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Comparative study of the effect of inorganic ions on the corrosion of Al 3003 and 6063 in carbonate solution

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Abstract

The effect of the addition of the oxo-anions $HPO_4{}^{2-}$, $MoO_4{}^{2-}$ and of the cations Ce^{3+}, Ce^{4+}, Li^+ and Mg^{2+} on the corrosion behaviour of the Al 3003 and Al 6063 alloys in carbonate solution is studied by electrochemical polarisation methods. The results show that these ions is the best inhibitor of Al 3003 alloy but only Ce^{3+} and Ce^{4+} are inhibitors for Al 6063 alloy. The inhibition efficiencies (IE%) of the $HPO_4{}^{2-}$, Ce^{3+}, Ce^{4+} and Mg^{2+} reached 90% at 10^{-2} M for Al 3003 alloy but of Ce^{3+}, Ce^{4+} is 50% at 10^{-2} M for Al 6063 alloy. Tafel lines of Al 6063 and Al 3003 alloys do not change with increasing of temperature in the presence and absence inhibitors. The IE% of Al 3003 of $HPO_4{}^{2-}$, Ce^{3+}, Ce^{4+} and Mg^{2+} is temperature independent. The increase of IE% of Li^+ from 76 to 99.6% at 25 and 70 °C, respectively, illustrates the performance of this inhibitor at elevated temperatures for Al 3003 alloy.

Keywords: Al 6063; Al 3003; Carbonate solution; Corrosion; Inhibition; Inorganic compounds

1. Introduction

Aluminium is used extensively for the protection, storage and preparation of food and beverages. Aluminium can be rolled into ultra-thin foils which are light, strong and have unique barrier and insulation qualities to preserve food, cosmetics, pharmaceutical products and protect from ultra-violet light, odours and bacteria. It resists to corrosion and it can be recycled many times with no loss of quality or properties. It is easy to sterilise for food and medical applications. The wide spread application of aluminium is attributed to its excellent properties like corrosion resistance, electrical, thermal conductivity, reflectivity and lightness. It also shows excellent mechanical properties at cryogenic temperatures [1,2].

The corrosion behaviour of aluminium in natural water depends on the nature and chemical composition of the water. Several works have been devoted to study the inhibition of aluminium by inorganic ions [3–12]. However, the majority of the reported works are focussed on chloride containing solutions because of their highly aggressive nature and their widespread occurrence in natural and plant environments [13–15]. A survey of the literature reveals that no systematic work has been devoted to the effect of the addition of metallic cations on the corrosion behaviour of aluminium alloys in media containing chlorides, sulphates or bicarbonates.

The present work aims to study the electrochemical effect of some inorganic compounds on the corrosion of Al 6063 and Al 3003 alloys in carbonate solution. The inorganic ions studied are: $HPO_4{}^{2-}$, $MoO_4{}^{2-}$, Ce^{3+}, Ce^{4+}, Li^+ and Mg^{2+}.

2. Experimental

The chemical compositions of the alloys used in the present study are given in Table 1.

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Table 1
Chemical composition (in weight) of Al 6063 and Al 3003 alloys

Alloy	Al	Mg	Si	Mn	Fe	Zn	Cu	Ti	Ni	Cr
6063	Balance	0.53	0.44	0.04	0.19	<0.002	<0.030	<0.002	<0.003	<0.002
3003	Balance	0.95	0.120	1.270	0.31	0.010	0.008	0.015	–	0.005

The aggressive solution of 0.1 M $NaHCO_3$ + 0.1 M NaCl is prepared by dilution with double distilled water. The inorganic compounds tested as inhibitors are the “Merck” commercial products.

Electrochemical measurements are carried out in a conventional three-electrode electrolytic cell. The working electrode is in the form of a disc cut from aluminium alloys and had a geometric working area of 0.5 cm^2. Saturated calomel electrode (SCE) and platinum electrode are used as reference and auxiliary electrodes, respectively.

The polarisation curves are carried out with a potentiostat (PGP 201), piloted by ordinate. The scan rate is 60 mV/min. All experiments are performed at temperature desired ±1 °C in a conventional electrochemical cell with three electrodes. Prior each experiment the electrode surface is polished with emery paper. The electrolyte magnetically stirred, is degassed by passing purified nitrogen through the solution for 30 min before starting the experiments. All tests are conducted at pH 8.

3. Results and discussion

3.1. Comparative study

Figs. 1 and 2 illustrate the polarization curves, recorded for the alloys studied in 0.1 M $NaHCO_3$ + 0.1 M NaCl in the absence and presence of the inhibitors at 10^{-2} M. Corresponding electrochemical parameters are summarised in Table 2.

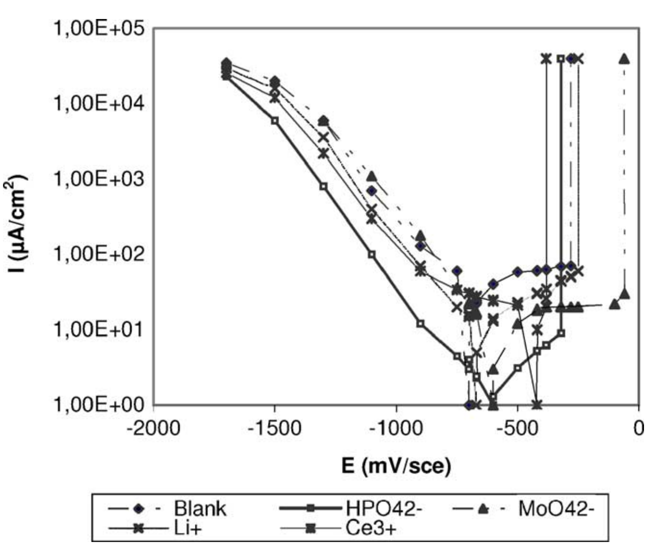

Fig. 1. Polarization curves of Al 3003 alloy in carbonate solution in the absence and presence of inhibitors at 10^{-2} M.

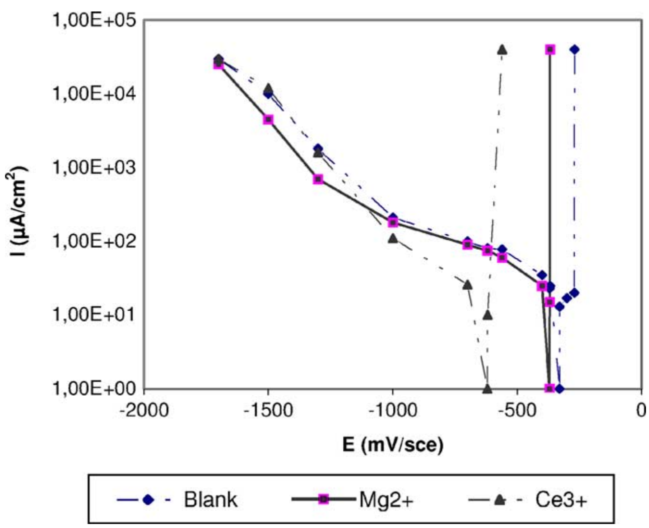

Fig. 2. Polarization curves of Al 6063 alloy in carbonate solution in the absence and presence of inhibitors at 10^{-2} M.

The corrosion inhibition efficiency (IE%) is defined as:

$$\mathrm{IE}(\%) = \left(1 - \frac{I'_{corr}}{I_{corr}}\right) \times 100 \quad (1)$$

I_{corr} and I'_{corr} are the uninhibited and inhibited corrosion current densities, respectively, determined by extrapolation of the cathodic Tafel lines to corrosion potential (E_{corr}). From

Table 2
Electrochemical parameters of Al 3003 and 6063 alloys in carbonate solution with and without inorganic compounds at 10^{-2} M and corresponding inhibition efficiencies (IE)

	E_{corr} (mV/ecs)	b_c (mV/dec)	I_{corr} (µA/cm^2)	E_{piq} (mV/sce)	IE (%)
Al 3003					
Blank	−700	450	50	−280	–
HPO_4^{2-}	−600	420	4	−320	92
MoO_4^{2-}	−600	420	9	−60	82
Ce^{3+}	−420	414	19	−380	62
Ce^{4+}	−460	416	3	−420	94
Li^{+}	−670	420	12	−250	76
Mg^{2+}	−620	430	4	−300	92
Al 6063					
Blank	−330	400	42	−270	–
HPO_4^{2-}	−380	430	40	−340	5
MoO_4^{2-}	−370	430	40	−340	5
Ce^{3+}	−620	460	20	−56	53
Ce^{4+}	−600	450	21	−340	50
Li^{+}	−380	420	40	−340	5
Mg^{2+}	−370	420	40	−330	5

Table 3
Electrochemical parameters of Al 3003 alloy and corresponding IE%

	C(M)	E_{corr} (mV)	b_c (mV/dec)	I_{corr} ($\mu A/cm^2$)	IE (%)
Blank	–	−700	450	50	–
Ce^{3+}	10^{-2}	−420	414	19	62
	10^{-3}	−420	420	38	25
Ce^{4+}	10^{-2}	−460	416	3	94
	10^{-3}	−400	420	11	78
	10^{-4}	−400	420	44	13
Li^{+}	10^{-2}	−670	420	12	76
	10^{-3}	−620	430	30	40
	10^{-4}	−600	425	45	10
Mg^{2+}	10^{-2}	−620	430	4	92
	10^{-3}	−600	415	4	92
	10^{-4}	−600	420	15	70
	10^{-5}	−600	435	41	18
$HPO_4{}^{2-}$	10^{-2}	−600	420	4	92
	10^{-3}	−380	420	12	76
	10^{-4}	−400	430	41	18
$MoO_4{}^{2-}$	10^{-2}	−600	420	9	82
	10^{-3}	−600	430	14	72
	10^{-4}	−620	440	25	50
	10^{-5}	−650	420	32	36

the analysis of Figs. 1 and 2 and Table 2, it can be seen that the cathodic Tafel lines are not altered by the presence of inhibitors both for Al 3003 and Al 6063 alloys. Parallel lines suggest that the addition of the tested compounds does not modify the mechanism of the cathodic process which corresponds to water molecule discharge:

$$2\,H_2O + 2e^- \rightarrow H_2 + 2\,OH^-$$

When inorganic compounds are added the corrosion potential of Al 3003 is shifted to more positive values and the corrosion potential of Al 6063 to more negative values. The addition of $HPO_4{}^{2-}$, $MoO_4{}^{2-}$, Ce^{3+}, Ce^{4+}, Li^{+} and Mg^{2+} ions at 10^{-2} M leads to a decrease of the corrosion current densities (I_{corr}) of Al 3003. In the case of Al 6063 alloy, only Ce^{3+} and Ce^{4+} ions inhibit corrosion while the others have practically no effect (Table 2). Only $MoO_4{}^{2-}$ offers a large domain of passivation. Metallographic observations allow to point out the formation of pits at E_{piq} [5,6]. Our results show that $MoO_4{}^{2-}$ ions act as a good inhibitor of both pitting and uniform corrosion of Al 3003 alloy in carbonate solution.

3.2. Detailed study

3.2.1. Influence of concentration

The electrochemical parameters deduced from polarisation curves of Al 6063 at various concentrations of $HPO_4{}^{2-}$, $MoO_4{}^{2-}$, Ce^{3+}, Ce^{4+}, Li^{+} and Mg^{2+} ions are given in Table 3.

From this table, it can be concluded that:

- Addition of inhibitors changes the values of E_{corr} but does not modify the Tafel slopes b_c.
- I_{corr} decreases with increasing inhibitors concentration.
- In the case of Mg^{2+} ions, the inhibition efficiency, reaches a maximum value at 10^{-3} M (IE% = 92%).

3.2.2. Influence of temperature

The electrochemical parameters of Al 3003 and Al 6063 alloys in carbonate solution with and without addition of $HPO_4{}^{2-}$, $MoO_4{}^{2-}$, Ce^{3+}, Ce^{4+}, Li^{+} and Mg^{2+} at 10^{-2} M determined at different temperatures in the range 25–70 °C are shown in Table 4. From these results it can be concluded that:

- The inhibition efficiencies IE% on Al 3003 alloy of $HPO_4{}^{2-}$, Ce^{3+}, Ce^{4+} and Mg^{2+} is independent of temperature. For Li^{+} ions, the increase of IE% from 76% at 25 °C to 99% at 70 °C illustrates the performance of this inhibitor at elevated temperatures. Only Ce^{3+} and Ce^{4+} are inhibitors for Al 6063 alloy.
- Tafel lines of Al 6063 and Al 3003 alloys do not change with increasing of temperature in the absence and presence of inhibitors.
- I_{corr} of Al 6063 in carbonate solution in the absence and presence of Ce^{3+} decreases with the rise of the temperature up to 50 °C. At 60 °C, I_{corr} increases rapidly until 70 °C, I_{corr} becomes important. Also, E_{corr} decreases with increasing temperature with and without addition of Ce^{3+}.

Results show that all the tested ions ($HPO_4{}^{2-}$, $MoO_4{}^{2-}$, Ce^{3+}, Ce^{4+}, Li^{+} and Mg^{2+}) are very efficient inhibitors towards corrosion of Al 3003 alloy and that only Ce^{3+} and Ce^{4+} have a medium inhibitive action on Al 6063 corrosion, $HPO_4{}^{2-}$, $MoO_4{}^{2-}$, Li^{+} and Mg^{2+} having practically no effect. Furthermore, Ce^{3+}, Ce^{4+}, Li^{+} and Mg^{2+} act also as a good inhibitor of pitting corrosion of Al 3003 alloy (Fig. 1). These ions integrate probably an oxide–hydroxide film, and reinforce its protective properties. In the case of $HPO_4{}^{2-}$ ions, inhibition efficiency (IE%) does not undergo a decrease until 60 °C. This result shows that the addition of these ions in aggressive media reinforces the passivation layer. For $MoO_4{}^{2-}$ and Li^{+}, IE% increases slightly from 25 to 70 °C to reach 97 and 99% respectively, and the pitting potential has tendency to move to more noble values with the rise of temperature. This result shows that Li^{+} or $MoO_4{}^{2-}$ exhibit an excellent behaviour toward the corrosion of Al 3003 alloy in aggressive media. The addition of Mg^{2+} inhibits the corrosion processes of Al 3003 alloy in all explored temperature. This is seen by the increase of IE% to attain 99% (Table 4). In addition Al 3003 become more sensitive to pitting when the temperature increases. So, Mg^{2+} ions favour the passivation of Al 3003 alloy at high temperature.

Table 4
Electrochemical parameters of Al 3003 and Al 6003 alloys in carbonate solution with and without some inorganic compounds (10^{-2} M) at different temperatures

	T (°C)	E_{corr} (mV/sce)	b_c (mV/dec)	I_{corr} (μA/cm^2)	E_{piq} (mV/sce)	IE (%)
Al 3003						
Blank	25	−700	450	50	−280	–
	40	−770	440	25	−230	–
	50	−800	430	150	−260	–
	60	−800	445	600	−260	–
	70	−850	450	2500	−250	–
HPO_4^{2-}	25	−600	420	1	−320	98
	40	−650	430	0.5	−290	98
	50	−550	435	1.5	−300	99
	60	−400	440	22	−290	96
	70	−400	450	220	−300	91
MoO_4^{2-}	25	−600	420	5	−60	82
	40	−600	425	8	−40	82
	50	−570	420	11	−40	93
	60	−550	430	30	−30	95
	70	−500	440	80	−20	97
Ce^{3+}	25	−420	414	19	−380	62
	40	−500	420	10	−400	60
	50	−500	430	45	−400	70
	60	−550	440	200	−430	67
	70	−650	450	790	−450	68
Ce^{4+}	25	−460	416	3.1	−420	94
	40	−460	420	1.5	−420	94
	50	−700	430	13	−550	91
	60	−700	430	22	−500	96
	70	−750	440	40	−520	98
Li^+	25	−670	420	12	−250	76
	40	−620	430	6	−230	76
	50	−600	440	7	−200	95
	60	−550	430	8	−100	99
	70	−550	420	10	−100	99.6
Mg^{2+}	25	−620	430	4	−300	92
	40	−700	430	2	−300	92
	50	−550	435	5	−100	99
	60	−500	440	13	−100	98
	70	−500	445	22	−50	99
Al 6063						
Blank	25	−330	400	42	−270	–
	40	−580	420	25	−360	–
	50	−870	430	15	−200	–
	60	−940	450	100	−270	–
	70	−1015	460	270	−200	–
Ce^{3+}	25	−620	460	20	−560	53
	40	−815	420	11	−400	56
	50	−900	430	7	−200	56
	60	−900	410	45	−300	55
	70	−950	400	120	−250	54

4. Conclusion

- HPO_4^{2-}, MoO_4^{2-}, Ce^{3+}, Ce^{4+}, Li^+ and Mg^{2+} are the best inhibitors of Al 3003 alloy but only Ce^{3+} and Ce^{4+} inhibit Al 6063 alloy corrosion.
- The inhibition efficiency of the HPO_4^{2-}, Ce^{3+}, Ce^{4+} and Mg^{2+} reaches 90% at 10^{-2} M for Al 3003 alloy but it does not exceed 50% at 10^{-2} M of Ce^{3+} or Ce^{4+} for Al 6063 alloy.
- The Tafel lines of Al 6063 and Al 3003 alloys do not change with increasing of temperature in the presence and absence of inhibitors.
- IE% of Al 3003 alloy of HPO_4^{2-}, Ce^{3+}, Ce^{4+} and Mg^{2+} are independent of temperature.
- The increase of IE% from 76 to 99% from 25 to 70 °C, illustrates the performance of Li^+ at elevated temperatures for Al 3003 alloy.

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