Pitting transients analysis of stainless steels at the open circuit potential

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Abstract

Metastable pitting of stainless steels in chloride containing oxidising electrolytes is investigated at rest potential using a new experimental technique allowing to record simultaneously the potential and corrosion current variations. Different industrial surface conditions (BA and 2B) are tested for both ferritic (FeCr type) and austenitic (FeCrNi type) stainless steels. It was shown that the number of pitting events decreases with the exposure time and that BA condition provides better resistance to pitting than 2B. As far as pitting mechanisms are concerned, the potential recovery after pitting does not reflect the pit repassivation but rather refers to the discharge of the surface capacity. Analysing the pitting transients provides quantitative information on the cathodic reaction through the passive film (transfer resistance and surface capacitance). Differences in pitting transient shapes are discussed as well.

Keywords: Pitting corrosion; Stainless steel; Open circuit potential; Potential transient; Current transient

1. Introduction

Electrochemical transient measurement techniques have been successfully used for many years to investigate localised corrosion processes and more particularly pitting
corrosion of passivable alloys [1–5]. Operating at open circuit potential allows to measure the signals spontaneously generated by the corroding interface, without any perturbation due to external polarization. Last, recording simultaneously the potential and the corrosion current variations is of great interest for the understanding of the pitting mechanisms. It is intended in this work to apply these techniques to different stainless steels, aiming to clarify the interpretation of the successive steps of the metastable pitting processes.

On stainless steels, open circuit metastable pitting potential transients consist of four successive stages (Fig. 1), what Hashimoto et al. [6] attributed respectively to (1) pit initiation, (2) growth start, (3) growth end and (4) pit repassivation. At the opposite, Isaacs [7–10] believes that step (4) rather corresponds to the discharge of the interface capacity on the repassivated surface, at least for slow cathodic reactions as oxygen evolution. Measuring simultaneously the corrosion current and the rest potential variations [1,2] should then bring a decisive information in this debate.

Moreover, it is well known that the pitting resistance of industrial stainless steel sheets depends not only of their chemical composition but also on their finishing condition, mainly the final annealing after cold working. Some typical finishing conditions are referred to as 2B and BA (bright annealing). The 2B surface condition is obtained when the cold rolled sheet is annealed in an oxidising atmosphere, then pickled in acid for removing the oxide scale. The BA condition (bright annealed) is the result of a final annealing carried out in an hydrogen or hydrogen + nitrogen atmosphere. The result is a bright surface, without any metal oxide and then no further pickling is needed. In the first case the passive film is formed during water rinsing after the pickling treatment and also further ageing in the in-service conditions. In the last one, the passive film is formed during the annealing treatment itself due to the water residual content in the hydrogen atmosphere [11]. It is out of the scope of this paper to discuss these points in more details, but is well known in industrial practice that the pitting corrosion resistance in chloride containing environments is much better for BA surface finishes than for 2B ones.

It is intended in this work to investigate the effect of these surface conditions on metastable pitting from an electrochemical point of view, with the significance of the successive steps observed at open circuit potential. In this purpose we developed a specific experimental procedure to record simultaneously the current and potential transients generated at rest potential by metastable pitting occurring in a chloride containing electrolyte. An

![Fig. 1. Schematic representation of the potential vs. time variations during metastable pitting [2]. Four successive steps are observed (see text).](image-url)
oxidising agent (FeCl₃) was added to promote pit initiation and to control the cathodic reaction around the pit.

2. Experimental and data processing

The electrochemical cell includes two identical working electrodes connected through a low impedance ammeter, and a standard calomel reference electrode (SCE), which allows to measure simultaneously the intensity and potential variations (Fig. 2) in open circuit conditions. The input impedance of the ammeter varies from 1 to 10⁶ Ω, depending on the used calibre. The input voltage drop is smaller than 250 µV and the accuracy of the measures is better than ±0.1%. The SCE input impedance voltmeter is close to 10¹³ Ω. The offset drift is lower than 100 µV and the accuracy of the measures is better than ±0.1%. During corrosion testing, the data sampling rate was \( f_s = 46.875 \) Hz, which gives a sufficient resolution without having to filter the signals (which could lead to a loss of information). Nevertheless, an anti-aliasing filter was additionally used. The cut-off frequency of this filter is set to \( f_s/2.35 \), hence the higher measurable frequency is of 20 Hz. All the set-up is made of low noise level components. The measuring instruments are made by Alpes Instruments® and are driven by the date acquisition processing software Mustig by Grésilog®.

The materials under investigation were some industrial ferritic Fe16Cr (AISI 430) and austenitic Fe18Cr9Ni (AISI 304) 1 mm thick stainless steels sheets (see chemical composition in Table 1), provided by the company Ugine-ALZ (Arcelor group) with 2B or BA surface conditions.

Tested specimen were some 10 mm diameter disks (exposed area = 7.1 cm²), cut from the industrial sheets. After degreasing in alcohol + acetone then rinsing, these specimen were immersed during 24 h in a NaCl containing aqueous solution (0.02 M for ferritic stainless steel and 1 M for austenitic stainless steel) at pH 6.6 and 23 °C. No metastable

![Fig. 2. Schematic representation of the experimental set-up with two identical working electrodes (subscripts 1 and 2) connected through a low resistance ammeter (ZRA). \( i_m \) is the measured current through the ammeter, \( i_k \) the cathodic current and \( i_a \) the anodic pitting current. \( V \) and \( Q \) are the potential and the charge of the electrodes.](image-url)
pit is observed within the time and the metal water interface is believed to simply stabilise. After 24 h the specimen are immersed in the corroding electrolyte, an aerated (0.02 M or 1 M) NaCl + \((2 \times 10^{-4} \text{ M})\) FeCl\(_3\) aqueous solution kept at 23 °C. The pH of this solution is close to 3.5 (which is larger than the depassivation pH of the investigated steels). Some current and potential transients are observed. Each current transient corresponds to a potential transient, which likely results to the initiation then repassivation of a metastable pit.

For each metastable pit, the electrical charge balance writes

\[
\frac{dQ_1}{dt} = -i_a + i_k + i_m = CS \frac{dV_1}{dt} \tag{1}
\]

and

\[
\frac{dQ_2}{dt} = i_k - i_m = CS \frac{dV_2}{dt} \tag{2}
\]

where \(S = 7.1 \text{ cm}^2\) is the electrode area, \(i_m, i_a (>0)\) and \(i_k (>0)\) respectively the measured, anodic and cathodic currents, \(Q\) the electrical charge and the subscripts 1 and 2 refer to the two working electrodes.

In this simplified model, \(C\) is the total interface capacitance, i.e., a combination of the Helmholtz capacitance, the space charge film capacitance, etc.

As the resistance of the electrolyte was found less than 100 Ω and the measured current \(i_m\) is close to or less than 10 μA, the potential difference between the two electrodes is smaller than 1 mV, which can be neglected regarding to the measured potential fluctuations (100 mV). Writing \(V = V_1 = V_2\), one obtains

\[
i_k = CS \frac{dV}{dt} + i_m \tag{3}
\]

and

\[
i_a = 2 \times i_m \tag{4}
\]

which are the master equations needed for further analysis of the current transients.

Linearizing the cathodic current potential dependence one finds

\[
i_k = \frac{V_0 - V}{R/S} \tag{5}
\]

where \(V_0\) is the metal electrolyte potential difference in the passive state, i.e., before or after any metastable pitting event, and \(R\) the electron transfer resistance at this potential. Eq. (3) writes now

\[
V_0 - V = RC \frac{dV}{dt} + \frac{R \cdot i_m}{S} \tag{3b}
\]

where \(RC\) is the time constant for the electron transfer through the passive interface.
3. Results

3.1. Typical signals

Typical potential and intensity signal are shown in Fig. 3. The sensitivity to pit nucleation can be first assessed by simply counting the number of transients (Fig. 4) during a 24 h experiment. One sees that

1. this number increases roughly logarithmically with time, which suggests a reinforcement of the passive film during the test, leading to the decrease of the pitting sensitivity;
2. this number is much smaller for the BA surface condition than for the 2B one. This is in accordance with the industrial evidence following which BA resists better to pitting corrosion than 2B;
3. the potential drops are larger for BA than for 2B specimen (Table 2).

![Fig. 3. Typical potential and current plots in metastable pitting condition (Fe16Cr). Positive and negative current transients correspond to metastable pitting on the two different working electrodes.](image)

![Fig. 4. Cumulative number of transients vs. immersion time for (a) Fe16Cr in NaCl 0.02 M pH 6.6 + FeCl₃ 2 × 10⁻⁴ M and (b) Fe18Cr9Ni in NaCl 1 M pH 6.6 + FeCl₃ 2 × 10⁻⁴ M.](image)
3.2. Single transients

At each metastable pit corresponds a potential and an intensity transient, characterized by a potential drop \( \Delta V \), a maximum current, and a current transient life-time (see Table 2). The following features are evidenced (Fig. 5):

1. The potential transient shows first a sharp decrease starting from the starting point A down to a minimum J (\( \frac{dV}{dt} = 0 \)). This decrease is followed by a slow exponential type increase.

2. Intensity first increases from the starting point A to a maximum M, close to (but not exactly on) an inflexion point observed on the potential transient. Then, the intensity decreases from this maximum to zero (point N) slightly after the potential minimum (point J). N corresponds to the pit repassivation and then the final potential increase (Fig. 1) does not point the pit repassivation but rather the discharge of the interfacial capacitance by the cathodic reaction (reduction of \( \text{Fe}^{3+} \) to \( \text{Fe}^{2+} \)), which validates the Isaacs model \([7–10]\) rather than the Hashimoto’s one \([6]\).

3. Intensity transients exhibit parabolic type shapes for Fe16Cr but nearly triangular ones for Fe18Cr9Ni. No effect of the surface finish is evidenced.

<table>
<thead>
<tr>
<th></th>
<th>Fe16Cr BA</th>
<th>Fe16Cr 2B</th>
<th>Fe18Cr9Ni BA</th>
<th>Fe18Cr9Ni 2B</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta V ) (mV)</td>
<td>60</td>
<td>175</td>
<td>300</td>
<td>25</td>
</tr>
<tr>
<td>( i_{\text{max}} ) (( \mu \text{A} ))</td>
<td>16.8</td>
<td>24</td>
<td>20.7</td>
<td>14.4</td>
</tr>
<tr>
<td>( T ) (s)</td>
<td>10.5</td>
<td>12</td>
<td>11.1</td>
<td>11.9</td>
</tr>
</tbody>
</table>

**Table 2**

Evolution of potential and current transient characteristics (potential drop—\( \Delta V \), maximum current, and current transient life-time—\( T \)) vs. time, at beginning (B), middle (M) and end (E) of immersion time.

Fig. 5. Typical potential and current transients obtained for (a) Fe16Cr in 0.02 M NaCl + 2 \( \times 10^{-4} \) M FeCl3 and for (b) Fe18Cr9Ni in 1 M NaCl + 2 \( \times 10^{-4} \) M FeCl3.
3.3. Transfer resistance and film capacitance

In the recovery stage (capacity discharge) the measured current $i_m$ is null. At the end of this stage $V$ is close to $V_0$. Eq. (3b) writes

$$V_0 - V = RC \frac{dV}{dt}$$

(6)

Plotting $(V_0 - V)$ vs. $dV/dt$ plot (Fig. 6) when $t \to \infty$ gives then the time constant $RC$.

At the beginning of the growth stage Eq. (3b) also applies with $i_m \neq 0$.

Plotting $(V_0 - V)/RC - dV/dt$ vs. $i_m$, when $t \to 0$ (Fig. 7), gives the transfer resistance $R$ and then the capacitance $C$.

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**Fig. 6.** Determination of the time constant $RC$ for Fe16Cr BA ($RC = 200/2.5 = 80$ s).

**Fig. 7.** Determination of the capacitance $C$ for Fe16Cr BA ($1/CS = 3 \text{ mF}^{-1} \to C = 47 \mu\text{F/cm}^2$).
The total results are shown in Figs. 8 and 9:

(1) The transfer resistance increases with the exposure time. At the opposite, the interfacial capacitances do not vary with time.

(2) The capacitances and the transfer resistance are lower in the BA condition than in the 2B one.

(3) The capacitances are larger, and the transfer resistance smaller, for the austenitic steels than for the ferritic ones. We should however keep in mind that the chloride concentration is much larger in the first case, suggesting a possible effect of the chloride adsorption.
4. Discussion and conclusions

As far as the successive stages of metastable pitting are concerned, the experiment that we carried out clearly show that the Isaacs model is suitable to explain metastable pitting transients at open circuit in ferric ions and chloride containing corrosive media: The potential recovery does not correspond to the repassivation but the discharge of the interfacial capacitance after the repassivation.

Furthermore, a metastable pitting event can be considered as an excitation of the cathodic reaction through the passive film and its analysis allows determining the electron transfer resistance and the interfacial capacitance.

(1) The shape [12–14] of the transient looks different for ferritic and austenitic steels. However, it could be simply the effect on Eqs. (3) and (3b) of the differences observed in transfer resistance and interfacial capacitance.

(2) The total capacitance $C$ does not vary with ageing time but is larger for austenitic steels. However, $C$ is a combination of the film capacitance (itself the combination of the dielectric and the space charge capacitances) and the double layer capacitance (including the effect of specific adsorption of chloride ions). As austenitic steels were tested in more concentrated chloride solutions, it may suggest that $C$ variations are controlled by chloride adsorption, and then that the capacitance of the passive film capacitance itself is constant during the transient.

(3) The transfer resistance increases with time. From another hand, the corrosion resistance seems to increase with time, which was already evidenced in former studies [11] but is confirmed here, since the total number of transient increases roughly as the logarithm of time, showing a smaller number of pitting events when ageing time increases. It suggests that for a given material and electrolyte chloride concentration, a large transfer resistance is correlated with a good resistance to pitting. However, this resistance looks larger for ferritic than for austenitic steels which were tested in more concentrated electrolytes, suggesting again an effect of the chloride adsorption. We are aware of the fact that suggestions (2) and (3) are only conjectural but we feel that they could be useful for further modelling, when confirmed by further works.

(4) Comparing BA and 2B surface conditions, by simply counting the number of metastable pitting events, clearly confirms that BA condition provides better pitting resistance than 2B. Furthermore, the capacitances and the transfer resistance are lower for BA condition than for 2B. Since the roughness is larger in the later case it cannot be an effect of the specific surface area. In case of a control of the capacitance by the chloride adsorption as discussed above, it suggests that this adsorption is less easy on BA than on 2B one. However, this work does not suggest any explanation for the difference between the transfer resistances.

5. Conclusions

Further works are needed to interpret all the information contained in those findings. Among them, modelling the potential and intensity time evolution during a transient should be fruitful and is currently a subject of investigation. However, the following results were clearly evidenced in this work:
(i) The last stage of metastable pitting is not the repassivation but the discharge of the surface capacity.

(ii) Analysing the pitting transient provides quantitative information on the cathodic reaction through the passive film (transfer resistance and surface capacitance).

(iii) Ageing in the corrosive solution improves the pitting resistance and increases the transfer resistance without changing the interfacial capacitance.

(iv) BA surface condition provides better resistance to pitting than 2B, but exhibits smaller transfer resistance and surface capacitance.

References