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Pitting transients analysis of stainless steels at the open circuit potential

G. Berthomé [a,*], B. Malki [a], B. Baroux [a,b]

[a] Institut National Polytechnique de Grenoble, LTPCM/ENSEEG, 1130, rue de la Piscine St. Martin d'Hères 38402, France
[b] Arcelor Research, France

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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

* Corresponding author. Fax: +33 (0)4 76 82 67 67.
E-mail address: berthome@ltpcm.inpg.fr (G. Berthomé).

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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

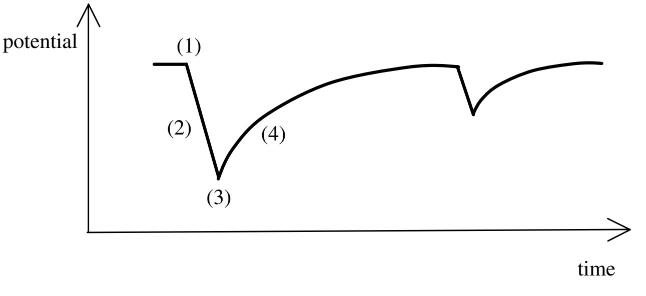

Fig. 1. Schematic representation of the potential vs. time variations during metastable pitting [2]. Four successive steps are observed (see text).