Initiation and Propagation of a single pit on stainless steel using SECM

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Introduction

Pitting corrosion has been in the focus for many decades for providing valuable information about the mechanisms, the shapes of growing pits, and the relationships linking various parameters such as temperature, pH and potential to the corrosion rate. Most of these researches were carried out directly in chloride containing solutions, giving rise to several pits on the metal surface. One of the main drawbacks of such an experimental approach is that data collected by means of global electrochemical techniques correspond to the overall surface of the sample rather than to the local behaviour of individual pits. Attempts to correlate the corrosion current to the evolution of a particular pit were limited by the complexity and variability of the collected data. Recently, focus has been laid on the generation of a single pit at a preselected site of the electrode surface in order to avoid the occurrence of random pits anywhere on the electrode surface and to allow a single event from its birth to its death to be observed using SVET [1] or SECM [2, 3]. The last technique is very promising since it allows very accurate chloride ions release close to the metallic substrate.

Experimental

Recently, two complementary devices using SECM has been developed for studying the evolution of a single pit. The first device consisted of an Ag/AgCl probe and allowed to focus on the understanding of pit initiation because with this technique, only limited amount of chloride ion can be generated. In such configuration, the electrochemical cell formed a cylindrical thin-layer-cell the thickness $z$ of which is equal to the probe-to-substrate distance ($z = 10 \mu$m), and of 1 mm in diameter, which is the diameter of the probe capillary. It was positioned accurately at the center of 316L substrate (1.5 mm in diameter).

In the second device, the Ag probe was substituted by a glass micro-capillary, positioned close to the electrode surface, in which chloride ions were injected at will with a syringe pump (Figure 1). This device allows working more on the understanding of pit propagation since a constant flux of chloride ion can be maintained at the close vicinity of the pit. The influence of potential, chloride concentration and the composition of the solution (0.5 M H$_2$SO$_4$ or 0.5M HClO$_4$) on the pit initiation and propagation on 316L stainless steel were investigated with both devices. To ensure reproducible results, the native oxide layer of each sample was reduced first by applying a cathodic potential of $-0.8$ V/SSE for 60 s. Then, a passive layer was formed \textit{in situ} by sweeping the sample potential towards positive values under quasi steady-state conditions (1 mV s$^{-1}$) from $-0.8$ V/SSE till the defined holding potential ($E_{316L} = -0.4$ V, 0 V or 0.4 V/SSE) was reached. Then, the electrode was biased at this potential for a controlled time to allow further growth of the passive layer. Finally, the chloride ions were injected in the solution and the corrosion test could start.
Results and Discussions

Initiation: Ag/AgCl probe

Initiations of a single pit were carried out on samples whose passive film was formed for different durations or at different potential. It was shown that when the duration (Figure 2) or the potential at which the passive film was built increased, pitting became more difficult to initiate. In both case, the pit may have started on a defective zone of the passive film (precipitate, inclusion). This behavior confirmed the influence of the passive film (thickness and/or structure) on the initiation of pitting [4, 5].

Once initiated, it was shown that the pit growth rate decreased with time (Figure 2). This is in agreement with the work of Moayed and Newman who suggested the formation of a salt film inside the pit and a diffusion controlled propagation [6]. However, while the outward diffusion of cations was suggested as limiting factor of the propagation rate, the chloride ions were present in limited amount in our test, so the diffusion of Cl$^-$ toward the pit bottom may have also been the limiting factor for maintaining an aggressive solution and preventing repassivation. Changing the anion of the solution from H$_2$SO$_4$ to HClO$_4$ impacted on the pit development as a function of time and as a function of potential. Indeed, first, it could be observed that repassivation was faster in HClO$_4$. Moreover, whereas in H$_2$SO$_4$ solution the amount of dissolved metal increased linearly with applied potential on 316L substrate, a decrease of pit growth rate was observed in HClO$_4$ over -0.2V/SSE (Figure 3): repassivation is favored which is in good agreement with the electrochemical behaviour of 316L in 0.5M HClO$_4$ as a function of potential. The behavior difference in both solutions may indicate the importance of the presence of other anions than Cl$^-$ in the pit development and competitive reaction between all the anions (Cl$^-$, OH$^-$, ClO$_4^-$, SO$_4^{2-}$) and the metallic substrate. These observations will be discussed in detail.
Figure 3: Pit current measurements as a function of time in (a) sulfate solution (0.5M) and (b) perchlorate solution (0.5M) at 0V/SSE.

Propagation: microcapillary with syringe
Tests using injection of low flowing chloride rich solution over 316L substrate showed that the pit morphology and the pit growth rate depended on the solution (H$_2$SO$_4$ or HClO$_4$). After 3h at 0V/SSE, the pit had the same diameter in H$_2$SO$_4$ than in HClO$_4$ (1.4 mm) but was deepest in the perchlorate containing solution (450µm and 580 µm respectively). Moreover, it was shown that the growth rate in the z-direction was potential independent in H$_2$SO$_4$. SEM images of the pit bottom in both media showed the presence of a “polished film” in H$_2$SO$_4$ whereas faceted surfaces were evidenced in HClO$_4$. All these results confirm that a salt film formed on the pit bottom surface in H$_2$SO$_4$ solution which controls the pit growth rate whereas no salt film was formed in HClO$_4$. In this last case, growth rate may have been controlled by an active dissolution process. As already evidenced by Frankenthal et al. in the past [7], the surface morphology of the pit is controlled by the composition of the electrolyte solution.

Conclusions
Initiation and propagation of a single pit were carried out using innovative devices with SECM. It was shown that the passive film (thickness and/or structure) impacts on the susceptibility of 316L to pitting. Once initiated, the pit growth rate and the surface morphology depend on the buffer solution. It appears that a rate controlling salt film formed in the bottom of pits in H$_2$SO$_4$ whereas the pit growth rate in HClO$_4$ is controlled by activation.

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References