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SHORT COMMUNICATION

Pit propagation in aluminium under anodic polarization in aqueous chloride electrolyte

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1. Introduction

We have already presented some aspects of pit initation in polycrystalline aluminium using voltammetry [1]. The determination of an apparent enthalpy of activation for pitting of ~ 11 kJ [1] indicated that the rate controlling process is likely to be the diffusion of soluble species. This communication records further experiments carried out using both rotating disc and potentiostatic pulse techniques.

2. Experimental

Rotating disc experiments were carried out in 3·42 M NaCl using an electrode of 99·999% purity (diameter 2 mm) which was polished on roughened glass lubricated with triply distilled water and then allowed to attain an oxide film by standing in air for 3 min. This electrode pretreatment was also employed in the potentiostatic pulse experiments which were carried out in 1 M NaCl; the transients being recorded on an X–Y plotter (Bryans 26000 A4).

3. Results and discussion

Both rotating disc and potentiostatic pulse experiments were confined to low anodic overpotentials[*] since previous work [1] has shown that at higher overpotentials the measured currents are iR controlled. Fig. 1 shows typical responses of a stationary aluminium electrode to a potentiostatic pulse from an initial potential of $-1{\cdot}0$ V[†] to a new potential such that $\eta = +25$ mV[*] for both short ($t < 12$ s, •) and longer (0) times. Examination of Fig. 1 shows that the initial i–t behaviour consists of an induction period where the current is independent of time and most probably corresponds to the film forming reaction after which the current increases with time. If the pitting reaction is considered to be charge-transfer controlled, and the current density within the pits constant, then for a single pit

$$i = zF\mathrm{k}S \qquad (1)$$

where k is the rate constant and S the pit area. The most likely pit geometry is hemispherical [2] hence

$$i = 2\pi zF\mathrm{k}r^2 \qquad (2)$$

To the authors' knowledge the time dependence of the pit radius (r) during anodic polarization for polycrystalline aluminium has not been determined. From solely geometric factors for the growth of hemispherical pits, a linear dependence of r upon time would be expected. Booth *et al.* [3], however, have found that during the pitting corrosion of aluminium in chloride containing waters that the pit depth (h) is given by

$$h = Kt^{1/3}. \qquad (3)$$

Hence for the instantaneous nucleation of N_0 centres (without overlap) the total current using (3) with $h = r$ is given by:

$$i = 2\pi zFN_0\mathrm{k}K^2t^{2/3} \qquad (4)$$

with

$$\frac{\partial \log i}{\partial \log t} = 0{\cdot}66.$$

For progressive nucleation the corresponding value would be expected to be 1·66. The line shown in Fig. 1 is drawn with a slope of 0·66.

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[*] With respect to E_p (pitting potential) taken from previous work [1].

[†] All potentials are quoted with respect to the saturated calomel electrode at 25° C.

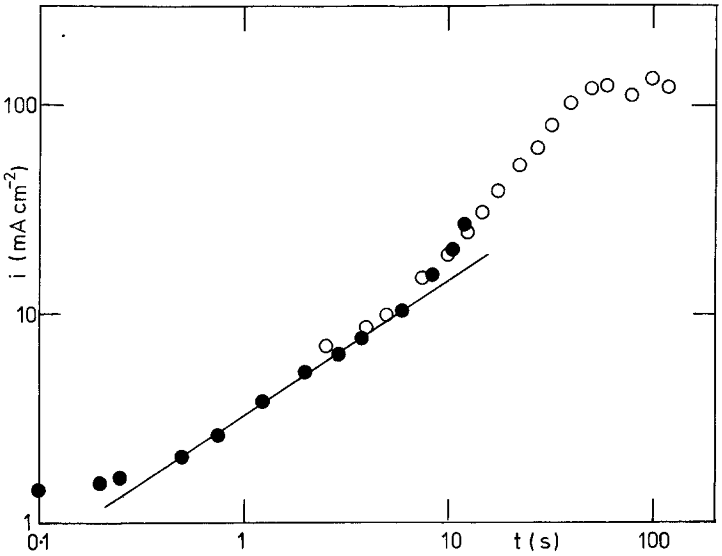

Fig. 1. Potentiostatic pulse response for polycrystalline aluminium. $E_1 = -1{\cdot}0$ V, $\eta = +25$ mV, 1 M NaCl, 25° C.

At value of $t > \sim 6$ s the current increases more rapidly with time and eventually attains an essentially time independent value at longer times ($t >$ 50 s). If, in this region (50 s $> t >$ 6 s) the graph is considered to be linear, a value of ~ 1·2 can be obtained for the slope. It is difficult to account for this acceleration of the pitting process in terms of a single specific physical effect; a number of processes may be involved. Overlap effects can be neglected since they would tend to cause the total current to fall, while the possibility of tunnel etching can also be neglected because of the low experimental temperature [2]. A value of ~ 1·2 may correspond to a change in the value of the exponent in Equation 3 to ~ 0·6 although it is difficult to envisage why this should occur. A more crystallographic attack‡ or a change in pit geometry may also be involved. Another possibility involves the undermining of the film due to pit growth. Stress within the film will produce new nucleation sites as cracks form and allow the electrolyte and metal to come in contact, thus increasing the total pitting current.

At longer times ($t >$ 50 s) the observed current may be the result of ohmic control, the production of an equilibrium (stabilized) surface or mass transfer effects within the pits.

No significant rotation speed dependence of the measured currents was observed at 25° C for fixed anodic overpotential values at any times. Experiments conducted at 90 ± 2° C showed the same behaviour. Hence mass transfer in the bulk can be eliminated as a rate controlling process during the pitting reaction, however, mass transfer within the pits would not be expected to be effected by rotating the electrode and, therefore, must be considered as a possible cause of current limitation.

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‡ Garz *et al.* [4] observed different values of log i/log t for the pitting of nickel single crystals depending on the crystallographic orientation.