Studying phosphate corrosion inhibition at the cut edge of coil coated galvanized steel using the SVET and EIS

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The work deals with the effect of sodium phosphate on the corrosion at the cut edge of electrogalvanized steel, studied by potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and the scanning vibrating electrode technique (SVET). Mapping of the ionic currents revealed that in non-inhibiting solution, the cathode shifts away from the anode as zinc corrosion products precipitate along concentric whitish lines that result from the location of the peak cathodic current. Sodium phosphate inhibits corrosion at the cut edge by precipitation of gel-like zinc phosphate clusters with barrier properties. Breakdown and repassivation of this layer can occur under certain conditions.

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1. Introduction

For coil-coated steel manufacturers, corrosion at cut edges is a major cause of delamination and consequent degradation, because of the unfavourable anode-to-cathode area ratio, which leads to accelerated dissolution of zinc [1].

During galvanic corrosion of a zinc/steel couple in neutral NaCl solution, Zn dissolves to form Zn^{2+} ions, whereas dissolved oxygen is reduced on the steel surface, to form hydroxyl ions:

anodic reaction : \( \text{Zn}(s) \rightarrow \text{Zn}^{2+}(aq) + 2e^- \) (1)
cathodic reaction : \( \text{O}_2(g) + 2\text{H}_2\text{O}(l) + 4e^- \rightarrow 4\text{OH}^-(aq) \) (2)

In a cut edge, the narrow dimensions of the zinc and steel electrodes, plus the immediate proximity of cathode and anode, cause strong chemical interactions and large concentration gradients of the intervenient species, thus affecting the chemistry of the process compared to self-corrosion of a homogeneous metallic material. As a consequence of this, there are important differences compared to the regular surface exposure. One of these changes has to do with the alkalisation of the solution near the cathode caused by reaction (2), which causes the precipitation of zinc corrosion products not over the zinc, as in self-corrosion conditions, but rather on steel.

The use of inhibitors for this form of galvanic attack is not trivial, because of the high electromotive force and high corrosion rates involved. Preliminary studies comparing various inhibitors have revealed sodium phosphate as a potential inhibitor for this situation. Phosphates are classified as non-oxidising anodic inhibitors for zinc, although their action as cathodic inhibitors has also been reported [2]. The mechanism by which phosphate acts is not totally understood but it is generally accepted that phosphate ions in solution react with metal cations released from the surface and precipitate a film with barrier properties at anodic areas. Enhanced cathodic inhibition may occur in the presence of Ca^{2+} or Zn^{2+} ions in solution, due to precipitation of calcium phosphate on the alkaline cathodic areas:

\( 2\text{HPO}_4^{2-} + 2\text{OH}^- + 3\text{Ca}^{2+} \rightarrow \text{Ca}_3(\text{PO}_4)_2 + 2\text{H}_2\text{O} \) (3)

This study deals with the effect of sodium phosphate on the galvanic corrosion of electrogalvanized steel at cut edges.

The scanning vibrating electrode technique (SVET) is particularly useful for systems where lateral resolution is important, due to its capability to map anodic and cathodic currents. Particularly, its previous applications to cut edge corrosion have provided relevant mechanistic information. Ogle et al. have followed the shift of the cathodic activity on steel away from the zinc-steel interface as zinc corrosion products precipitate on steel starting from the anode and related it with the pH gradients on the steel surface resulting from oxygen reduction [3]; the existence of different areas on the steel surface was also reported, the area near the zinc being under cathodic inhibition and thus with hardly any cathodic activity, while at central area the cathodic reaction proceeded [4]. The SVET was also used by Worsley et al. [5] to show that application of different organic coatings on the two sides of galvanized steel results in anodic delamination on the side with the less porous coating, due to differential aeration. Other studies are also reported.

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in the literature, namely the effect of the thickness of the sacrificial coating or of the effect of magnesium additions \[6,7\].

In our work the SVET was used to monitor the evolution of the galvanic currents and compared with the results from electrochemical impedance spectroscopy.

2. **Experimental**

2.1. **Materials and solutions**

For the EIS and the potential measurements, samples consisted of cross-cut specimens of electrogalvanized steel (zinc layer with 7 µm on both sides of a 800 µm steel sheet) mounted in resin and polished up to 4000 grit. With this setup, Zn/Fe galvanic couples were exposed, with an area ratio of approximately 1 Zn:50 Fe and a total exposed area of 0.10 cm². Measurements were made until 48 h of immersion. Electrodes of steel and of pure zinc (Goodfellow) were also resin-mounted. Surface preparation consisted of polishing the mounted electrodes with SiC and diamond paste down to grade 1 µm, followed by rinsing with water and degreasing with ethanol. In order to minimize any smearing of zinc or steel at the cut edge, polishing was made only parallel to the zinc–steel interface. Before starting the experiments, microscopy inspection of the electrodes was made, in order to avoid any defects. The electrodes had typically an area of ∼0.1 cm², except for the SVET measurements, for which a length of 2 mm or less was delimited using adhesive tape. No signs of preferential corrosion under the tape were seen. The electrochemical study was made at room temperature using a naturally aerated 0.1 M NaCl aqueous solution, with a Na₃PO₄ concentration of 0.01 M or 0.001 M. The exception to this was the SVET study, for which a lower NaCl concentration was used – 0.01 M – in order to decrease the conductivity and thus increase the electric field. All the solutions were prepared using distilled water.

2.2. **d.c. and EIS measurements**

The d.c. electrochemical measurements were made using an AUTOLAB PGstat 20 apparatus, using the saturated calomel electrode (SCE) as reference and a platinum counter electrode. Potentiodynamic polarization was made separately on steel and on zinc electrodes, at a scan rate of 1 mV/s, starting from the open circuit potential. The results are referred to an area of zinc of 0.02 cm² and for iron, of 1 cm², in order to make them correspond to the actual area ratio at a cut edge.

For the impedance measurements a 1250 Frequency Response Analyser + 1286 electrochemical interface (both from Solartron) were used. Impedance spectra were collected at the open circuit potential, in the frequency range 50 kHz to 0.01 Hz, with signal amplitude of 10 mV rms.

The inhibition efficiency was determined from impedance measurements made on each of the pure metals and using Eq. (4):  
\[
\text{efficiency} = 1 - \frac{R_{ct}}{R_{0ct}} \times 100\% 
\]

in which \(R_{ct}\) and \(R_{0ct}\) correspond to the charge transfer resistance in the inhibited solution and in the blank solution respectively, for the same exposure times, determined from the low frequency impedance, for which 12.6 mHz was chosen.

2.3. **SVET measurements**

The scanning vibrating electrode technique (SVET) was applied using a setup from Applicable Electronics Inc. and the ASET program (Scieneewares). The vibrating electrode was made of platinum-iridium coated with polymer (Microprobe Inc.), leaving only an uncovered tip with a black platinum deposit with ∼20 µm diameter. The probe works as a pseudo-reference elec-

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**Fig. 1.** Polarization curves of steel and pure zinc in 0.1 M NaCl, for 0 h and 1 h of immersion. Currents referred to a steel area of 1 cm² and a zinc area of 0.02 cm².

**Fig. 2.** EIS of steel (a) and of pure zinc (b) in NaCl 0.1 M, at the beginning of exposure and after 24 h and 48 h.
trodé, sensing the potential vs. a stationary Pt electrode. Conversion of potential measurements to local ionic currents was made using previous calibration. The probe was used to scan the surface at a constant height of 200 μm, with vibration amplitude of 20 μm; the frequencies of vibration were 325 Hz and 124 Hz in the vertical and horizontal directions, respectively. Maps were made on a 2 mm × 3 mm area with a matrix of 21 × 31 points. Only the normal (vertical) component of the current is shown.

3. Results and discussion

3.1 Behaviour in the non-inhibiting solution

The electrochemical reactions involved in the galvanic corrosion of the cut edge are the oxidation of zinc at the anode and the reduction of oxygen at the cathode. The polarization plots for the anodic branch on zinc and the cathodic branch on steel (Fig. 1) show a high electromotive force for the galvanic process, of nearly 600 mV in the initial stages. The coupling potential is very close to the corrosion potential of zinc, because the reaction is controlled by the diffusion rate of oxygen to the steel surface. For later stages, if the two electrodes were left under conditions of self-corrosion, there is significant cathodic polarization of steel, caused by a decrease in the oxygen limiting diffusion plateau, which, in the absence of other effects, can be expected to reduce the galvanic current, as observed in the intersection of the two curves for 1 h of immersion. Naturally, the results obtained by this procedure do not reveal the effect of the zinc oxide precipitated on steel, which would decrease the cathodic current even further. The effect on zinc is less pronounced, with only small variations in the currents measured. Extrapolation of the currents to the corrosion potential reveals that for self-corrosion, the corrosion rates of the two metals remain nearly constant. This is confirmed by the impedance plots of each of the two metals – Fig. 2 – where we observe a low frequency impedance in the range 200–1000 Ω cm², indicating active corrosion. In both cases there was a slight impedance drop in the first day of immersion, but after that the spectra remained practically stable until the 48 h.

For the galvanic couple the impedance measured in the first hour of immersion was comparable to that of the isolated metals – Fig. 3. The total impedance was 300–400 Ω cm² and increased with time, becoming four times larger after 48 h of immersion. This reveals some degree of self-healing at the cut edge, resulting from the precipitation of the zinc corrosion products over the steel surface. The Bode plot reveals two time constants. For the first instants of immersion, the process at ~200 Hz is attributed to the charge transfer process, whereas the low frequency process may be related to the diffusion limitations caused by the high reaction rate. The response of the charge transfer becomes shifted to lower frequencies as the active area expands, increasing the capacitance. Meanwhile, another process, with very low resistance, appears at high frequencies. This process appears at approximately 200 Hz but the evolution of the system suggests that it is a new process. Its origin is not clear but it may result from the cathodic reaction or from the precipitation of zinc hydroxide:

\[
\text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2
\]

According to the Pourbaix diagram for zinc, zinc hydroxide is stable at pH values above 8, a value that is easily reached over steel[18]. Further, carbonates can also form, eventually leading to hydrozincite,

---

**Table 1**

Values used in the fitting of equivalent circuit, in 0.1 M NaCl (blank solution).

<table>
<thead>
<tr>
<th>T/h</th>
<th>(Y_1 (\Omega^{-1} \text{ cm}^2 \cdot \text{s}^\alpha))</th>
<th>(R_1 (\Omega \text{ cm}^2))</th>
<th>(Y_2 (\Omega^{-1} \text{ cm}^2 \cdot \text{s}^\beta))</th>
<th>(R_2 (\Omega \text{ cm}^2))</th>
<th>(Y_1 (\Omega^{-1} \text{ cm}^2 \cdot \text{s}^\delta))</th>
<th>(R_3 (\Omega \text{ cm}^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cut edge</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>(3 \times 10^{-4})</td>
<td>(-)</td>
<td>(-)</td>
<td>(7 \times 10^{-5})</td>
<td>362</td>
<td>0.02</td>
</tr>
<tr>
<td>24</td>
<td>(3 \times 10^{-4})</td>
<td>30</td>
<td>(5 \times 10^{-4})</td>
<td>670</td>
<td>(-)</td>
<td>(-)</td>
</tr>
<tr>
<td>48</td>
<td>(3 \times 10^{-4})</td>
<td>12</td>
<td>(1 \times 10^{-3})</td>
<td>1166</td>
<td>(-)</td>
<td>(-)</td>
</tr>
<tr>
<td>Zinc</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>(3 \times 10^{-4})</td>
<td>(-)</td>
<td>(-)</td>
<td>(7 \times 10^{-5})</td>
<td>246</td>
<td>0.01</td>
</tr>
<tr>
<td>24</td>
<td>(9 \times 10^{-4})</td>
<td>17</td>
<td>(1 \times 10^{-3})</td>
<td>205</td>
<td>0.3</td>
<td>80</td>
</tr>
<tr>
<td>48</td>
<td>(9 \times 10^{-4})</td>
<td>22</td>
<td>(1 \times 10^{-3})</td>
<td>198</td>
<td>0.11</td>
<td>233</td>
</tr>
</tbody>
</table>
According to [9]:

\[ \text{Zn(OH)}_2 + 4\text{Zn}^{2+} + 4\text{OH}^- + 2\text{CO}_3^{2-} \rightarrow \text{Zn}_5(\text{CO}_3)_2(\text{OH})_6 \downarrow \]  

Most of the publications applying impedance to corroding systems use continuous metals and not galvanic couples. In such a system, the interpretation of impedance spectra may be facilitated by the results for the separate metals. In this case, it is interesting to note the resemblance between the spectrum for the cut edge and that of zinc in self-corrosion. This can be explained by the fact that the two relaxations processes are geometrically in parallel and therefore the process with lower impedance, i.e., the anodic process is the one that predominates.

Fitting of the spectra of the sample exposed to the non-inhibiting solution – Fig. 4 – has two relaxation constants. Although the response derives essentially from the anodic reaction, there may be also a slight effect of the cathodic reaction, as discussed above, suggesting the separation of cathodic and anodic areas. The capacitive components have high values, possibly revealing diffusion influence. The results from the fitting – Table 1 – confirm the similarity between the impedance of the cut edge and of zinc.

3.2. Effect of sodium phosphate

Addition of Na₃PO₄ to the salt solution led to an impedance rise of steel by nearly one order of magnitude (Fig. 5). This inhibition was fairly stable, with only a slight decay for long exposure times. At intermediate frequencies the capacitive slope becomes shifted to higher \(|Z|\) values, revealing a decrease in the capacitance and consequently a decrease of the active area, whereas an increase of the low frequency resistance reveals a decrease of the corrosion rate. On zinc the spectrum was truncated due to the low frequency noise (Fig. 6), but the effects discussed above, of the decrease of capacitance and the increase of resistance were more pronounced than on steel. Finally, on the cut edge the effect of

Fig. 5. EIS of steel after 24 h in NaCl 0.1 M, with (■) and without (□) sodium phosphate.

Fig. 6. EIS of zinc after 24 h in NaCl 0.1 M, with (■) and without (□) sodium phosphate.

Fig. 7. Impedance spectra of cut edge in 0.1 M NaCl, with (filled) and without (open) phosphate addition. Time: 0 h (square) and 24 h (triangle) hours of immersion.

Fig. 8. Impedance spectra of cut edge after 24 h in 0.1 M NaCl with Na₃PO₄. Fitting parameters: \(Y_1 = 1 \times 10^{-4} \text{ cm}^{-1} \text{ s}^2\); \(n_1 = 0.80\); \(R_1 = 7400 \Omega \text{ cm}^2\).

phosphate is evidenced not so much on the capacitance, but rather by the rise of the low frequency impedance – Fig. 7. In contrast with the non-inhibiting solution, the spectrum of the sample in the phosphate-containing solution remains fairly stable, meaning that the system changes within the first hour and then remains pseudo-stationary. The equivalent circuit revealed only one time constant – Fig. 8 – with higher resistance values compared to the blank test. The capacitive component is in the same range as in the absence of phosphate, indicating lower corrosion rates. Further, the shape of the spectrum changed deeply, namely the response of the zinc processes observed above is not evident any more, suggesting that either the corrosion mechanism or at least the processes on the zinc have changed. The inhibiting efficiency after 24 h determined from the low frequency impedance was 99% for zinc, 78% for iron and 87% for the cut edge, for the 0.01 M phosphate concentration.

The ionic current maps reveal diverse features of the activity at the cut edge in the presence and in the absence of the phosphate. The values of the local ionic currents decrease to roughly half to one third of those in the blank test – Fig. 9. Naturally, these correspond to peak values and not to average values, and thus cannot be used to estimate the inhibiting efficiency. Compared to the behaviour in the blank NaCl solution, the phosphate causes smaller anodes, with shorter lifetime, due to the formation of a colloidal white precipitate at the anodic sites. These anodes apparently grow until they become plugged by the zinc phosphate precipitate. This corresponds to a significant change in the healing effect: the phosphate acts locally on zinc, whereas in the blank NaCl solution the self-healing results from the precipitation of zinc hydroxide on the cathodic steel. Since under natural conditions the corrosion at the cut edge occurs under oxygen diffusion control at the cathode, then this anodic inhibition can only occur with a change in the rate control to mixed activation control. This means that the precipitation of the sparingly soluble zinc phosphate [10] on the surface:

\[
3Zn^{2+} + 2(PO_4)^{3-} \rightarrow Zn_3(PO_4)_2
\]

(7) is capable of drastically polarizing the zinc oxidation, up to the point of changing the rate control from cathodic to mixed activation control.

Inspection of the surface at the end of the experiment has shown that, compared to the zinc hydroxide, the precipitation of zinc phosphate is not driven by the alkaline pH over the steel, since the deposits are mostly centered on the zinc surface – Fig. 10(a). These deposits contain essentially zinc phosphate, as confirmed by EDS – Fig. 10(b).
4. Conclusions

The effect of sodium phosphate on the galvanic corrosion of a cut edge was studied. The behaviour of the cut edge was compared to that of self-corrosion of steel and of zinc. The inhibiting efficiency indicated moderate inhibition for the cut edge, with values below those for zinc but higher than for steel.

The protection mechanism involves trapping of zinc ions released over the anode, which precipitate over the anode and later over the cathode. The SVET technique provided information concerning the lifetime of anodes and cathodes and revealed some repassivation of local anodes by the precipitation of zinc phosphate. In the presence of phosphate, zinc dissolution was more localized and the lifetime of local anodes was shorter than in the non-inhibiting NaCl solution.

Acknowledgement

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References


Fig. 10. Micrograph of precipitate formed over the zinc in phosphate solution (a) and EDS analysis (b) on steel (···) and on precipitate (—).