Effect of electrolyte temperature on the polarization characteristics of an Al–Li–Cu–Mg alloy in NaOH

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Abstract. The effect of electrolyte temperature on the polarization characteristics of an Al–Li alloy of composition Al–1·90 Li–1·80 Cu–1·00Mg–0·09 Zr in 0·1 M NaOH solution was studied by the potentiodynamic polarization method. The electrolyte temperature was the equilibrium temperature established due to the prevailing weather conditions at different times in the year. The alloys exhibited active–passive behaviour at all the temperatures. It was found that the temperature of electrolyte affected the polarization behaviour of the alloys. The zero current potential and the open circuit potential were nobler with decreasing temperature. The corrosion current density, critical current density and passive current density increased with temperature, indicating the activated nature of the electrochemical process. The passive range was higher at 35°C compared to other temperatures. The temperature effect on polarization behaviour has also been explained by considering the dissolved oxygen concentration in the electrolyte at different temperatures. The ennoblement of Cu on the Al–Li alloy surface has also been addressed.

Keywords. Al–Li alloys; polarization behaviour; temperature effect; surface enrichment.

1. Introduction

The attractive combination of weight saving benefits and increased stiffness of Al–Li alloys has rendered them as candidate materials for aerospace applications (Sankaran and Grant 1980; Lavernia *et al* 1990). The substitution of Al–Li alloys in place of conventional 7XXX series Al alloys in aircraft components would entail a saving of 8 to 10% of the structural weight along with an increase of 15% in the elastic modulus, therefore providing an extra margin of safety for critical aerospace applications.

In addition to being fuel efficient, aircraft structures are also required to be corrosion resistant for long service life. In this regard, several studies have shown that Al–Li alloys are susceptible to environmental degradation (Christodoulou *et al* 1983; Holroyd *et al* 1985; Binsfield *et al* 1987; Meletis and Huang 1989; Balasubramaniam *et al* 1991; Wang *et al* 1992). The presence of the active element Li renders the corrosion behaviour of these alloys different from the conventional Al alloys. They have been observed to be more susceptible to corrosion by Niskanen *et al* (1981) and Ricker and Duquette (1983). As a complement to a detailed study on the hydrogen embrittlement (HE) of two Al–Li alloys (Thakur and Balasubramaniam 1997a, b), the polarization behaviour of these alloys in 0·1 M NaOH (the solution used for cathodic hydrogen charging in the HE study) was evaluated and the nature of the surface film formation under these conditions also characterized (Thakur and Balasubramaniam 1997c). Interestingly, it was observed that the polarization curves obtained in the summer months were different in nature compared to those obtained in the winter months, although the curves themselves were highly reproducible in any given particular

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season. The present paper addresses the polarization behaviour of two Al–Li alloys in 0·1 M NaOH as a function of electrolyte temperature, with the electrolyte temperature being varied due to seasonal conditions rather than by thermostatic water bath control.

2. Experimental

The Al–Li alloy (designated as 1441) used in the present study was supplied by the Defence Metallurgical Research Laboratory, Hyderabad. The composition of the alloy was 1·90% Li, 1·80% Cu, 1·00% Mg, 0·09% Zr and balance Al. Incidentally, the polarization behaviour of another Al–Li alloy, designated as 1440 and having the composition Al–2·30 Li–1·24 Cu–0·80 Mg–0·12 Zr, was also studied in detail and its behaviour was similar to that of the 1441 alloy, which is reported in this communication. Peak aged (aged at 170°C for 18 h) coupons of 1 cm² cross-sectional area were sectioned from the sheet and later all the surfaces were ground to 600 grit surface finish. Specimen coupons were connected with a conductive wire and this assembly was mounted in a cold setting epoxy. Specimen surfaces were polished to 1 μ surface finish and were thoroughly cleaned with acetone prior to each polarization experiment. Polarization experiments were performed in a one-litre polarization cell containing the working and counter electrodes which were controlled by a potentiostat interfaced to a personal computer. A platinum foil of 1 cm² area was used as the counter electrode. 0·1 M NaOH solution of pH = 13 was the electrolyte used in the present study as this was the solution in which cathodic hydrogen precharging was conducted for HE studies (Thakur and Balasubramaniam 1996a, b). In the case of polarization studies, the temperature of the electrolyte was that of the ambient temperature. The open circuit potential was monitored continuously immediately from the time of immersion, versus saturated calomel electrode (SCE). Before the start of each polarization experiment, the specimen was allowed to attain a stable potential. The data of potential versus time was obtained. After having obtained the steady open circuit potential, the potential was scanned at the rate of 1 mV/sec from − 1800 mV to + 1800 mV followed by a reverse scan from + 1800 mV towards active potentials. All the potentials reported in this paper are with respect to SCE.

3. Results and discussion

It was observed that the nature of the polarization curve depended upon the season in which the experiments were conducted, i.e. it was different when the experiments were conducted in winter and when conducted in summer. The polarization curves were themselves highly reproducible in any particular season. The only difference in the experiments conducted during these times was the ambient temperature (15°C in winter and 35°C in summer). The electrolyte's temperature was similar to that of the ambient temperature. Therefore, this was the main variable in the experiments conducted in the different seasons. The effect of this variable on the polarization characteristics is addressed below.

3.1 *Variation of open circuit potential with time*

The nature of variation of open circuit potential (OCP) with time of immersion in the alkaline solution at 35°C is presented in figure 1. The nature of OCP stabilization curve
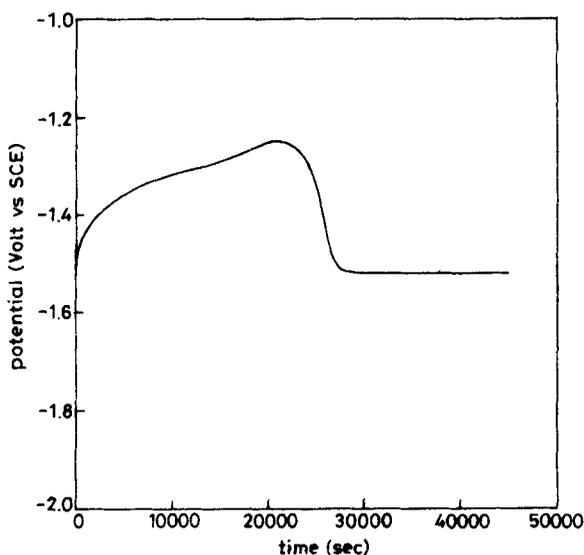
Figure 1. Variation of the open circuit potential as a function of time in 0·1 M NaOH solution at 35°C. The nature of the curves are similar at 15°C and 25°C.

in the NaOH electrolyte at different temperatures was similar. It is seen that the OCP stabilizes only after a fairly long amount of time (on the order of 8–10 h). The open circuit potential is at a very active value immediately upon immersion and then rapidly rises in the initial period to about − 1400 mV. This initial steep rise in Al alloys has been attributed to ohmic drop and the charging of the double layer next to the surface (Epelboin and Keddam 1978). The potential still continues to rise after this value is reached but the rate of increase is much slower. The OCP reaches its maximum value after ∼ 5 h and then it decreases rapidly until it reaches a value of about − 1450 mV. It is important to note that this behaviour was observed in a large number of independent experiments. After the fall of potential, the OCP stabilizes at all temperatures and remains fairly constant even for long immersion times. Interestingly, it was earlier observed by Colvin *et al* (1986) that a ternary Al–Li–Ge alloy took fairly long times (18–36 h) for stabilization of OCP in deaerated 3·5% NaCl solution. Very few investigators have mentioned the OCP stabilization nature of Al–Li alloys. In a detailed study of the polarization behaviour of several Al–Li alloys in 3·5% NaCl solution of different pH, Ambat and Dwarakadasa (1992) mentioned that the experiments were conducted once the stable potential was obtained and they did not provide the time for stabilization. The nature of stabilization curve is due to the type and nature of surface film forming on Al–Li alloys in the electrolyte and this has been addressed in detail elsewhere (Thakur and Balasubramaniam 1997c).

3.2 *Potentiodynamic polarization*

Potentiodynamic polarization experiments were performed at different seasons when the temperature of the electrolyte was 15°C, 25°C and 35°C. The temperature of the electrolyte used in the polarization cell was not controlled and therefore it was allowed

to equilibrate with the ambient temperature of the environment. In all the cases, the polarization scan was begun from an active potential of -1800 mV and scanned in the noble direction up to $+1800$ mV, at a constant scan rate of 1 mV/sec. The scanning direction was reversed after the potential of $+1800$ mV was attained. The potentiodynamic polarization curves for the 1441 alloy in 0·1 M NaOH at temperatures 15°C, 25°C and 35°C are provided in figures 2 through 4, respectively. In all these figures, it can be noticed from the forward polarization scan that the alloy exhibited active–passive behaviour in this electrolyte. On reversal, the polarization scan nearly traces the original forward polarization curve and this is indicative of the good re-passivation nature of the alloys in this electrolyte. The behaviour of the 1440 alloy was similar and therefore its polarization curves are not being reported here. Interestingly, the nature of polarization curve was also similar in different heat treatment conditions (i.e. under aged, peak aged and over aged) of the alloys and very minor variations were observed in the parameters of the polarization curves for the different aging conditions.

Table 1 presents the various parameters obtained from the polarization curves for the 1441 alloy in electrolytes at temperatures of 15°C, 25°C and 35°C. The zero current potential during the forward scan (ZCP_f) and the stabilized OCPs become active with increasing solution temperature. The zero current potential is the potential at which the cathodic and anodic currents balance (i.e. the mixed potential) during a potentiodynamic polarization sweep. In order to differentiate between the ZCP that is obtained on forward polarization scan (i.e. from active to noble potentials), the ZCP obtained on forward scanning is termed as ZCP_f and that obtained on reverse polarization scan (i.e. from noble to active potentials) is termed as ZCP_b. The primary passivation potential (E_{pp}) and the complete passivation potential (E_{cp}) are similar at
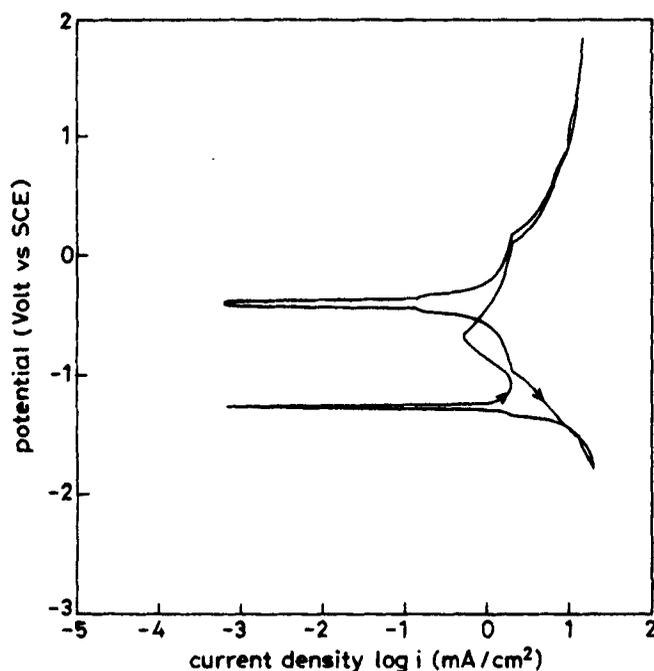

Figure 2. Cyclic potentiodynamic polarization curve in 0·1 M NaOH solution at 15°C.
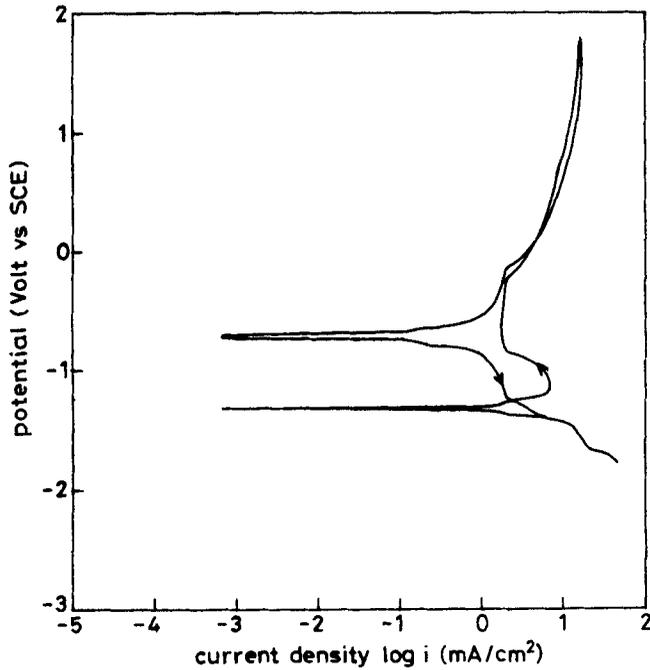
Figure 3. Cyclic potentiodynamic polarization curve in 0·1 M NaOH solution at 25°C.
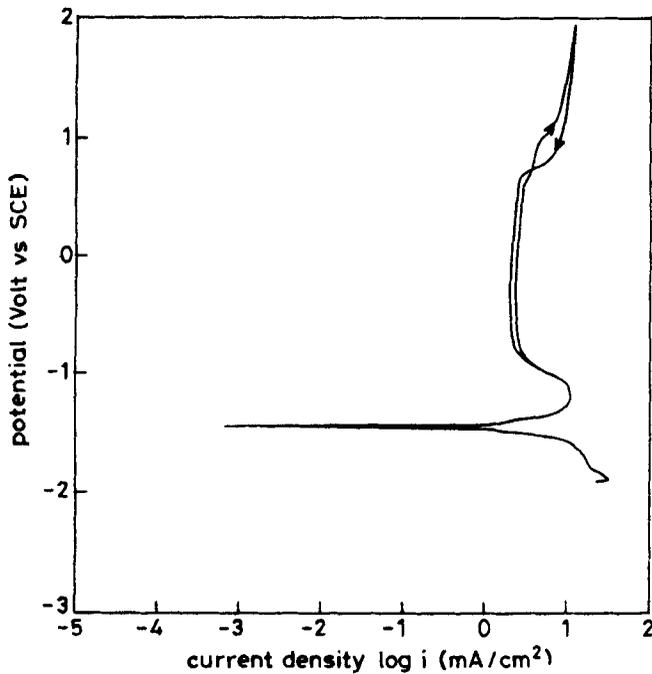

Figure 4. Cyclic potentiodynamic polarization curve in 0·1 M NaOH solution at 35°C.

the different temperatures. The critical current density for passivation (i_{crit}) and the passive current density (i_{pass}) increases with increasing solution temperature, indicating that the corrosion process is an activated phenomenon in the range of temperatures

Table 1. Electrochemical parameters obtained from the polarization curves of the Al–Li alloy in 0·1 M NaOH solution at different temperatures.

Temp. (°C)	OCP (mV vs SCE)	ZCP_f (mV vs SCE)	Passive range (mV)	i_{crit} (mA cm^{-2})	i_{pass} (mA cm^{-2})	i_{corr} (mA cm^{-2})
15	− 1450	− 1250	700	1·8	0·5	0·3
25	− 1458	− 1320	700	6·3	1·6	0·5
35	− 1520	− 1450	1550	10·0	2·0	0·8

investigated. Moreover, the corrosion current density (i_{corr}), estimated by Tafel extrapolation in the active region, increases with increasing solution temperature (table 1). Incidentally, this is the normal effect of temperature on these parameters of the anodic polarization curve of an active–passive metal (Jones 1990). The order of i_{crit} and i_{corr} are comparable to the critical current density and corrosion rate obtained by Ambat and Dwarakadasa (1992) for a number of Al–Li alloys in alkaline pH. The passive range is similar at 15°C and 25°C, but lower than the range at 35°C. Ambat and Dwarakadasa (1992) observed that the breakdown potential of several Al–Li alloys to be about − 500 mV in alkaline pH = 12 NaCl solution and this is lower than the breakdown potentials obtained in this study as the presence of chloride ions leads to easier destabilization of passive films on the surface of Al–Li alloys (Schnuriger *et al* 1987). On reversing the scan, the zero current potential (i.e. ZCP_b) is nobler in the case of the solution at 15°C than in the case of solution at 25°C (see figures 2 and 3). In the case of the solution maintained at 35°C, the ZCP_b was not attained as the scanning was stopped at − 1000 mV due to memory limitations of the potentiostat, but nevertheless it must be at a more active value than for the other two cases.

The change in the parameters of the potentiodynamic polarization curves obtained in the solution at different temperatures can be explained by considering the activated nature of the corrosion process, as it was observed that i_{corr}, i_{crit} and i_{pass} increased with increasing temperature. Moreover, the dissolved oxygen content, which depends on the temperature of the electrolyte, could also affect the polarization behaviour. It is well known that the polarization behaviour of Al is influenced by the oxygen content in the electrolyte (Pourbaix 1971; Tohma and Takeuchi 1979). The solution at higher temperature contains a lower amount of dissolved oxygen than the solution at lower temperature. For example, the oxygen concentration in fresh water or water of low salinity is 11·3 ppm at 10°C and 6·5 ppm at 40°C (Garg 1990). The effect of oxygen content is also reflected by the observation that the i_{crit} for passivation is lower with increasing oxygen concentration in the solution, thereby implying the easy formation and establishment of passivity (by the formation of hydrated oxide) on the surface of the alloy polarized in a solution with higher dissolved oxygen concentration. Moreover, the stabilized OCP and ZCP_f are nobler with increasing oxygen concentration in the solution (table 1). Ricker and Duquette (1983) found that the aeration of solution reduced the passive current density and increased the ZCP_f of Al–Li–Mg alloys. Moreover, Tsao and Pizzo (1985) studied the effect of oxygen content (between 0·5 and 15 ppm) on the polarization behaviour of several Al–Li–Cu alloys and showed that the ZCP_f shifts to noble values with increasing oxygen concentration with E_{pp} remaining essentially unaffected. The results of the present study (table 1) are in conformity with

these earlier studies. The shift in the ZCP$_f$ as a function of aeration has been explained by Pourbaix (1971) by the mixed potential theory.

It was earlier noted that the stabilized OCP was obtained only after a long period of immersion in the electrolyte. One of the characteristic features observed after the OCP versus time curve attains a flat shape (i.e. the maximum after the initial period of increase), was that there were thin ruptures on the surface film from which vigorous hydrogen evolution was observed. The rupture of the surface film leads to the exposure of the fresh metal surface to the electrolyte. Thus corrosion of Al in the alkaline medium proceeds according to

$$Al + 2H_2O = AlO_2^- + 4H^+ + 3e^-.$$

The electrons liberated by the above oxidation reaction are consumed by the cathodic reaction, one of the important of which is the hydrogen liberation reaction which occurs in the alkaline medium according to

$$2H_2O + 2e^- = H_2 + 2OH^-.$$
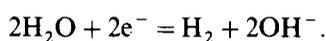
Therefore, the localized rupturing of the film formed on these Al–Li alloys under open circuit conditions results in the liberation of hydrogen according to the above equation. It is reasonable to assume that the presence of oxygen in higher amounts in the electrolyte would result in a lower amount of rupturing thereby stabilizing the potentials at a nobler value.

The nature of the polarization curves obtained can be explained by the mixed potential theory. The cathodic polarization curve (due to oxygen reduction and/or hydrogen reduction) intersects the anodic polarization in the active region and therefore, the specimen is in a state of active corrosion on immersion in the electrolyte. On the reversal of scan, it was observed that the ZCP$_b$ is obtained at a much more noble potential compared to the ZCP$_f$. This can be explained by noting that corrosion occurring during the forward scan causes the surface to be enriched with Cu due to dealloying of Al and Li (Buchheit and Stoner 1989). During the reverse scan, the exchange current density for hydrogen reduction reaction is higher because the surface is richer in Cu as it is known that the exchange current density for hydrogen evolution reaction is higher on Cu than on Al (Kortum and Bockris 1951). Therefore, the ZCP$_b$ is shifted to positive potentials. It is interesting to note that a similar explanation has been provided by Buchheit and Stoner (1989) to explain the shift of ZCP$_b$ for Al$_2$CuLi in NaCl solution. Incidentally, the enrichment of Cu on the surface film formed on the Al–Li alloys used in the present study under open circuit conditions has been experimentally verified by X-ray diffraction analysis and scanning electron microscopy (Thakur and Balasubramaniam 1997c). The amount of Cu, present as Cu(OH)$_2$, on the surface was minimal at small times of immersion and it became significant with increasing times of immersion. Moreover, it was visually observed that the film on the surface of the Al–Li alloy turned greenish in colour after stabilization of OCP and greenish-yellow after polarizing the specimen past the passive region during the forward polarization scan. The colour change is indicative of Cu enrichment as copper compounds are generally green in color. Craig *et al* (1987) in their study of local chemistry of pits in Al–Li–Cu–Mg alloys noticed that the solution in the pits became alkaline, unlike conventional Al alloys, and also that under these conditions the pits were packed with a greenish hydrous material with both metallic copper and oxidized

copper particles in and around the pits. Therefore, Cu enrichment occurs on the surface of Al–Li–Cu–Mg alloys exposed to alkaline environments and the shift in the ZCP_b in the noble direction during reverse polarization can be explained. The shift is more pronounced when the electrolyte temperatures are lower and this implies that the amount of Cu ennoblement on the surface is higher in this case, thereby resulting in nobler ZCP_b on reversal of scan. This would at first sight look anomalous since the corrosion rate in the active state is higher at higher temperatures (table 1). However, this can be resolved by noticing in figures 2 through 4 that the alloy remains in the pitted state for a longer time during the polarization scan at the lower temperatures due to the lower breakdown potentials in these cases compared to that at 35°C. The surface ennoblement of Cu arises due to this reason.

4. Conclusions

The polarization behaviour of an Al–Li–Cu–Mg alloy in 0·1 M NaOH solution at temperatures 15°C, 25°C and 35°C has been evaluated. It required a fairly long time to stabilize the open circuit potential at different temperatures. The alloy exhibited active–passive behaviour in the electrolytes at all the three different temperatures. Higher corrosion, critical and passive current densities were obtained at higher temperatures indicative of the activated nature of the corrosion process in the temperature range investigated. The effect of dissolved oxygen on the polarization behaviour has also been briefly discussed. Surface enrichment of Cu on the surface of the alloy is indirectly indicated by noble zero current potential obtained on reverse scan.

Acknowledgements

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