IN-SITU ACOUSTIC EMISSION MONITORING OF ZINC-PHOSPHATE COATING FORMATION ON MILD STEEL

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Abstract

In the present work, acoustic emission (AE) technique, along with potential electrode measurements, is used to study the zinc-phosphate coating formation obtained on mild steel by cathodic electrochemical treatment (-15 mA.cm\(^{-2}\)) at ambient temperature. The AE activity recorded during the phosphate-coating formation shows evident links between this activity and the coating parameters such as potential electrode and coating weight. The principal component analysis (PCA) of AE parameters reveals the presence of three well-separated populations, A, B and C. The A population shows peak frequencies <180 kHz, high energy and lower rise time, the B population presents specific peak frequencies between 214-260 kHz, lower energy and longer rise time and the C population has peak frequency range at 280-320 kHz, lower energy and rise time. These events were respectively attributed to the evolution and release of hydrogen bubbles, the formation and growth of the phosphate layer, and the stress release generated by the hydrogen bubbles trapped in the coating pores.

1. Introduction

Acoustic emission (AE) has been developed for more than three decades as a non-destructive evaluation technique and is a useful tool for research on metallic materials. This technique can also be applied to characterize the electrochemical formation of coatings such as phosphatation. This phosphatation treatment is an industrially proven process with excellent corrosion resistance [1], a good adhesion and lubricating properties [2]. Generally, phosphatation processes reported in literature require high operating temperatures [3]. However different ways of accelerating phosphatation treatment at low temperatures have been explored. These require specific electrochemical methods. Sylla et al. [4] obtained Zn-Mn films by potentiostatic electro-deposition at potentials between -1.8 and -2 V/SCE at room temperature in aerated conditions. Jegannathan et al. [5] formed zinc-phosphate coating at 27°C by cathodic electrochemical treatment (CET). Thus, during the coating formation on steel, several phenomena occur simultaneously on the sample surface: hydrogen-bubble release and phosphate-coating growth. Different authors have demonstrated the AE sensitivity for detecting the hydrogen-evolution phenomenon during the corrosion of metallic materials. Indeed, Mazille et al. [6] showed that AE can be used to detect the pitting corrosion. Idrissi et al. [7, 8] have reported that the hydrogen-bubble release is the main AE source recorded during the pitting corrosion of aluminum alloys and the general corrosion of steel organic coating. Fregonese et al. [9] have also found this phenomenon on the pitting of AISI 316L austenitic stainless steel.

In this paper, we combine the AE technique, electrochemical measurements, microscopic (SEM, EDS) and XRD analysis in order to characterize and monitor phosphate-coating growth obtained by CET. The aim was to investigate if there is a qualitative or quantitative correlation between the AE parameters and electrochemical measurements, and to elucidate and characterize the different stages observed during CET. This study will in the long term allow one to control the process in order to obtain films having the desired properties (anti-corrosion, thickness, weight).
2. Experimental

Samples are made from mild steel rods FeE500 classically used in civil engineering. These rods are 8 mm in diameter and 60 mm in length. The samples have been chemically pickled with 36.5% HCl for one minute, then rinsed several times with deionized water to remove any acid residue formed during the pickling process, and finally a 5.5-cm² area is immersed in the bath. The samples were treated at a constant stirring rate of 100 rpm, under an applied current density of -15 mA.cm⁻² at ambient temperature.

The phosphatation bath (pH = 2.2) is used to investigate the in-situ zinc-phosphate coating formation and has the following composition:

\[ \text{Zn}^{2+} (0.2 \text{ M}) + \text{PO}_4^{3-} (0.35 \text{ M}) + \text{Ni}^{2+} (0.02 \text{ M}) + \text{NO}_3^- (0.08 \text{ M}) \]

The growth of the phosphate coating \(m_{\text{phosph}}\) was calculated as Zimermann et al. [10], according to: \(m_{\text{phosph}} = m_1 - m_2\), where \(m_1\) is the weight after phosphating and \(m_2\) is the weight remaining after eliminating the phosphate coating by immersion in a \(3.6 \times 10^{-4} \text{ M} \ (\text{NH}_4)_2\text{Cr}_2\text{O}_7 + 0.7 \text{ M NH}_3\) solution for 5 min.

The device used (Fig. 1) is composed of a classical 3-electrode electrochemical cell: reference electrode (SCE), platinum counter-electrode with 50 cm² area and working electrode (its area is 5.5 cm²).

AE acquisition device used in this study is composed of a wideband piezoelectric transducer (PAC WD) (100 kHz-1200 kHz), a pre-amplifier (EPA 1220A with 60 dB gain), and an acquisition card run with the MISTRAS 2001. Acquisition threshold is 28 dB and sampling rate is 5 MHz. After recording, AE features (signal number, hit number, peak frequency, rise time, duration, energy and waveform) have been analyzed.

The morphology and the coating compositions were studied by scanning electron microscopy (SEM) in SEI and EDS modes. Coating crystallographic structure was identified by X-ray diffraction measurement (XRD) using Cu K-\(\lambda(2,3)\) radiation.

3. Results and Discussion

3.1. Zinc-phosphate coating formation

Figure 2 shows SEM micrographs with the morphology of zinc-phosphate coatings obtained after different treatment durations. After one minute of treatment, the first grains grow on the steel surface (Fig. 2a). It can be observed that several small crystals, in a range of 0.2-3 µm in size cover a minor part of the steel surface. Two minutes later, the crystals are more developed and partially cover the surface (Fig. 2b). After 5 minutes, the surface is totally coated (Fig. 2c). The crystals are organized in a cauliflower-type structure, and this kind of structure has already observed from SEM micrographs on phosphate coatings by Lian et al. [11].

EDS analysis of the coating formed after 5-minute treatment shows the presence of phosphorus, zinc, iron and oxygen. According to Simescu [12] the formed phosphate coatings contain three phases: hopeite \((\text{Zn}_3(\text{PO}_4)_2.4\text{H}_2\text{O})\), phosphophyllite \((\text{Zn}_2\text{Fe(PO}_4)_2.4\text{H}_2\text{O})\) and metallic zinc.

3.2. Evolution of AE and electrochemical measurements correlation

The mild steel potential-time evolution and the AE detected during the CET are quite well correlated (Fig. 3). This evolution can be divided into three stages:

- Stage I: For the initial 2 minutes of depositing time, the measured potential strongly decreases towards more cathodic values and AE activity slightly increases.
- Stage II: From 2 to 5 minutes, the potential tends to stabilize and AE activity strongly increases.
Stage III: From 5 to 15 minutes, the stabilization of potential is almost reached and AE activity decreases and remains stable after 12 minutes of treatment.

3.2.1. Stage I: During the first stage of the phosphatation process, further reduction of oxides occurs, which were previously formed on the substrate surface by short contact with ambient air before treatment. This reduction leads to a strong decrease of the potential. After one minute of treatment the first grains of metallic zinc and non-metallic zinc phosphate appeared (Fig. 2a) simultaneously with the coalescence and release of hydrogen bubbles on the steel surface.

The principal component analysis (PCA) is applied on selected AE parameters (rise time, duration, energy and peak frequency) using NOESIS software. K-means clustering is used as an unsupervised method for the PCA analysis. The projection of correlation matrix obtained by PCA (first principal components PC1 versus zeroth principal components PC0) shows the presence of a population (noted A), which corresponds to a type of signal due to the hydrogen-bubble evolution (Fig. 4). The population A has high energy, low rise time and a peak frequency below 180 kHz (Fig. 5 and Table 1). These values are in accordance with those determined by Idrissi et al. [7] and Didier et al. [13] during the release of bubbles from metal surface.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>A</th>
<th>B</th>
<th>C</th>
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<tbody>
<tr>
<td>Rise time (µs)</td>
<td>&lt;75</td>
<td>&lt;100</td>
<td>50</td>
</tr>
<tr>
<td>Duration (µs)</td>
<td>&lt;200</td>
<td>&lt;150</td>
<td>80</td>
</tr>
<tr>
<td>Energy (aJ)</td>
<td>&lt;200</td>
<td>&lt;15</td>
<td>&lt;25</td>
</tr>
<tr>
<td>Peak frequency (kHz)</td>
<td>130-180</td>
<td>214-260</td>
<td>280-320</td>
</tr>
</tbody>
</table>
3.2.2. Stage II: From 2 to 5 minutes, the potential begins to stabilize and AE strongly increases. This AE intensification is due not only to a strong hydrogen bubble evolution \([2H^+ + 2e^- \rightarrow H_2]\), but also to the formation of metallic zinc \([Zn^{2+} + 2e^- \rightarrow Zn]\) and zinc phosphate crystals on the sample surface (Fig. 2b). Donofrio [2] has shown that these two reactions result in the increase of local pH at metal-solution interface, which facilitates the precipitation of insoluble phosphates according to the following reactions:

\[
\begin{align*}
3Zn^{2+} + 2H_2PO_4^- + 4H_2O + 6e^- & \rightarrow Zn_3(PO_4)_2.4H_2O + 3H_2 \\
2Zn^{2+} + Fe^{2+} + 2H_2PO_4^- + 4H_2O + 6e^- & \rightarrow Zn_2Fe(PO_4)_2.4H_2O + 3H_2
\end{align*}
\]  

Figure 6 shows the projection of correlation matrix obtained by PCA (PC1 versus PC0) in Stage II. This plot clearly shows the presence of two well-separated populations A and B, corresponding to two types of signals due to release of hydrogen bubbles and formation and growth of phosphate coating (Fig. 5). The population A was also detected during Stage I.

The population B has lower energy, longer rise time, and a peak frequency between 214 and 260 kHz (Table 1). This population was due to the metallic Zn and non-metallic Zn-phosphate coating formation (hopeite and phosphophyllite). The same frequencies were reported by Chotard et al. [14, 15] during the characterization of early stage of calcium-aluminate cement hydration and by Ramadan and Idrissi [16] during the calcium-carbonate deposition on Cu surface.

3.2.3. Stage III: After 5 minutes, the surface is completely coated. Consequently, hydrogen evolution and AE activity decreased. The potential tends to increase slightly, acting as a marker of zinc phosphate coating growth as it was observed also by Jegannathan et al. [17].

Plot of the third principal components (PC3) versus second principal components (PC2) shows three separate directions. This means that AE signals are divided into three populations A, B and C. We also note that the hit number of population A is much less important than for the two other populations recorded during this stage (Fig. 7). The new population (noted C) has low
energy and rise time. These C signals have typical frequencies between 280 and 320 kHz (Fig. 5). The C signals are attributed to the stress release generated by hydrogen bubbles trapped in the coating pores [18, 19]. The signals with frequencies located around 300 kHz was also attributed by Assouli et al. to the stress release phenomenon during selective corrosion of α-β’ brass [20].

To validate this classification a test using k-nearest-neighbor (kNN) method was applied on selected AE parameters. In the kNN algorithm, the classification of a new sample is determined by the class of its k-nearest neighbors. This method gives 1.6% error and confirms the existence of three well-separated populations. Table 2 shows the feature discriminated statistics of AE parameters.

### Table 2 Feature discriminated statistics from PCA analysis.

<table>
<thead>
<tr>
<th>AE parameters</th>
<th>Wilk’s R</th>
<th>Rij</th>
<th>Tou</th>
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</thead>
<tbody>
<tr>
<td>Rise time</td>
<td>0.9501</td>
<td>1.0912</td>
<td>1.1611</td>
</tr>
<tr>
<td>Duration</td>
<td>0.9814</td>
<td>5.8311</td>
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<tr>
<td>Energy</td>
<td>0.9884</td>
<td>6.2549</td>
<td>0.2067</td>
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<tr>
<td>Peak frequency</td>
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<td>17.1653</td>
<td>0.1061</td>
</tr>
</tbody>
</table>

Fig. 7. PCA of AE parameters (a) and 3D plot of AE parameters during Stage III.

### 3.3. Correlation between the kinetic of phosphate growth and AE evolution

Figure 8 shows the evolution of cumulative AE activity as well as the phosphate coating weight increase vs. phosphtation time. The tendency of these curves is similar, showing that the kinetics of phosphate-coating formation on the mild steel can be followed qualitatively by the AE technique. This result is useful for industrial applications. The AE technique can be considered as a potential tool to characterize the coatings growth. This “passive technique” allows a continuous and *in-situ* monitoring of coating formation.

Fig. 8. (a) Cumulative AE signals and (b) phosphate-coating weight variation vs. CET.

The growth kinetics of phosphate-coating show that the coating-formation process starts slowly in the beginning (0-2 minutes), and then it increases rapidly between 3 and 10 minutes (Fig. 8b). After 10 minutes, the coating growth is slow. The low weight increase during this time period could be explained, firstly by the dissolution followed by the precipitation of the phosphate coating and, secondly by the pH increase at the sample-solution interface, which, after Jegannathan et al. [17], interferes with the zinc-phosphate precipitation. Under these conditions, phosphatation rate is quasi-constant.
4. Conclusions

The results presented in this paper show that AE techniques coupled to electrochemical measurements could be used as a reliable tool to monitor the phosphate-coating formation and the possibility of forming a well-crystallized coating on mild steel surface. This technique allows a continuous and in-situ monitoring of phosphate formation.

The potential-time measurements coupled to AE show a good correlation, especially for the decrease of released hydrogen during this coating growth. Thereby, three populations (A, B and C) detected during the phosphatation process have been identified in this work. They were attributed to typical frequencies of:

1- The coalescence and the release of hydrogen bubbles (f<180 kHz).
2- The formation of metallic zinc and non-metallic zinc-phosphate coating: Zn₃(PO₄)₂.4H₂O, Zn₂Fe(PO₄)₂.4H₂O, Zn (214 kHz ≤ f ≤ 260 kHz).
3- The stress release generated by hydrogen bubbles trapped in the coating pores (280 kHz ≤ f ≤ 320 kHz).

The AE evaluation allows correlating each physical process that occurs during coating formation to a specific AE activity. In further works, this technique would be applied to control other types of electrochemical coatings and to draw in-situ qualitative criteria (thickness, porosity, crystallization) by differentiating various AE parameters, such as specific AE peak frequencies, rise time, energy, duration or waveform.

Acknowledgment

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References