ANALYSIS OF CURRENT TRANSIENTS AND MORPHOLOGY OF METASTABLE AND STABLE PITTING ON STAINLESS STEEL ABOVE PITTING POTENTIAL[*]

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Abstract – In order to record metastable pit current transients, a 904L austenitic stainless steel was polarized potentiostatically by applying 750 mV (Ag/AgCl) in 1 M NaCl solution at 45, 49 and 54°C, knowing that the alloy CPT is 56°C. Stable pit current transients were recorded employing the same potential and test solution but at 62°C. It was found that the metastable pit current, I, follows a power law relation ship of $I \propto t^n$ during the initiation and growth prior to repassivation. The value of n was found to vary with temperature, however, values of 0.5 to 1.5 were obtained in all cases. The results of Scanning Electron Microscopy (SEM) studies on these transients showed two types of pit morphology: small pits associated with the small transients, whose interior surface were not visible, and open pit cavities with polished surface for larger transients, recorded at temperature closed to the CPT. Current transients from the stable pits showed an initial shape similar to that of stable pit. The stable pit currents rises approximately in proportion to $t^{1/2}$, but only for a few seconds and then continues to increase proportion to $t^{1/2}$ without repassivation. The SEM studies also revealed that stable pits are covered with a lace-like pattern with polished interior surface.

Keywords – Pitting corrosion, stainless steel, metastable pit, stable pit

1. INTRODUCTION

Metastable pit growth is a well-documented early stage in pitting corrosion of stainless steel in chloride solution. Metastable pitting can be observed as potential fluctuations in open circuit condition or galvanostatic investigations, or current fluctuations under potentiostatic control. Each event reflects the initiation, growth and repassivation of a micropit. Metastable pit transients can be recorded at potentials preceding the breakdown potential [1] (at temperatures above the critical pitting temperature) and over a wide range of potentials during polarization below the critical pitting temperature [2, 3]. Most of the investigations on metastable pit current transient on stainless steels have been carried out by applying an anodic potential less than pitting potential but above the alloy CPT. These investigations are classified into two main groups; stochastic approach to the transition from metastable to stable pit growth [4], and other works on individual current transients from metastable pits under potentiostatic control [1]. Frankel and co-workers [5] showed that the current increased approximately with the square of time ($I \propto t^2$), but that it frequently increased more sharply (owing to opening of a hole in the pit cover) just before the decay due to repassivation. The transients

showed lifetimes between 5 and 15 seconds and their magnitude varied from 4 nA to as much as 20 μA. Williams *et al.* [6] showed that metastable pit transients shapes varied from a form showing $I \propto t^{1/2}$, through a linear to some which showed $I \propto t^2$ for a short time. In the study of metastable pit current transients of several commercial stainless steels, Ezuber and Newman [7] proposed that transients with $I \propto t^{1/2}$ relationship occur in relatively occluded cavities and $I \propto t^2$ in more open cavities. Their result showed that increasing the potential gave a relatively higher proportion of t^2 transients, favouring pitting in relatively open cavities. Balkwill et al. [8] expressed that if the current is limited by the resistance of the solution outside the pit, or the resistance to current flow of a cap of corrosion products over the pit, then the relationship of $I \propto t^{1/2}$ is expected. As the potential becomes more anodic higher rates of active dissolution result in higher currents and a shift in the distribution of the shapes of transients occurs from transients which are resistance limited ($I \propto t^{1/2}$) to transients which show mixed area and resistance control ($I \propto t$).

2. EXPERIMENTAL PROCEDURE

a) Specimen preparation

Specimens from plate of stainless steels of 904L (6 mm thickness) were cut with a surface area of 5 cm^2 for the CPT measurements and 1 cm^2 for recording metastable and stable current transients. The specimen was welded to Nichrome wire for electrical connection. The Nichrome wire was covered with a heat shrinkable plastic tube to provide insulation from the external environment. Specimens were mounted in Metset resin, and allowed to set overnight in air. The working electrodes used in this work were mechanically wet polished to 3 μm diamond paste mirror, finish employing silicon carbide papers and diamond paste. After polishing to 3μm paste, the specimens were degreased with ethanol prior to drying with air. In order to prevent crevice corrosion, the gap between Metset resin and the specimen was masked with a masking material (type: 45-stopper lacquer) and dried with warm air. To record the CPT and metastable pit transients, surface areas of 4 and ~ 0.1 cm^2 were used, respectively.

b) Electrochemical cells and electrodes

The electrochemical cell employed in this work was a 250 ml beaker open to air. In general, 150-200 ml of test solution was used for each test. A commercial Ag/AgCl electrode was used as a reference electrode for all experiments. The stability of the reference electrode potential was compared regularly with respect to an unused reference electrode. The auxiliary electrode used was a bright platinum sheet, area ~ 2 cm^2, assembled on a glass tube. The cell was suspended in a water bath (Model: Grant X) to control the solution temperature. The solution temperature was measured by a thermometer, which was inserted into the test solution, close to the working electrode but without interfering with the cell current flow. A highly alloyed 904L austenitic stainless steel supplied by Avesta-Sheffield was employed as a working electrode. The alloy composition is given in Table 1.

Table 1. Compositions of the alloy used in this work

Grade	Alloying elements, Wt.% (balance Fe)				
	Cr	Ni	Mo	Mn	N
904L *	20.06	25.04	4.32	1.41	0.00

(*) Actual composition supplied by Avesta-Sheffield

c) Electrochemical equipment

Throughout this work an ACM potentiostat (ACM instruments) was used to control the electrode potential. The current between working and auxiliary electrodes was measured either by a digital electrometer in series with the cell or across a resistor inserted into the circuit. The analogue output of the electrometer or current output of the potentiostat was connected to an A/D card and the data were stored in a 486 personal computer. A schematic drawing of the DC polarization measurement is shown in Fig. 1. In order to investigate the detail of stable pit morphology, it was necessary to remove the pit cover from the pit mouth. To achieve that, the as-pitted specimens were immersed into a 100 ml beaker filled with methanol and the beaker dipped into the ultrasonic bath filled with deionised water. The specimens were exposed to the ultrasonic treatment for 10 to 15 minutes and then dried prior to SEM examination. Scanning electron microscope (AMRAY 1810) with energy dispersive X-ray facilities was used to examine the detailed features of as-pitted and ultrasonically cleaned specimens. Surface conductivity of the specimen was improved by carbon coating. A voltage range up to 20 kV was used.
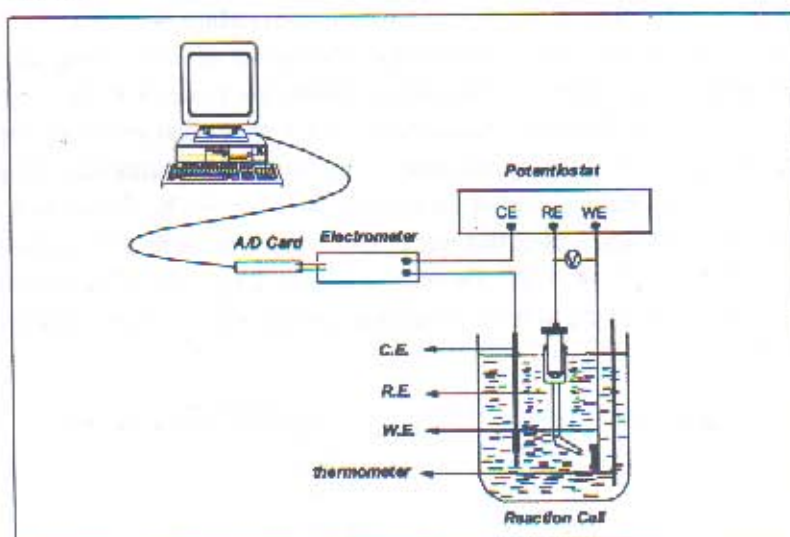

Fig. 1. A schematic of three electrodes electrochemical cell and circuit

d) Electrochemical techniques

The potentiostatic CPT determination procedure involves polarization of the working electrode by applying a potential more noble than the pitting potential with continuously increasing temperature. The specimens were mounted into a cell containing 200 ml of 1 M NaCl with a temperature of ~5 °C. In this work, all the specimens were allowed to stabilize at their open circuit potential for 5 min, at the starting temperature. After initial temperature stabilisation, an anodic potential of 750 mV (vs. Ag/AgCl) was applied and the electrolyte temperature was changed at a rate of ~0.4°C/min. In another work [9] the CPT has been evaluated at which the current density exceeds 100 μA/cm^2. Recording of metastable pit transients as large as 160 μA led us to define the CPT as the temperature at which the current starts to increase rapidly with no repassivation after 2 min.

The metastable pit and stable pit current transient measurements were carried out in a beaker of 250 ml capacity open to air containing 150 ml of solution at 750 mV, in 1 M NaCl at several temperatures. The main aim of these experiments was to record individual transients. To achieve this, small working electrodes of ~0.1 cm^2 were used to record separated metastable pit events with no