Study of the metastable pitting of Stainless Steels by computer simulations

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Introduction

This paper is a summary of research done to describe using analytical and numerical modelling the metastable pit transition. Understanding how the polarization conditions as well as the role of the pit chemistry as a function of its geometry influence this transition is the major purpose of the work.

Analytical modelling

It was necessary to first develop a 1D analytical modeling framework using a cylindrical pit geometry in how the metastable active/passive is extensively investigated. The basis of the model is to use a generic passivatable system in dilute chloride solutions. Basic chemistries that govern corrosion processes are considered. The study is focus on the role of hydrolysis reactions in trigging the local acidities. How the geometry (noticed by a structural parameter $\gamma = l.r^{-1/2}$ where l and r are respectively the length and the mouth of the considered a pit) affects the repassivation transition was extensively researched. We looked especially at how the pH transition pH_T at the passive/active (p/l) areas evolves (see Figure 1). A parabolic behaviour with a minimum was then found (see Figure 1 too). It was concluded that giving a depassivation pH_d for a given stainless steel system, the passive/active transition is governed principally by a <u>critical potential</u> V_C and a structural factor $\gamma = l.r^{-1/2}$ as illustrated in figure 2. Consequently, it was deduced that the commonly observed pit transients namely type I and II correspond respectively to over-critical and under-critical propagation conditions (see figure 2).

Numerical modelling

In this second part of the work, a method is proposed for modeling in 2D dimension the pit chemistry using the finites elements method. We aim to take into account particularly the influence of alloying elements namely Chromium and Nickel on the repassivation reaction that plays an fundamental role in the metastable pitting of stainless steels systems [5]. The idea is based on an assumption that those elements trigger the local pH evolution, which in turn governs the inner repassivation reaction. Based on these general equations, the numerical techniques applied to solve the resulting system are explained and commented. The modeling results are compared to analytical conclusions and discussed in the light of various models and simulation results [1-5].

Keywords: metastable pitting corrosion; modelling chemistry, finite element method
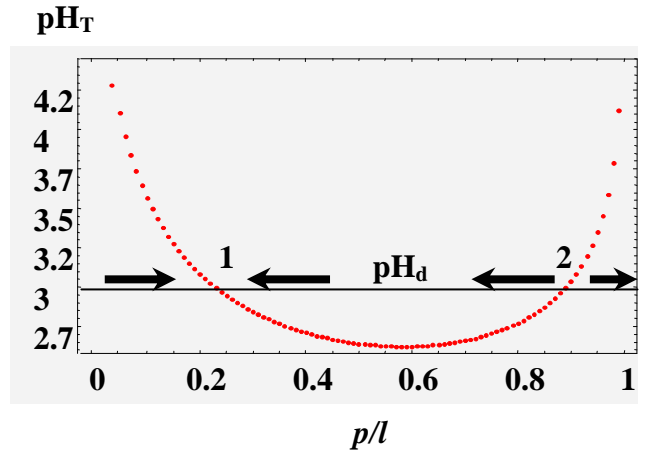
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Figure 1: Evolution of the local pH at the passive/active transition as a function of passive/active (**p/l**) areas for a cylindrical pit geometry. For a given depassivation pH (pH_d) a stable pit is obtained each time $pH_T < pH_d$. (1) and (2) are respectively stable and instable points.
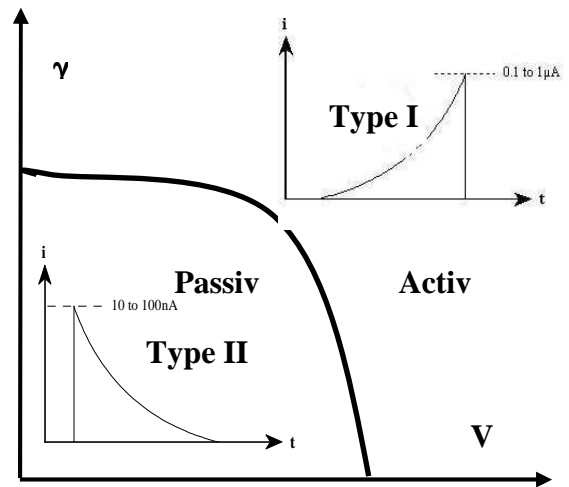

Figure 2: Schematic illustration of the major factors which govern the active/passive transition in a cylindrical pit geometry system.

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