

PIT NUCLEATION AND GROWTH FROM MICROELECTRODES

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The measurement of current transients from emanating from localized breakdown of passivity of microelectrodes is presented. Microelectrodes require special electrochemical handling because of the very small currents generated, even when the current density is quite large. The present method involves a two-electrode potentiostatic circuit in which the metal is held under constant potential against a reference electrode, the latter of which also acts as a counter electrode. This reference/counter electrode was a 21 cm² sheet of silver which had been pre-anodized in HCl to generate a film of AgCl. The equilibrium potential of this reference/counter electrode is a function only of the chloride concentration for a given temperature. The working electrolyte, of known chloride concentration was used for equilibration. This reference/counter electrode was unpolarized when subject to the very small currents carried by the working electrode, and thereby operated successfully in the dual role. Microelectrodes made from stainless steel and titanium were subject to a series of experiments involving constant potential in a range of electrolytes containing chloride. The electrodes were fabricated from wires which were either bought or cut, ground and polished from sheet. These had diameters typically of 50 µm, although larger and smaller ones were also used. The wires were mounted by first threading through a plastic tube which had been slit down its length, and then pouring a cast of epoxy resin into the tube. When set, the end was ground to reveal a circular electrode surface.

The polarizing source was a simple bank of dry-cell batteries linked in parallel, and connected to a voltage divider to provide a maximum polarization of 1.5 V relative to the Ag/AgCl reference. The use of such d.c. polarizing sources helps to minimize noise in the signal. Because the work was carried out on microelectrodes, the pick-up from extraneous sources could be quite sensitive. The data were recorded digitally via an analogue-to-digital interface.

The glass cell was of ca. 100 cm³ capacity, with the reference/counter electrode housed in a separate vessel and linked to the working cell via a plastic tube. The ohmic potential drop was at all times negligible because of the tiny currents from the working microelectrodes. The cell and reference compartment were housed in a double concentric earthed Faraday cage to minimize electrical interference. The amplifier used to detect the small current transients was housed in a separate, adjacent earthed Faraday cage. The two cages were ca 1 cm apart, and the cable link passed through holed between the two.

The cell was equipped with a home-built immersion heater, consisting of a fine nichrome wire heating element inside a glass tube which acted as a finger in the working cell. The heater was powered from a d.c. supply. To minimize switching transients which would be achieved by a thermostatically controlled temperature system, the present experiments did not involve a thermostat. Instead, heat was controlled simply by controlling the constant current through the heating element, and allowed to reach a steady state by natural heat loss from the cell. Since the cell was deaerated with pure nitrogen, the flowing gas aided fairly rapid achievement of a thermal steady state. Temperatures up to 50°C were maintained in this fashion.

Experiments consisted of fixing the electrode potential and recording the current as a function of time. Measurements over long periods of time were achieved by recording at a frequency not so fast the inordinately large volumes of data were recorded, but sufficiently large to allow observation of the fast current transients which nucleate pitting corrosion (13.5 Hz). In this way, experiments were run for periods of up to 39.5 min at a time before transferring the data to an independent storage device, but the measurement could then be continued in further 39.5 min periods.

Results are presented which describe pit nucleation and the early stages of growth of stainless steel and on titanium in chloride solution. The metals show substantially the same form of nucleation behavior in chloride solution, with a sharp nucleation current spike followed by either a decay to the steady state, representing repassivation of the event, or a partial decay followed by a propagation step. The statistics of the occurrence of these events is presented. Pit nucleation on stainless steel is very frequent, but the frequency decays with time of exposure, provided the potential is below the pitting potential. On titanium, pit nucleation is far rarer, consistent with the much higher pitting potentials. However, the frequency of occurrence for titanium shows no evidence of decay with time. The observations show that nucleation of pits on stainless steels occurs from discrete sites, but that on titanium does not. Effects of some other variables are described.