
Synergistic interaction of indium and gallium in the activation of aluminium alloy in aqueous chloride solution

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Keywords

Aluminium, Alloys

Abstract

Aluminium alloys are being employed very widely as galvanic anodes for cathodic protection. Aluminium-zinc-mercury and aluminium-zinc-indium are the popular alloys that are used as anodes. In general, the alloying ingredients activate aluminium and maintain uniform dissolution. In the present investigation, the role of addition of gallium in the ternary alloy of aluminium-zinc-indium has been studied by making use of polarisation studies, capacity measurements and galvanic current measurements.

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Introduction

Cathodic protection is a unique method of corrosion prevention revived at the time of the Second World War, after Davy's successful demonstration of the principles and their application in 1824 (Davy, 1824). It can be imparted either by using an impressed current system, or by use of a sacrificial anode system. Cathodic protection by aluminium sacrificial anodes is widely used for protecting steel structures in marine environments.

Pure aluminium corrodes by a pitting mechanism in brine solutions, which leads to irregular corrosion patterns. Therefore, aluminium anodes are being formulated with appropriate alloying elements to eliminate passivation and hence to promote surface activation. Thus, the addition of alloying elements prevents the formation of a continuous, adherent and protective oxide film on the alloy surface, and enhance the galvanic action of aluminium.

The effect of various alloying elements on aluminium anodes in seawater has been reported by Reding and Newport (1966). In the case of binary alloys they found that manganese and copper cause a positive shift whereas zinc, cadmium, magnesium and barium cause a slight negative shift in the potential. However, gallium, mercury, tin and indium cause a more significant negative shift. Of the ternary alloy aluminium-zinc-mercury, aluminium-zinc-tin and aluminium-zinc-indium show high capacity at potentials of about $-1,050\text{mV}$ Vs SCE.

Sakano *et al.* (1966) reported that aluminium alloy anodes composed of aluminium-zinc-indium ternary alloys exhibited 90 per cent anode efficiency. Several papers (Murai *et al.*, 1974; Peterson *et al.*, 1975; Ponchel and Horst, 1968; Schreiber and Murray, 1988) addressed the development as well as the mechanism of dissolution of indium activated ternary aluminium alloy anodes.

Similarly the ternary alloy (AlZnGa) anode was reported to exhibit > 80 per cent anode efficiency (Aragon *et al.*, 1977). Addition of gallium reduces induced negative shift in the free corrosion potential. Although the solubility of gallium in aluminium is very high, the efficiencies of the alloy are

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comparatively low. It was postulated that partial segregation in these alloys might account for the observation.

In consequence, it was of interest to study the combined influence of indium and gallium, as activating elements in aluminium-zinc systems, which seems to improve the efficiency of the anode. Both gallium and indium do not appear to cause pollution problems and exhibit higher efficiency, whereas mercury-activated anodes pose pollution problems (Haney and Kurr, 1976) in confined water and foundry areas. Hence, the study of the quaternary alloy anode with two activating alloying elements is another milestone in the development of improved sacrificial anodes.

So far, the combined effects of indium and gallium have not been elaborately studied. Therefore, an attempt has been made in the present investigation to study the behaviour of aluminium-zinc-indium-gallium quaternary alloys in comparison with the aluminium-zinc-indium ternary alloys. In particular, the influence of the addition of gallium on the electrochemical behaviour of the ternary alloy (AlZnIn) has been investigated. The electrochemical results thus obtained are presented and discussed.

Experimental

Aluminium alloy specimens were prepared by adding the activator elements and casting in cast iron cylindrical moulds. The aluminium used in this casting was high pure grade. The composition analyses of these alloys are given in Table I. Then the specimens were machined and polished to the required size. For polarization studies rod shape specimens of 1cm² exposure area have been employed. For all other tests, rod shape alloys with 10cm² exposure area have been employed. Before testing, the specimens were processed by

cleaning in acetone and distilled water. All the experiments were carried out at 28 ± 0.5°C.

Potentiostatic polarisation studies were carried out using a potentiostat (EG&G 173) and a universal programmer (EG&G 175). The polarization curves were recorded in aerated 3 per cent NaCl solution using a X-Y recorder (Rikadenki R102 T). The potential was scanned in the anodic direction from the initial polarising potential at a rate of 1mV/sec. Potentials in the text refers to the SCE scale.

The anode capacity test has been carried out as per the DNV standards (Det Norske Veritas Industri Norge, AS, 1993). The specimens were subjected to different current densities, i.e. at 1.5, 0.4, 4.0, 1.5mA/cm² for four days in ten litres aerated 3 per cent NaCl solution under static conditions. After completion of test period, the specimens were cleaned by using a solution containing 4 per cent CrO₃ + 10 per cent H₃PO₄ at 80°C. Then they were rinsed with tap water and ethanol successively, dried and weighed to a precision of 0.1mg. The capacity of the anode was calculated as:

$$C = \frac{I \times 1,000}{W}$$

where:

- W = specimen weight loss in grammes;
- C = capacity of the anode; and
- I = total current charge in ampere-hour.

Autocorrosion tests were carried out with these specimens in 3 per cent aerated NaCl solution for 15 days. Throughout the test period, a day-by-day record of the potential of each individual specimen under test was made. After the test period, the same weighing and cleaning procedures were followed as in the case of capacity test.

The galvanic behaviour of the alloys was also investigated by coupling it to a low carbon steel cathode. An anode/cathode area ratio of 1:10 was used. The cell current and

Table I Composition analysis of Al-Zn-In-Ga alloys

Alloy	Zinc (%)	Indium (%)	Gallium (%)	Iron (%)	Silicon (%)	Manganese (%)	Copper (%)	Aluminium (%)
AlZnIn 0% Ga	3.92	0.14	—	0.11	0.07	0.01	0.004	Remainder
AlZnIn 0.005% Ga	3.87	0.13	0.005	0.12	0.06	0.01	0.003	Remainder
AlZnIn 0.010% Ga	3.85	0.12	0.0091	0.10	0.07	0.01	0.002	Remainder
AlZnIn 0.020% Ga	3.91	0.13	0.0190	0.11	0.05	0.01	0.002	Remainder
AlZnIn 0.050% Ga	3.90	0.14	0.0481	0.11	0.06	0.01	0.002	Remainder
AlZnIn 0.100% Ga	3.84	0.13	0.0972	0.11	0.07	0.01	0.003	Remainder

the potential of the couple were recorded as a function of time for a period of seven days.

Results

The potentiodynamic polarisation curves for gallium-activated aluminium anodes in 0.5M NaCl solution are shown in Figure 1. Initially the electrodes were polarised to a potential of 1,200mV, and kept at the same potential for 60 seconds, then scanned in the anodic direction up to the breakdown potential. The parameters derived from the polarisation curves are given in Table II. From Table II, it can be observed that except for the ternary alloy all quaternary alloys (Ga activated) showed corrosion potential more negative than -900mV. The corrosion current obtained for these alloys was found to be low for the particular quaternary alloy containing 0.02 per cent Ga.

The anodic Tafel slope was found to be more or less the same for all the electrodes, suggesting that the dissolution behaviour is similar. However, the slope values greatly vary in cathodic hydrogen reaction from 120 to 30mV suggesting, the influence of the surface oxide film on the polarisation behaviour. The current density falls to a minimum value of $\sim 200 \mu\text{A}$ in all the quaternary alloys.

Table II Parameters derived from the polarisation curves

Alloy composition	E_{corr} (mV Vs SCE)	I_{corr} (A/cm^2)	b_a (mV/dec.)	b_c (mV/dec.)
AlZnIn 0% Ga	-850	5.5×10^{-6}	5	120
AlZnIn 0.005% Ga	-928	5.0×10^{-6}	24	24
AlZnIn 0.010% Ga	-972	2.8×10^{-6}	28	66
AlZnIn 0.020% Ga	-928	2.2×10^{-6}	16	62
AlZnIn 0.050% Ga	-952	3.7×10^{-6}	14	46
AlZnIn 0.100% Ga	-924	5.6×10^{-6}	10	30

Table III gives the average capacity of the alloys in Ah/kg, the average efficiency, expressed as a percentage (%IE), the auto corrosion weight loss and the average potential of each alloy samples at the end of the capacity test. The results clearly indicate that the AlZnIn alloy containing 0.02 per cent gallium gives a higher capacity value of the order of 2,549Ah/kg, thus achieving 95 per cent of efficiency (Figure 2). However, the mean polarised potential was found to be -970mV, which was nobler than the AlZnIn ternary system. Here it is worth mentioning that the capacity was found to increase with the addition of gallium and after a critical concentration, the capacity was found to decrease with increase in concentration of gallium in the alloy.

The auto corrosion test results are presented together with the capacity test data in Table II. In earlier reports (Ashworth and

Figure 1

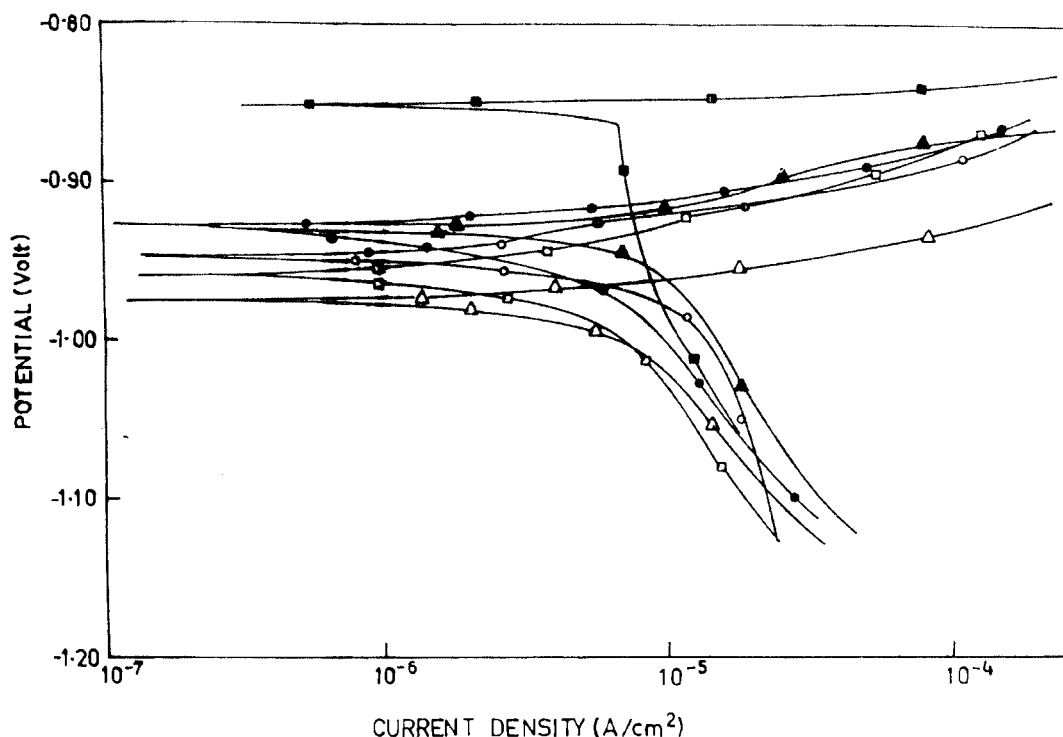
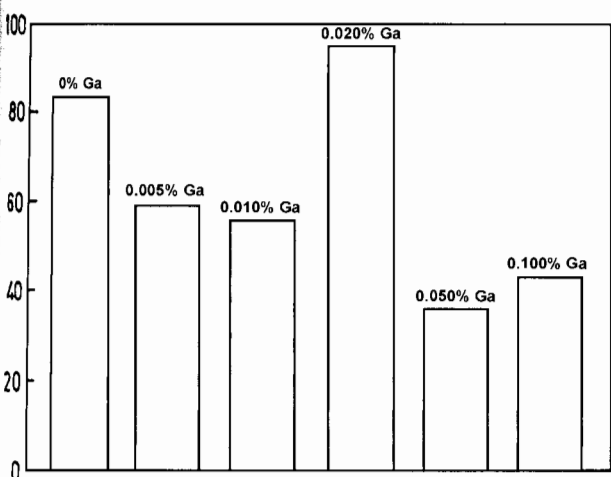


Table III Efficiency and auto corrosion test data

Alloy composition	Mean capacity (Ah/Kg.)	Mean efficiency (%)	Auto-corrosion weight loss (g)	Mean potential capacity test (mV)	Closed circuit potential (mV)
AlZnIn 0% Ga	2,133	82	1.813	-920	-967
AlZnIn 0.005% Ga	1,485	59	2.238	-980	-970
AlZnIn 0.010% Ga	1,226	56	2.711	-970	-970
AlZnIn 0.020% Ga	2,549	95	1.304	-971	-1000
AlZnIn 0.050% Ga	974	36	3.414	-971	-980
AlZnIn 0.100% Ga	1,151	43	2.889	-972	-970

re 2



Googan, 1993), it was suggested that low capacities at elevated temperatures were associated with a stimulation of local action of cathodic reactions. In this work, the autocorrosion test was conducted on the basis that rapid corrosion kinetics would manifest in higher natural corrosion rates in 3 per cent NaCl solution. The test result indicated that weight loss accounts to a minimum of 1.391gm/10cm² mass loss compared with efficiency of 95 per cent for the quaternary alloy system. Thus as the efficiency decreases the auto corrosion weight loss was found to increase.

The open circuit potential, as a function of time obtained for 15 days, is shown in Figure 3. From Figure 3, it can be seen that a favourable negative shift in the potential was observed for the quaternary systems.

The galvanic currents measured with time for these alloys are shown in Figure 4. It can be seen that the cell current falls very rapidly to ~200µA in all the alloy systems from an initial value of ~700µA. During the test period, the maintenance current was found to be ~170µA. On the other hand the cathode (steel) is polarized to ~200-300mV from its

Figure 3

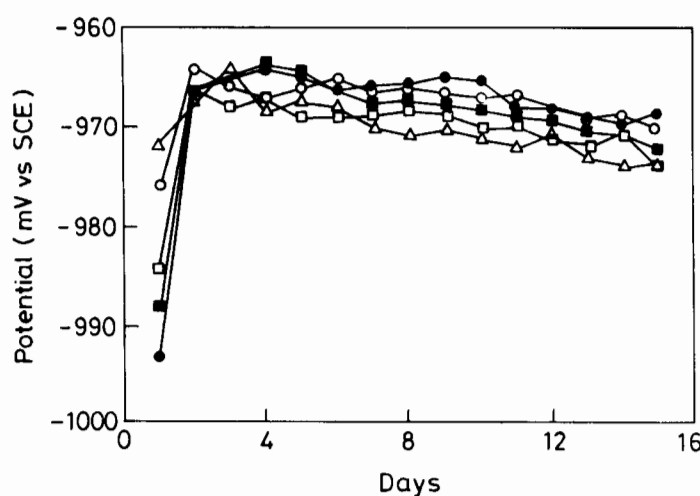
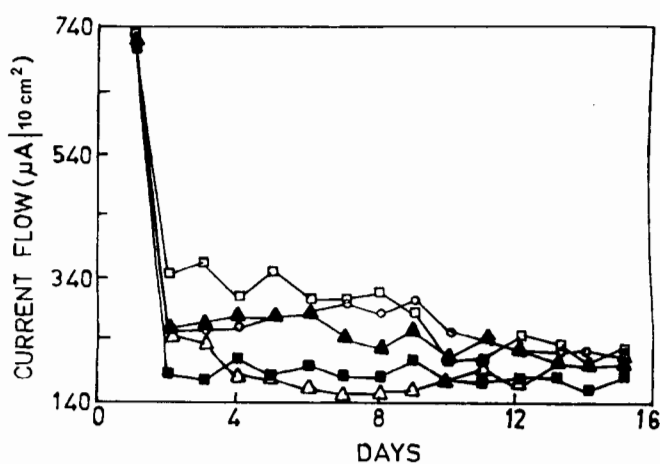


Figure 4



open circuit potential. Hence, it was evidenced that the steel specimens were adequately protected throughout the experiment. This conclusion was confirmed by a uniform non-corroded surface of steel observed during the experiment.

The morphology of dissolution can be demonstrated by the visual observation. In general, the dissolution pattern of anodes in

brine is markedly uneven. Parts of the surface are heavily attacked while extensive areas remain less affected. However, the areas of attack on anodes with a better performance (0.02 per cent Ga) were often relatively smooth with uniform open pits. By contrast the poor performance anodes often show adherent corrosion products; deeply undercut pits and evidence of spalling, i.e. mechanical loss.

Discussion

From the results it is clear that better performance of AlZnIn alloy activated with gallium was observed due to the synergistic activation by the addition of indium and gallium.

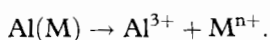
Earlier it was reported that the mechanisms of activation of aluminium by indium and gallium are quite different (Gimenz, 1982). The indium present in the alloy is reduced at local site (Reboul and Delatte, 1980) when the alloy is coupled to the steel structure. The reduced indium ions produce a highly polarizing condition, which promotes chloride migration and adsorption, thereby enhancing the dissolution of aluminium from the alloy matrix by forming chloride complex.

The addition of gallium (Tuck *et al.*, 1976) activates the alloy since gallium is present in the liquid state in the alloy boundaries at room temperature ($T_M = 29.6^\circ\text{C}$). The existence of gallium in the liquid state at grain boundaries would allow mechanical break, resulting in lower efficiencies.

Breslin and Caroll (1992) reported that with the addition of gallium (0.025-0.1 wt.) to Al-Zn the alloy showed no significant change in electrochemical behaviour. However, with higher contents up to 2.6 wt., the corrosion potential was made significantly more negative.

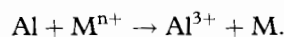
A three-step mechanism (Reboul *et al.*, 1984) has been proposed to explain the activation of minor alloying addition of elements in the aluminium alloy anodes:

- (1) Aluminium and the alloying elements present in the solid solution of aluminium oxidize on galvanic coupling and produce cations in the electrolyte:



- (2) The cations produced during the first step plate back on to the aluminium

surface, since the alloying elements are cathodic to aluminium according to the electrochemical exchange reaction:



- (3) Here, the aluminium oxide film is separated locally.

Thus, the efficiency of the alloy improves if the oxide film can easily be ruptured by the chloride ions present in the electrolyte allowing the alloy to be available for further uniform dissolution.

It can be seen from Tables II and III that at 0.02 per cent gallium addition, I_{corr} is the lowest, while mean capacity and mean efficiency values are the highest. Below or above 0.02 per cent gallium addition, I_{corr} value is drastically reduced. This shows that for a given indium concentration (0.10 per cent), 0.02 per cent gallium is the critical concentration. This can be explained as follows: Indium enters the surface oxide film as trivalent ions and there it creates some additional cation vacancies. These additional vacancies are occupied by the gallium ions, which further improves the surface activation, thus proving the synergistic activity. In this present investigation 0.10 indium added, has created a fixed amount of cation vacancies. These entire vacancies are correspondingly filled by gallium ions only at 0.02% concentration. At lower values, some vacancies remain unfilled, producing negative effect. At concentrations greater than 0.02 per cent, excess gallium ions remain in the grain boundaries producing again negative effect. Synergistic effect is produced only when the cation vacancies of indium are exactly filled up by gallium ions.

Conclusion

Our studies have clearly shown that for a given indium percentage there is a critical concentration of gallium which will have the positive and synergistic effect. In the present case, 0.02 per cent gallium is the critical concentration. Above or below this value the efficiency as well as capacity decreases drastically producing a negative effect of gallium. This critical concentration of 0.02 per cent gallium addition enhances the efficiency of the anode to 95 per cent from 82 per cent obtained for the ternary alloy (AlZnIn)-system.

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