Microprobe Study of pH Change During the Induction Period Preceding Crevice Corrosion

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Crevice corrosion processes in metals and alloys can belong to one of two groups, those that occur immediately upon contact with the electrolyte and those that occur after an induction period. This paper addresses the latter and focuses on the induction period, in particular how pH and electrode potential, *E*, change with time and distance, *x*, into the crevice, where *E(x)* is given by the magnitude of the *IR* voltage at *x* (1).

In two cases of delayed crevice corrosion, one a spontaneously active system (2) and the other a spontaneously passive system (3), *E* at the bottom of the crevice, $E(x = 10\text{ mm})$, sharply decreased at the same time the current increased to the mA range, signaling not only the end of the induction period and start of crevice corrosion but also the involvement of *IR* voltage. For the spontaneously passive system (3), an active peak formed in the polarization curve of the crevice solution during the induction period (its formation being caused by a drop in pH) and by $E(x = 10\text{ mm})$ stabilizing in this newly formed active region. Thus, *E(x)* and active peak growth via a decreasing pH with time were instrumental in ending the induction period and starting crevice corrosion. In principle, crevice corrosion does not necessarily occur at the peak's first appearance because the *IR* voltage may not be large enough to satisfy the $IR > \Delta\phi^*$ criterion (1, 4), i.e., $E(x = 10\text{ mm})$ is still more positive than the potential of the active/passive transition, $E_{A/P}$, of the crevice solution. But as $E_{A/P}$ becomes more positive with time, at some moment this criterion will be satisfied and the current will rise suddenly and steeply as crevice corrosion commences.

It is this proposed role of *IR* voltage, pH(*x*) decrease, and active peak formation (1, 4, 5) that this paper investigates using a recently developed pH/*E* microprobe to in-situ measure in real time both pH(*x*) and *E(x)* in the crevice electrolyte (6, 7). Both are measured simultaneously at the same *x* value, because the potential of a specific ion microelectrode can only be correlated with ion concentration after the contribution of potential from the *IR* voltage is taken into consideration. Since the *IR* voltage can be several hundred mV mm^{-1}, it is also necessary to have the sensing area confined to a very small Δx. This is accomplished by covering the combined pH/*E* microelectrode with an insulating material and then cutting the coated microelectrode perpendicular to its length. This exposes only the two-dimensional cross sectional areas of the pH and *E* electrodes, which are appropriately prepared PdH and saturated calomel electrodes, respectively (6). The microprobe consisting of the pH and *E* electrodes is positioned at desired depths in the crevice using a micromanipulator. The crevice arrangement has the crevice opening facing upward and the bottom of the crevice closed so that the crevice solution is stagnant.

The spontaneously passive metal/electrolyte system being investigated is the same as in Reference (3): iron in 0.2M Na_2SO_4 + 0.025M K_2CrO_4 of pH 9.0. The system is well characterized and is also a convenient system to investigate because it undergoes crevice corrosion after a relatively short induction period. In that time the pH decreases to 4 or 5, causing the formation of an active peak and the conversion of the metal/crevice-electrolyte system to a spontaneously active system. As such, iron in sodium sulfate / chromate solutions may be a model system for studying crevice corrosion in spontaneously passive systems.

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