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Pit formation in relation to the etching of aluminium in chloride solutions

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The pitting potential, E_p, has been determined by steady-state and linear potential sweep methods. E_p is is shown to be a logarithmic function of the chloride concentration; the form of the function yields information about the equilibria between electrode and electrolyte species at E_p. Values of the enthalpy of activation for the pitting process have been determined by measuring the rate of pit propagation at constant driving potential at a series of temperatures. An 'ad hoc' interpretation of the data has been avoided and an attempt made to present the results using a more theoretical approach.

1. Introduction

The transition undergone by a metal electrode passing from a passive state to an active or quasi-active state under attack by an aggressive anion is frequently marked by the development of pits on the metal surface. Initially covered by a protective oxide (or basic salt) layer, these pits develop when there is a pointwise breakdown of the passive layer. Surveys of the literature of pitting have been given from time to time; important ones are by Kolotyrkin [1] and Szkarska-Smialowska [2]. The main interest in pitting lies in the study of the corrosion of metal fabrics and containers. However, the capacitor manufacturing industry, using aluminium and tantalum to produce a film of metal oxide on the corresponding metal bases, relies on the presence of tunnels formed by the development of pits to provide a sufficiently large surface area. The basis of the process is to initiate pits in the capacitor metal surface and then drive tunnels through the metal lattice using a sufficiently positive potential.

The two major interests cited above are to some extent reflected in the two generally used methods of investigating pitting phenomena. The first of these in which at constant potential, a certain concentration of aggressive ion is added to the system and the current flowing at the electrode is measured as a function of time, corresponds to the corrosion situation. The second technique uses a linearly varying potential applied to the electrode, and the various reactions occurring can be inferred from the current flowing. This latter technique is extremely useful for the investigation of anodic processes of industrial significance where high rates of reaction are desirable.

This paper records the results of experiments undertaken in order to provide further information about the first stages of the etching of aluminium. For capacitor production this process employs strong sodium chloride solution as the etchant and such solutions form the main ones of present interest at temperatures up to 100°C as is industrial practice.

2. Experimental

Galvanostatic experiments were made using a conventional battery/resistance circuit. Differential capacitiance measurements were made with a polarizable Schering bridge circuit fed with a.c. (5 mV peak-to-peak) from a signal source (Solatron type CO 564.2), the balance being detected using a tuned amplifier (General Radio type 1232-A). Linear sweep voltammetric experiments at a sweep rate of 1·35 mV sec^{-1} were made using a potentiostat (Chemical Electronics type TR 2A) coupled with a linear sweep generator (O.R. Brown). Temperature control was achieved using thermostats

25 ± 0·5°C, 90 ± 2°C. All chemicals were of A.R. quality, water was triply distilled from deionized stock. Counter electrodes were made of platinum gauze of large surface area. Reference electrodes were calomel, in contact with KCl, saturated at all temperatures. Aluminium rod was 99·999% (supplied by Halewood Chemicals Ltd), and electrodes were constructed by encasing them in polyethylene and sectioning at right angles to the long axis so as to expose the cross section of the rod. Immediately before experiments were commenced the electrode was polished on glass lubricated with triply distilled water and allowed to attain an oxide film by standing in air for 3 min.

Solutions of NaCl in the concentration range 0·01–5·12 M were investigated in the temperature range 25–90°C. At 3·4 M NaCl concentration, additional experiments were made in which additions of Na_2SO_4 and $NaNO_3$ were made in the ranges 0·01–1 M and 0·1–3 M respectively.

3. Results

Fig. 1 shows the results of anodic galvanostatic polarization at a series of low current densities in NaCl solution. From the time of closing the circuit the potential shifted to more positive values. However, after a time this was reversed and a steady-state value resulted. The final potential depended strongly on the applied current, the higher the current density the more positive the steady-state potential.

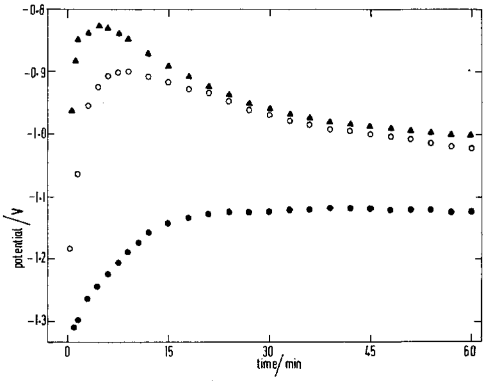

Fig. 1. Typical potential-time data for Al in 3·42 M NaCl at 25°C: ▲, 50 $\mu A\ cm^{-2}$; ○, 10 $\mu A\ cm^{-2}$; ●, 2·4 $\mu A\ cm^{-2}$.

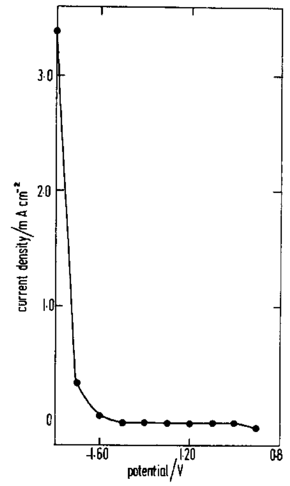

Fig. 2. Faradaic current-bias potential curve for Al in 3·42 M NaCl at 25°C.

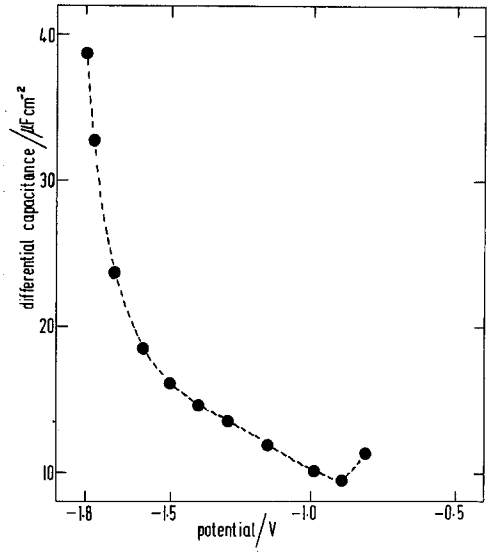

Fig. 3. A typical differential capacitance curve for Al in 3·42 M NaCl electrolyte, 1 KHz, 25°C.

Fig. 2 shows steady-state faradaic currents plotted against bias potential. Lattice disruption began at ~ −900 mV* and hydrogen evolution at ~ − 1600 mV. Within these limits there existed an experimentally polarizable region; the differential capacitance data corresponding to this region are shown in Fig. 3.

* All potentials are given on the saturated calomel scale at 25°C. Where temperatures differed from 25°C, correction was made for the shift in the reference electrode potential using data given in Ives and Janz [3].

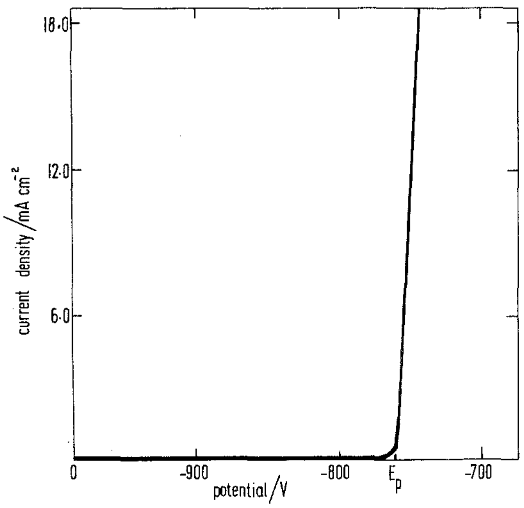

Fig. 4. Typical current-potential sweep (versus SCE at 40°C) for Al in 1 M NaCl at 40°C.

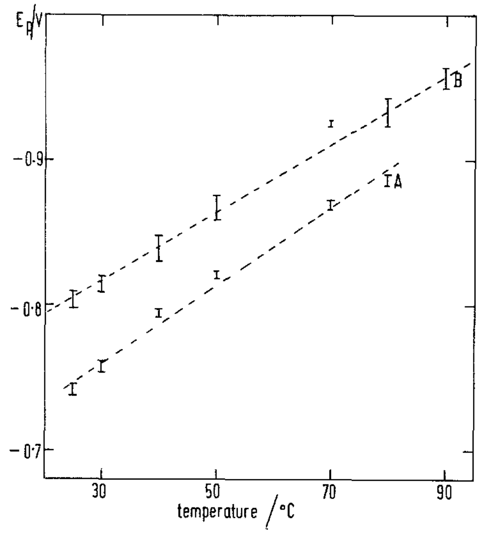

Fig. 5. Typical critical pitting potential-temperature data for Al in NaCl electrolyte: (A) 1·71 M; (B) 5·12 M.

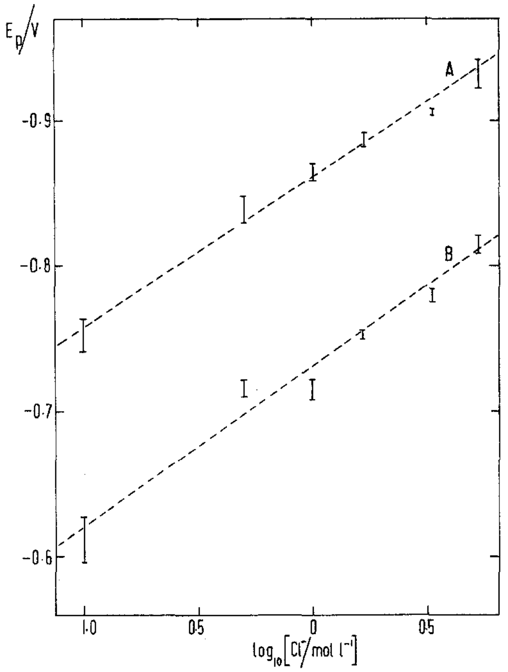

Fig. 6. Typical critical pitting potentials of Al in various concentrations of NaCl: (A) 80°C; (B) 30°C.

Table 1. Enthalpies of activation

[NaCl] mol dm^{-3} at 25°C	*[Na_2SO_4] mol dm^{-3} at 25°C*	*[$NaNO_3$] mol dm^{-3} at 25°C*	*Apparent activation enthalpy (kJ)*
0·01	–	–	8·4
0·5	–	–	6·5
1·0	–	–	10·0
3·42	–	–	12·8
5·12	–	–	12·6
3·42	0·01	–	4·0
3·42	0·1	–	5·9
3·42	0·5	–	11·2
3·42	1·0	–	25·9
3·42	–	0·1	14·9
3·42	–	0·5	11·4
3·42	–	1·0	11·2
3·42	–	3·0	11·3

Fig. 4 shows typical linear sweep potentiograms. No current flows at the more cathodic potentials, but as the electrode is driven more positive a large current flows as soon as a critical potential is exceeded. Around the foot of this increase only a very small region exists in which the current obeyed the Erdey–Gruz and Volmer relationship [4]; the current rapidly became of the linear form indicating ohmic control. The pitting potential, E_p, (see Discussion) was determined by extrapolation of the sharp rise of current back to the potential of zero current.

The effect of temperature on E_p is shown in Fig. 5, and the dependence of E_p on the chloride concentration of the etching solution is shown in Fig. 6; Figs. 5 and 6 are typical of all concentrations and temperatures investigated.

Additions of nitrate ion to the chloride solutions

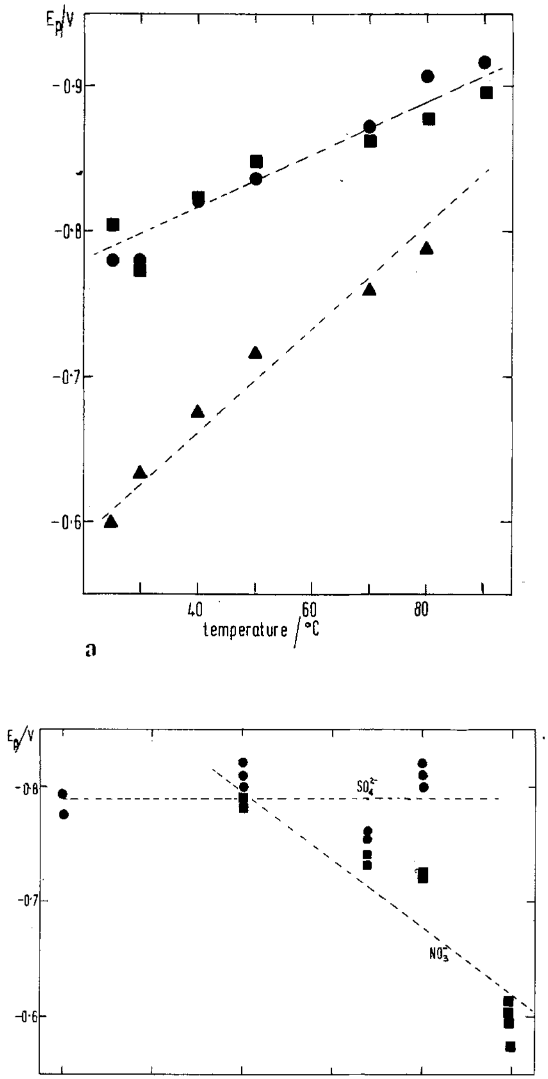

Fig. 7. (a) Critical pitting potential-temperature data for Al showing effect of SO_4^{2-} and NO_3^- additions: ●, 3·42 M NaCl; ■, 3·42 M NaCl containing 1 M Na_2SO_4; ▲, 3·42 M NaCl containing 3 M $NaNO_3$; (b) critical pitting potentials of Al in 3·42 M NaCl with Na_2SO_4 and $NaNO_3$ additions, 25°C.

caused a progressive shift in E_p to more positive values whereas the effect of sulphate on E_p was not significant. Typical data are shown in Fig. 7a and b and Table 1. The points shown in Fig. 7a are each the average of several determinations.

4. Discussion

The galvanostatic results shown in Fig. 1 show that the system is complicated. Similar behaviour to that reported here has been reported by Richardson and Wood [5] and interpreted as evidence for the importance of film formation and pitting attack at the bases of flaws in the surface 'oxide' film as a competitive process. The active area of the electrode (total pitting area) increases simultaneously with the thickening of the oxide film leading to a maximum in potential. At the peak potential, the rate of increase in (anodic) potential due to film formation is balanced by the rate of decrease in potential due to surface area development. In agreement with this, the magnitudes of the peak heights clearly depend upon the applied currents as do the final potentials as required by initial and final current control by the growing oxide layer.

The low magnitudes of the differential capacitance values shown in the curves of Fig. 3 confirm the presence of a film at the electrode. The increase in capacitance at ~ -900 mV indicates that chloride ions can penetrate the film possibly via a pore or structural defect giving rise to a faradaic pseudocapacitance due to pitting. This is confirmed by the faradaic current curve (Fig. 2). Although the electrode capacitance due to the double layer may increase slightly due to the onset of pitting, this geometrical area increase will be small. Therefore, the differential capacitance increase indicates the onset of pitting and is tantamount to taking the definition of E_p to be when the aggressive ions penetrate the protective layer to reach the metal with point dissolution. This method of determining E_p corresponds to an equilibrium situation and is clearly independent of the corrosion rate.

The results of the linear sweep experiments confirm that the system is complex. In the experimental range of potential at the more negative potentials and temperatures near normal, the electrode is efficiently protected by the oxide layer. Even at the highest temperatures investigated no hydrogen evolution (net cathodic) current was observed from the electrode.

The onset of the pitting process results in a very rapid increase in positive (anodic) current immediately the potential is more positive than E_p. The value of E_p can be unequivocally obtained by extrapolating back the current-potential curve to zero current. The value of E_p obtained is in reasonable agreement with values from differential capacitance measurements although it should be emphasized that such agreement is unlikely at rapid sweeping speeds.

The mechanism of pit initiation is still in doubt. Vetter [6] considers that pitting occurs when there is equilibrium between the protective oxide and the salt of the metal and aggressive ion; Uhlig [7] considers that the equilibrium involved is between the aggressive ion and oxygen for adsorption sites; Vermilyea [8] considers that at E_p, reaction to form a salt of the aggressive ion is just thermodynamically favoured over reaction with water molecules to form the oxide. This latter theory leads to an approximately correct theoretical value for E_p in the case of Al in chloride media. The theories suggested so far are not completely dissimilar for it is clear that if the chloride ion is to act in an aggressive manner in pit formation, then it must approach sufficiently close to the surface to react. Driving the electrode positive will increase the interaction of both Cl^- and oxygen dipoles with the surface. However, as the surface becomes more positive the Cl^-—Al interaction will overshadow that between H_2O—Al. At more negative potentials the Al—O will predominate; thus, as the potential varies positively in the experimental range the interactions at the electrode will change from protective to pitting. A simple explanation of why chloride ion is aggressive might be the obvious one of the solubility of the aluminium salts of the ion coupled with its adsorbability *vis-à-vis* the oxide. The pitting potential for a particular ion is therefore that potential required to bring Al ions in the lattice into equilibrium with Al^{3+} species and aggressive ions in the pit at the localized (microscopic) pitting conditions. Bogar and Foley [9], using a supporting medium of H_2SO_4 solution, find that the primary pitting reaction is:

$$\mathrm{Al} + 4\mathrm{Cl}^- = \mathrm{AlCl}_4^- + 3\mathrm{e}. \qquad (1)$$

Vermilyea considers that the pit solution is almost concentrated $AlCl_3$ solution and the pitting reaction to be:

$$\mathrm{Al} + 3\mathrm{Cl}^- = \mathrm{AlCl}_3 + 3\mathrm{e}. \qquad (2)$$

Thus E_p represents an equilibrium potential, albeit a rather special case where a net cathodic process would be difficult to demonstrate.

The nature of the equilibrium within the freshly initiated pore cannot be examined readily. However, Fig. 6 shows the effect of bulk chloride concentration on E_p. The slope of the E_p versus log $[Cl^-]$ curve is 100 ± 10 mV, and agrees fairly well with those of Böhni and Uhlig [10] (124 mV) and Kaesche [11] (124 mV) although these investigators used different methods for the determination of E_p. The present value indicates that Reaction 1 is more likely to be the correct one for pitting. It should, however, be noted that an aggressive reaction:

$$\mathrm{Al} + n\mathrm{Cl}^- \rightarrow \mathrm{AlCl}_n^{(n-3)-} + 3\mathrm{e} \qquad (3)$$

will not be exactly represented by an E_p dependence on bulk $[Cl^-]$

$$E_p = E_p^0 + 2{\cdot}3n\frac{RT}{3F}\log_{10}[\mathrm{Cl}^-],$$

since the chloride ion concentration at the electrode will be related to that in the bulk by an isotherm which is not necessarily linear. It is interesting to note that the value of E_p^0 observed in the present work (−0·757 V) compares well with Kaesche's [11] value of −0·746 V.

It is desirable to calculate the apparent enthalpy of activation for the process of pitting. Conventionally this is best done by measuring the rate of pitting at a constant driving potential as a function of temperature and measuring the slope of the resulting Arrhenius plot* as $\Delta H^{\neq}/2{\cdot}3R$. In the present case, an apparent enthalpy of activation for the pitting process can be found by measuring the rate of pit propagation (anodic pitting current) at a fixed potential increment (20 mV) from E_p at a series of temperatures. Typical plots are shown in Fig. 8. The values of the enthalpies of activation obtained from these plots are shown in Table 1. In calculating the apparent activation enthalpies it is recognized that the area of the electrode is increasing continuously with the time of the experiment. The method used here to derive the apparent activation enthalpies attempts to minimize this since the rate of reaction was determined under 'standard' conditions of potential (rather than at the equilibrium potential). Also, using L.S.V., the

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* True enthalpies of activation cannot be obtained for electrochemical reactions since the reversible potential of the reference system varies with temperature. This can only be assessed by measurements against a reference electrode at constant potential. Such measurements fail because of the presence of an unknown thermo-liquid junction potential [12].

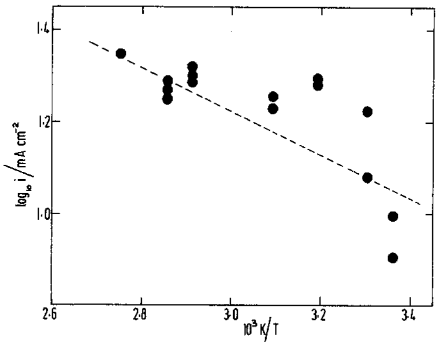

Fig. 8. Arrhenius plot for Al in 1 M NaCl at constant anodic driving potential ($\eta = 20$ mV).

extent of the uncertainty in area from experiment to experiment could be minimised since only a small amount of Faradaic charge is passed across the interphase during the time of the experiment. Nevertheless it is realized that the apparent activation enthalpies derived here may contain some degree of uncertainty. These values are not to be compared with Bogar and Foley's [9] value for the enthalpy of activation for the chloride breakdown of the oxide film on aluminium of ~ 80 kJ. These authors calculated the enthalpy from the temperature dependence of the induction time and it is clear that a different phenomenon from that presently being examined was involved. The magnitude of values of ~ 10 kJ suggests that the rate determining step is diffusion in solution; the diffusion of Cl^- from the bulk to the reaction site at the pit and diffusion of products from the pitting site determining the magnitude of the current flow. The effect of temperature on pitting is also to drive E_p to more negative values. Discussions of these phenomena are difficult, in common with discussions of all thermochemical effects. However it seems reasonable to expect the threshold potential for pit initiation to move to more negative potentials as the temperature is raised.

The effects of the addition of sulphate and nitrate ion on the onset of pitting are shown in Fig. 7. Sulphate is only a very weak inhibitor in chloride solutions of the concentrations investigated, E_p being negligibly displaced by relatively large sulphate additions. It is interesting to note that in 5 mM Cl^-, Böhni and Uhlig [10] found that sulphate shifted E_p by ~ 480 mV per decade of added $[SO_4^{2-}]$ at 25°C.

The addition of nitrate did, however, move E_p to more positive values to the extent of ~ 130 mV per decade of $[NO_3^-]$. Again this value should be compared with an earlier reported value of ~ 2300 mV per decade of $[NO_3^-]$ at a base $[Cl^-]$ of 0·1 M. It is clear therefore that the effect of the inhibiting ion is minimized by a high level of aggressive ion and that under etching conditions the sulphate ions are not effective as inhibitors.

Consideration of the relative adsorbability of sulphate and nitrate suggests that competitive adsorption is not the mode of inhibition of the nitrate ion under etching conditions. This follows from the expected greater tendency for adsorption of the doubly charged sulphate ion over that of the nitrate ion.

The effects of the added ions on the enthalpies of activation are shown in Table 1. The values of the enthalpies for chloride pitting in presence of sulphate and nitrate are more or less similar to the values for chloride solutions indicating that the energetics of the rate determining reaction are unaltered.

The presence of nitrate ion, during the tunnel etching of Al in chloride solutions, is known to result in both an increase in the size and a decrease in the number of tunnels produced [13]. It is therefore suggested that the mechanism of inhibition by nitrate ions is via a more perfect oxide layer promoted by the oxidizing anion. Under these conditions the potential across the more mechanically perfect oxide layer required to bring chloride ions into contact with the metal is greater in the presence of nitrate. Therefore E_p is driven more positive. An alternative explanation of the inhibition by nitrate ion has been given by de Wexler and Galvele [14] who considered that the removal of hydrogen ion by nitrate ion (to form nitrogen gas) retarded the rate of the corrosion reaction. Which explanation is the correct one is difficult to say: both may be involved.

5. Conclusions

(1) E_p can be readily measured by differential capacitance measurements. L.S.V. measurements at low rate give similar results.

(2) E_p depends on bulk $[Cl^-]$ with a shift of 100 ± 10 mV per decade of $[Cl^-]$.

(3) Nitrate ions inhibit pitting by shifting E_p to more positive values.

(4) The determination of an approximate activation enthalpy is useful in that although the value is not in any sense absolute, it provides additional data with which certain effects can be explained. $\Delta H^{\neq}$ for pitting is ~ 11 kJ.

(5) The rate determining process for pitting is likely to be the diffusion of soluble species.

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