Journal of Applied Electrochemistry **31**: 115–119, 2001.

Influence of alloying additives on corrosion and hydrogen permeation through commercial aluminium in alkaline solution

M. PARAMASIVAM and S. VENKATAKRISHNA IYER
Central Electrochemical Research Institute, Karaikudi-630 006, Tamil Nadu, India

Received 14 March 2000; accepted in revised form 27 July 2000

Key words: alkaline solution, alloying additives, commercial aluminium, electropermeation, open circuit potential, self corrosion rate

Abstract

The influence of alloying additives on the extent of corrosion and hydrogen permeation through aluminium of different grades such as 2S, 3S, 26S and 57S, in 0.01 M NaOH has been investigated using weight loss measurements and electropermeation. It is found that the extent of self corrosion and hydrogen permeated through different grades of commercial aluminium follow the order: 3S > 2S > 26S > 57S. The influence of incorporating zinc and indium either alone or in combination on self corrosion and permeation current has also been studied. It is found that ternary alloys of both 26S and 57S containing zinc and indium give considerably lesser values of self corrosion rate and permeation current.

1. Introduction

Aluminium, having attractive properties such as high energy density and high negative potential in alkaline media, combined with its abundance, offers an attractive choice as galvanic anode in primary alkaline batteries. However, it has drawbacks such as its high rate of self corrosion and gassing. It has been reported that a combination of calcium and complexing agents like citrate and tartrate can reduce the self corrosion of commercial grades of aluminium such as 2S, 3S, 26S and 57S in 1 M NaOH and also the extent of gas evolution [1]. The self corrosion and gassing can also be reduced by incorporating different alloying additives such as zinc, indium, thallium, tin and bismuth in commercial aluminium [2–4]. Among these additives zinc and indium are found to be more effective in improving electrochemical properties of aluminium in addition to gassing and self corrosion. It is also of interest to investigate whether the incorporation of these alloying additives in aluminium has any significant influence on the extent of hydrogen permeation through aluminium in alkaline solution.

Devanathan and Stachurski's electropermeation method [5] has recently been improved [6] and has been used for hydrogen permeation studies on steel in corrosive medium. This technique has been widely used for hydrogen uptake studies using palladium, steel and other transition metals [7–10]. Little work has been reported on permeation studies using aluminium. Chang et al. [11] have studied hydrogen permeation through pure aluminium using the hydrogen permeation method. Onochukwu and Trasatti [12] studied the permeation of hydrogen through the aluminium alloy AA 1060 in alkaline medium. Onochukwu et al. [13] also studied the influence of different anions and temperature on the extent of hydrogen permeation through aluminium AA 1060 in alkaline medium. In the present study the influence of alloying additives such as zinc and indium on the self corrosion rate and the extent of hydrogen permeated through different grades of commercial aluminium and their binary and ternary alloys has been studied using weight loss measurements, open circuit potential measurements and the hydrogen permeation method.

2. Experimental details

2.1. *Materials and solution*

Specimens used for the study were different grades of aluminium namely 2S, 3S, 26S and 57S and their compositions are given in Table 1. All the above grades are commercial alloys manufactured by Indian Aluminium Company Ltd, Calcutta. Various binary and ternary alloys of aluminium were obtained by incorporating different weight percentages of alloying additives such as zinc and indium. These alloys were cast by melting the constituents in a graphite crucible and then casting in a graphite mould in the form of sheets of 0.025 cm thickness.

Specimens for corrosion rate measurements, open circuit potential and electropermeation studies were

Table 1. Composition of different grades of commercial aluminium

Grade	Composition (normal) / wt/wt					
	Al	Mn	Mg	Cu	Si	Fe
2S	99.0	–	0.1	0.2	0.3	0.4
3S	97.8	1.1	1.1	–	–	–
26S	93.3	0.8	0.8	4.3	0.8	–
57S	97.7	2.0	0.3	–	–	–

rectangular strips of different grades of aluminium of size 5 cm × 2 cm × 0.025 cm. These specimens were buffed with a cloth, polished with pumice powder and finally degreased with trichloroethylene. Zinc of 99.75% purity was procured from Binani Zinc Ltd, Aluwa, Kerala and indium of 99.9% purity was procured from Nuclear Fuel Complex, Hyderabad. Sodium hydroxide was of reagent quality (E.Merck). All solutions were prepared using triply distilled water.

2.2. *Procedure*

2.2.1. *Corrosion rate measurements*

Triplicate specimens of different grades of commercial aluminium and their alloys were kept immersed in 0.01 M NaOH solution for 30 min. At the end of the period, specimens were removed, washed well with distilled water, dried and weighed.

2.2.2. *Open circuit potential measurements*

Open circuit potentials of specimens undergoing self corrosion in alkaline solution were noted 10 min after immersion with reference to a Hg/HgO, 0.01 M NaOH electrode using a high impedance multimeter (HIL). Reproducibility of the potential measured is ± 5 mV.

2.2.3. *Electropermeation studies*

The sketch of the cell used in this study is shown in Figure 1. The cell consists of two double walled compartments A and B, which have provisions for circulating water from a thermostat to maintain at a temperature of 30 ± 2 °C. The right compartment (B) has two openings, one for the platinum auxiliary electrode and the other for the Hg/HgO, 0.01 M NaOH electrode. The left compartment (A) also has two openings, one for the aluminium electrode and the other for inserting a thermometer. The aluminium membrane was tightly held between the two compartments using Teflon bushings clamped intact.

A polished and cleaned aluminium specimen, using cotton soaked in 0.5 M NaOH was used for measurements. It was coated on one side (side B^1) using palladium to enable the ionization of hydrogen at a faster rate than hydrogen atom combination. The aluminium membrane was inserted in the clamp and screwed tightly. The anode compartment was filled with palladium plating solution containing deoxygenated 0.001 M $PdCl_2$ and 0.01 M KNO_2 in 3.5% NaCl as the background electrolyte. Plating was carried out at 100 μA for a duration of 90 min using platinum as the counter electrode. A potential of −76 mV with respect to Hg/HgO, 0.01 M NaOH electrode was impressed between the palladium coated aluminium electrode and the reference electrode by means of potentiostat (Wenking model POS 73) to ionise the hydrogen arising from electrodeposition completely. Thereafter, the chemical evolution of hydrogen was started in the compartment A by adding 0.01 M NaOH solution to come into contact with the aluminium membrane surface (side A^1). The concentration of NaOH used corresponded to the maximum permeation current with minimum attack on the membrane surface [12]. The ionization potential was maintained steady and constant until the hydrogen evolved due to corrosion was ionised and detected as a current of hydrogen ions. The hydrogen permeation rate was monitered with time for this aluminium membrane. After reaching a steady state of permeation, the corroding solution was removed from the compartment A, which was rinsed repeatedly with distilled water.

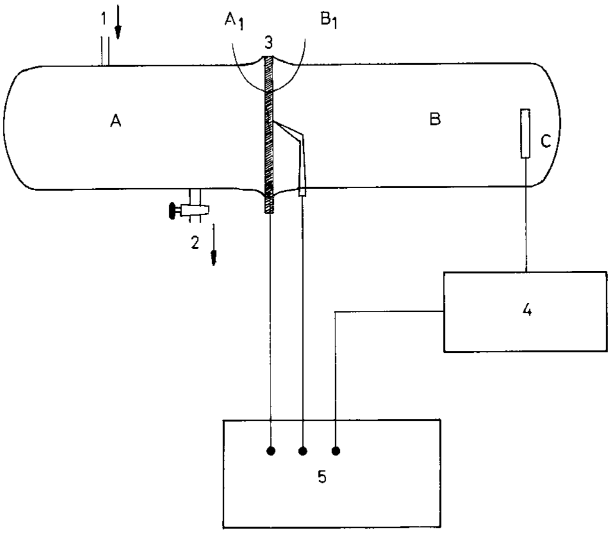

Fig. 1. Sketch of the cell and the electrical circuit for the hydrogen permeation studies. (1) Opening for introducing 0.01 M NaOH solution; (2) 0.01 M NaOH solution removal; (3) Aluminium membrane; (4) X-y-t recorder; (5) Potentiostat; (A^1) Side of the membrane where corrosion takes place; (B^1) Side of the membrane where hydrogen ionisation is detected.

The experiment was repeated three times and a fresh sample was used each time.

3. Results and discussion

Earlier studies on hydrogen permeation through metals depend on electrolytic hydrogen charging in which hydrogen is generated by applying a current between a platinum auxiliary electrode and a steel/aluminium working electrode. Hydrogen formation can be stopped once the current is out off. But the present method employs a chemical reaction method, in which aluminium reacts strongly with alkaline solution to evolve hydrogen on one side of the aluminium membrane.

Moreover, in the case of aluminium, cathodic generation of hydrogen is not possible as it is not an electrocatalytic surface.

The overall chemical reaction of aluminium dissolution can be written as [14]

$$\mathrm{Al(S)} + 2\,\mathrm{OH^-(aq)} \rightarrow \mathrm{AlO_2^-} + \mathrm{H_2}\uparrow \tag{1}$$

During hydrogen evolution [15, 16] hydrogen is initially adsorbed as atomic hydrogen on the metal surface. Subsequently it can either recombine to give a gaseous hydrogen molecule or be absorbed [17, 18]. The mechanism is

$$\mathrm{H_2O(l)} + \mathrm{e^-} \rightarrow [\mathrm{H}] + \mathrm{OH^-} \tag{2}$$

$$\mathrm{Al(S)} + [\mathrm{H}] \rightarrow \mathrm{Al{-}H_{ad}} \begin{array}{ll} \nearrow \mathrm{Al{-}H_{ab}} & \quad (3) \\ \searrow \mathrm{Al(S)} + \mathrm{H_2}\uparrow & \quad (4) \end{array}$$

The fact that it is possible to monitor the anodic current on the other side of the aluminium sheet proves the occurrence of hydrogen permeation via Step 3.

Figure 2 gives the hydrogen permeation against time curves for different grades of commercial aluminium in 0.01 M NaOH. Table 1 gives the values of open circuit potential, corrosion rate and permeation current for different grades of commercial aluminium. Permeation current against time curves have almost similar features to those reported for pure aluminium in alkali [11]. For all grades of aluminium, there is a delay of a few seconds for the evolution of hydrogen and thereby for the recording of hydrogen current. This 'time lag' can be attributed to the presence of a passivation surface oxide film, which delays, to some extent, the reaction of aluminium metal with alkali. It is also found that the permeation current increases with time and becomes steady after a certain time. The extent of hydrogen permeation through different grades of commercial aluminium follows the order 3S > 2S > 26S > 57S.

Values of corrosion current for different grades of commercial aluminium follows a similar order. The above observation can be explained as follows. Manganese, being a cathodic impurity, plays a significant role in the extent of corrosion of different grades of commercial aluminium depending on its content. Thus, 3S grade, having maximum manganese content, shows maximum self corrosion followed by 26S and 57S in decreasing order. Moreover, the presence of an anodic impurity, namely magnesium in different percentages in 26S and 57S leads to cathodic polarization (cathodic protection) of the base metal aluminium, resulting in less corrosion for 57S than 26S. Similarly the differences in corrosion rate between 26S and 57S can be explained on the basis of the presence of cathodic impurities such as copper, iron and silicon.

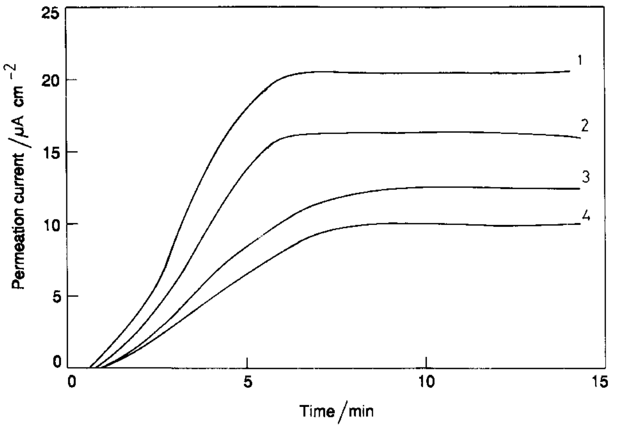

Fig. 2. Variation of permeation current with time for different grades of commercial aluminium: (1) 3S, (2) 2S, (3) 26S and (4) 57S.

It has already been reported that ternary alloys of commercial grade aluminium containing zinc and indium function very effectively as galvanic anodes for the cathodic protection of submerged structures and in primary alkaline batteries [19, 20]. So it is of interest to study the influence of the incorporation of zinc and indium on self corrosion and the hydrogen permeation current for aluminium in alkali. As 2S and 3S grades of aluminium show higher corrosion rates and permeation currents, these grades have not been made use of in further studies reported in this paper. Table 3 gives the self corrosion rate, open circuit potential and hydrogen permeation current for different binary alloys of 26S and 57S grade aluminium containing different percentages of zinc. Permeation current against time curves obtained for 26S and 57S aluminium containing different concentrations of zinc have exactly similar features as observed for 26S and 57S aluminium alone. As the solid solubility of zinc in aluminium lies in the range 3–5.5% by weight, zinc content in the alloy cannot be increased to a value higher than 5.5%. It can be seen from Table 2 that self corrosion rates for both grades of aluminium decrease with increase in zinc content up to 4% by weight and then increase for a concentration of 5% zinc. As zinc is cathodic to aluminium its incorporation in increasing concentrations is found to make open circuit potential values less negative up to 4% zinc addition and then the open circuit value becomes more negative. A proportionality is observed between the values of corrosion rate and permeation current for different percentages of zinc incorporated in the aluminium. This

Table 2. Values of open circuit potential, corrosion rate and permeation current for the corrosion of different grades of commercial aluminium in 0.04 M NaOH solution

Grade	Open circuit potential vs Hg/HgO, 0.01 M NaOH /V	Corrosion rate /mg $\mathrm{cm^{-2}\,min^{-1}}$	Permeation current /μA $\mathrm{cm^{-2}}$
2S	−1.426	0.1250	16.2
3S	−1.438	0.1876	20.6
26S	−1.396	0.0526	12.4
57S	−1.372	0.0498	10.6

Table 3. Values of open circuit potential, corrosion rate and permeation current for different grades of binary alloys 26S and 57S containing different percentages of zinc

Binary alloys	Zinc (wt/wt) /%	Open circuit potential vs Hg/HgO, 0.01 M NaOH /V	Corrosion rate /mg cm^{-2} min^{-1}	Permeation current /μA cm^{-2}
26S	–	−1.396	0.0526	12.4
	1.00	−1.390	0.0502	12.1
	2.00	−1.382	0.0486	11.5
	3.00	−1.376	0.0424	10.9
	4.00	−1.388	0.0394	9.2
	5.00	−1.379	0.0516	12.6
57S	–	−1.372	0.0498	10.6
	1.00	−1.358	0.0482	10.2
	2.00	−1.342	0.0418	8.8
	3.00	−1.334	0.0352	7.9
	4.00	−1.285	0.0326	7.1
	5.00	−1.362	0.0478	10.6

observation can be explained as follows. In any electrochemical reaction, the rates of anodic reaction (i.e., metal dissolution) and cathodic reaction (i.e., gas evolution) are equal. So, if the rate of anodic reaction is greater than that of the cathodic reaction will be greater still. When corrosion rate increases with incorporation of higher percentages of zinc, hydrogen evolution increases. This, in turn, leads to higher permeation of hydrogen through the metal membrane. Thus, the incorporation of 4% zinc in both 26S and 57S aluminium has a favourable influence in bringing down the self corrosion and permeation current. But the binary alloy of 57S performs better than that of 26S.

Table 4 gives values of self corrosion rate, open circuit potential and permeation current for 26S and 57S aluminium containing 4% zinc and different concentrations of indium ranging from 0.01–0.05%. It is found that the incorporation of different weight percentages of indium in both 26S and 57S aluminium is found to make open circuit potentials more negative. This observation can be ascribed to the fact that the incorporation of indium, as with mercury, is known disrupt the protective oxide layer to such an extent that aluminium becomes an unstable material in the presence of air. This makes it more active in corrosive environments and the open circuit potential becomes more negative [21]. Moreover the corrosion rates are also found to increase with increase in indium concentration. But the extent of hydrogen permeated is found to decrease with increase in indium content up to 0.025% of indium and then found to increase. In this case a proportionality is not observed between corrosion rate and the extent of hydrogen permeation. This can be attributed to higher cathodic overvoltage caused by the presence of indium in the alloy like mercury and tin. The presence of indium causes a decrease in hydrogen evolution and thereby reduces hydrogen permeation. The better performance of ternary alloys of 26S and 57S containing zinc (4%) and indium (0.025%) can be explained as follows.

Table 4. Values of open circuit potential, corrosion rate and permeation current for different grades of ternary alloys 26S and 57S containing different percentages (wt/wt) of indium

Binary alloys	Indium (wt/wt) /%	Open circuit potential vs Hg/HgO, 0.01 M NaOH /V	Corrosion rate /mg cm^{-2} min^{-1}	Permeation current /μA cm^{-2}
26S	–	−1.368	0.0394	9.2
	0.01	−1.376	0.0382	8.8
	0.02	−1.378	0.0308	8.0
	0.03	−1.394	0.0342	6.8
	0.04	−1.400	0.0389	8.2
	0.05	−1.415	0.0398	8.9
57S	–	−1.285	0.0326	7.10
	0.01	−1.292	0.0312	6.56
	0.02	−1.304	0.0302	6.28
	0.03	−1.306	0.0285	5.94
	0.04	−1.314	0.0295	6.12
	0.05	−1.320	0.0316	6.38
		−1.324	0.0325	6.82

Zinc forms a solid solution in aluminium as its concentration is within the range 3–5.5% weight. Indium incorporated as the third element may be precipitated in the grain boundaries and this is responsible for the better electrochemical properties of Al–Zn (4%) In (0.025%) alloy in alkaline medium. Similar observations have been made earlier by Kapali et al. who have examined the suitability of Al–Zn–In alloy as a galvanic anode for use in sea water for the cathodic protection of submerged structures [19]. The ternary alloy of 57S aluminium is found to perform better than that of 26S, as it has lower corrosion rate and permeation current.

4. Conclusion

(i) Corrosion rates of different grades of commercial aluminium in 0.01 M NaOH follow the order 3S > 2S > 26S > 57S.

(ii) Permeation currents for different grades of aluminium in 0.01 M NaOH follow a similar order.

(iii) Binary alloys of 26S and 57S aluminium containing 4% zinc give both lower corrosion rate and permeation current.

(iv) Incorporation of indium (0.025%) in binary alloy of 26S and 57S aluminium containing zinc gives a ternary alloy with lower corrosion rate and permeation current.

(v) The ternary alloy of 57S containing 4% zinc and 0.025% indium performs better than the ternary alloy of 26S.

References

1. V. Kapali, S. Venkatakrishna Iyer and N. Subramanyan, *Brit. Corros. J.* **4** (1969) 305.

2. K.B. Sarangapani, V. Balaramachandran, V. Kapali and S. Venkatakrishna Iyer, Proc. Annual Technical Meeting, Electrochemical Society of India, Bangalore, India (July 1985), p. 13.
3. A. Sheik Mideen, M. Ganesan, M. Anbukulandainathan, K.B. Sarangapani, V. Balaramachandran, V. Kapali and S. Venkatakrishna Iyer, *J. Power Sources* **27** (1988) 235.
4. V. Kapali, S. Venkatakrishna Iyer, V. Balaramachandran, K.B. Sarangapani, M. Ganesan, M. Anbukulandainathan and A. Sheik Mideen, *J. Power Sources* **39** (1992) 263.
5. M.A.V. Devanathan and Z. Stachurski, *Proc. Roy. Soc.* A **270** (1962) 90.
6. K.N. Srinivasan, M. Selvam and S. Venkatakrishna Iyer, *J. Appl. Electrochem.* **23** (1993) 358.
7. M.A.V. Devanathan and Z. Stachurski, *J. Electrochem. Soc.* **111** (1964) 619.
8. J.O'M. Bockris, M.A. Genshew and M. Fullenwider, *Electrochim. Acta* **15** (1970) 47.
9. H. Vondrak, *Electrochim. Acta* **29** (1984) 1191.
10. L.V. Babenkova, N.M. Popova and I.N. Blagovesh Chenskaya, *Usp Khim.* **54** (1985) 177.
11. Chu Young Chang, Yin Heyun and R.M. Latanision, Proc. 10th International Congress on 'Metallic Corrosion', Central Electrochemical Research Institute, Karaikudi, India (Nov. 1997), p. 2379.
12. A.I. Onochukwu and S. Trasatti, *Electrochim. Acta* **10** (1988) 1425.
13. A.I. Onochukwu, S.P. Trasatti and S. Trasatti, *Corros. Sci.* **36** (1994) 1815.
14. A.I. Onochukwu and O.D. Obande, *J. Chem. Ed.* **63** (1986) 269.
15. S. Trasatti, *J. Electroanal. Chem.* **39** (1972) 163.
16. L.I. Krishtalik, *J. Electroanal. Chem.* **130** (1981) 9.
17. A.I. Onochukwu, *J. Electrochem. Soc.* **130** (1983) 1078.
18. A. Saraby-Reeintjes, *Electrochim. Acta* **31** (1986) 251.
19. V. Kapali, K.N. Srinivasan, B. Venkataraman and K. Balakrishnan, Proc. 10th International Congress on 'Metallic Corrosion', Central Electrochemical Research Institute, Karaikudi, India (Nov. 1987), p. 955.
20. M. Paramasivam and S. Venkatakrishna Iyer, Proc. International Conference on 'Corrosion', CONCORN 97, NACE International, India Section and Mumbai, India (Dec. 1997), p. 974.
21. A.R. Despic, D.M. Drazic, M.M. Purenovic and N. Cikovic, *J. Appl. Electrochem.* **6** (1976) 527.