

Stochastic Aspects of Pit Initiation at Passive Iron

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Introduction – Pitting corrosion at a passive metal such as pure iron can occur, if critical conditions are fulfilled with respect to e. g. the critical pitting potential E_p and the critical concentration c_p of an aggressive anion. When all critical conditions are met, the first pit accompanied by a fast rise of anodic current appears after some time t_i of incubation. Mean values of \bar{t}_i change by many orders of magnitude depending on experimental conditions. Individual values of t_i are described by a broad distribution function. At times $t < t_i$ the current is noisy. At $t > t_i$ the surface concentration of pits rises to stationary values.

Experimental – Usually, passive iron was kept at constant electrode potential and the concentration of chloride in a solution of defined pH was increased step-wise. Electrodes had areas $A \approx 1 \text{ cm}^2$, but microelectrodes were used e.g. for noise measurements in order to obtain intrinsic electrode noise not influenced by external noise. Distribution functions of t_i were obtained with cells in which up to 20 working electrodes were kept under identical conditions.

Results– Mean incubation times \bar{t}_i as a function of electrode potential E are described by

$$\lg \bar{t}_i / t_0 = E_0 / (E - E_p) \quad (1)$$

with the critical pitting potential E_p . The minimum incubation time t_0 depends only little on E and the chloride concentration c . Both E_p and the reciprocal slope E_0^{-1} are linear functions of the $\log c$. Experimental values

$$E_0^{-1} = S \lg c/c_p \quad (2)$$

extrapolate to the critical concentration c_p . The slope S decreases linearly with pH.

The probability P to observe the first pit at the time t after establishing the critical conditions is described by

$$P(t) = \exp(-At) \quad (3)$$

with the frequency function

$$A(t) = [1 - \exp(-t/\tau_1)][a + b \exp(-t/\tau_2)] \quad (4).$$

Eqs. (3) & (4) were established by analyzing several hundreds of pit incubation times. All the 4 parameters in eq. (4) were found obey the potential dependence analogous to the one in eq. (1). The same critical pitting potential was obtained from each of the parameters.

The differences $\bar{t}_i - t^*$ are a linear function of the reciprocal electrode area. The shortest incubation times t^* are observed at large electrodes. At microelectrodes the incubation times can become very long even in concentrated chloride solutions.

Spectral densities S_U of the intrinsic voltage noise were obtained from spectral densities S_I of current noise and from impedance spectra $Z(f)$

$$S_U = S_I |Z(f)|^2 \quad (5)$$

both measured under potentiostatic conditions. According to measurements in borate buffer solutions not containing aggressive anions, S_U is described by a Lorentz function

$$S_U = \frac{K}{1 + [(f^2 - f_0^2)/\Gamma f]^2} \quad (6)$$

with a central frequency $f_0 = 0$ and a characteristic frequency $\Gamma = 1.4 \text{ mHz}$ in a frequency range $1 \text{ } \mu\text{Hz} < f < 10 \text{ Hz}$. The amplitude $K = 470 \text{ } \mu\text{V}^2 \text{ Hz}^{-1}$ and Γ were independent of E for potentials $E > E_F$ sufficiently positive to the Flade potential E_F . Shallow maxima of S_U were observed around 1 kHz depending on nature and concentration of non-aggressive anions. Immediately after addition of chloride, additional noise S_U around a central frequency $f_0 \approx 4 \text{ Hz}$ was observed with the amplitude decaying from a maximum to a steady state. Finite central frequencies indicate oscillatory behavior.

Simultaneously with the noise there is a negligible increase of the mean current, but a relatively large and noisy increase of the ferric in dissolution rate observed with the rotating ring disc electrode. The mean ferric ion dissolution rate grows linearly with the chloride concentration. No ferrous ions are dissolved during the incubation time.

After appearance of the first pit, the number of further pits increases rapidly at a rate increasing with $E - E_p$ and with c . After some time a steady state surface concentration N_o of pits is attained. N_o increases with $E - E_p$ and c and decreases with pH. Again, N_o becomes zero at the critical pitting potential.

Pits are evenly distributed on a surface of macroscopically even dislocation structure. Cold work increases N_o . Pits are known to grow at dislocations emerging at the surface. The probability $P(r)$ to find a pit at a radial distance r from any pit is described by a Poisson function. However, there is an exclusion zone around the pits in which no new pits appear. The width of the exclusion zone decreases with c and increases with pH, but is independent of E .

Discussion – Pit initiation can be understood in terms of local thinning of the passivating oxide film due to the enhancement of the oxide dissolution rate by adsorbed chloride which is removed from the surface by iron(III) chloride complexes. The dissolution apparently is localized, because islands of a condensed adsorption phase are formed at chloride concentrations in solution exceeding a critical value. Another possibility with similar consequences is the preferential adsorption of chloride at atomic steps. On areas of thinned oxide the film may either grow again or may dissolve further until it is eventually removed completely at some spot. Such a mechanism explains the enhanced noise and iron(III) dissolution rate. If a bare spot appears at the site of a suitable emerging dislocation, growth of pits covered by a monolayer of chloride starts by dislocation etching producing at first etch pits with typical crystallographic shapes which upon further growth may assume a hemispherical shape. The demand for chloride to cover the growing pit is the apparent reason for the exclusion zone.

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