

## EFFECT OF CARBONATE AND LITHIUM IONS ON THE CORROSION PERFORMANCE OF PURE ALUMINIUM

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**Abstract**—The effect of the presence of lithium ions in carbonate solutions on the corrosion behaviour of aluminium was studied taking into consideration the particular importance of the use of lithium-containing aluminium alloys in aeronautics. *dc* electrochemical polarization measurements were performed on pure aluminium (99.999%) in mixed solutions of  $\text{Na}_2\text{CO}_3$  and  $\text{Li}_2\text{CO}_3$ , the results showing that the presence of  $\text{Li}^+$  in solution improves the passivation of aluminium, but only above a critical concentration of carbonates. The presence of chlorides in those solutions above a certain level is deleterious for the passivation films, since it leads to localized attack. This process seems to be related to the easy formation of lithium chloride containing species, which promote local film dissolution.

**Key words:** aluminium, corrosion, lithium, carbonate solutions.

### INTRODUCTION

Lithium-containing aluminium alloys have been envisaged with interest in the past years since they could constitute an alternative to the more traditional high strength aluminium alloys. This is of special importance in aerospace applications, where the stiffness-to-density ratio of the materials used is a critical parameter.

Determining the effect of lithium on the corrosion resistance of aluminium alloys has been the object of many different studies[1–4]. The specimens can suffer different types of localized attack such as pitting corrosion, crevice corrosion and stress corrosion cracking, in which localized solution chemistry with high dissolved metal ion content can develop[5].

Since, in contact with the atmosphere, carbonates can be formed due to the presence of  $\text{CO}_2$  and humidity, the influence of carbonate and lithium ions in solution on the electrochemical behaviour of aluminium deserves attention.

With this objective, studies[5–7] have been carried out in solutions containing sodium or potassium carbonates on one hand or lithium carbonate on the other. The present work aims at the study of the combined effects of carbonate and lithium ions, by testing the behaviour of aluminium in solutions with mixtures of sodium carbonate and lithium carbonate in different proportions.

Since chlorides are present in most environments in which aircraft operate, the effect of the chloride concentration in solutions of lithium carbonate and sodium carbonate was also studied.

### EXPERIMENTAL

Anodic polarization studies on 99.999% pure aluminium in solutions of  $\text{Na}_2\text{CO}_3$  and  $\text{Li}_2\text{CO}_3$  were carried out.

The specimens were cut into discs of 10 mm diameter from an aluminium bar, embedded in epoxy resin, and the surface mechanically polished with silica carbide paper up to 1000 grit.

Solutions of  $\text{Na}_2\text{CO}_3$  and  $\text{Li}_2\text{CO}_3$  with  $\text{pH} \approx 11$  were prepared from Analar reagents. In one set of experiments the concentration of carbonate was kept constant:

A—0.10 M  $\text{Na}_2\text{CO}_3$ ,

B—0.09 M  $\text{Na}_2\text{CO}_3$  + 0.01 M  $\text{Li}_2\text{CO}_3$ ,

C—0.05 M  $\text{Na}_2\text{CO}_3$  + 0.05 M  $\text{Li}_2\text{CO}_3$ ,

D—0.10 M  $\text{Li}_2\text{CO}_3$ ,

whereas in the other set, the concentration of  $\text{Li}^+$  was kept constant:

E—0.01 M  $\text{Li}_2\text{CO}_3$ ,

F—0.01 M  $\text{Li}_2\text{CO}_3$  + 0.04 M  $\text{Na}_2\text{CO}_3$ ,

G—0.01 M  $\text{Li}_2\text{CO}_3$  + 0.07 M  $\text{Na}_2\text{CO}_3$ ,

H—0.01 M  $\text{Li}_2\text{CO}_3$  + 0.09 M  $\text{Na}_2\text{CO}_3$ .

Reference solutions of only  $\text{Na}_2\text{CO}_3$  or  $\text{Li}_2\text{CO}_3$  (A, D, E) were also used.

The effect of chloride concentration was also studied in the three following solutions: 0.10 M  $\text{Li}_2\text{CO}_3$ , 0.01 M  $\text{Na}_2\text{CO}_3$  and 0.10 M  $\text{Na}_2\text{CO}_3$ . The chloride was added as  $\text{NaCl}$  in concentrations ranging from 0.001 to 0.020 M.

The experiments were performed in a three-electrode conventional cell with a graphite counter electrode and a bridge to an external reference saturated calomel electrode (*sce*).

All the solutions were previously  $\text{N}_2$ -bubbled for 1 h and were used at room temperature (18–20°C).

The potential was controlled with a Thompson 251 Ministat and swept by a Thompson DRG-16 Ramp Generator at a rate of  $0.1 \text{ mV s}^{-1}$  from the free corrosion potential.

The potential and current outputs of the potentiostat were connected to two Solartron 7150 digital voltmeters, which were connected via a HPIB interface to an HP-87 microcomputer. This set-up allowed automatic data acquisition.

## RESULTS AND DISCUSSION

### *Effect of the presence of Li<sup>+</sup> ions in solution*

Figure 1 shows anodic polarization plots for pure aluminium in a series of solutions which are always 0.10 M in CO<sub>3</sub><sup>2-</sup>, with concentrations of Li<sup>+</sup> varying between 0 and 0.20 M. The objective is to observe the effect of the concentration of Li<sup>+</sup> ions in carbonate solutions on the aluminium behaviour.

As evident from the results, the presence of lithium ions in solution leads to passivation of the metal. At potentials *ca.* -1.7 to -1.6 V the current suddenly drops, becoming 10<sup>3</sup> to 10<sup>4</sup> times lower. On the other hand, although the current density in the passive region decreases with the increase of the concentration of Li<sup>+</sup> ions, it was observed that only a small amount of Li<sup>+</sup> was necessary for the passivation of the aluminium.

The effect of lithium in solution on the anodic behaviour of aluminium has been related to the incorporation of lithium in the film of corrosion products[5-7]. According to Gui and Devine[5] the formation of a passive film in solutions containing only Na<sub>2</sub>CO<sub>3</sub> is facilitated by high pH of the solution, the same occurring in solutions of lithium carbonate at low values of the applied potential. However, at higher potentials, those authors observed the formation of a passive film with a significant amount of lithium incorporated from the solution.

The protective effect of the presence of lithium was attributed by Craig and Newman[6] to the formation of lithium meta-aluminate (LiAlO<sub>2</sub>), which is sparingly soluble, precipitating at the metal surface and stabilizing the passive film.

### *Effect of the CO<sub>3</sub><sup>2-</sup> on passivation in Li<sup>+</sup> containing solutions*

To elucidate the effect of carbonate ions on passivation, solutions with a fixed concentration in Li<sup>+</sup>

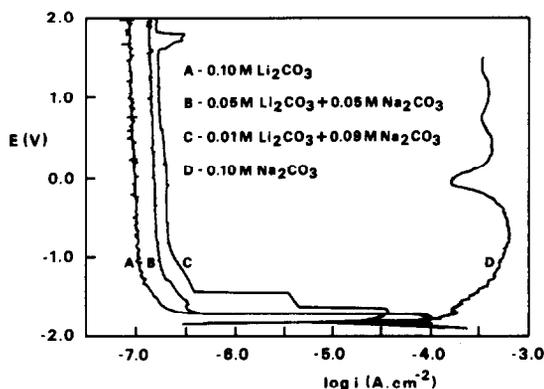


Fig. 1. Anodic polarization plots for aluminium in lithium carbonate and sodium carbonate solutions, with a total concentration in CO<sub>3</sub><sup>2-</sup> equal to 0.10 M.

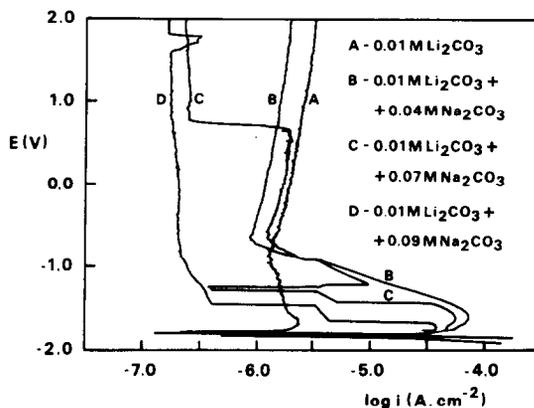


Fig. 2. Anodic polarization plots for aluminium in lithium carbonate and sodium carbonate solutions, with a total concentration of Li<sup>+</sup> equal to 0.02 M.

(0.02 M) and different concentrations of carbonate ions were used.

The plots (Fig. 2) show that an increase in the carbonate concentration leads to the formation of a more protective film, although it is only for a concentration of carbonate of 0.10 M that passivation really takes place.

### *Effect of the presence of Cl<sup>-</sup> in solution*

The polarization plots in Fig. 3 were obtained in 0.10 M Li<sub>2</sub>CO<sub>3</sub> solutions without and with chlorides. In the passive region, an increase of chloride concentration corresponds to a slight increase of the recorded currents.

The breakdown of the passive film occurs for concentrations of chlorides of 0.01 M and 0.02 M, but not for 0.001 M which seems to indicate that the critical concentration of chlorides for breakdown lies between 0.001 and 0.010 M. Moreover, the pitting potential decreases with the increase of chloride concentration, as expected.

Results were also obtained for chloride concentrations of 0.005 M. However, the reproducibility of these results was poor, the breakdown occurring only in some of the experiments. This fact also supports

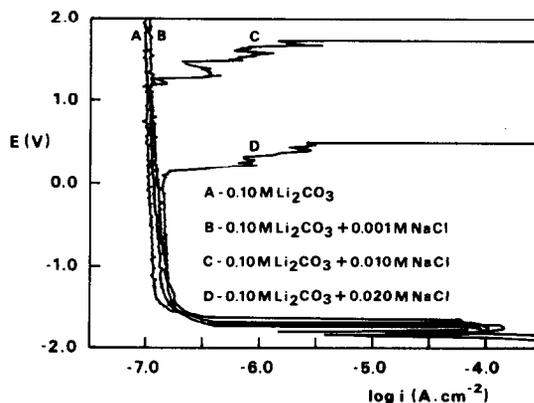


Fig. 3. Anodic polarization plots for aluminium in 0.10 M, Li<sub>2</sub>CO<sub>3</sub> solution without chlorides and with 0.001 M, 0.010 M and 0.020 M of NaCl.

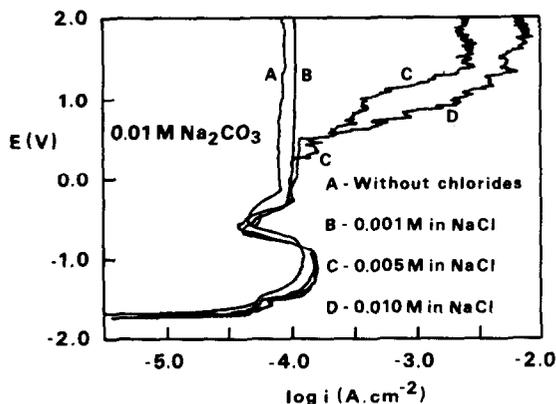


Fig. 4. Anodic polarization plots for aluminium in 0.01 M  $\text{Na}_2\text{CO}_3$  solution without chlorides and with 0.001 M, 0.005 M and 0.010 M of NaCl.

the idea that the critical chloride concentration is in the above mentioned range.

Polarization tests were also performed in  $\text{Na}_2\text{CO}_3$  without and with various concentrations of chlorides, Figs 4 and 5. For the 0.01 M  $\text{Na}_2\text{CO}_3$  solution, the effect of chloride addition in the passive region up to 0 V is only a slight increase of current (Fig. 4), the same behaviour occurring for more anodic potentials in the case of solutions 0.001 M in chloride. For solutions with larger chloride contents ( $\geq 0.005$  M), the localized breakdown of the film occurs at potentials between 0 and 0.5 V, originating pits that can easily be detected by optical microscopy.

Tests carried out in solutions with higher  $\text{Na}_2\text{CO}_3$  concentrations (0.10 M) and with the same chloride concentrations as previously mentioned, showed that no pitting occurred, the curves being in all cases nearly coincident. For simplicity only one of these curves is shown in Fig. 5.

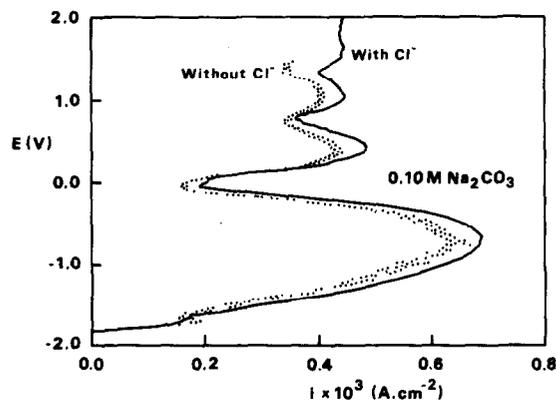


Fig. 5. Anodic polarization plots for aluminium in 0.10 M  $\text{Na}_2\text{CO}_3$  solution without chlorides and with 0.005 M NaCl.

The differences in the passive behaviour found for aluminium in the absence and presence of  $\text{Li}^+$  might be explained by the different nature of the films formed. In the former case the film is constituted by aluminium oxide/hydroxide, which provides little protection[8], whereas in the latter case lithium is incorporated in the film, making it more protective. However, the lithium-containing films seem to be more prone to chloride attack than the non-containing ones, *ie* the ones formed only in sodium carbonate solutions, due probably to a tendency to more easily form lithium chloride species (rather than aluminium chloride) which are soluble and lead to film breakdown.

## CONCLUSIONS

The passivation of aluminium in carbonate solutions requires only a small amount of  $\text{Li}^+$  in solution, although an increase in  $\text{Li}^+$  concentration improves the protection conferred by the passive film. However, the passivation caused by lithium is only effective in the presence of a minimum concentration of carbonate.

Chloride ions, above a certain concentration, are able to destroy locally the passive films formed in carbonate solutions, originating pits. The lithium-containing films, *ie* those formed in presence of  $\text{Li}_2\text{CO}_3$ , need a lower concentration of chloride to initiate breakdown. Thus, although lithium makes the films more protective, it also makes them more prone to localized attack.

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