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Characterization of aluminium alloys in tetrahydrofuran media

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Rest potential measurements and voltammetric scans at different rates (0.01–1 V min^{-1}) have been carried out on aluminium alloys in a tetrahydrofuran (THF) environment. The solvent contained either chloride, perchlorate or trifluoromethane sulfonate ions. For the Al–Mg alloys in chloride environments, the voltammograms observed for low scan rates show electrode passivation with the formation of a magnesium salt layer. For Al–Li alloys, rest potential measurements indicate the selective dissolution of lithium. The maximum dissolution current is sensitive to the lithium content in the alloy and limited by the solubility of lithium chloride. In chloride environments, the passivity breakdown potential E_b and the protective potential E_p have similar values and do not depend on the type of alloy. In contrast, large differences between these potentials are observed in the presence of $CF_3SO_3^-$ ions

1. Introduction

Lithium may be added to aluminium to form an alloy with enhanced elasticity and reduced density [1]. The corrosion resistance is also modifed, however the electrochemical tests generally used to characterize corrosion properties in aqueous environments cannot be employed since the phases (AlLi) precipitated at the grain boundaries react in this environment [2–4].

We have already presented an investigation of the electrochemical behavior of high purity aluminium and binary Al–Li alloys in various organic electrolytes [5]. THF was selected as the best solvent due to its stability with respect to aluminium and lithium and the solubility of the salts concerned (LiCl and $AlCl_3$). The case of binary alloys is however very limited, so we have since studied various aluminium alloys containing other elements such as magnesium, copper and zinc. The present study is an attempt to class the studied alloys in terms of their reactivity using potentiometric measurements and voltammetric scans.

Table 1. Alloy compositions (%)

Alloys		*Li*	*Mg*	*Cu*	*Zr*
Al-Li	1268	1.7	–	–	0.12
Al-Li	1156	2	–	–	< 0.10
Al-Li	1518	2.5	–	–	< 0.10
Al-Mg	1507	–	1	–	< 0.10
Al-Li-Mg	1600	1.35	1	–	< 0.10
Al-Li-Mg	1522	2.4	0.9	–	0.12
Al-Cu-Li-Mg	1299	2.4	1	1.3	0.10

2. Experimental details

The experimental apparatus is the same as described in our previous paper [5]. The alloy compositions are given in Table 1. These alloys were subjected to heat treatment (annealing) before use. The electrolyte was tetrahydrofuran (THF) containing either chloride, perchlorate or aluminium and/or lithium trifluoromethane sulfonate salts.

3. Results

3.1. *Al–Li alloys*

Al–Li alloys with lithium contents ranging from 1.7 to 2.5% by weight were used. Rest potential measurements and voltammetric scans at different rates were carried out. The results obtained for the potentiometric measurements are given (Fig. 1) for alloys 1268, 1156 and 1518 in THF environments containing

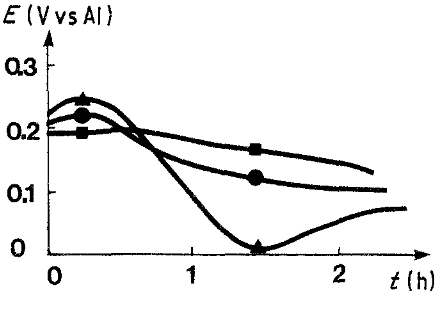

Fig. 1. Potential evolution with time. Electrolyte: THF + LiCl (0.1 M) + $AlCl_3$ (0.9 M). (■) Al–Li–Zr (1268); (●) Al–Li (1156); (▲) Al–LiZr (1518).

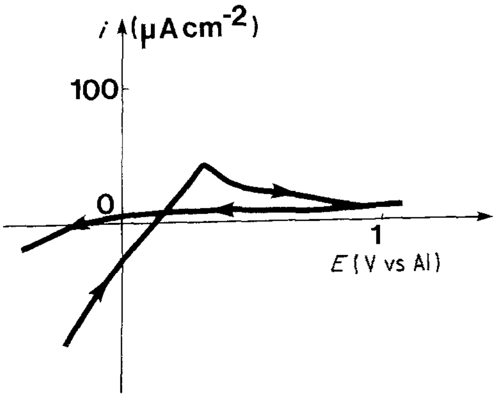

Fig. 2. Cyclic voltammogram at Al–Li–Zr (1268). Electrolyte: THF + LiCl (0.1 M) + $AlCl_3$ (0.9 M); scan rate: 10 mV min^{-1}.

LiCl and $AlCl_3$. In all three cases, the rest potential decreased before stabilization (2 h). The voltammetric results for alloy 1268 show that the dissolution of this alloy is accompanied by a limiting dissolution current (Fig. 2). Similar results were obtained (Fig. 3) for alloy 1156 with however a higher limiting dissolution current. For higher lithium contents (alloy 1518), fast alloy dissolution is observed for high scan rates (Fig. 4), however a limiting current persists for low scan rates.

Our results indicate that the preferential dissolution of lithium (the most electropositive element) could lead to local saturation in terms of LiCl at the electrode surface. This localized precipitation (observed at low scan rates) offers an explanation of the observed discrepancies between different scan rates. Similarly, for the potentiometric measurements, the preferential dissolution of the lithium appears to result in an aluminium surface enrichment and a corresponding change in the rest potential.

3.2. *Al–Mg alloys*

The rest potential measurements and voltammetric scans were repeated on the alloys Al–Mg 1507, Al–Li–Mg 1600 and Al–Li–Mg–Cu 1299. These alloys differ from those studied above by the presence of either magnesium alone or in conjunction with lithium or lithium and copper. The rest potentials obtained for these alloys in the electrolyte THF + $AlCl_3$ + LiCl are plotted in Fig. 5. In all three cases, a rapid variation of the initial potential different from that of the reference electrode (Al) is observed.

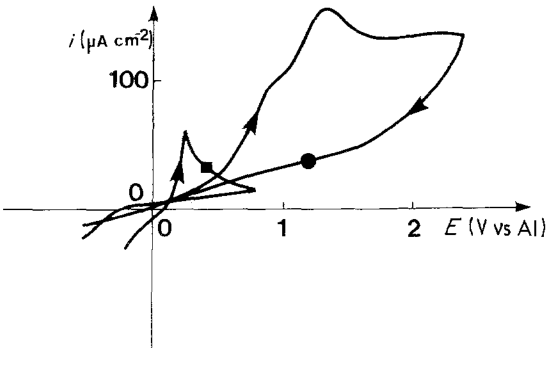

Fig. 3. Cyclic voltammogram at Al–Li (1156). Electrolyte: THF + LiCl (0.1 M) + $AlCl_3$ (0.9 M). (■) Scan rate 10 mV min^{-1}; (●) scan rate 1 V min^{-1}.

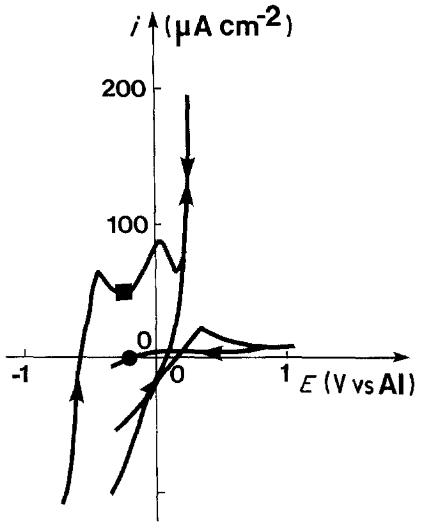

Fig. 4. Cyclic voltammogram at Al–Li–Zr (1518). Electrolyte: THF + LiCl (0.1 M) + $AlCl_3$ (0.9 M). (●) Scan rate 10 mV min^{-1}; (■) scan rate 1 V min^{-1}.

The voltammograms for the Al–Mg alloy are shown in Fig. 6. For slow scans, passivation is observed for this alloy. The oxidation current remains limited even with large overvoltages. A similar passivation phenomenon is observed with the Al–Li–Mg alloy (Fig. 7).

For high voltammetric scan rates, major anodic dissolution takes place only for the Al–Mg–Li–Cu alloy (Fig. 8). We also tested the solubility of magnesium chloride in THF. The results show very low solubility in this environment. This low solubility is likely responsible for the electrochemical properties of these alloys. A passive layer of insoluble magnesium chloride is formed at the surface either during rest voltage measurements or slow voltammetric scans. For the sake of comparison, note that high purity aluminium can be dissolved in this electrolyte and that its rest voltage is, in that case, stable.

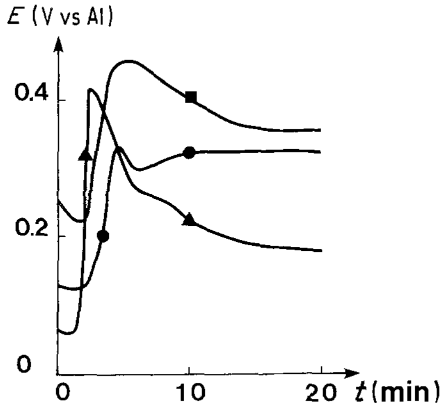

Fig. 5. Potential evolution with time. Electrolyte: THF + LiCl (0.1 M) + $AlCl_3$ (0.9 M). (▲) Al–Mg (1507); (■) Al–Mg–Li (1600); (●) Al–Mg–Li–Cu (1299).

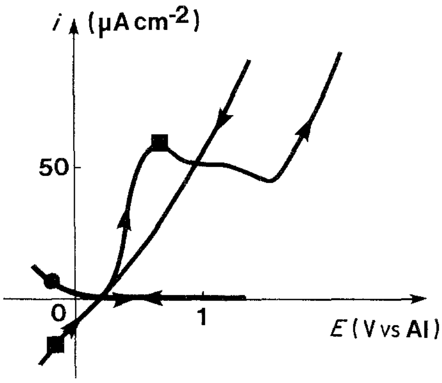

Fig. 6. Cyclic voltammogram at Al-Mg (1507). Electrolyte: THF + LiCl (0.1 M) + $AlCl_3$ (0.9 M). (●) Scan rate 10 mV min^{-1}; (■) scan rate 600 mV min^{-1}.

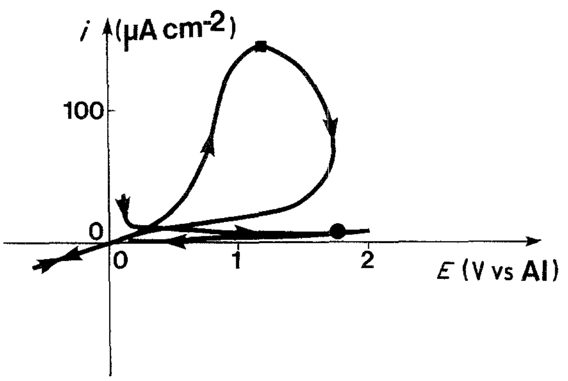

Fig. 7. Cyclic voltammogram at Al-Mg-Li (1600). Electrolyte: THF + LiCl (0.1 M) + $AlCl_3$ (0.9 M). (●) Scan rate 10 mV min^{-1}; (■) scan rate 600 mV min^{-1}.

3.3. *Other alloys*

A third family of alloys containing various elements in varying contents was tested. Their compositions are given in Table 2.

Measurements of the rest voltage and the passivity breakdown and protective potentials (E_b and E_p respectively) were made in THF electrolytes containing either $Al(ClO_4)_3$ or $Al(ClO_4)_3$ + $LiCF_3SO_3$. Figures 9 and 10 show that the rest potentials of these alloys rapidly approach that of the high purity aluminium electrode. Voltammetric scans were used to determine the values of the breakdown and protective potentials. The results are presented in Tables 3 and 4.

The voltammograms obtained for the two scan rates are not the same. In the perchlorate environment, the Tl phase is nearly passive, different from the other alloys. The two alloys 4104 and CP274 have similar breakdown and protective potentials.

These results show that none of the three anions tested can be used to characterize all the alloys

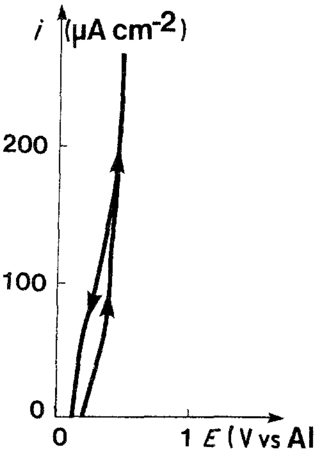

Fig. 8. Cyclic voltammogram at Al-Mg-Cu-Zr (1299). Electrolyte: THF + LiCl (0.1 M) + $AlCl_3$ (0.9 M); scan rate: 600 mV min^{-1}.

Table 2.

Alloys	*Element (%)*						
	Li	*Si*	*Mg*	*Cu*	*Zr*	*Ti*	*Fe*
Al 4104	–	0.10	1.58	–	–	–	–
Al T1	yes	–	–	–	–	–	–
Al delta	yes	–	–	yes	–	–	–
Al CP274	1.90	0.03	1.40	2.00	0.08	0.02	0.02

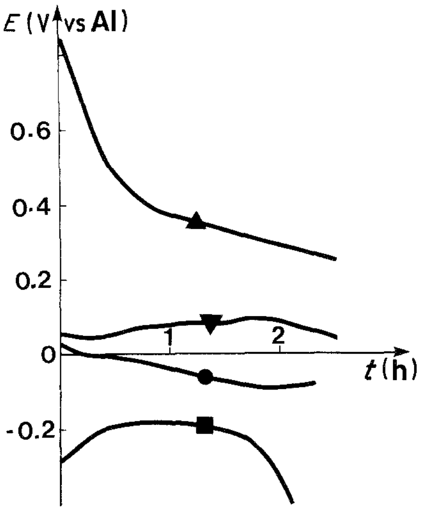

Fig. 9. Potential evolution with time. Electrolyte: THF + $Al(ClO_4)_3$ (0.1 M). (●) Al; (▲) Al-Li (AlTl); (▼) Al-Mg-Si (4104); (■) Al-Mg-Li-Cu (CP274).

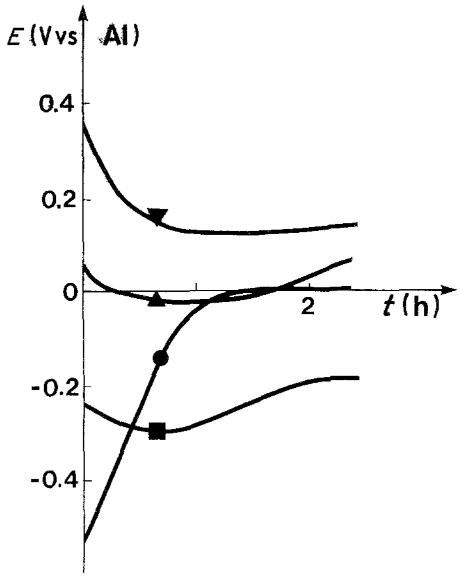

Fig. 10. Potential evolution with time. Electrolyte: THF + $Al(ClO_4)_3$ (0.05 M) + $LiCF_3SO_3$ (0.15 M). (●) Al; (▲) Al-Li (AlTl); (▼) Al-Mg-Si (4104); (■) Al-Mg-Li-Cu (CP274).

Table 3. E_b and E_p values for aluminium alloys in THF for different anions ($v = 10\,\mathrm{mV\,min^{-1}}$)

Electrolyte	*$Al(ClO_4)_3$*		*$Al(ClO_4)_3 + LiCF_3SO_3$*	
	0.1 M		0.05 M	0.15 M
Alloys	E_b(mV vs Al)	E_p(mV vs Al)	E_b(mV vs Al)	E_p(mV vs Al)
Al 4104	732	260	470	49
Al T1	Passivation	Passivation	−74	−272
Al CP274	−4	−125	785	-

Table 4. E_b and E_p values for aluminium alloys in THF for different anions ($v = 100\,\mathrm{mV\,min^{-1}}$)

Electrolyte	*$Al(ClO_4)_3$*		*$Al(ClO_4)_3 + LiCF_3SO_3$*	
	0.1 M		0.05 M	0.15 M
Alloys	E_b(mV vs Al)	E_p(mV vs Al)	E_b(mV vs Al)	E_p(mV vs Al)
Al 4104	419	−48	1595	121
Al T1	Passivation	Passivation	−198	−179
Al CP274	395	−53	240	−380
Al delta	-	-	1390	535

studied. The $CF_3SO_3^-$ ion is better suited to the characterization of alloys containing lithium, while the perchlorate ion proves to be best suited to the study of aluminium alloys containing magnesium. Chloride ions permit, in each case, the rapid dissolution of all types of alloys. All the passivity breakdown and protective potentials (E_b and E_p respectively) are close and fall within the same band of experimental values and reproducibility. Note that the E_b values depend on the electrode surface finishing. The scratch technique proposed by Pessall and Liu [6] offers improved measurement reproducibility.

4. Conclusion

Aluminium alloys containing very electropositive elements (Li, Mg) have been studied in organic environments (THF). The electrochemical behavior of these alloys was tested in the presence of chlorides, perchlorates and trifluoromethane sulfonate. Rest voltage measurements and voltammetric scans were carried out.

Two types of results were obtained depending on the alloy family studied. For the Al–Li alloys, the lithium content modifies the maximum dissolution current. The lithium content can be characterized by voltammograms obtained at low scan rates. The preferential dissolution of lithium leads in this case to the local precipitation of lithium chloride. For the Al–Mg alloys, the low solubility of magnesium chloride in THF would appear to be responsible for the results obtained, with the possible formation of a passivation layer of magnesium salt on the electrode.

Generally speaking, whatever the aluminium alloy considered, the voltammograms obtained in chloride environments give close values of the passivity breakdown and protective potentials, E_b and E_p, respectively. In $CF_3SO_3^-$ environments, dissolution takes place for both Al–Li and Al–Mg alloys. $CF_3SO_3^-$ would appear to be the most suitable ion for the characterization of Al–Li alloys, giving rise to the greatest difference between E_b and E_p.

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