

THE INFLUENCE OF Li ON THE ELECTROCHEMICAL BEHAVIOUR
OF PURE ALUMINIUM

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The favourable effect of lithium addition on the stiffness to density ratio of aluminium have generated a great deal of interest in the Al-Li family of alloys for use as aircraft components. Environmental degradation problems causing either general localized corrosion have received little attention so far.

This paper reports on the influence of lithium addition to the solution and aims to assess its influence on the resistance to corrosion of aluminium 99.999%.

An electrochemical study was conducted using a sodium carbonate solution as base electrolyte.

Fig.1 shows the E-t profile for Al 99.999% in 0.05M LiCO₃ solution. A potential displacement towards noble values reaching -500mV(SCE) after 50h exposure is evident. This profile is indicative of a film formation process. The absence of lithium gave as a result are the end of 50h exposure, values of \approx -1640mV as shown in Fig.2 (evolution during the first hours is shown in the inserts of the figures).

Observation on the optical microscope agreed with the

indicated E-t profiles. Lithium incorporation into the film on aluminium was confirmed qualitatively by ESCA and by nuclear reactions.

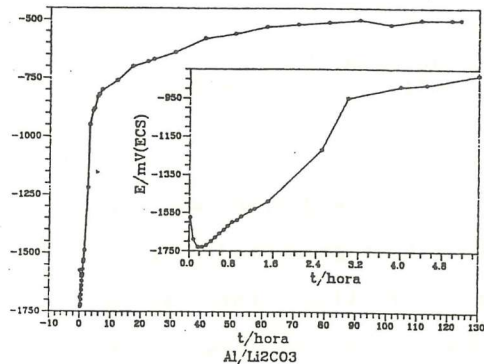


Fig.1. E-t curve for the system Al 99.999% in 0.05M Li₂CO₃.

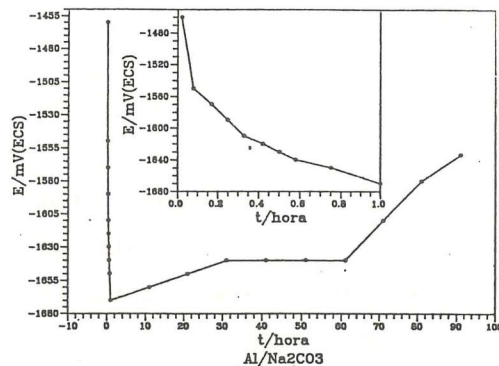
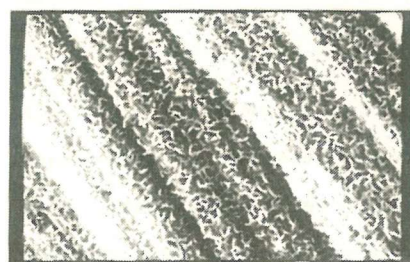
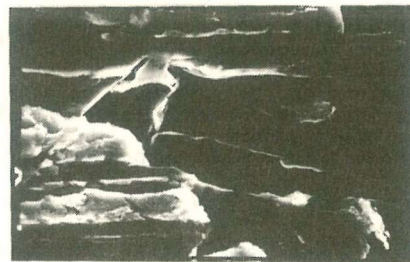


Fig.2. E-t curve for the system Al 99.999% in 0.05M Na₂CO₃.

Morphology of the films formed in the presence and absence of lithium was observed on the scanning electron microscope (SEM). Fig.3a and 3b show the typical SEM image for Li₂CO₃ and Na₂CO₃ at the open circuit potential.



(a) 2900 x



(b) 2900 x

Fig.3. Morphology of the film observed on the SEM for Al 99.999% in Li₂CO₃ (a) and Na₂CO₃ (b) at the open circuit potential.

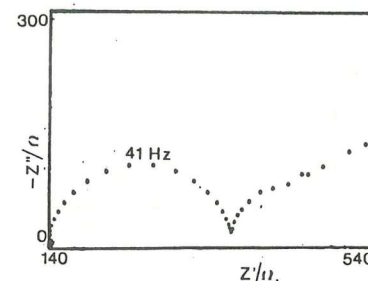
A porous structure is observed in the absence of Li

whisit a more compact film with acicular precipitates is on the bases of the protecting character of Li.

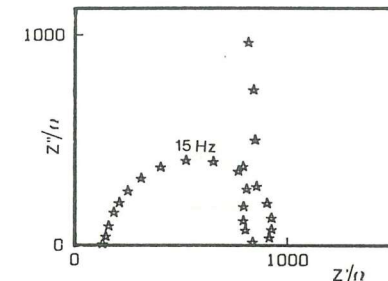
Polarization curves were run in the same media. The presence of lithium indicated that the formation of a polarization film is at the base of the observed decrease in current throughout the whole scanned potential interval.

The anodic behaviour of the system in the presence and absence of lithium was studied by AC Impedance at potentials considered of interest along the E-I curves.

At -1.60V(SCE) the Nyquist plot (Fig.4a) evidences a charge transfer process showing diffusion at low frequencies. At more positive potentials the Impedance spectra show a loop followed by a vertical line, characteristic of a capacitive film (Fig.4b). At even higher potential the picture is the same, indicating a dissolution process occurring on a film covered surface.



(a)



(b)

Fig.4. AC Impedance diagrams for Al 99.999% in 0.01M Na₂CO₃ at -1.60V(SCE) (a) -1.20V(SCE) (b).

Additions of lithium to the system (0.01M Li₂CO₃) at

-1600mV(SCE) bring as a consequence the formation of a film of different nature judging by the obtained capacitive values. Data indicate a charge transfer process that might involve localized corrosion (Fig.5a).

An increase of lithium in solution (0.05M Li_2CO_3) at the same potential improves the quality of the film with probably more incorporated lithium and the absence of localized corrosion (Fig.5b). SEM observation of tested samples confirmed it.

For 0.05M Li_2CO_3 , an increase in potential give an AC response that evidenced the formation of a film, a charge transfer process and also diffusion at low frequencies.

The quantification of Li profiles using RBS and other techniques is under way in order to characterized film composition under potentiostatic control.

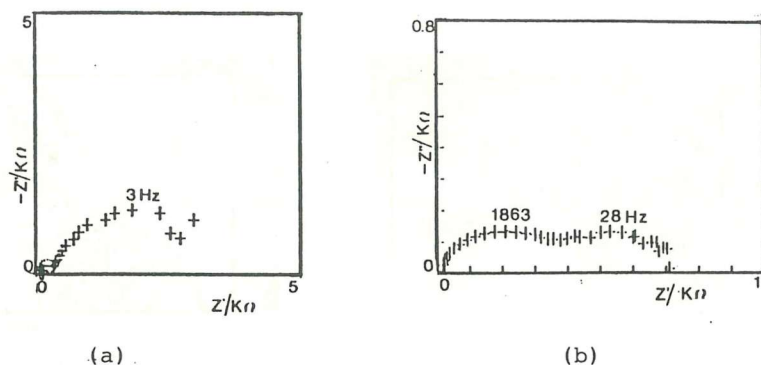


Fig.5. AC Impedance diagrams for Al 99.999% in Lithium containing solutions at 1.60V(SCE)
0.01M Li_2CO_3 (a)
0.05M Li_2CO_3 (b).

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STUDIES ON ALUMINIUM CORROSION IN HYDROCHLORIC ACID SOLUTION

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Corrosion of aluminium usually results in the formation of a porous or barrier type oxide film on its surface [1]. The film can be formed anodically, except at low pH, or cathodically even at low pH due to local pH increase at the aluminium surface associated with hydrogen evolution. The corrosion rate is enhanced by the presence of chloride ion in solution through a pitting mechanism, procedure employed in the etching of aluminium by hydrochloric acid for use in dielectric capacitors [2].

The corrosion behaviour of aluminium in 0.1M HCl has been studied in this work by three techniques. A cylinder of pure aluminium, diameter 0.5cm, was encased in Teflon and made into the form of a rotating disc electrode. Experiments were conducted with and without electrode rotation, and in aerated and de-aerated solution. Firstly, the variation of corrosion potential, E_{corr} , with time was measured for freshly polished smooth and deliberately roughened aluminium. Secondly, the polarization resistance, R_p , of the aluminium/solution interface was measured using small amplitude cyclic voltammetry at slow scan rate at potentials within 20mV of the corrosion potential. Thirdly, impedance spectra were recorded over a frequency range of $10^{-2} \rightarrow 10^4$ Hz at a variety of applied dc potentials using a 5mV rms