

IN-SITU DETERMINATION OF CHLORIDE ION ACCUMULATION IN A CORRODING MODEL CREVICE

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A novel chloride ion sensitive microelectrode system was developed. This system permits the determination of the chloride concentration inside a crevice during crevice corrosion even in the presence of a pronounced potential drop within the crevice. It consists of a planar silver electrode, covered with silver chloride. The outer diameter of this electrode is about 0.2 mm, the diameter of the active area 0.05 mm. At exactly the same depth into the crevice there is the tip of a Luggin capillary, leading to a calomel reference electrode, REF1. Both electrodes are connected to a micromanipulator and can be positioned at desired depths into the crevice. A second calomel reference electrode, REF2, is positioned in the bulk of the electrolyte, outside the crevice. With these two calomel electrodes one can measure the potential inside the crevice with respect to the potential in the bulk solution. The potential difference between the silver/silver chloride electrode and the reference REF1 is determined by the chloride ion activity inside the crevice. After calibration of the microelectrode system with NaCl solutions of known chloride ion concentrations with and without the buffer one can measure the time dependence and the position dependence of the chloride ion concentration during crevice corrosion.

The model crevice consisted of pure iron; the electrolyte was 0.5 M sodium acetate + 0.5 M acetic acid + sodium chloride, c_{Cl^-} , varying between 0 and 10 mM. With increasing time of crevice corrosion one finds a pronounced chloride ion accumulation in the region where the passive/active transition occurs in the crevice. A tentative mechanism for the chloride ion transport into the crevice will be discussed.