

**THE EFFECT OF INHIBITOR ANIONS ON THE CORROSION OF
ALUMINIUM IN CHLORIDE-CONTAINING SOLUTIONS**

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ABSTRACT

A comparative study of the inhibition of aluminium corrosion by nitrite and chromate ions in chloride media was carried out. Results indicate that negative of the pitting potential nitrite is the more effective inhibitor, whereas at more positive potentials nitrite loses its inhibiting power and chromate remains effective through its aiding oxide formation.

Protection of metals against corrosion can be done by coatings, electrochemical protection of the corroding surface, or through addition of soluble inhibitors to the contacting liquid. In this work a comparison of the inhibition of the corrosion of aluminium by two oxy-anions, nitrite and chromate, added to solutions at near-neutral pH was carried out.

In chloride media, the naturally-formed oxide film on aluminium is readily attacked, often leading to pits in the electrode surface [1]. Inhibitor adsorption on the metal surface can physically impede attack by aggressive ions, inhibitors can react preferentially so as to block the corrosion anodic half-reaction, or they can increase the hydrogen overpotential [2].

Characterisation of the corrosion mechanism was done by using measurements of the open-circuit potential and its variation with time, linear sweep voltammetry, potential step experiments and electrochemical impedance spectroscopy. These were complemented by scanning electron microscopy.

Experiments were carried out with disc electrodes of pure aluminium, area 0.2cm^2 . Electrodes were freshly polished and rinsed with acetone before each experiment. Aqueous solutions of potassium salts with variable composition were employed, containing concentrations of chloride ion up to 0.10M , and inhibitor up to 0.20M ; the ionic strength was kept constant at $\sim 1.2\text{M}$ by addition of potassium sulphate electrolyte. The pH of the bulk solution was adjusted to be between 8 and 9. Unless stated otherwise, solutions were not deaerated.

The time-variation of the open-circuit potential was measured for solutions of various compositions. After an initial period of rapid change from values which were usually in the region of -1.2V to -1.0V vs. SCE, the potential varied linearly with $\log t$, as illustrated by the examples of Fig.1. This suggests that the anodic reaction is rate-limiting, and the slope of the plots is proportional to the rate of oxide growth [3]. In the case of nitrite, the values of the open-circuit potential were continuously affected by its concentration, but the rate of oxide growth remained almost unaltered. With regard to chromate ion inhibitor, it was found that above a concentration of 0.05M , the open-circuit potential became concentration independent. It was also found that the slopes of the plots were higher with chromate than nitrite. In nitrite-containing solution, deoxygenation gave a lower slope on the E vs. $\log t$ plot, but for chromate there was a slight increase. This suggests a more complicated interaction in the latter case, which is evidenced in other types of experiment.

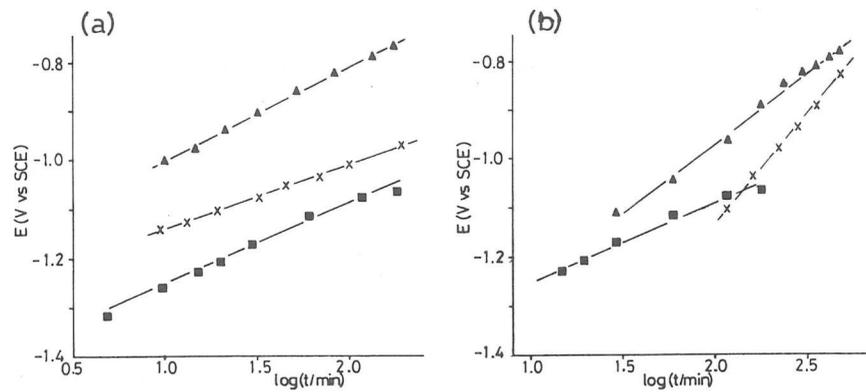


Fig.1 Plots of open circuit potential vs. $\log(\text{time})$ for solutions containing: ■ chloride ion (0.10M) and (a) nitrite anion 0.10M , (b) chromate ion 0.20M , with (▲) and without (×) dissolved oxygen.

The form of the potentiodynamic curves is that of a metal undergoing pitting corrosion, even with high concentrations of inhibitor. However, currents are lower, and after leaving the electrode in the electrolyte for a period of half an hour, initiation of pitting occurred for more positive potentials. Pitting potentials were generally found to be between -0.7V and -0.6V vs. SCE. Tafel plots were constructed from data recorded at low scan rates (5mV s^{-1}) and corrosion currents were calculated. These diminished with increasing inhibitor concentration, from values of $60\mu\text{A}$ in 0.10M chloride solution to $0.3\mu\text{A}$ in chloride plus 0.10M chromate inhibitor. Low values for the anodic transfer coefficient suggest a strong interaction between Al and OH species.

Potential step chronoamperometric transients, recorded in the zone of potentials where the corrosion rate was not large, stepped from an initial value of -1.1V vs SCE, to successively more positive potentials, were fitted to plots of I vs. $t^{1/2}$ and I vs. t^{-1} . Best linearity and good correlation between intercepts on the current axis and currents in the raw transients corresponding to infinite time was achieved with the latter plots. This dependence on t results from a mechanism of homogeneous oxide growth [4], and occurs for both inhibitor anions. Observed currents were lower for chromate than for nitrite ion.

Impedance spectroscopy showed effects of anion adsorption and competition with the adsorption of chloride ions. It also showed the differences between nitrite and chromate ions. Fig.2 shows some results obtained with chromate anion.

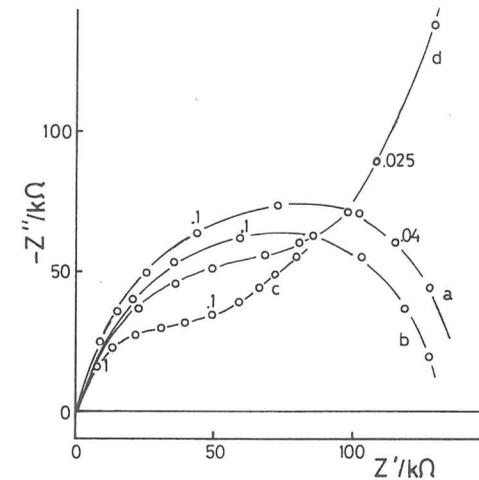


Fig.2 Complex plane impedance spectra of aluminium in a solution containing 0.10M KCl, 0.10M K_2CrO_4 and 0.27M K_2SO_4 at potentials of: (a) -1.0V , (b) -0.8V , (c) -0.6V , (d) -0.4V vs. SCE. Frequencies in Hz.

Modelling shows that, positive of the pitting potential, chromate ion is associated with a large pseudo-capacitance of the order of $150\mu\text{F cm}^{-2}$, clear from the low-frequency variation. At these potentials, nitrite ion does not inhibit the corrosion process.

Scanning electron microscopy of the surfaces of the aluminium electrodes submitted to an applied potential of -0.5V vs. SCE for 20 minutes showed crystallographically etched pits for chloride and for chloride plus nitrite solutions, but no visual evidence of pitting for chromate-containing solutions. Thus, this and the impedance results point to the strong adsorption of chromate ion at potentials positive of the pitting potential and its aiding oxide growth and repair of defects in the oxide film, probably through reduction of the chromate ion with simultaneous production of oxide ions.

In conclusion, the inhibitor action for both these anions has been demonstrated and both of them adsorb and compete with chloride ion on the aluminium surface. At potentials more negative than the pitting potential, nitrite is the more effective inhibitor, but this situation is reversed at more positive potentials, due to the ability of chromate ion to aid oxide film growth. Of the electrochemical techniques employed, impedance is that which gives most information about the electrode processes occurring.

REFERENCES

1. C.M.A. Brett, *Corrosion Sci.*, 1992, **33**, 203 and references therein.
2. G. Trabanelli, *Corrosion*, 1991, **47**, 410.
3. A.M. Shams El Din and N.J. Paul, *Thin Solid Films*, 1989, **189**, 205.
4. J.W. Schültze, M.H. Lohrengel and D. Ross, *Electrochim. Acta*, 1983, **28**, 973.

A VOLTAMMETRIC STUDY OF SILVER DEPOSITION ON CARBON MICROELECTRODES

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The development of microelectrodes has made an impact in the electrochemistry domain, opening up new opportunities for the investigation of in situ properties of several systems. This has led to the evolution of a major number of theoretical methods which model the properties of such systems. Due to the high quality and precision of the experimental data acquired with microelectrodes novel concepts have been achieved and hitherto inaccessible parameters have been determined.

It has been shown elsewhere [1] that it is possible to obtain a complete description of the single and double potential step experiments associated to the metallic nucleation process. The basic reason why it is possible to do this is that the time dependence of the radius can be determined.

Linear sweep voltammetry (LSV) measurements have the advantage that they traverse the whole range of potentials. The disadvantage is that one cannot obtain a complete closed form analytic description of the experiments. The reason is that it seems impossible to integrate the non-linear inhomogeneous expression

$$\frac{dr}{dt} = \frac{Mk_{Ag^+}}{\rho} = \frac{Mk_{Ag^+}^0}{\rho} \frac{\left\{ \exp\left(\frac{-\alpha_{Ag^+}Fv t}{RT}\right) - \exp\left(\frac{(1-\alpha_{Ag^+})Fv t}{RT}\right) \right\}}{\left\{ 1 + \frac{rk_{Ag^+}^0}{D_{Ag^+}C_{Ag^+}^\infty} \exp\left(\frac{-\alpha_{Ag^+}Fv t}{RT}\right) \right\}} \quad (1)$$

where r (cm) is the radius of the particle, t (s) is the time, K_{Ag^+} and $K_{Ag^+}^0$ ($\text{mols cm}^{-2}\text{s}^{-1}$) are rate constants of crystal growth, M (g mol^{-1}) is the molecular weight, ρ (g cm^{-3}) is the density, α_{Ag^+} are the transfer coefficients, v (V s^{-1}) is the potential sweep rate, $C_{Ag^+}^\infty$ (mol cm^{-3}) is the bulk concentration, T ($^\circ\text{C}$) is the temperature, D_{Ag^+} ($\text{cm}^2 \text{s}^{-1}$) is the diffusion coefficient and F (C mol^{-1}) is the Faraday constant. It is only possible to do this numerically and, in such numerical procedures, one can be guided by the parameters established for the potentiostatic experiments. So far, theoretical simulations were drawn for the two limiting conditions, i.e., diffusion controlled growth and kinetically controlled deposition [1].