Effect of Heat Treatments on Al-Zn-Sn Alloys as Sacrificial Anode

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LABORATORY tests were carried out to study the electrochemical behaviour of Al-Zn-Sn alloys (5 wt % Zn and 0.067 to 0.5 wt % Sn) being coupled with mild steel in synthetic sea water. The alloys were given various heat treatments in these studies and their suitability as sacrficial anodes were compared with those of non-heat treated alloys. Corrosion rate of mild steel changed considerably and differently when coupled to these alloys. Anode outputs of these alloys for protection of mild steel were compared for different heat treatment conditions.

DUE to its high electronegetivity and electrochemical equivalence (3.6 and 1.5 times as much as that of the zinc and Magnesium respectively), Aluminium promises to be an attractive alternative as sacrificial anode for cathodic protection systems[1-3]. However, there are certain draw-backs in its application. Firstly, the self adjusted potentials attained by the oxide film covered aluminium and most of its alloys are quite noble. Nobility obtained sometimes is so much that in many cases these potentials are more positive than even those attained by steel which is to be protected. Secondly, in the presence of chloride, anodic polarization of aluminium (when coupled to steel) may lead to pitting of aluminium. This highly localised dissolution of the anode contrary to the requirement of uniform dissolution leads to unpredictable and inefficient performance. Finally, the potential in sea-water of aluminium alloy, even when coupled to steel is likely to be sufficiently negative to induce hydrogen evolution reaction (HER)[4]. Hence, the anode output is likely to be severely reduced unless the hydrogen over voltage of the sacrificial anode is made very high, or the oxide film formed on aluminium is kept un-disrupted at the anodic current densities which is determined by the current needed to prevent corrosion of the steel at the area ratio used.

It is because of these consideratios that pure aluminium is unsuitable as sacrificial anodes for cathodic protection of steel in sea-water. However, by means of suitable alloying additions and heat treatments the above disadvantages can be minimised. The addition of Zn, Mg and Cd as alloying elements show a potential 0.1 to 0.3 volts and the addition of minute quantities of In, Hg, Sn, and Ga cause a potential 0.3 to 0.9 volts more electronegative than that of unalloyed aluminium[5]. Al-Zn alloys become progressively more electronegative up to zinc content of 5% but increases only slightly with further additions of zinc. In sea-water, anodes of Al-9% Zn alloys have an average anode output of 725 amp. hr./lb. Aluminium alloyed with tin show[9] expectionally high electronegative potentials to start with and gets polarised soon on coupling with mild steel and gives rise to low anode output within a short time.

Many authors[6-8,10-11] have suggested ternary alloys as sacrificial anodes which provide both high anode output and high electronegative potentials. The alloys which became popular are Al-Zn-Hg[10], Al-Zn-Sn[8] and Al-Zn-In[6]. The latter two require a critical and closely controlled heat treatment, otherwise, unpredictable low current efficiency will be observed. On the other hand, Al-Zn-Hg anodes require no heat treatment and show very high anode output.

Information on the effect of various types of heat treatments of Al-Zn-Sn alloys on their suitability as sacrificial anodes, is not available in the literature. An attempt has been made in this article to present laboratory data on the performance of heat treated Al-5 Zn-Sn alloys as sacrificial anodes in sea water.

EXPERIMENTAL

Ternary alloys of Al-Zn-Sn containing 5 wt. % Zn and 0.067 to 0.5 wt % Sn were cast into cylindrical rods of 1.0 cm. diameter. These were

homogenised and given various heat treatments as shown in Table 1. The alloys were then subjected to polarisation and galvanic coupling studies.

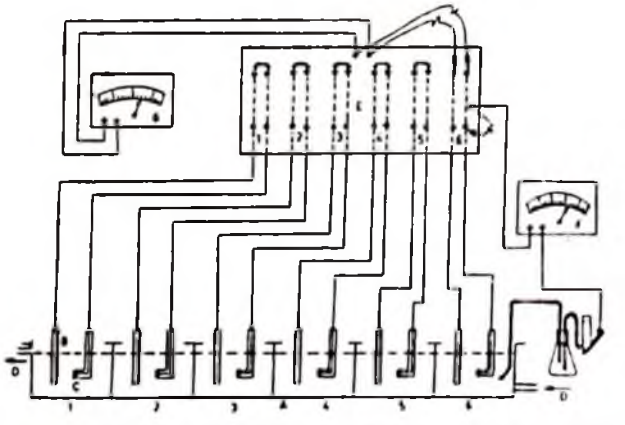
TABLE 1

Heat treatments given to Al-5 Zn-Sn alloys

Convention	Heat Treatment
X	As cast (homogenised)
A	Heated for 3 hrs. at 300°C and quenched
B	Heated for 3 hrs. at 300°C and Fec. cooled
C	Heated for 3 hrs. at 150 C and quenched
D	Heated for 3 hrs. at 150 C and Fec. cooled

Polarisation studies[11] were carried out potentio-statically using synthetic sea-water as electrolyte. An area of 0.78 cm^2 of the polished and degreased aluminium alloys was exposed to the electrolyte. The alloys were potentiostatically polarised anodically and at each selected potential the steady state current was noted.

The galvanic studies were carried out by coupling the mild steel (ASTM-A 106), to be protected to the Al-alloys. An area of 200 : 1 of mild steel to Al alloys is maintained in all the experiments. Fig (1) gives the diagram of multi-



A-GALVANIC CELLS (NOS 1 - 6) B-MILD STEEL C-Al-5Zn-Sn ALLOYS D-Sea WATER E-MULTI CHANNEL BOARD F-V.T.V.M G-LOW IMPEDENCE D.C MICRO AMMETER

FIG 1. CIRCUIT DIAGRAM FOR GALVANIC COUPLING STUDIES USING MULTI CHANNEL SYSTEM

channel system used for galvanic coupling studies (The diagram shows the arrangement for measuring the galvanic current and the coupled potential of the 6th cell). The steel and Al alloys samples were coupled through a low impedence micro-ammeter and exposed to running synthetic sea-water for about 180 hrs. A flow rate of 10 lit/hr. of synthetic sea-water with aeration was maintained thoughout the experiment. At regular intervals, the coupled potentials of steel and Al alloys were measured. Weight loss of steel when coupled to Al-alloy were also found out periodically. The ammeter readings were noted regularly and plotted versus time.

RESULTS AND DISCUSSION

Polarisation studies : The anodic polarisation curves of all the heat treated and as cast Al-alloys show that the passivation tendency of the alloys decreases with increase in tin content. It can be seen from Fig. (2) that the Al-5 Zn-0.065 Sn alloy

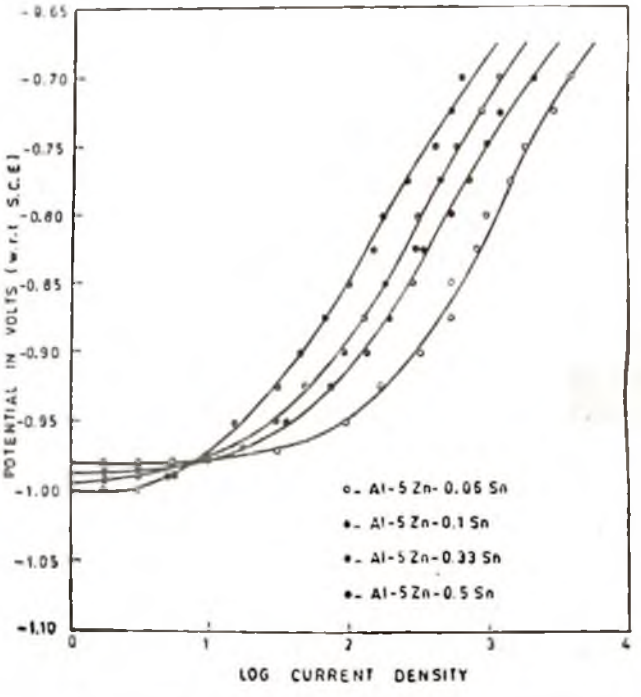


FIG 2. ANODIC POLARISATION CURVES OF NON-HEAT TREATED Al-5 Zn-Sn ALLOYS

has a lesser tendency to get passivated compared to other alloys. However, with the same tin content, the annealed alloys are more passive compared to the quenched alloys and also, the alloys which were quenched from higher temperature show still less passivity. Fig. (3) gives the anodic polarisation curves of heat treated Al-5 Zn-0.1 Sn alloys. It can be reduced by quenching the alloys from higher temperature and also by selecting very low tin content.

Galvanic coupling studies : It is observed that the potentials of mild steel coupled to quenched Al-alloys were in general more electro-negative than —0.84 volts with respect to S C.E. which is the protection potential of mild steel. In

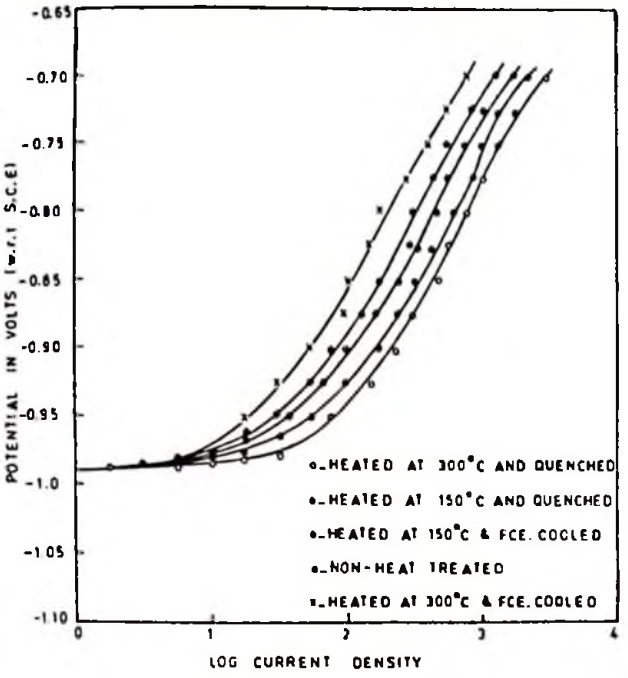


FIG. 3. ANODIC POLARISATION CURVES OF HEAT TREATED Al-5 Zn-0.1 Sn ALLOYS

a few instances only, the potential was found to slightly cross the protection potential towards the positive side. The coupled potentials of mild steel, coupled to annealed and as cast Al-alloys, were found regularly slightly above towards positive side of the protection potential except in the first few hours where it was more electronegative than —0.84 volts. This indicates that the quenched Al-5 Zn-Sn alloys give better protection to mild steel than those of annealed or as cast alloys.

Table-2 gives the corrosion rate (mpy) of mild steel when coupled to various heat treated alloys calculated by wt. loss method. It is observed that the quenched alloys are giving better protection than those of annealed and as cast alloys when coupled to mild steel. Also, the alloys with higher tin content give less protection than those of lower tin content up to 0. 1%, below which corrosion rate of mild steel increases again due to insufficient tin content. Amongst quenched alloys, the alloys quenched from higher temperature show less corrosion rate of mild steel. Fig. (4) gives the corrosion rates of mild steel coupled to various heat treated Al-5Zn-0.1 Sn alloys.

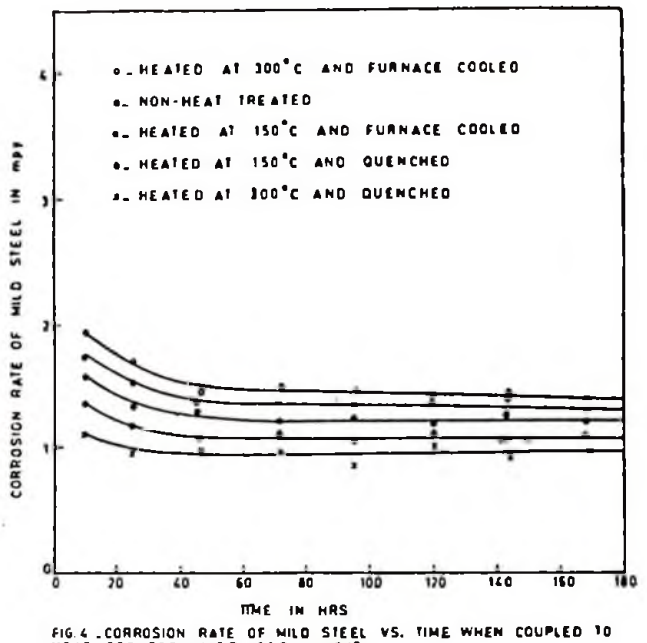


FIG. 4. CORROSION RATE OF MILD STEEL VS. TIME WHEN COUPLED TO HEAT TREATED Al-5 Zn-0.1 Sn ALLOYS

The galvanic current generated during the coupling of Al-alloys to mild steel were plotted against time and the anode output (amp. hr/lb) of the alloys were calculated. Though there is a slight variation in the galvanic current with the variation of tin content of the alloys (Fig. 5) under various heat treatments (Fig. 6), the anode output of the alloys vary considerably. This is mainly due to the remarkable changes in wt. loss of Al-5Zn-Sn alloys subjected to various heat treatments. The annealed alloys which give higher wt. loss as compared to quenched alloys thus show lower

TABLE 2

Corrosion rates of Mild steel coupled to various heat treated Al-5 Zn-Sn alloys

Alloys	Rest (without coupling) pot. of Al alloy in Volts w.r.t. S.C.E.	Corrosion rate (mpy) of mild steel coupled to				
		As cast alloys	Heat treated Al-5 Zn-Sn Alloys			
		X	A	B	C	D
Al-5 Zn-0.067 Sn	—0.98	1.414	1.045	1.641	1.109	1.282
Al-5 Sn-0.1 Sn	—0.99	1.327	0.980	1.506	1.068	1.195
Al-5 Zn-0.33 Sn	—9.994	1.605	1.178	1.783	1.192	1.217
Al-5 Zn-0.5 Sn	—1.00	1.619	1.250	1.845	1.378	1.540

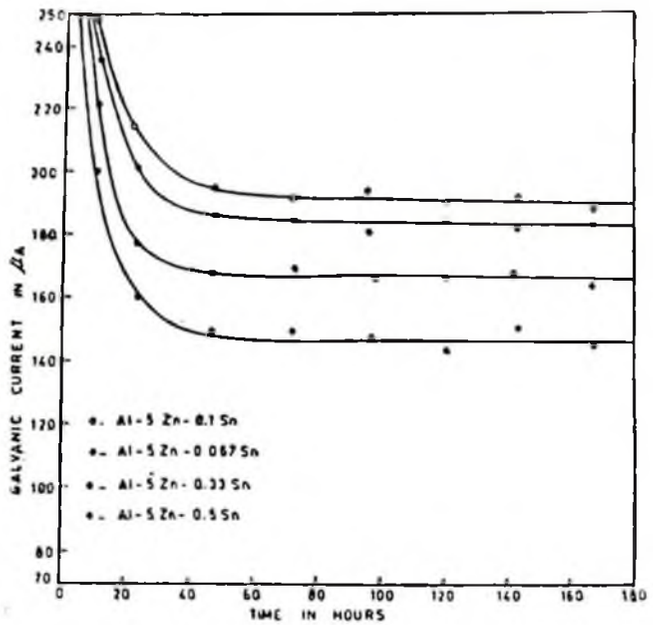


FIG. 5. CURRENT VS. TIME CURVES FOR NON-HEAT TREATED Al-5 Zn-Sn ALLOYS COUPLED TO MILD STEEL

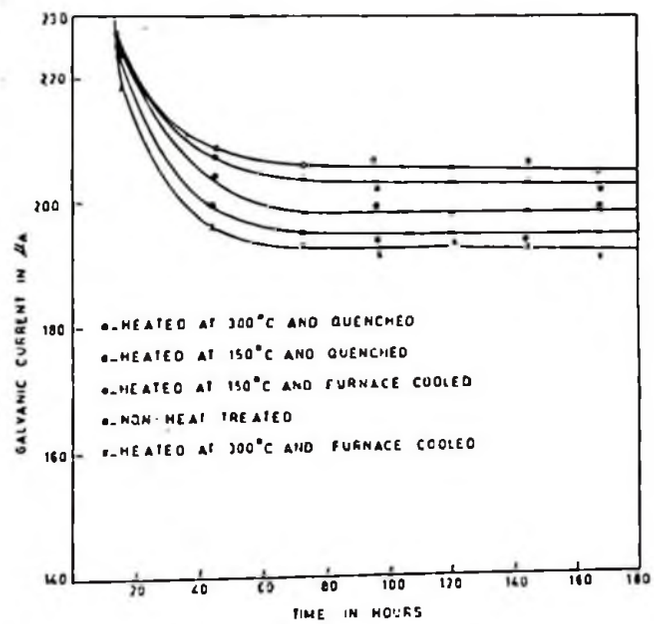


FIG. 6. CURRENT VS. TIME CURVES FOR HEAT TREATED Al-5 Zn-0.1 Sn ALLOYS COUPLED TO MILD STEEL

anode outputs. (Fig 7) Table-3 gives the anode output and current efficiency of various alloys.

The higher weight loss of the annealed and as cast Al-5 Zn Sn alloys compared to corresponding quenched alloys can be explained by an examination of scanning electromicrographs of exposed alloys. Generally, the grain boundary attack is

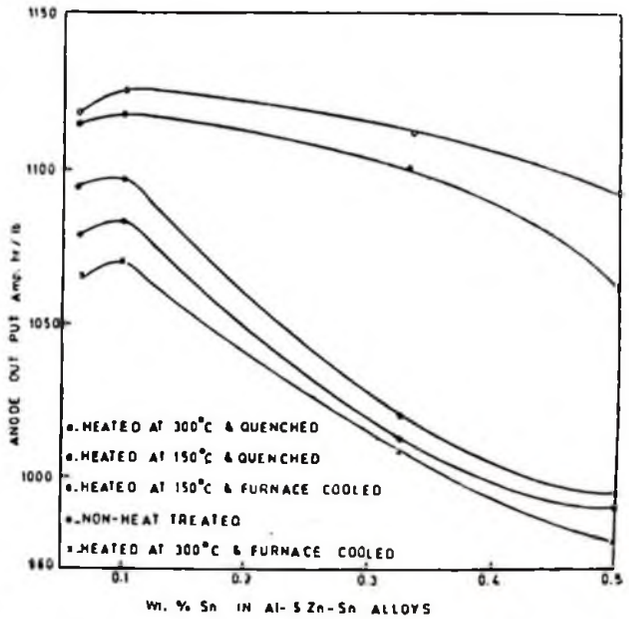


FIG. 7. ANODE OUT PUT (Amp. hr/lb) VS. Wt. % Sn IN Al-5 Zn-Sn ALLOYS

observed in all annealed and as-cast Al-alloys. This type of attack is likely to cause the isolation of grains which are assumed to fall in electrolyte in due course giving rise to an extra loss in aluminium. The extent of grain boundary attack increases with increase in tin content of the alloys. In Fig. (8) the plates (a) and (b) show grain boundry attack of annealed Al-5Zn-0.1 Sn and Al-5Zn-0.5 Sn alloys. The latter shows a wider

TABLE 3

Anode out put and current efficiency of various heat treated Al 5 Zn Sn alloys coupled to Mild Steel

Alloys	Anode out (Amp. hr/lb) and current efficiency (C.E. %)									
	As cast alloys		Heat treated Al-5 Zn-Sn Alloys							
	X		A		B		C		D	
	Amp. hr/lb	C.E.%	Amp. hr/lb	C.E.%	Amp. hr/lb	C.E.%	Amp. hr/lb	C.E.%	Amp. hr/lb	C.E.%
Al-5 Zn-0.067 Sn	1079	79.93	1117	82.74	1065	78.89	1115	82.59	1095	81.11
Al-5 Zn-0.1 Sn	1083	80.22	1125	83.33	1070	79.26	1111	82.81	1097	81.26
Al-5 Zn-0.33 Sn	1012	74.96	1111	82.30	1009	74.74	1100	81.48	1020	75.56
Al-5 Zn-0.5 Sn	991	73.41	1093	80.96	980	72.59	1062	78.67	995	73.70

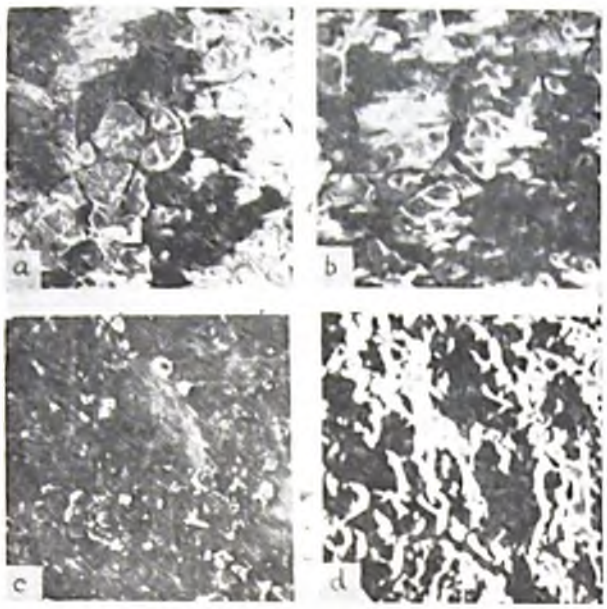


FIG. 8 Scanning electron microscopic images (800×) of heat treated Al-5 Zn-Sn alloys after exposing in sea-water for cathodic protection of mild steel

a) Al-5 Zn- 0.1 Sn (annealed) b) Al-5 Zn-0.5 Sn (annealed)
c) Al-5 Zn- 0.1 Sn (quenched) c) Al-5 Zn-0.5 Sn (quenched)

attack than that of former. Plate (c) shows uniform corrosion of quenched Al-5Zn-0.1 Sn alloys. This uniformity in corrosion decreases with increase of tin content. Plate (d) shows relatively non-uniform corrosion of quenched Al-5Zn-0.5 Sn alloys.

Immersed in sea-water, conditions are favourable for formation of a thin oxide film on active metals like aluminium and its alloys. Free corrosion occurs through this film and the rate is regulated by the physiochemical characteristics of this film.Poor ionic and electronic conductivitics of the oxide film formed on pure aluminium and many of its conventional alloys is probably the reason for their attaining noble immersion potentials.

It is seen from the results that the beneficial effect of adding tin to Al-5 Zn alloys depends on the amount of tin added and the type of heat treatment the alloy undergoes. Besides, it is seen that more than the galvanic current, it is the anode output which is greatly influenced by the variations in the tin content and the type of heat treatment. The general trend being that the benefits are accrued only when tin remains in the alloy in a very low concentration without being precipitated out due to its limited solubility in aluminium. It appears that the presence of dissolved tin modifies the oxide film formed favourably, allows the alloys to attain more electronegative potential and makes the film more conducting both electronically and ionically which in turn reduces the anodic polarisation of the alloys.

It is quite possible that the presence of dissolved tin, due to its surface active property, helps in its being selectively adsorbed at alloy oxide interface and migrating by process of surface diffusion to the places of disruption in the film. Thereby the possibility is increased for a high hydrogen overvoltage at such places of disruption or rupture in the film. In other words, the small addition of tin is likely to help in preventing free evolution of hydrogen wherever the film is broken and the fresh metal is exposed. The situation is quite different whenever the conditions of preparing the alloy has favoured precipitation of tin due to its limited solubility. Here, the disrupted film not likely to be uniform. The alloy in this case contains the segregated excess tin in its grain boundaries giving rise to weakening of grain boundaries. Extensive grain boundary attack as seen in the experiments seems to offer an evidence for this.

A higher concentration of tin can be assumed to be adsorbed in the alloy oxide interface whenever the alloy is maintained at a higher temperature. Quenching retains such higher concentration of tin at the alloy oxide interface. This higher concentration gives an effective coverage of the films at its disrupted places.

CONCLUSION

In summary, it is observed that for tin addition to be effective, the alloys prepared should be quenched after homogenising at the highest possible temperature. Alloys so prepared show the least passivation tendency, high galvanic current and very good current efficiency with regard anode out put.

Of all the alloys studied, the Al-5 Zn-0.1 Sn, alloy which is quenched from 300°C gives better protection to mild steel in sea-water. It attains an anode output of about 1125 Amp. hr/lb, when coupled to mild steel (1 : 200 area ratio), giving rise to a current efficiency of 83.33% in sea water.

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