JOURNAL OF APPLIED ELECTROCHEMISTRY **24** (1994) 814–818

Behaviour of Al–Sn alloy on the negative side of the open-circuit potential

M. KLIŠKIĆ, J. RADOŠEVIĆ, LJ. ALJINOVIĆ

Faculty of Technology, Split, Croatia

Received 1 November 1993; revised 31 January 1994

The influence of the addition of small quantities of tin to high-purity aluminium (99.999%) on its electrochemical behaviour at high cathodic potentials was investigated. Cathodic current-time transients were recorded on Al–Sn alloys immersed in neutral 2 M NaCl, when subjected to a potential pulse from a potential around the open-circuit potential to different negative values. Hydration of the oxide layer occurs at potentials more negative than −1600 mV vs SCE (for alloys with 0.02% and 0.09% Sn), −1750 mV (Al–0.2% Sn) and −1900 mV (Al–0.4% Sn), whereupon hydrogen is evolved at the metal–hydrated oxide interface. Anodic current responses to the return of the potential to the rest values were also recorded, and the charges required for oxidation of the substances created during the cathodic processes are discussed.

1. Introduction

Aluminium alloys are widely used in everyday practice, primarily as construction materials, due to their exceptional mechanical properties and corrosion resistance. In recent years increasing attention has been given to a number of aluminium alloys, in which aluminium is electrochemically active, e.g. with indium, gallium, tin etc. [1–5].

Corrosion processes have been extensively investigated at pure aluminium [6, 7]. There are, however, few data on the behaviour of aluminium at high cathodic potentials, for both the inert and electrochemically active types.

In this work an attempt was made to examine the behaviour of Al–Sn alloy during cathodic polarization up to high negative potential values. Al–Sn alloy is interesting for uses such as batteries and sacrificial anodes, alone or with In, Ga etc.

2. Experimental details

The Al–Sn alloys, obtained by courtesy of Alcan International, had been prepared with high purity (99.999%) aluminium as the primary component. The alloying components had been added in amounts ranging from 0.02 wt %–0.4 wt % Sn. This corresponds to a mole ratio in the range 5×10^{-5}–10^{-3} Sn. After alloying the metal was homogenized at 600 °C for more than 1 h. At this temperature tin has its maximum solubility in aluminium of approximately 0.10% Sn. The alloy was quenched in cold water. The electrodes were cut into cubes of 1 cm^3 and made into electrodes by inserting insulated copper wires and protecting all sides but one by epoxy resin. The open side was mechanically polished to a mirror finish, degreased in alcohol and left in the air to attain the 'natural' oxide film, prior to immersion into solution.

A standard closed electrochemical cell was used with a SCE reference electrode and a platinum counter electrode in separate compartments. The solution was 2 M NaCl made of reagent grade salt and triply distilled water. The electrolyte and the electrode were placed in the cell and the solution was purged free of oxygen by purified nitrogen. The temperature was maintained at 25 ± 0.1 °C. Electrochemical measurements were performed with a potentiostat (PAR M 273) driven by a computer (PC 386SX).

Potential sweeps at very low sweep rate ($0.5\,\text{mV}\,\text{s}^{-1}$) were applied to the Al–Sn electrodes starting from the pitting potential in the negative direction down to −2.0 V vs SCE and back. The current response was converted to a logarithmic scale and the resulting Tafel plots, covering up to six orders of current density, were obtained on the plotter.

With the potentiostatic pulse method the time dependence of the cathodic current density on the electrode potential pulses ranging from −1300 mV to −2000 mV vs SCE with pulse duration of 1 s, were followed. The time dependence of the anodic current response, which appears after a certain cathodic polarization, when the potential is returned to a value slightly more positive than open circuit potential, was also recorded.

3. Results and discussion

During the cathodic polarization of Al–Sn alloys of small Sn contents (0.02 and 0.09%) no significant

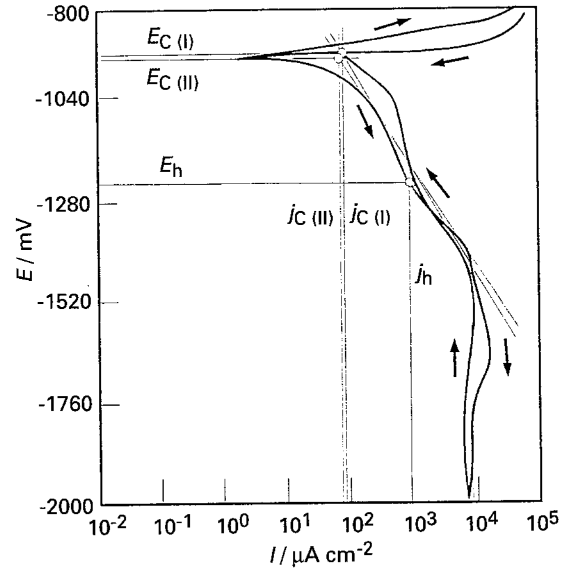

Fig. 1. Tafel plots of Al–0.02% Sn in 2 M NaCl solution (pH 1).

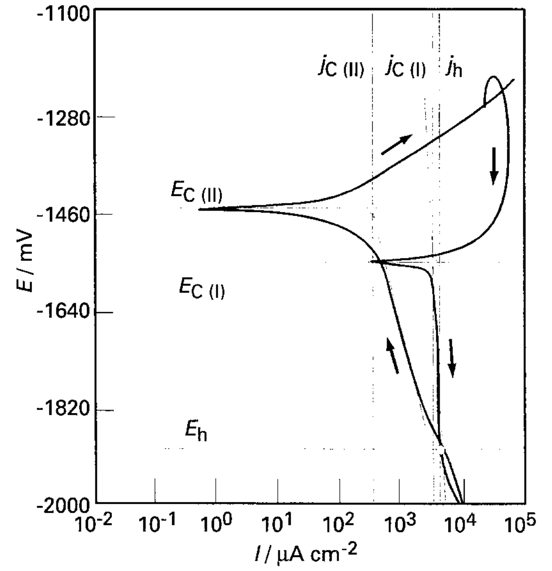

Fig. 2. Tafel plots of Al–0.4% Sn in 2 M NaCl solution (pH 1).

change with respect to the Tafel plot for pure aluminium was noted [8].

An analysis of polarization characteristics (Tafel functions obtained by means of slow potential changes) showed that there is no dependence on pH for pH > 2. At a pH of 1 a diffusion limiting current appears, which can be seen in Fig. 1. At that pH corrosion by means of H^+ ions appears to be dominant, whereas at higher pH the corrosion process, as well as the cathodic evolution of hydrogen, occurs by discharge of water.

The parameters obtained from the voltammograms for other pH values are shown in Table 1, with parameters of the cathodic Tafel functions characterizing the cathodic process, as are the corrosion potentials E_c(I) and E_c(II) and corrosion currents, j_c(I) and j_c(II) for the negative and the positive direction of the sweep responses, as well as the points of occurrence of hydration of the oxide layer characterized by E_h and j_h. They are compared with those for pure aluminium, as well as for other investigated alloys.

As seen in Table 1, for Al–0.02% Sn and Al–0.09% Sn alloys, except at pH 1 and 2, hydration and rapid current increase are shifted towards the negative values compared to pure aluminium. For alloys with higher tin contents, the initiation of hydration is, at all pH values, significantly shifted in the negative direction. In the case of Al–0.4% Sn alloy, as seen in Fig. 2, at potential change from −1300 mV vs SCE in the cathodic direction, cyclic voltammograms first show some depassivation and then assume the expected course to the corrosion potential E_c(I). The appearance of depassivation as for pure aluminium was not registered [8].

Apart from the results at pH 1, where the increase in cathodic polarization leads to a limiting current of 50 A m^{-2}, at higher pH values the cathodic process takes place all the way up to the hydration potential, E_h, with similar currents of the order of magnitude of 1 A m^{-2} and virtually with the same slope and the same E_h (evident in Table 1).

It is interesting to note that, for the alloy with the highest tin content, the E_c(II) is usually more positive than E_c(I), which may be explained in terms of the loss of tin in the surface layer. However, this loss is large as E_c(II) is still very negative. For this alloy, at pH values between 5 and 10, a double corrosion potential sometimes appears on return from the cathodic in the anodic sweep direction; this can be seen in Fig. 3.

This may be understood if it is assumed that the first $E_c(II)_1$ is determined by an anodic process involving a cathodic product e.g. hydride [6]. As a consequence, the process is slowed down to give the second $E_c(II)_2$. For alloys containing 0.2 and 0.4% Sn, at pH 1 and 2, voltammograms with limiting currents were obtained. At other pH values voltammograms similar to those for Al–0.4% Sn were obtained. When starting the voltammograms in the cathodic direction from positive potentials (−1300 mV vs

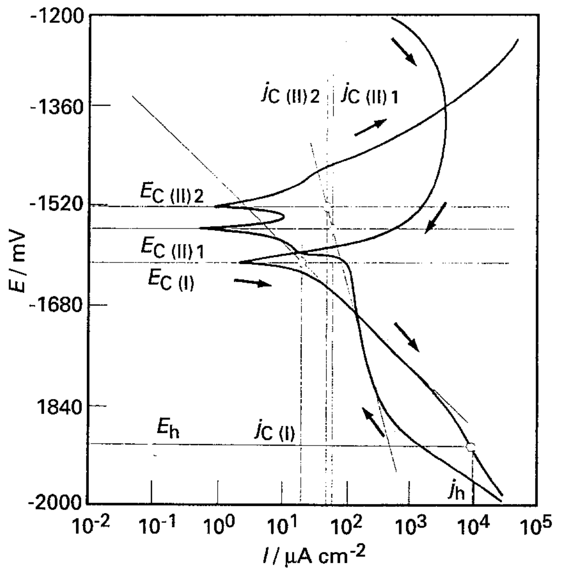

Fig. 3. Tafel plots of Al–0.4% Sn in 2 M NaCl solution (pH 5).

Table 1. Characteristic features of the cathodic Tafel plots of aluminium and Al–Sn alloys in 2 M *NaCl solutions*

	pH	$E_c(I)$/mV	$j_c(I)\times 10^2$/Am^{-2}	$E_c(II)$/mV	$j_c(II)\times 10^2$/Am^{-2}	E_h/mV	$j_h\times 10^2$/Am^{-2}
Al(5N)[9]	5	−1170	4.0	—	—	−1480	10
Al–0.02% Sn	1	−920	82.5	−904	68.0	−1252	1000
	2	−952	21.5	−1112	1.9	−1473	197
	3	−1020	12.1	−1272	2.6	−1705	95
	4	−1004	3.0	−1628	5.6	−1721	85
	5	−1057	1.8	−1604	1.3	−1765	356
	6	−1061	1.2	−1632	5.1	−1737	251
	7	−992	5.0	−1608	18.0	−1721	311
	8	−1020	2.0	−1624	9.0	−1737	130
	9	−1000	0.3	−1576	1.6	−1785	256
	10	−1081	0.5	−1628	5.0	−1649	17
Al–0.09% Sn	1	−1551	7498.0	−1377	383.0	−1928	8254
	2	−1123	100.0	−1109	16.0	−1770	510
	3	−1143	24.0	−1215	0.1	−1591	115
	4	−1152	2.4	−1598	4.2	−1751	85
	5	−956	5.0	−1436	4.6	−1559	75
	6	−922	2.0	−1310	0.6	−1731	2066
	7	−942	2.0	−1583	5.0	−1392	133
	8	−1090	0.6	−1617	14.7	−1499	40
	9	−1080	1.6	−1588	3.8	−1707	119
	10	−965	0.4	−1622	8.2	−1723	120
Al–0.2% Sn	1	−1776	5623.0	−1546	3831.0	−1745	9240
	2	−1580	1780.0	−1449	1000.0	−1860	1957
	3	−1580	56.0	−1508	0.4	−1797	147
	4	−1595	30.0	−1619	4.0	−1754	62
	5	−1600	18.0	−1633	3.8	−1792	51
	6	−1614	8.0	−1643	4.0	−1846	100
	7	−1597	12.0	−1623	2.0	−1749	24
	8	−1609	2.0	−1596	0.7	−1836	110
	9	−1609	10.0	−1556	0.6	−1753	38
	10	−1607	9.0	−1600	1.5	−1709	12
Al–0.4% Sn	1	−1546	3162.0	−1447	348.0	−1913	5109
	2	−1565	178.0	−1484	3.8	−1882	383
	3	−1586	68.0	−1525	7.5	−1840	196
	4	−1578	75.0	−1503	4.0	−1801	196
	5	−1611	16.0	−1611	80.0	−1900	9980
	6	−1597	68.0	−1652	31.6	−1840	261
	7	−1580	68.0	−1498	1.9	−1795	262
	8	−1603	56.0	−1658	46.4	−1865	316
	9	−1580	110.0	−1497	2.1	−1812	287
	10	−1580	1509.0	−1509	5.6	−1806	215

SCE) all alloys show signs of passivation in the anodic branch, whereas on the return sweep this phenomenon was not noticed.

A typical current-time response during the cathodic polarization of the Al–0.4% Sn alloy, obtained with a potentiostatic pulse, is shown in Fig. 4.

Characteristic sequences of cathodic pulses registered in the 2 M NaCl solution (pH 5.5) for Al–0.02% Sn and Al–0.4% Sn alloys are shown in Fig. 5.

Two potential regions were found:

(i) For the alloys with lower tin contents (0.02% and 0.09%) pulsation resulted in typical potentiostatic charging curves up to −1600 mV vs SCE. The limit shifted to −1750 mV (for 0.2% Sn) and −1900 mV (for 0.4% Sn). In the indicated potential regions the initial current peaks were fairly stable and the values were in the vicinity of 10^{-2} A m^{-2}.

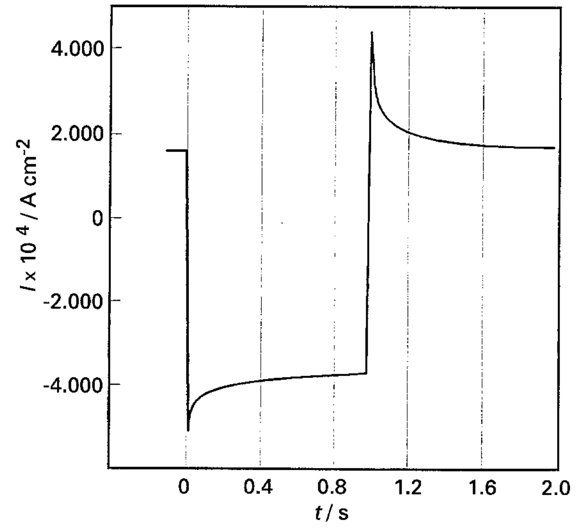

Fig. 4. Sequences of cathodic and anodic current–time responses to potential pulse from −1300 mV vs SCE to −1550 mV and back for Al–0.4% Sn. Pulse duration: 1 s.

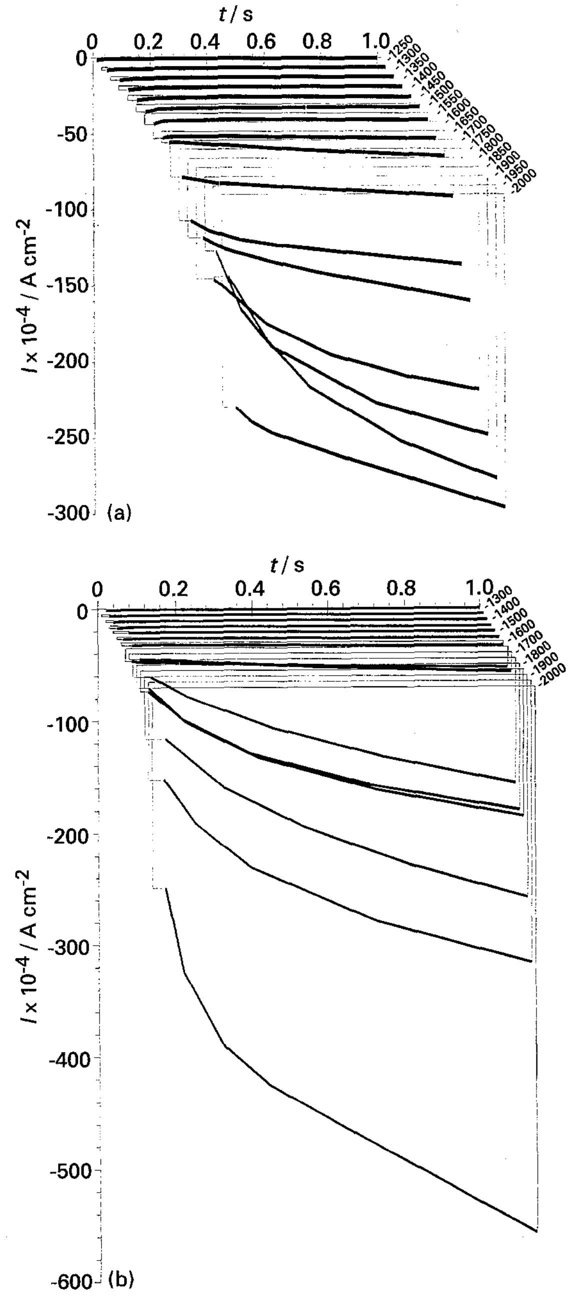

Fig. 5. Sequences of cathodic current–time responses to potential pulses from the rest potential to different negative values (indicated in the Figure) and back, for (a) Al–0.02% Sn and (b) Al–0.4% Sn.

(ii) Pulsation to potentials more negative than the earlier values (for each alloy separately) led to complex current-time functions. In these potential regions, as seen in Fig. 5, after the charging current decay, the current density was found to rise again.

In a relatively wide potential region, i.e. to the occurrence of hydration, the oxide film appears to preserve its properties as the cathodic current responses follow a simple exponential decay. The changes taking place in the second potential region reflect oxide hydration penetrating from the interface, on which hydrogen gas is evolved, all the way to the surface of the metal itself. The shifting of the potentials in the negative direction makes possible the occurrence of other substances which are stable in that potential region, such as AlH_3, AlH_2^+, AlH^{2+} [9]. The return of the potential to the rest value results in the appearance of significant anodic currents decaying with time (Fig. 4), following a complex exponential function. It may be assumed that this function reflects both charging of the interfacial capacitance due to a sudden change of potential, and the oxidation of the substances accumulated during the cathodic process, which did not diffuse

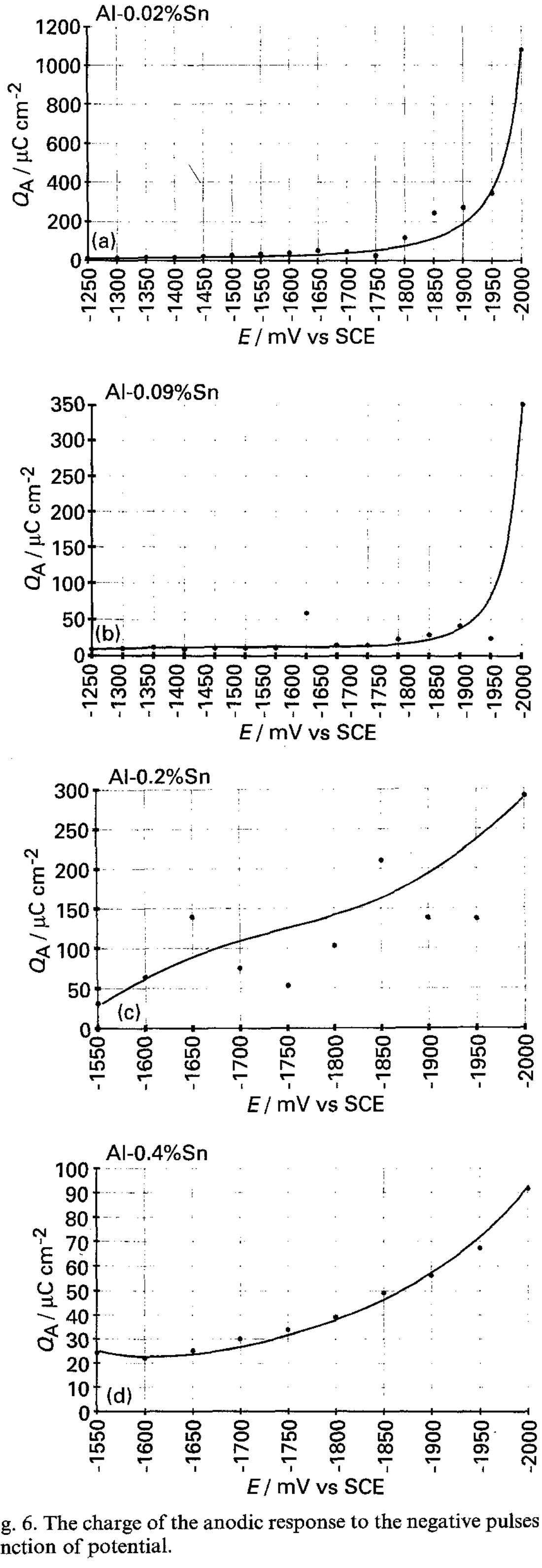

Fig. 6. The charge of the anodic response to the negative pulses as a function of potential.

Table 2. Charge obtained by integration of current–time responses to return of the potential to the rest value

E/mV	$Q_A \times 10^2/\mathrm{C\,m^{-2}}$			
	Al–Sn 0.02%	*Al–Sn 0.09%*	*Al–Sn 0.20%*	*Al–Sn 0.40%*
−1250	11	—	—	—
−1300	14	9	—	—
−1350	16	10	—	—
−1400	17	12	—	—
−1450	20	9	—	—
−1500	29	11	—	—
−1550	36	11	31	24
−1600	42	12	64	22
−1650	53	49	138	25
−1700	47	15	75	30
−1750	27	15	53	34
−1800	120	23	102	39
−1850	246	29	209	49
−1900	272	41	137	56
−1950	272	24	136	67
−2000	1078	350	291	91

further and which are unstable at the more positive potentials.

By integrating currents with time [6] at the return of the potential to the rest value, quantities of charge, Q_A, were evaluated for each alloy within 1 s, and are shown in Table 2. It is obvious that, with increase in tin content in an alloy, the Q_A value is reduced, which means that a significantly smaller quantity of the substance which stays at the surface of the metal is formed in the cathodic process. This is probably due to the fact that the beginning of hydration of the oxide film, for the alloys with larger tin content, is shifted towards the more negative potentials, so that during the shorter time the cathodic process takes place at the bare metal, a considerably smaller amount of the readily oxidizing substance is created.

As can be seen in Fig. 6(a) and (b) the charge Q_A in the two negative potential regions are basically different for the Al–0.02% Sn and Al–0.09% Sn alloys from those of the Al–0.2% and Al–0.4% Sn alloys (Fig. 6(c) and (d)). The charge quantities on the latter, as obtained in the two negative potential regions, are much smaller and similar.

4. Conclusion

If small quantities of Sn are added to high-purity aluminium in 2 M NaCl solution, changes in the behaviour during cathodic polarization occur, but only if these contents are higher than 0.2%. Otherwise the addition of tin has virtually no effect.

Cyclic voltammetry showed that (except at pH 1 and 2, where cathodic process evidently included H^+ ion reduction) at all pH values, the presence of tin affects the anodic process as well as the corrosion potential. The cathodic process takes place over the oxide film by reduction of water molecules, which accounts for the absence of pH dependence.

By studying the dependence of the beginning of hydration on tin content in aluminium alloys, it was found that with increase of the former the hydration shifts towards a more negative potential. The presence of tin tends to stabilize the oxide film.

The Q_A values also confirm the increased stability of the oxide film with increase in tin content in the alloy.

Cathodic polarization activates the alloy for anodic dissolution, so that at −1300 mV current densities of several hundred $\mathrm{A\,m^{-2}}$ are attained, which indicates significantly more active dissolution of aluminium than for the pure metal.

References

[1] T. Valand and G. Nilsson, *Corros. Sci.* **17**(11) (1977) 931.

[2] A. Mance, D. Cerović and A. Mihajlović *J. Appl. Electrochem.* **14** (1984) 459.

[3] *Idem, ibid.* **15** (1985) 415.

[4] Lj. Krstulović and B. Kulušić, *Kem. Ind.* **40**(2) (1991) 49.

[5] D. S. Keir, M. J. Prior and P. R. Sperry, *J. Electrochem. Soc.* **116**(3) (1969) 319.

[6] J. Radošević, M. Kliškić, P. Dabić, R. Stevanović, and A. Despić, *J. Electroanal. Chem.* **277** (1990) 105.

[7] A. Despić, J. Radošević, P. Dabić and M. Kliškić, *Electrochim. Acta* **35** (1990) 1743.

[8] J. Radošević, M. Kliškić and A. Despić, *J. Appl. Electrochem.* **22** (1992) 649.

[9] G. G. Perrault, *J. Electrochem. Soc.* **126** (1979) 199.