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## THE ELECTROCHEMICAL BEHAVIOUR AND CORROSION OF ALUMINIUM IN CHLORIDE MEDIA. THE EFFECT OF INHIBITOR ANIONS

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**Abstract**—The effect of nitrite and chromate inhibitor ions in varying concentrations on the corrosion of aluminium in near-neutral chloride solution has been studied using measurements of the open circuit potential and its variation with time, cyclic voltammetry, potential step chronoamperometry and electrochemical impedance measurements. A concentration dependence is shown, more marked in the case of chromate, as is the effect on oxide film growth through the variation of corrosion potential with the logarithm of time. Differences between the mode of action of the two inhibitors are demonstrated, particularly by impedance measurements. At potentials close to the corrosion potential, nitrite is the more effective inhibitor, acting through strong adsorption. Above the pitting potential, nitrite becomes ineffective and chromate acts through repairing the oxide film and aiding oxide growth, as shown through corrosion potential, chronoamperometry and impedance data.

### INTRODUCTION

THE MANY important applications of aluminium and its alloys have resulted in research into its electrochemical behaviour and corrosion resistance in a wide variety of media, including investigation of the properties of the surface oxide film, formed naturally or by anodization.<sup>1</sup> Generally, this consists of a thin barrier film adjacent to the metal (~25 nm thick) covered by a thicker porous oxide layer. In aggressive media, such as chloride solution, localised corrosion can occur leading to the breakdown of the passive layer and pit formation.

The electrochemistry of aluminium in chloride solution at a wide variety of pH values has been widely investigated, e.g. Refs 2–10. Some work has been directed specifically to the mechanism of pit initiation and to artificially produced pits in chloride media.<sup>11–15</sup> The effect of the presence of different ions in solution on the electrochemical behaviour, inhibiting or enhancing corrosion, has also been studied.<sup>16–21</sup>

Pit formation can occur by migration (i.e. absorption) of aggressive ions to within the porous oxide layer due to the high electric field, via film cracking due to anion adsorption causing local mechanical stresses, and through formation of soluble complex ions by chemical reaction.<sup>22</sup> It is clear that these processes will occur most easily at defects in the oxide film, or where the film is thinnest. Thus, useful corrosion inhibition must protect against attack of this kind.

In this work, the inhibition of aluminium corrosion by two soluble inhibitor anions, chromate and nitrite, was studied. Techniques employed include the variation of open circuit potential with time, linear sweep and potential step voltam-

metry, impedance spectroscopy and scanning electron microscopy. Inhibitors can act by competitive adsorption with the aggressive ion, by making the anodic reaction more difficult (possibly by aiding oxide film formation), or by increasing the hydrogen evolution/oxygen reduction overpotential—perhaps through a pH increase.<sup>23</sup>

### EXPERIMENTAL METHOD

Disc electrodes of area 0.20 cm<sup>2</sup> made from pure aluminium (Johnson Matthey, 99.999% purity) and surrounded by a Teflon sheath were polished metallographically down to 1 μm particle size before use and rinsed carefully with acetone. The cell also contained a platinum gauze counter electrode and a Radiometer K401 saturated calomel reference electrode (SCE).

Voltammetric experiments were carried out using an in-house-constructed potentiostat, with a bounce-free flip-flop switch for potential step experiments. Voltammograms were recorded on a HP7035B XY recorder, and current transients on a Gould Advance OS4020 Digital Storage Oscilloscope, being transferred to the XY recorder afterwards. Impedance spectra were recorded using a Solartron 1250 Frequency Response Analyser coupled to a Solartron 1286 Electrochemical Interface, with a 5 mV rms perturbation. Scanning electron microscopy was done with a Jeol T330 scanning electron microscope.

Solutions were made from analytical grade reagents and tridistilled water, and contained varying concentrations of potassium chloride, potassium chromate and sodium nitrite, made up to a constant ionic strength of ~1.2 mol dm<sup>-3</sup> with potassium sulphate electrolyte. Experiments were conducted at 25 ± 1°C, and solutions were not de-aerated unless otherwise stated.

### EXPERIMENTAL RESULTS AND DISCUSSION

Results obtained for the different media will be presented by technique, rather than by solution constitution. Comparisons will be made for each technique separately and the information given by each technique will then be discussed, leading to the final conclusions.

#### *Open circuit potential*

Freshly polished aluminium electrodes were introduced into the various solutions and the variation of open-circuit potential,  $E_{\text{corr}}$ , with time was monitored. This information is shown for several concentrations of chloride ion and nitrite (Fig. 1a and b) or chloride and chromate (Fig. 2a and b). Differences between the  $E_{\text{corr}}$  vs  $t$  plots in Figs 1a and 2a are evident, although the trend in all cases is for  $E_{\text{corr}}$  to become more positive with time, due to oxide film growth. In particular, initial values in chromate-containing solution are more negative than in nitrite-containing solution; also the dependence of  $E_{\text{corr}}$  on concentration is much more marked for nitrite than the chromate. This suggests that the nitrite ion is strongly and rapidly adsorbed at these potentials.

More information can be extracted by considering the variation of  $E_{\text{corr}}$  with the logarithm of time,  $\lg t$ , at longer times. The following expression has been proposed for the variation of the potential,  $E$ , in situations where there is growth of anodic oxide and that its formation is the rate-limiting step<sup>24</sup>

$$E = \text{constant} + 2.303(\delta/B) \lg t,$$

in which  $\delta$  is the rate of oxide film thickening per decade of time and  $B$  is given by

$$B = (nF/RT)\alpha\delta'.$$

Here  $\alpha$  is a transference coefficient and  $\delta'$  is the width of the energy barrier traversed by the metal ion during oxide formation; all other symbols have their usual meaning.

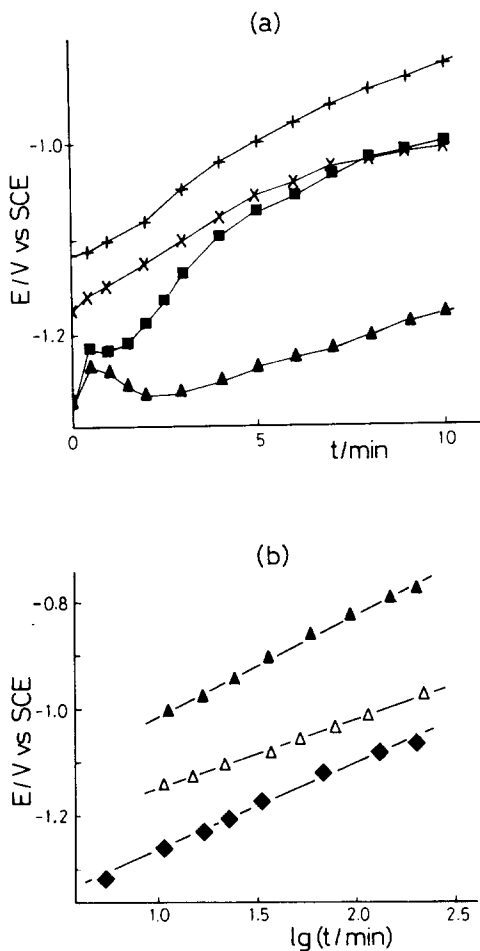


FIG. 1. Open circuit potential data for solutions containing chloride and nitrite anions; K<sub>2</sub>SO<sub>4</sub> electrolyte added such that the ionic strength,  $I \sim 1.2 \text{ mol dm}^{-3}$ . (a) Variation of  $E_{\text{corr}}$  vs  $t$ : (+) 0.01 M NaNO<sub>2</sub> + 0.01 M KCl; (■) 0.05 M NaNO<sub>2</sub> + 0.05 M KCl; (×) 0.10 M NaNO<sub>2</sub> + 0.05 M KCl; (▲) 0.10 M NaNO<sub>2</sub> + 0.10 M KCl. (b) Plots of  $E_{\text{corr}}$  vs  $\lg t$  for: (◆) 0.10 M KCl; (▲) 0.10 M NaNO<sub>2</sub> + 0.10 M KCl; (△) 0.10 M NaNO<sub>2</sub> + 0.10 M KCl (de-oxygenated solution).

Thus, if there is a linear relation between  $E$  and  $\lg t$ , as indeed occurs (see Figs 1b and 2b), then the slope of the plot is directly proportional to the rate of oxide growth.

We would expect that: (i) a strongly adsorbed inhibitor ion has little effect on oxide growth rate (or possibly diminishes it in the absence of the aggressive ion); (ii) an inhibitor ion that aids oxide growth leads to a higher slope on the plot; (iii) in de-oxygenated solution, lower slopes are obtained.

Examination of Figs 1b and 2b therefore suggests that nitrite is strongly adsorbed and that the rate of film growth is not higher in relation to solutions containing chloride only. Strong anion adsorption would tend to impede oxide growth. Thus, the chromate ion, which is not so strongly adsorbed, aids oxide growth, as shown by

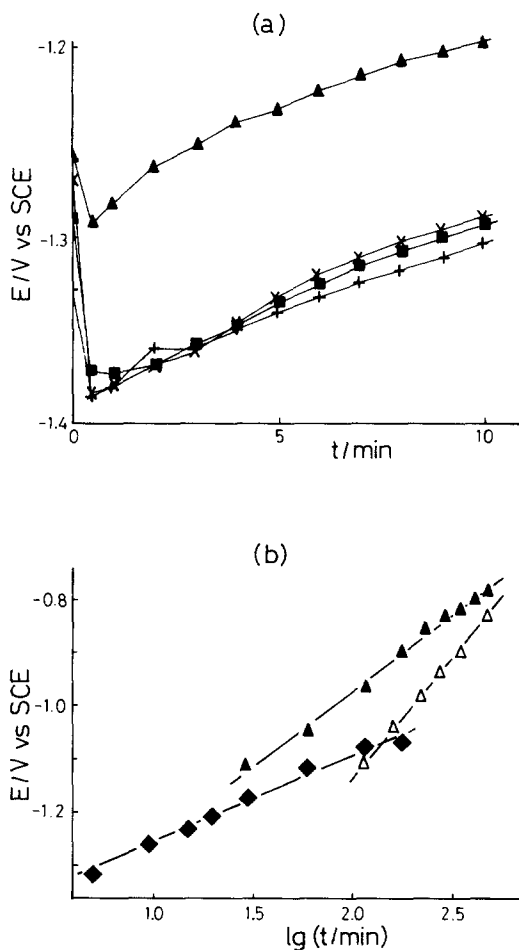


Fig. 2. Open circuit potential data for solutions containing chloride and chromate anions:  $K_2SO_4$  electrolyte added such that the ionic strength,  $I \sim 1.2 \text{ mol dm}^{-3}$ . (a) Variation of  $E_{corr}$  vs  $t$ : (+) 0.01 M  $K_2CrO_4$  + 0.01 M KCl; (■) 0.05 M  $K_2CrO_4$  + 0.05 M KCl; (×) 0.10 M  $K_2CrO_4$  + 0.05 M KCl; (▲) 0.20 M  $K_2CrO_4$  + 0.10 M KCl. (b) Plots of  $E_{corr}$  vs  $lg t$  for: (◆) 0.10 M KCl; (▲) 0.20 M  $K_2CrO_4$  + 0.10 M KCl; (△) 0.20 M  $K_2CrO_4$  + 0.10 M KCl (de-oxygenated solution).

the higher slopes in the  $E_{corr}$  vs  $lg t$  plots. In both cases, lower slopes were found in de-oxygenated solution, as predicted above.

### Cyclic voltammetry

Figure 3 shows some linear sweep voltammograms in solutions containing chloride only, chloride plus nitrite, and chloride plus chromate ions. It is seen that the effect of chromate ion is much greater than the effect of nitrite ion. Inclusive, the pitting potential in the latter case is shifted to much more positive values. Recording the current-voltage profiles in the region of the corrosion potential at lower scan rates permits the extrapolation of plots from which the corrosion current and corrosion potential may be calculated. This leads to reasonable agreement with

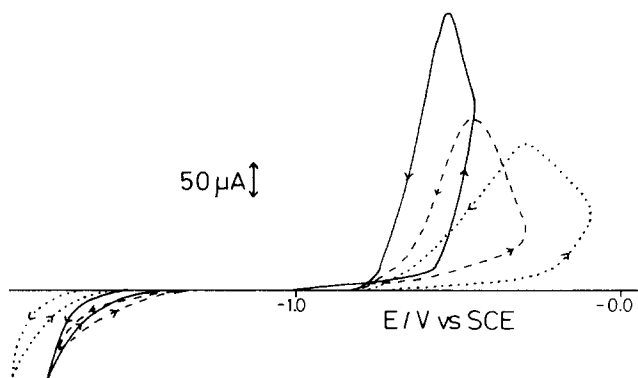


FIG. 3. Illustrative cyclic voltammograms in solutions containing (—) 0.10 M KCl; (- - -) 0.10 M NaNO<sub>2</sub> + 0.10 M KCl; (· · · · ·) 0.10 M K<sub>2</sub>CrO<sub>4</sub> + 0.10 M KCl, in addition to K<sub>2</sub>SO<sub>4</sub> electrolyte.  $\nu = 20 \text{ mV s}^{-1}$ .

open circuit potential values. The corrosion current decreased with increasing inhibitor concentration and was lower for chromate than for nitrite-containing solutions.

Once again the difference between nitrite and chromate ions is shown, although no specific clues as to the mechanism are evident.

#### Potential step

In these experiments, the potential applied to the aluminium electrode was stepped from  $-1.1 \text{ V(SCE)}$  (a value close to the potential of freshly polished electrodes) to more positive values, and the shape of the current transient analysed according to a power law  $I \propto t^n$ . Figure 4 shows some of the transients obtained for a final potential of  $-0.3 \text{ V}$ ; note that the current scale is different in each case. In general, it was found that the currents are higher the higher the chloride concentration and the lower the inhibitor concentration. Below the pitting potential, nitrite was more effective than chromate in reducing the current, although above the pitting potential chromate continued to inhibit, whereas, after a 3 s induction period, nitrite became ineffective.

It was found in all cases by means of log-log plots that the best value of the  $t^n$  dependence was with  $n = -1$ . This implies a uniform, homogeneous growth of oxide film on the surface, due to a strong electric field,<sup>25</sup> as would be predicted from the semiconductor nature of aluminium oxide. Example plots are given in Fig. 5. Where the current began to rise after an induction period, the transient was analysed only before this time. The intercepts of these plots agree well with the measured values for  $I(t \rightarrow \infty)$ . It can be deduced that the oxide continues to grow during this period at a lower rate than without inhibitor, which implies adsorption of the species and partial blocking of the surface.

In chloride-containing solutions and where the final potential is positive of the pitting potential an induction period of about 3 s is usually found, after which the current begins to rise in a slightly irregular way. Analysis of this portion of the  $I-t$  curve shows a power law of  $I \propto t^{3/2}$ , which is indicative of diffusion control in pitting nucleation.

For solutions containing chromate, two interesting features are seen. First, there is no increase in current at long times for final potentials positive of the pitting

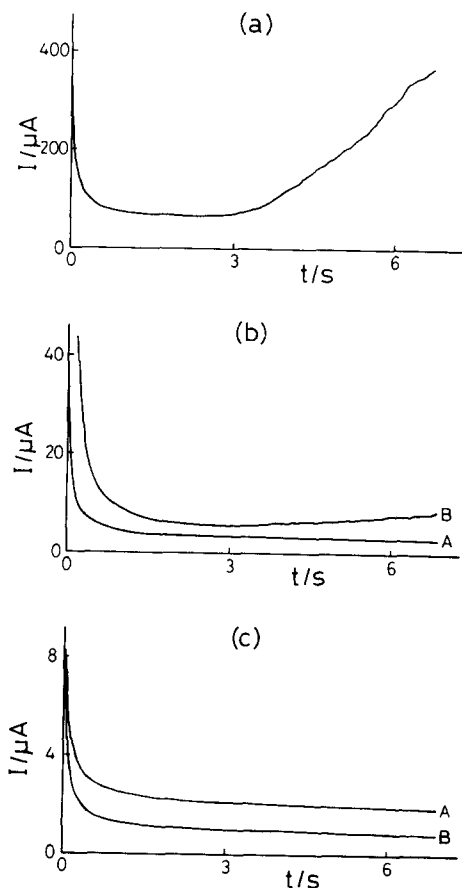


FIG. 4. Examples of chronoamperometric transients obtained by potential step from  $-1.1$  V to  $-0.3$  V vs SCE in solutions containing: (a)  $1.10$  M KCl +  $0.37$  M  $K_2SO_4$ ; (b)  $0.10$  M  $NaNO_2$  with A:  $0.37$  M  $K_2SO_4$ , B:  $0.10$  M KCl +  $0.33$  M  $K_2SO_4$ ; (c)  $0.10$  M  $K_2CrO_4$  with A:  $0.38$  M  $K_2SO_4$ , B:  $0.10$  M KCl +  $0.27$  M  $K_2SO_4$ .

potential, as mentioned above. Secondly, the more positive the final potential, the lower the current as  $t \rightarrow \infty$ . Also, see Fig. 4c, the current is lower in the presence of chloride than in its absence. This unexpected result suggests that there is an interaction between the chromate and chloride ions which leads to a reordering of the surface layers of the oxide. As for previous data obtained by other techniques, the conclusion is that chromate is aiding oxide film growth.

#### *Impedance spectroscopy*

Impedance spectra probably show the differences between the two inhibitor ions most clearly, as described elsewhere.<sup>26</sup> Figure 6a and b shows spectra at  $-1.0$  V and  $-0.6$  V(SCE) in chloride solution in the presence of nitrite and chromate inhibitor ions, respectively. The higher the inhibitor concentration for a given chloride concentration, the larger the semicircle radius.

At  $-1.0$  V the spectra in Figs 6a and b are qualitatively similar and can be

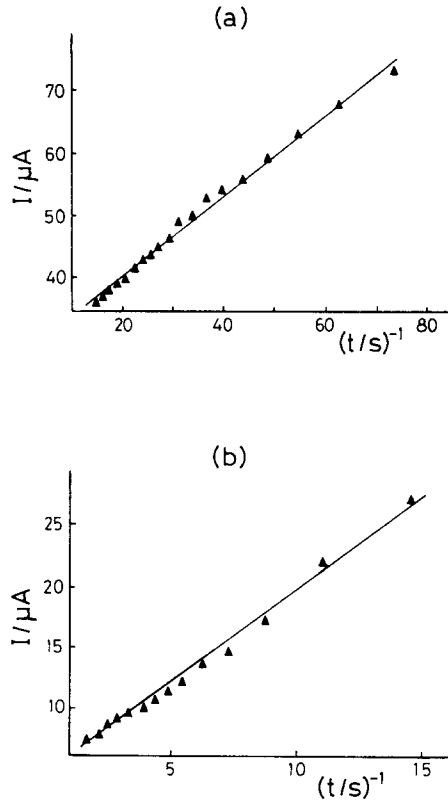


FIG. 5. Typical plots of  $I$  vs  $t^{-1}$  from chronoamperometric transients of (a) 0.10 M  $\text{NaNO}_2$  + 0.10 M  $\text{KCl}$ ; (b) 0.10 M  $\text{K}_2\text{CrO}_4$  + 0.10 M  $\text{KCl}$ .

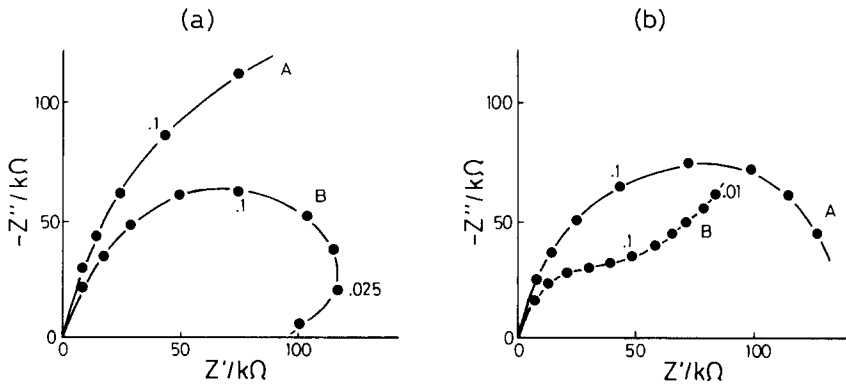


FIG. 6. Complex plane impedance plots at potentials of A  $-1.0$  V and B  $-0.6$  V vs SCE for solutions containing, besides  $\text{K}_2\text{SO}_4$  electrolyte: (a) 0.10 M  $\text{NaNO}_2$  + 0.10 M  $\text{KCl}$ ; (b) 0.10 M  $\text{K}_2\text{CrO}_4$  + 0.10 M  $\text{KCl}$ . Frequencies in Hz.

modelled by a parallel RC combination representing the oxide film on the aluminium substrate; the radius of the semicircle is much larger in the case of nitrite. By  $-0.6$  V, slightly above the pitting potential, the semicircle for nitrite-containing solution is now smaller than before and begins to show evidence of film relaxation effects at low frequency. The resistance of the parallel RC combination is much smaller in the absence of nitrite anion, and with just chloride ions present. At this applied potential, chromate-containing solutions begin to show indications of a capacitance in series with the parallel RC combination, which becomes more accentuated at more positive potentials. Calculated values of this capacitance are of the order of  $100\text{--}150\ \mu\text{F cm}^{-2}$ . In the case of nitrite, as for chloride solutions alone, no inhibition at more positive potentials occurs, the current fluctuates wildly and it is not possible to record reproducible impedance spectra.

### *Comparison of results*

All these experiments show that both nitrite and chromate ions lead to a concentration-dependent inhibitor action, but that their mechanism of action is different. No evidence was found for enhanced corrosion at low inhibitor ion concentrations due to reduction of the ions themselves.

The nitrite ion appears to act primarily by strong adsorption, such that it is competing with the chloride ion for adsorption sites. Below the pitting potential, this is sufficient to inhibit corrosion effectively, and this is shown particularly by the potential step and impedance results. Above the pitting potential, chloride becomes sufficiently active so as to overcome this adsorption effect. This is corroborated by SEM of aluminium surfaces such as that of Fig. 7, where a typical crystallographically etched pit is shown. Pits tend to be shallow and wide, not hemispherical as found in other solution media.<sup>12,15</sup>

The adsorption of chromate appears not to be so strong as nitrite, and open circuit potential data suggest that chromate is actively partaking in the oxidation process by promoting oxide film growth, as shown by the higher slopes in the  $E_{\text{CORR}}$  vs  $\lg t$  plots. Thus it is not surprising that above the pitting potential, this process should continue. Strong evidence of chromate adsorption is found from the impedance spectra. SEM micrographs of surfaces exposed to chromate and chloride solution taken under similar conditions to those used to produce Fig. 7 show no evidence of pitting, but rather a fuzziness which could be attributed to a small increase in oxide film thickness. The role of chromate has been noted before in other contexts, e.g. Refs 27 and 28 and was suggested to occur through the reduction of Cr(VI) to Cr(III) producing oxide ions which help repair defects in the oxide film and aid oxide growth, such that pitting is avoided. Our data confirm this, the role in oxide growth particularly through plots such as those of Fig. 2b.

## CONCLUSIONS

This work shows, using a number of electrochemical techniques, that nitrite and chromate ions are both reasonably successful inhibitors. At potentials close to the corrosion potential, nitrite is the more effective inhibitor, whereas at more positive potentials, positive of the pitting potential chromate is effective, but nitrite is not. This is particularly shown by potential step and impedance results, although open circuit potential data are valuable in showing the role of chromate ion in aiding oxide film growth. Additions of potassium chromate to potassium chloride solutions





FIG. 7. Scanning electron micrograph showing pit formation after exposure for 20 min at  $-0.5$  V(SCE) in a solution containing  $0.10$  M  $\text{NaNO}_2$  +  $0.10$  M  $\text{KCl}$  +  $0.33$  M  $\text{K}_2\text{SO}_4$ .

proved more successful in inhibiting pitting corrosion of pure aluminium than addition of nitrite; this could be due to improved film repair conditions.

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