

# CRITICAL PITTING TEMPERATURE OF ALUMINIUM IN NITRIC AND HYDROCHLORIC ACIDS

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Pitting corrosion of metals occurs by the action of an aggressive ion on a surface which is otherwise passive. The most commonly encountered aggressive ion towards aluminium is  $\text{Cl}^-$  although  $\text{NO}_3^-$  (amongst others) can also cause pitting<sup>1-3</sup>. The usual method of characterising pitting is through the pitting potential. This parameter can have many ambiguities and uncertainties, such as the effects of electrode size, potential scan rate etc. Nevertheless, some comparisons can be made. In this context, aluminium in chloride solutions has a pitting potential of *ca.*  $-0.75 \text{ V(SCE)}^2$ , a low-potential pitting process. By contrast, pitting of aluminium in nitrate solution is a high-potential process, with a pitting potential of *ca.*  $+1.5 \text{ V(SCE)}^{2,3}$ ; indeed this pitting potential is so high that nitrate ions act often as a corrosion inhibitor and can raise the pitting potential of the metal in chloride solution<sup>2</sup>. In order to examine these processes more sensitively, we have developed a technique designed to record the critical pitting temperature. The critical pitting temperature has been measured on stainless steel, but the method involves constant temperature, constant potential measurements. As a consequence, no hysteresis data can be established.

We have developed a technique for sweeping the temperature of a specimen whilst it is held at constant potential<sup>4</sup>. The temperature can be swept up and back, with continuous logging of the current. Analogous to cyclic voltammetry, we term this "cyclic thermammetry", meaning measurement of current as a function of temperature. The method works by equipping a standard three-electrode electrochemical cell with an immersion heater for heating the cell, and a thermistor for measuring and controlling the temperature. The output from the thermistor is fed into an electronic feedback circuit which supplies power to the heater in order to maintain constant temperature. In this new technique the temperature control unit can be programmed by a voltage signal to generate a number of temperature programmes. This paper describes the technique as it can be applied to measurement of critical pitting temperatures. We have applied linear sweep temperature scans up to  $70 \text{ }^\circ\text{C}$  to the cell by programming the equipment with a linear ramp potential. The temperature scan rate has a number of limitations, including the heat capacity of the cell and its contents. The measurements presented here were generated cyclically at a rate of  $7 \text{ mK s}^{-1}$ .

In this paper we describe the results obtained from aluminium in hydrochloric and nitric acids using cyclic thermammetry. High purity aluminium wire (1 mm

diameter) mounted in epoxy resin was polarised in the pitting solutions at potentials below the ambient-temperature pitting potential and the electrolyte temperature was swept upwards linearly. The current density rises with increase in temperature continuously, but at the pitting temperature, it rises more sharply. The critical pitting temperature is thereby measured. On the reverse temperature sweep the current remains high to temperatures lower than those at which pitting occurs on the upward sweep. Hysteresis is thus generated, in which the metal continues to pit below its pitting temperature. This phenomenon is analogous to that observed during potential sweeps, and in a similar nomenclature to the repassivation potential, we observe a repassivation temperature. The fact that pitting had taken place on the aluminium surface was confirmed by examination under the scanning electron microscope. We also see a change in the form of the data when plotted as an Arrhenius relationship, and demonstrate tentatively that the activation energy is similar above and below the critical pitting temperature even though the reaction rate is different. We also observed that there was significant noise in the current noise once the critical pitting temperature had been exceeded. Particularly, the current density noise in the negatively sweeping scan is significantly lower than that in the positively sweeping scan, even when temperature is still above the critical pitting temperature; this is consistent with the continual breakdown and repair of the oxide film during pitting under circumstances of high overall current density. Discussion of the cyclic thermammetry method is presented. The observations obtained from these cyclic thermammetric measurements are discussed in terms of mechanisms of breakdown and propagation, and the role of temperature in the pitting of aluminium. The work shows similarities and differences between pitting of aluminium in chloride and in nitrate solutions.

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