameters included the mean current I and the standard deviation of current fluctuation σ_I.

In **Figures 1 - 2** the values of the shot noise parameter q estimated for (a) and (b) type of specimen had been plotted for different times of immersion under experimental conditions mentioned above. It can be seen that most q values obtained for (a) type of specimen lie in the range 10^{-8} - 10^{-7} C, while the most q values obtained for (b) type of specimen were between 10^{-10} - 10^{-9} C. From the point of shot noise analysis, the higher value of q, the more charge in each event representing active-passive transition, the more mass is being close in each anodic event. From **Figure 1** can be seen that active-passive transition is complicated for (a) type of specimen, probably due to defects formation in Al coating influenced by the presence of weld area on internal surface. In fact rather higher degree of localized corrosion development seems to be observed already after 27 h of exposure.

Table 1 Values of I and σ_I for (a) and (b) type of specimens after different time of exposure

exposure time (h)	(a) type specimen		(b) type specimen	
	I (A)	σ_I (A)	I (A)	σ_I (A)
1	6.992×10^{-6}	1.928×10^{-6}	27.572×10^{-9}	21.580×10^{-9}
23	7.298×10^{-6}	1.843×10^{-6}	0.557×10^{-9}	13.849×10^{-9}
27	2.332×10^{-6}	0.419×10^{-6}	8.602×10^{-9}	17.762×10^{-9}
47	5.390×10^{-6}	3.971×10^{-6}	188.985×10^{-9}	22.269×10^{-9}
51	5.411×10^{-6}	3.593×10^{-6}	228.859×10^{-9}	34.854×10^{-9}
71	6.813×10^{-6}	4.956×10^{-6}	730.236×10^{-9}	123.657×10^{-9}
75	4.642×10^{-6}	1.159×10^{-6}	642.864×10^{-9}	89.842×10^{-9}
95	7.065×10^{-6}	4.562×10^{-6}	651.422×10^{-9}	191.311×10^{-9}
99	6.366×10^{-6}	4.423×10^{-6}	632.067×10^{-9}	192.192×10^{-9}

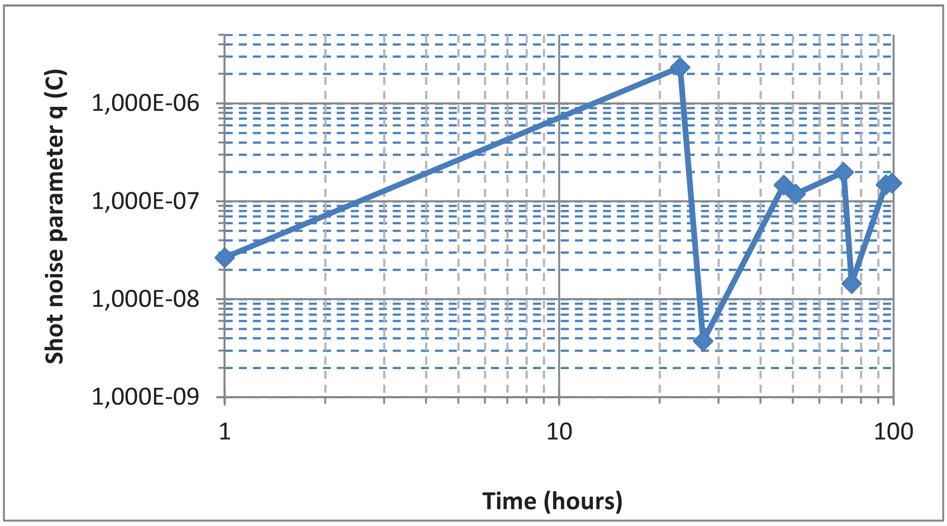

Figure 1 Shot noise parameter q development with time of exposure in oxygen free water (pH = 8.2) at 60 °C for (a) type of specimen

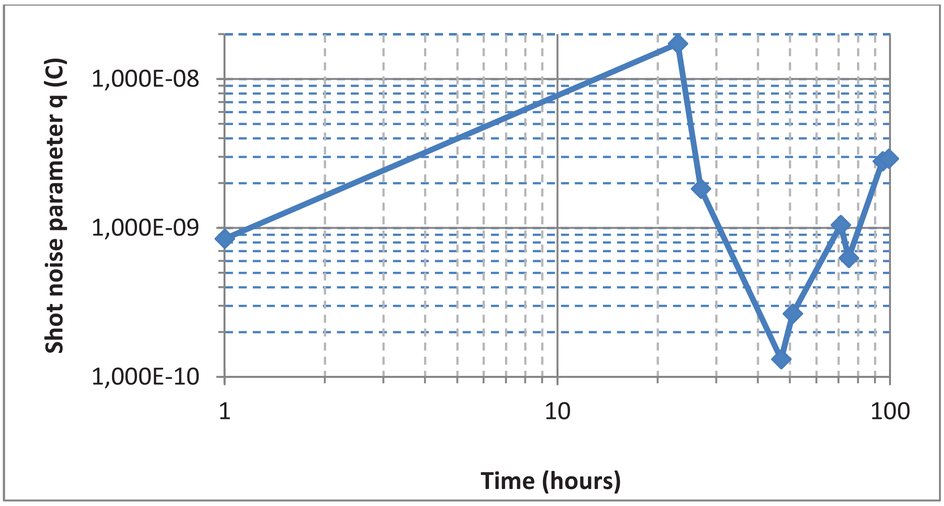

Figure 2 Shot noise parameter q development with time of exposure in oxygen free water (pH = 8.2) at 60 °C for (b) type of specimen

On the other hand as can be seen from **Figure 2** active-passive transition is not so complicated for (b) type of specimen and after 47 h of exposure rather case of passivity can be considered for this specimen with possible low degree of localized corrosion development after 99 h of exposure. When metallographic analysis was performed after the test of (a) and (b) specimens the metallographic evaluation and the EN results showed a reasonable experimental correlation (see **Figures 3 - 4** compared with **Figures 1 - 2**).

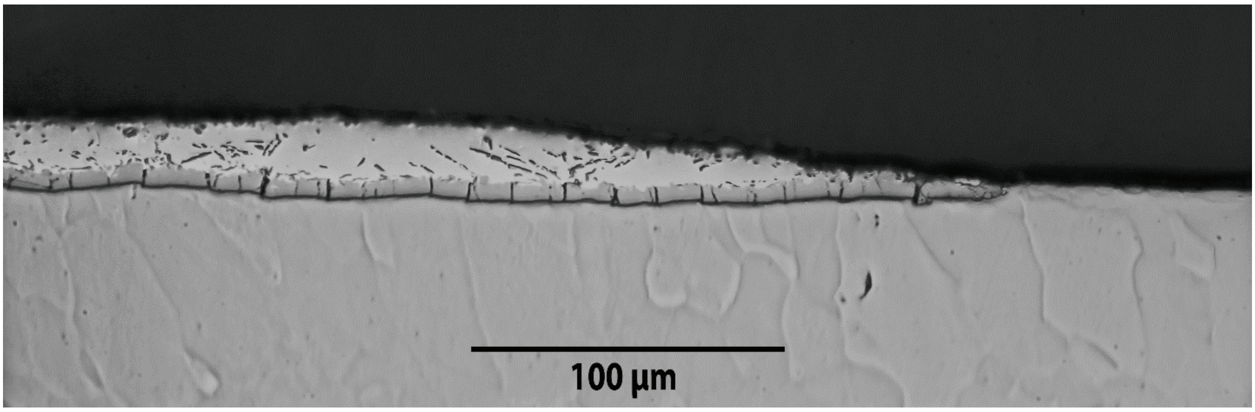

Figure 3 Cross-section of (a) type of specimen after 99 h of exposure in oxygen free water (pH = 8.2) at 60 °C

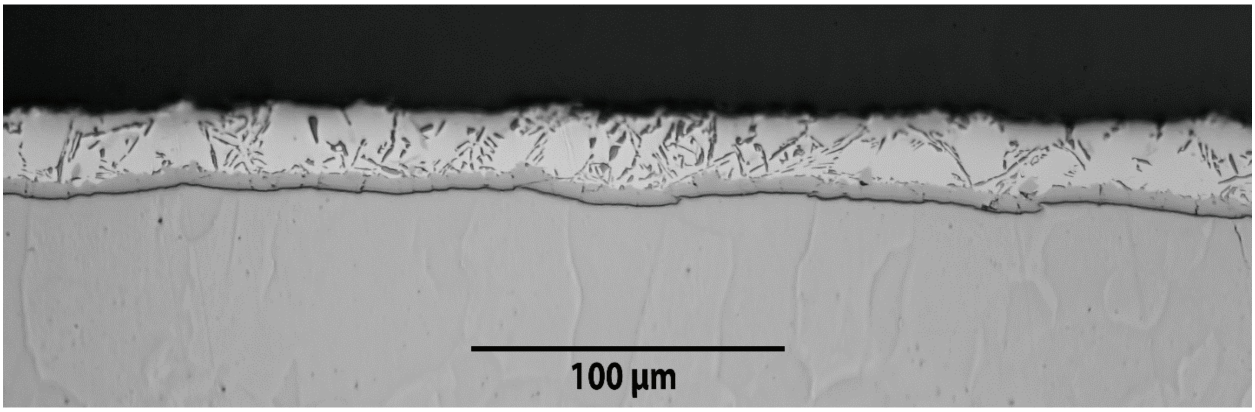

Figure 4 Cross-section of (b) type of specimen after 99 h of exposure in oxygen free water (pH = 8.2) at 60 °C

As can be seen from **Figure 3** cracks formation in interlayer at the coating-steel interface as well as partial delamination aluminized layer occurs for (a) type of specimen after test, while no cracks formation in interlayer and no delamination is observed for (b) type of specimen. Although these results showed some tendency relating metallographic observations and EN data for studied system, further investigations are required to explain possible impacts of time development of expected active-passive transitions in Al coating on kinetics of underlying steel corrosion process.

4. CONCLUSION

The presence of weld area on internal surface of cooling tubes manufactured of aluminized carbon steel seems to be problematic for application in deaerated water systems at 60°C even when inhibiting anions for stabilization of pH under critical value are present. More information is necessary for good prediction of corrosion risk expected at industrial applications.

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