

Active Peak Formation 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 group and involves experiments designed to determine (i) if an active peak forms during the induction period in the otherwise all passive bulk solution polarization curve, (ii) if a decrease in pH with time is responsible for formation and growth of this active peak, and (iii) if the induction period ends when the electrode potential of the active/passive transition of the growing active peak, which becomes more positive with time, and the electrode potential at the bottom of the crevice, which becomes more negative with time, coincide.

This focus was an initial attempt by Al-Zahrani (1) to understand the relationship between the roles of IR voltage and crevice solution composition for initiating the delayed form of crevice corrosion. IR voltage is known to modify the electrode potential on the crevice wall such that there is a distribution of $E(x)$ values on the wall, representing a decreasing overpotential, η , for the metal dissolution reaction with increasing distance, x , into the crevice. This role of IR voltage is necessary and often sufficient for initiating the immediate form of crevice corrosion. Our previous studies established that for crevice corrosion to immediately occur, the magnitude of the IR voltage has to be greater than the difference between the potential on the outer surface and the potential of the active/passive transition in the polarization curve, $\Delta\phi^*$ (2, 3). Thus, the criterion for the onset of crevice corrosion becomes $IR > \Delta\phi^*$. Since the immediate form of crevice corrosion precludes significant changes in composition of the crevice solution, other factors that are involved in the delayed form of crevice corrosion -- i.e., acidification and/or aggressive ion accumulation-- and are thought by some to be the main cause of crevice corrosion, are not involved in initiating the immediate form of crevice corrosion. In the case of delayed crevice corrosion, changes in composition of the crevice solution during the induction period combined with the $E(x)$ distribution on the crevice wall, have been proposed by more than one group to end the induction period and initiate crevice corrosion (2, 4, 5), and it is this hypothesis that this paper investigates.

Samples for the study were cut from Carpenter Electrical Iron to the final size of 20 mm x 10 mm x 5 mm. The dimensions of the iron crevice wall were 10 mm x 5 mm, and the other crevice walls were Plexiglas; the dimensions of the outer iron surface were 20 mm x 5 mm. These two iron surfaces were mechanically polished to a mirror finish. The crevice opening faced upward and the bottom of the crevice was closed so that the crevice solution would be stagnant. The iron sample and outer

Teflon mount were fully immersed in the 0.2M Na_2SO_4 + 0.025M K_2CrO_4 electrolyte of pH 9.0. The polarization curve of this metal/electrolyte system exhibits only passive behavior and no tendency for the immediate form of crevice corrosion. The pH of the crevice solution was measured before and after the induction period. The microprobe for measuring the potential inside the crevice consisted of a very fine (≤ 0.05 mm OD) glass capillary filled with the test solution and connected to a reference electrode. A 3D micromanipulator was used to adjust the position of the tip of the glass capillary inside the crevice opening at $x = 10$ mm which was the bottom of the crevice. The Luggin capillary tip of the SCE used to control the potential of the outer iron surface was placed close to the crevice opening in order to minimize the bulk solution IR voltage drop.

A potential well in the passive region (650 mV_{SCE}) was applied to the outer surface of the iron and the current was monitored as a function of time. A rise in current above the passive value was recorded after several minutes and indicated the end of the induction period and start of crevice corrosion. At this same time the electrode potential at the bottom of the crevice, $E(x=10)$, sharply decreased, confirming the onset of crevice corrosion. When the current became nearly stable at approximately 5 mA cm⁻² of exposed iron surface, the potentiodynamic part of the experiment was started by scanning backward (in the less noble direction) to 150 mV_{SCE} which is below the corrosion potential, E_{corr} . During this scan the top of the active peak (above 5 mA cm⁻²) was seen, indicating that an active peak formed during the induction period. The crevice solution was now found to be pH 4. The polarization curve of this iron/pH 4 system exhibits an active peak and a passive region. Its active/passive transition coincided with that measured in the reverse scan. All these results strongly indicate the integrated roles of pH change and the $IR > \Delta\phi^*$ criterion as being the explanation for the ending of the induction period and the onset of the delayed form of crevice corrosion.

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