

Inhibition of aluminium corrosion in chloride media: an impedance study

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Inhibition of the corrosion of pure aluminium by nitrite and chromate anions in near neutral aqueous chloride solution has been studied by electrochemical impedance spectroscopy, keeping the ionic strength constant by addition of potassium sulphate electrolyte. Negative of the chloride pitting potential impedance spectra show that both anions are successful in reducing corrosion through adsorption, nitrite more than chromate. Positive of this value, nitrite becomes ineffective, whereas chromate remains adsorbed and continues to prevent pitting corrosion, probably through its ability to repair defects in the oxide film. Impedance techniques successfully show the qualitative and quantitative differences between the two inhibitors.

1. Introduction

The electrochemical behaviour and corrosion of aluminium and its alloys has been the subject of a large number of studies, due to its widespread application, technologically and otherwise, and has been recently reviewed [1]. These applications are often possible because of the natural tendency of aluminium to form a passivating oxide layer, which can be formed artificially by anodization processes. However, in aggressive media the passivating layer can be destroyed, as occurs with pitting corrosion in chloride media. This is used to good effect in hydrochloric acid etching for the electronics industry and in highly alkaline solution for the aluminium/air battery.

Several methods can be used to protect metals or alloys against corrosion. These are the formation of a protective coating on the surface, protection of the substrate electrochemically through an applied potential or current, or the addition of species to the solution in contact with the surface in order to inhibit the corrosion reaction and reduce the corrosion rate [2]. It is the last of these which has been studied here.

The effect of the presence of a number of ions in solution on aluminium corrosion has been investigated, some enhancing and others reducing the corrosion rate [3–7]. By probing the influence of ions, and especially inhibitor ions, on the electrochemical partial corrosion reactions, it can be determined whether they increase the overpotential of the cathodic reaction or make the anodic metal oxidation reaction more difficult, and the importance of inhibitor ion adsorption can be evaluated.

Electrochemical impedance spectroscopy (EIS) has proved a powerful tool for studying metallic corrosion

processes [8, 9]. It has been used to elucidate aspects of the corrosion and electrochemical behaviour of aluminium and anodized aluminium in a variety of media [10–19].

Voltammetric experiments have been carried out on the inhibition of aluminium corrosion in chloride media by the addition of nitrite or chromate ions [20]. In relation to the corrosion of iron, these have both been classed as Type II inhibitors [21], acting through inhibition of the anodic reaction by adsorption. Linear sweep and potential step techniques together with measurements of open circuit potential, suggest that the anodic reaction is rate-limiting [20]. Open circuit potential variation with time showed a linear E against $\log t$ relationship which is indicative of continuous oxide growth. Voltammetric results showed that nitrite does not increase the rate of oxide growth in chloride-containing solution but that chromate ion does, including at potential values more positive than the pitting potential (-0.65 V vs SCE).

In this work EIS is employed to investigate the inhibition of aluminium corrosion in chloride media by nitrite or chromate ions, with a view to elucidating and distinguishing their mode of action.

2. Experimental details

Experiments were performed on pure aluminium (99.999%) disc electrodes of area 0.20 cm² made from cylindrical sections and embedded in a Teflon[®] sheath, with a copper wire connection made by silver epoxy resin. A platinum gauze counter electrode and Radiometer K401 SCE reference electrode were employed, with the reference electrode tip placed close to the aluminium surface by means of a Luggin capillary. The aluminium electrodes were polished metallographically down to 1.0 μ m particle size and rinsed carefully in acetone before use.

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Solutions were made from analytical grade reagents and tridistilled water: containing 0.10 M KCl, 0.10 M NaNO₂ or 0.10 M K₂CrO₄ (both inhibitors) and 0.10 M KCl + 0.10 M inhibitor, the ionic strength being made up to 1.2 mol dm⁻³ with potassium sulphate (the equivalent of 0.4 M K₂SO₄ electrolyte), besides 0.4 M K₂SO₄ electrolyte alone as a reference solution. The concentration of added K₂SO₄ in mixed electrolyte solutions corresponded to an excess, confirmed by varying its concentration. Lower concentrations of chloride and inhibitor ion were also employed, with qualitatively similar results, and so only data obtained for these highest concentrations will be presented. Solutions were not deaerated, and experiments were conducted at 25 ± 1 °C.

Impedance spectra were recorded using a Solartron 1250 frequency response analyser coupled to the Solartron 1286 electrochemical interface, and used a 5 mV r.m.s. perturbation. The electrode was freshly polished before each spectrum recording and left in solution at open circuit for 10 min before beginning the experiment. Spectra were recorded in all six solutions described above at applied potentials that lay approximately in the range from the open circuit potential ≈ -1.0 V to -0.3 V vs SCE (where this was possible without too high a corrosion rate) and in the frequency range 0.01 Hz to 65 kHz with five frequency points per decade. A high corrosion rate manifested itself in EIS as irregularly varying currents and highly dispersed spectra.

Scanning electron microscopy was done with a Jeol T330 scanning electron microscope equipped with a Tracor energy dispersive X-ray microanalysis accessory.

3. Results

Electrochemical impedance spectra were recorded in all types of solution. However, it was observed experimentally that the effect of the inhibitor ions was such that spectra from inhibitor-ion-containing solutions with or without chloride ion were almost identical in the potential range where inhibition occurred. In itself, this suggests strong adsorption of the inhibitor ion on the aluminium surface. Thus, spectra for inhibitor-containing solutions are shown only with chloride ion. Representative spectra are given in Figs 1 to 4; bode plots led to no indication of hidden features at high frequency.

Three possible equivalent circuits for this type of interface are shown in Fig. 5. Uncompensated solution resistance is not included as this is negligible in comparison with the interfacial impedance. The first circuit, Fig. 5(a), assumes a continuous oxide layer with charge transfer by ionic migration. The second, Fig. 5(b), leads to two capacitive features with an intermediate inductive feature, and has been successful in describing spectra at aluminium electrodes in a variety of chloride media [16]. The third, Fig. 5(c), describes a capacitive oxide/solution interfacial

region in series with the oxide layer. At high frequencies, both the second circuit (putting $R = R_1 + R_2$) and the third (assuming $C_1 \gg C$) reduce to the parallel RC combination of Fig. 5(a).

Figure 6 plots values of R and C for the 'high frequency' semicircles assuming a parallel RC combination for these data.

3.1. Potassium sulphate electrolyte

The spectra of Fig. 1 indicate the occurrence of a charge-transfer ion migration across the oxide film, which becomes slightly faster as the potential becomes more positive. Finally, at -0.3 V vs SCE (not shown), there is a change in the form of the spectra and small pits are observed in the aluminium surface. Since the applied potentials used in the presence of chloride, described in subsequent sections, are significantly more negative than -0.3 V, as the currents are already too large and irregular to lead to meaningful results, the effect of sulphate ions on the rate of corrosion is small. An exception is the case of chromate-containing solutions, but here the chromate effect dominates, as discussed later.

3.2. Chloride-containing solution without inhibitor

It is well documented that chloride ion causes pitting, and in general gives rise to two capacitive loops, at high and low frequency, with an intermediate inductive loop associated with relaxation processes in the oxide film [16, 17, 22], as described by the circuit in Fig. 5(b). Figure 2 shows that with a mixture of chloride and sulphate anions rather than just chloride, this behaviour is modified in that the inductive loop begins to appear at higher frequencies and is less accentuated. This must be due to some adsorption of sulphate ions, reducing the corrosion rate and altering the rate of oxide film relaxation. It was not possible to record reproducible spectra positive of -0.6 V vs SCE (pitting potential -0.65 V), owing to the high, irregularly varying values of the currents.

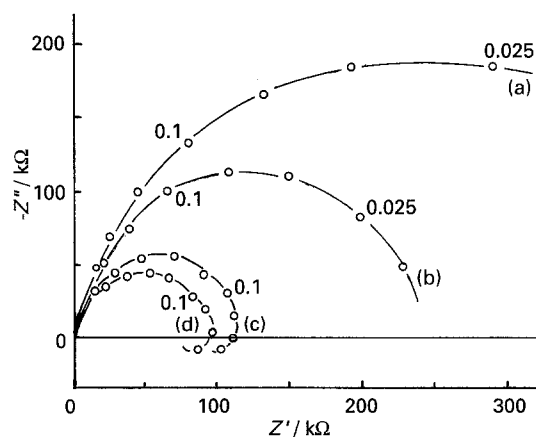


Fig. 1. Complex plane impedance spectra of Al in 0.40 M K₂SO₄ at potentials: (a) -1.0 V, (b) -0.8 V, (c) -0.6 V, (d) -0.4 V. Frequencies in hertz.

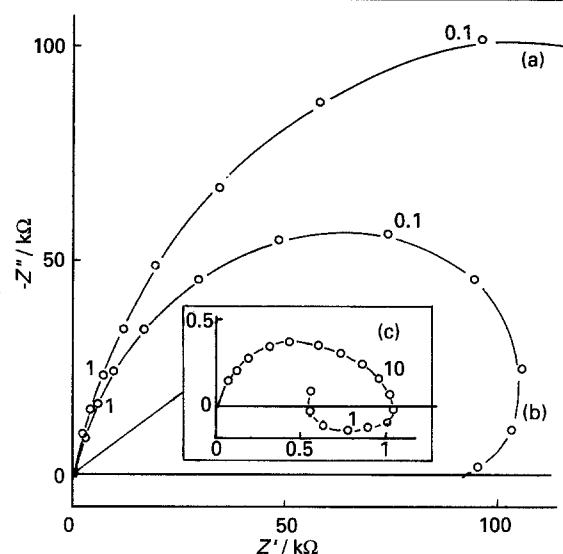


Fig. 2. Complex plane impedance spectra of Al in (0.10 M KCl + 0.37 M K₂SO₄) at potentials: (a) -1.0 V, (b) -0.8 V, (c) -0.6 V. Frequencies in hertz.

3.3. Nitrite-containing solution

The results presented in Fig. 3 are those of the mixture of nitrite and chloride ions. For potentials negative of -0.6 V vs SCE, the spectra from solutions containing 0.10 M NaNO₂ and (0.10 M NaNO₂ + 0.10 M KCl) are almost indistinguishable, which means that nitrite adsorption dominates over chloride and prevents the latter's adsorption. At -0.6 V there is still significant inhibition of the corrosion reaction, manifested in the impedance values (compare with Fig. 2). However, at more positive potentials nitrite no longer inhibits; the inhibition potential region therefore extends up to -0.6 V.

3.4. Chromate-containing solution

As is the case for nitrite inhibitor, spectra in the presence of and in the absence of chloride are

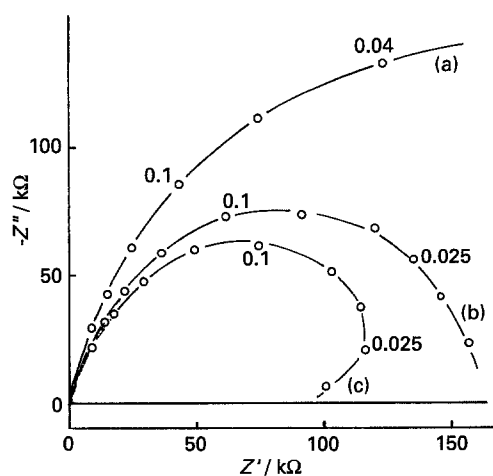


Fig. 3. Complex plane impedance spectra of Al in (0.10 M NaNO₂ + 0.10 M KCl + 0.33 M K₂SO₄) at potentials: (a) -1.0 V, (b) -0.8 V, (c) -0.6 V. Frequencies in hertz.

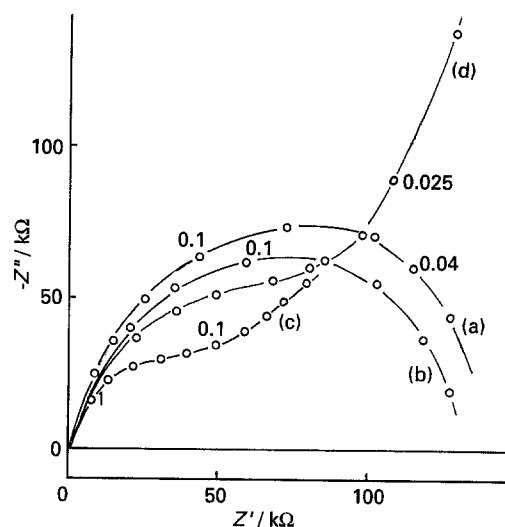


Fig. 4. Complex plane impedance spectra of Al in (0.10 M K₂CrO₄ + 0.10 M KCl + 0.27 M K₂SO₄) at potentials: (a) -1.0 V, (b) -0.8 V, (c) -0.6 V, (d) -0.4 V. Frequencies in hertz.

almost identical. However, the form of the spectra is substantially different from that of nitrite-containing solutions close to the pitting potential at -0.6 V, and even more so for more positive values of the applied potential, Fig. 4. Thus, from -0.6 V there is a change into an RC parallel combination in series with a pseudo-capacity, see Fig. 5(c). This pseudocapacity is calculated as in the region of 100 μF cm⁻², and suggests strong chromate adsorption on the electrode surface impeding passage of other ions. The corrosion rate is very low.

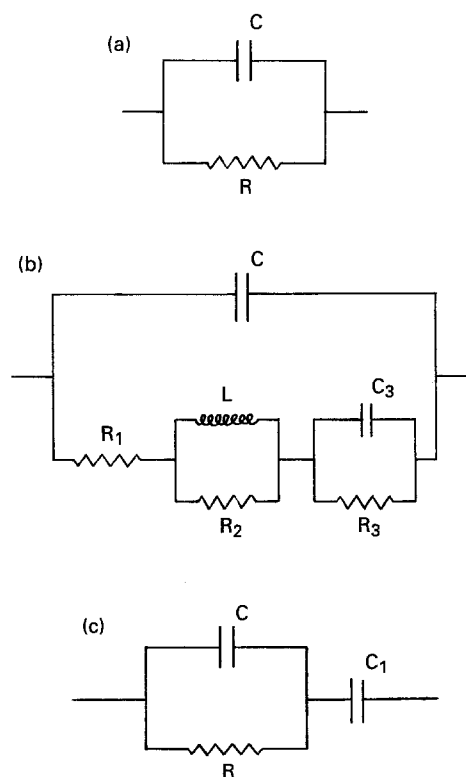


Fig. 5. Equivalent circuits for modelling impedance data of aluminium electrodes.

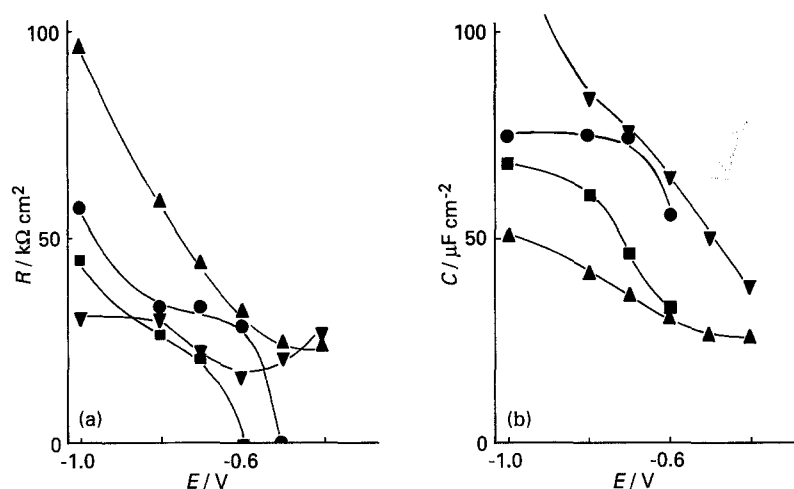


Fig. 6. Plots of R and C vs potential from the high frequency features for Al in: (▲) 0.40 M K_2SO_4 ; (■) 0.10 M KCl + 0.37 M K_2SO_4 ; (●) 0.10 M $NaNO_2$ + 0.10 M KCl + 0.33 M K_2SO_4 ; (▼) 0.10 M K_2CrO_4 + 0.10 M KCl + 0.27 M K_2SO_4 .

4. Discussion

4.1. Comparison between different solutions

Comparison between the different solutions is aided by Fig. 6, where the values of R and C calculated from the high-frequency feature of Figs 1 to 4 are plotted. In this discussion 'nitrite' refers to solutions containing nitrite plus chloride ions, and 'chromate' to solutions containing chromate plus chloride ions.

In Fig. 6(a) the decrease in R values as the potential becomes more positive is clear. At -1.0 V the order in R is sulphate > nitrite > chloride > chromate. It is interesting that sulphate leads to significantly higher R values, which probably reflects physical blocking of the aluminium surface. Except for the case of chromate, the R values decrease significantly as the potential is increased. For chloride and nitrite, just positive of the pitting potential they fall to values close to zero. It is evident that sulphate continues to block the surface at more positive potentials. The chromate values pass through a minimum and then begin to increase: such a variation is best attributed to an increase in oxide layer thickness due to the chromate ion, as discussed further below.

Figure 6(b) shows the capacity values decreasing with increasing potential. This is to be expected since a more positive potential implies a thicker oxide layer. The order at -1.0 V of chromate > nitrite > chloride > sulphate is maintained, nitrite and chloride ceasing to appear for potentials more positive than -0.6 V. The presence of the different ions therefore leads to some differences in the capacity values of the high frequency feature. In agreement with the strong adsorption of chromate the corresponding C values are higher.

If a simple parallel-plate capacitor model is used then, per unit area,

$$C = \frac{\epsilon\epsilon_0}{d_{ox}}$$

where d_{ox} is the thickness of the oxide film, ϵ the relative permittivity and ϵ_0 the vacuum permittivity. On substituting $\epsilon = 9$ for alumina [23] and $\epsilon_0 = 8.854 \times$

$$10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ mol}^{-1},$$

$$C = \frac{8.0}{d_{ox}}$$

where C is in $\mu\text{F cm}^{-2}$ and d_{ox} in nm. Thus oxide layers are predicted to be extremely thin, of the order of 0.2 nm, putting $C = 50 \mu\text{F cm}^{-2}$ as a typical oxide film capacity. Although this simple model gives the observed dependence of capacity with potential, for very thin films it is unlikely that the relative permittivity is that of bulk alumina: higher values of ϵ would lead to higher values of d_{ox} , which is physically more acceptable. An alternative model recognises a surface state capacity in parallel with the semiconducting oxide layer (space charge) capacity and reduces the values of the measured space charge capacity [24]. The effect on the form of the complex plane spectra is to flatten the semicircles, which occurs to a small extent: a contribution from surface states can therefore be considered. The adsorbed anions will, for very thin oxide films, probably have the effect of increasing the relative permittivity, since the ions will be effectively incorporated in the surface film.

The existence of a pseudo-capacity in series with the parallel RC combination for chromate positive of the pitting potential (the same behaviour is observed in solutions without chloride ion), as shown in Fig. 4, implies the existence of significant charge separation at the oxide/electrolyte interface, caused by strong chromate ion adsorption, impeding adsorption or absorption of chloride ion.

4.2. Surface morphology

The above deductions are corroborated by the surface morphology, revealed by scanning electron microscopy (SEM) of the aluminium surface. SEM of electrodes exposed to the various solutions at -0.5 V vs SCE (where pitting due to chloride ion can already occur), shows the total absence of pits in the case of solutions containing chloride with chromate inhibitor, and some evidence of surface roughening and oxide growth. This agrees with reports in the literature that chromate can aid the formation of the oxide

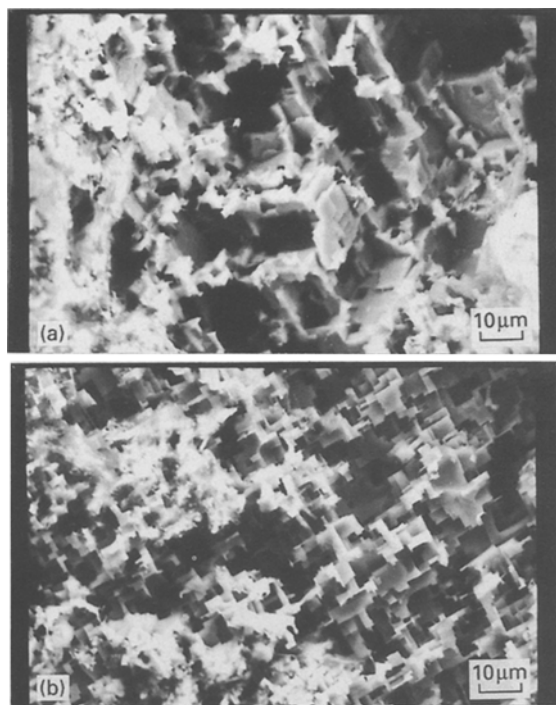


Fig. 7. SEM micrographs of corrosion pits in aluminium after application of -0.50 V vs SCE for 20 min in (a) 0.1 M KCl + 0.37 M K_2SO_4 and (b) 0.1 M $NaNO_2$ + 0.10 M KCl + 0.33 M K_2SO_4 .

layer by repairing defects [5]. For chloride and chloride plus nitrite solutions, non-uniformly distributed and irregularly sized pits are formed. Figure 7 shows typical morphology within the pits. There is clear evidence of crystallographic etching, though this is more perfect in solutions containing nitrite as well as chloride anions. Pits have a shallow wide form, and are not hemispherical as found in some solutions [25, 26]. Microanalysis showed no evidence of absorption of any of the ions within the surface layer or within the pits. This might have been expected due to the high electric field attracting anions to within the oxide layer and the fact that chloride can act as a chemical reaction partner [27]. However, microanalysis does not have sufficient resolution for the very thin oxide layer thicknesses in this case.

4.3. Mode of inhibitor action

The mode of inhibitor action is now considered: by physical adsorption and/or chemical reaction. One of the ways in which inhibition involving oxyanions can occur is via reduction of the oxyanions themselves which, in general, and if their concentration is too low, can enhance corrosion, or if their concentration is sufficiently high, then oxide formation is promoted. Using concentrations of either inhibitor anion varying from zero up to 0.1 M, no evidence for this effect was found.

It can be deduced that there are two factors contributing to the inhibition mechanism. First, and most important, competitive adsorption between the inhibitor anion and chloride anion on the aluminium surface negative of the pitting potential. Second, for

chromate, direct interference in anodic dissolution which would occur through the formation of chloro- and oxychlorocomplexes by reduction of CrO_4^{2-} to Cr(III) producing oxide anions [28–30]. In fact, in potential step voltammetric experiments to values positive of the pitting potential [20], it was found that, although the growth of oxide is uniform and homogeneous, satisfying a I vs t^{-1} linear relationship, in nitrite-containing solutions the effect of the presence of chloride is to increase the observed currents, whereas in the case of chromate with chloride the opposite occurs. This second factor explains the tendency of chromate ion to aid oxide film repair. Impedance spectra give direct evidence of its strong interaction with the oxide surface.

5. Conclusions

The distinction between the mode of action of nitrite and chromate inhibitor anions has been demonstrated successfully by electrochemical impedance spectroscopy. Nitrite anion is more strongly adsorbed than chromate and thus exhibits a greater inhibitor effect negative of the pitting potential. At more positive potentials chromate remains strongly adsorbed and is able to protect the surface against chloride-induced corrosion owing to its ability to assist oxide formation; impedance spectra clearly show this strong adsorption. At these potentials nitrite ceases to have any inhibition effect.

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