

## **CORROSION BEHAVIOUR OF Al AND Al ALLOYS CONTAINING Zn, Sn AND Cu IN SEAWATER**

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### **ABSTRACT**

The corrosion behaviour of aluminium (Al) alloys in seawater medium was investigated using potentiodynamic technique, complemented by Scanning Electron Microscopy (SEM) and EDAX. SEM was carried out to characterize the corroded surface and to observe the extent of corrosion attack on the Al alloys tested in seawater. EDAX analysis was used to identify elements present on the specimen surface. The results indicate that zinc (Zn), stannum (Sn) and copper (Cu) as alloying elements enhance corrosion behaviour of the aluminium in seawater by shifting the potential to a more negative value. In the presence of those elements, the Al alloys becomes more active, having potential of more than  $-1.0 V_{SCE}$  and showed active corrosion behaviour.

### **INTRODUCTION**

It is known that the addition of certain elements to aluminium, such as mercury (Hg), gallium (Ga), stannum (Sn), indium (In), magnesium (Mg), zinc (Zn), cadmium (Cd) and barium (Ba) results in alloys with more anodic potentials than unalloyed aluminium (Al) [1]. On the exposure to the atmosphere, the passive film formed on Al and retards further corrosion of the metal [2,3]. Although the anodic oxide film of pure aluminum is a good electrical insulator, it is not good in the presence of chloride ions. The most frequent form of Al and Al alloys in seawater is pitting corrosion [4] due to localized breakdown of oxide film by chloride attack. This reaction serves as a first step in pitting and crevice corrosion [5]. Commercially produced Al anodes are alloyed with Zn and activators such as Hg, In or Sn [6]. This paper reports the experimental results of corrosion behaviour study of Al alloys containing Zn, Sn and Cu in seawater. It will lead to a better understanding of the dissolution process occurring at the activation potential of Al alloys containing Zn, Sn and Cu and their performance in seawater.

### **EXPERIMENTAL AND METHOD**

Pure Al (99.99%), Zn (99.9%), Sn (99.8%) and Cu (99.8%)(Aldrich Chemical) in granule form were used for samples preparation. The selected samples compositions were melt up to 800°C in a cylindrical graphite crucible in ambient environment. The

molten was homogenized by stirring with a high density graphite rod and then poured into the preheated split steel mould 1.5 cm in diameter and 16 cm in height. Prior to test, samples were cut to 1.5 cm in diameter and 0.3 cm in height and mechanically ground up to 2400 grit SiC paper and washed thoroughly with distilled water followed by acetone and drying.

The electrochemical analysis was carried out by Tafel and potentiodynamic method provided by Gamry Instrument, using CMS 100 software. All potential values of 72 hours immersion in seawater are measured with respect to a Saturated Calomel Electrode (SCE) reference electrode. Following the potentiodynamic test, samples were further characterized by Scanning Electron Microscope (SEM) (FEI 400) instrument equipped with an Energy-dispersive using X-ray analyzer (EDAX)(Genesis 7000) to study morphology and elemental content.

## RESULTS AND DISCUSSION

The surface chemical composition of as cast samples analysed by EDAX and measured open circuit potential (OCP) of the alloys are as shown in Table 1 (a) and (b).

Table 1: Composition (a) and OCP for samples (b)

Sample	Zn	Sn	Cu	Al
A	-	-	-	Pure
B	5.35	-	-	Bal.
C	5.40	0.97	-	Bal.
D	5.77	0.85	0.24	Bal.

(a)

Sample	Voltage ( $V_{SCE}$ )
A	-0.7812
B	-1.0034
C	-1.3380
D	-1.0988

(b)

The potential values for samples measured at room temperature are shown in Table 1(b). It shows that the potential value for each Al alloy is greater than  $-1.0 V_{SCE}$  while pure Al (sample A) has a value of  $-0.7 V_{SCE}$ . With the lower potential, pure Al has more tendency to form passive oxide layer on the surface. Where as a binary alloy, Al-Zn (sample B), shows 0.22V higher potential value than pure Al. The presence of zinc and indium on Al leads to a displacement of the activation potential in approximately 0.3 V towards more negative values in seawater [7]. Al-Zn alloys with the presence of Sn and

Cu activators (sample C and D), show OCP increased significantly in the negative (active) direction for 72 hours immersion in seawater. Therefore, the addition of the alloying elements has shifted the potential towards more negative value.

Fig.1 shows the Tafel plot for samples A, B, C and D and Table 2 shows corrosion rate, current density and polarization resistance of the samples extrapolated from Tafel plot technique. The lowest current density and corrosion rate shows by sample A (pure Al) is due to compact and adherent passive layer formed of  $\gamma\text{-Al}_2\text{O}_3$  on its surface as shown clearly by SEM micrograph in Fig.3(a). This layer prevents further dissolution of pure Al as displayed by higher resistance ( $R_p$ ) value. Current density and corrosion rate of Al increased with addition of alloying elements. Sample C shows the highest value of current density and corrosion rate.

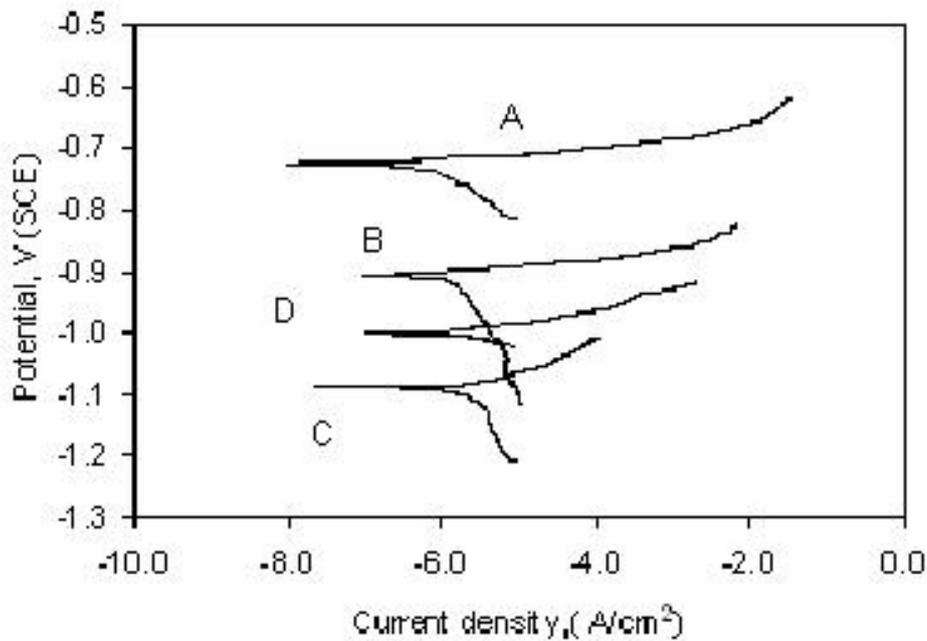


Fig. 1. Tafel plot for samples A, B, C and D in seawater medium

Table 2: Result from Tafel plot

Sample	Corrosion rate (mm/yr)	$I_{corr}(\text{A}/\text{cm}^2)$	$R_p(\text{Ohm}\text{Cm}^2)$
A	0.004	$4.052 \times 10^{-7}$	$4.751 \times 10^4$
B	0.018	$1.630 \times 10^{-6}$	$5.172 \times 10^3$
C	0.082	$6.506 \times 10^{-6}$	$3.084 \times 10^3$
D	0.058	$5.169 \times 10^{-6}$	$2.493 \times 10^3$

The polarization curves of the alloys (Fig. 2) show corrosion potential ( $E_{corr}$ ) of more than  $-1.0 \text{ V}_{SCE}$  was found for the Al containing alloying elements.

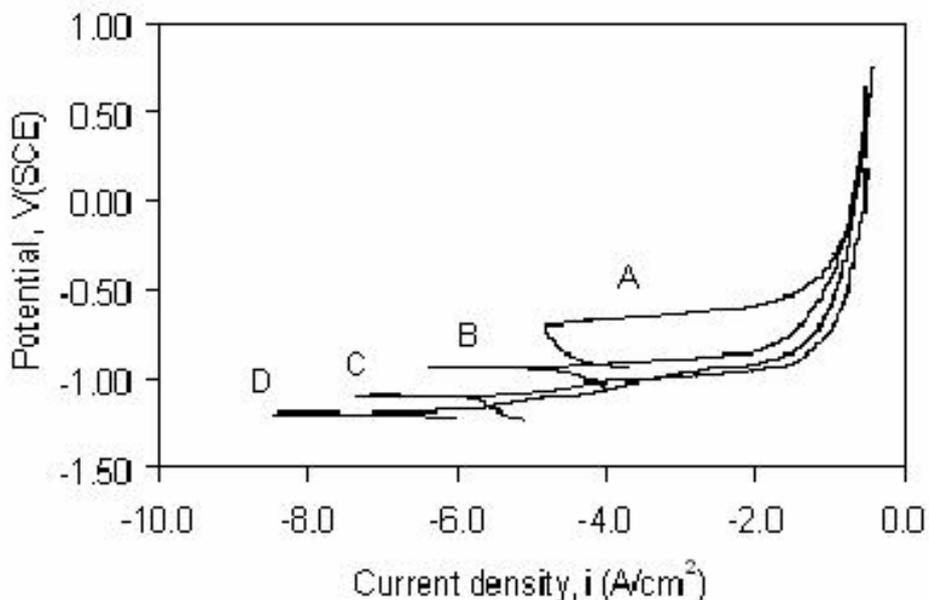


Figure 2: Anodic potentiodynamic of specimens in aerated seawater of  $\text{pH} = 7.8 \pm 0.1$  at room temperature.

Anodic curves for alloys are similar to that of pure Al, but have shifting the corrosion potential towards more negative values. Due to their high anodic dissolution rate, those potentials practically in stable state in the current density ranging from  $10^{-8}$  to  $10^{-1}$   $\text{A/cm}^2$ . The more negative potential found in the case of Al alloys containing Sn and Cu may be attributed to the absence of cathodic impurities. These elements enhance the hydrogen evolution, which in turn polarized the system and shifting the surface potential to more negative values.

The relationship between morphological structure and electrochemical results was examined and particular attention paid to the influence of alloying elements on activation of Al alloys. Preferential attack was not observed for pure Al but at higher magnification (i.e. 500X) appearance of several cavities can be observed (Fig. 3).

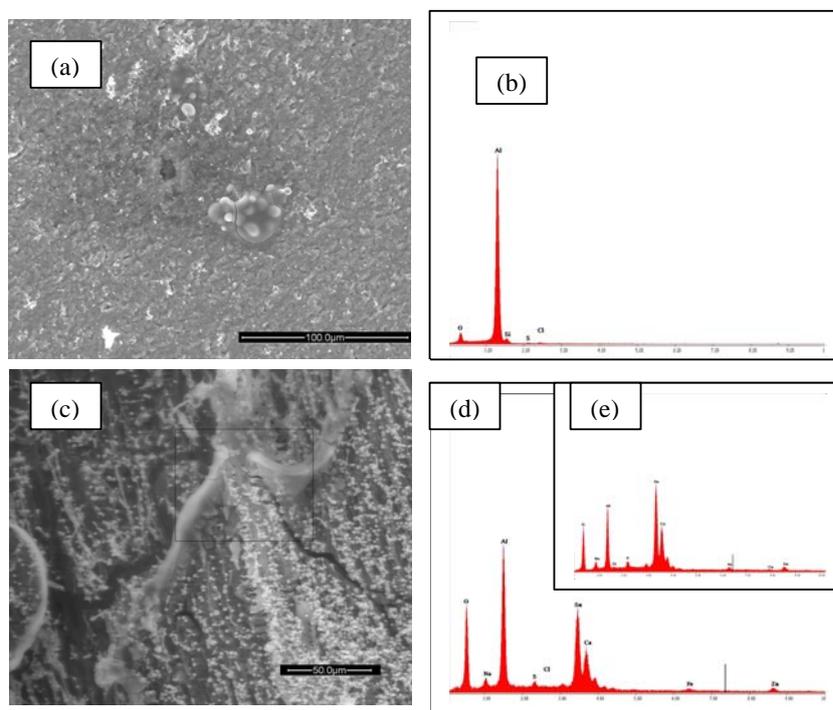


Fig.3 SEM micrograph (500x) and EDAX analysis of sample A (a & b) and sample C (c & d, e).

According to Breslin et al. [8], the presence of Zn as alloying elements promotes the nucleation of  $ZnAl_2O_4$  spinel, which gives rise to increase defects and cracking of protective layer. A minimum content of 5%Zn in the alloy is necessary to achieve a proper amount of intermetallic compound in order to provide the breakdown of passive layer and related anodic activation [9]. Fig. 3c shows the growth of porous corrosion product that might have been removed from the surface and leaving a large area of fresh exposed metal having cracked surface. The irregular morphology (Fig.3c. marked area) is believed due to non-uniform Sn precipitation. This assumption is supported by EDAX analysis that spectrum revealed higher concentration of Sn (Fig.3e). Sn definitely believed to serve as cathodic sites in the corrosion process of Al alloy. Morphology of sample D (Fig.4) which containing Cu shows more severity of corrosion. According to [4] for Al alloyed with Cu, corrosion of Al is aggravated by copper corrosion product and it decreases resistance to corrosion. From the SEM surface examination, the presence of alloying elements in Al matrix were found to affect the morphology of their surface with formation of region covered with shrunken, porous and cracked surface deposits.

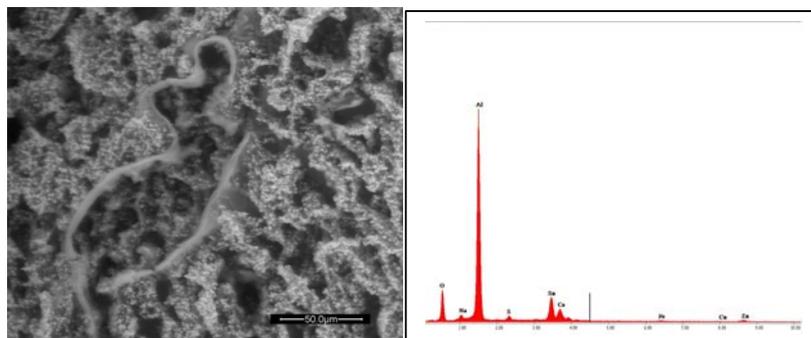


Figure 4: SEM micrograph and EDAX analysis sample D

## CONCLUSION

According to this study, the results indicate that alloying elements in Al matrix play important role on the improving corrosion behaviour of Al alloys in seawater. The attack initiation of the Al alloys is due to higher potential achieved with the addition of Zn, Sn and Cu in Al. The corrosion resistance of Al decreased significantly with the addition of alloying elements and this, in turn assures the active dissolution of the Al matrix.

## REFERENCES

- [1]. J.T. Reding and J.J.Newport, (1966); The Influence Of Alloying Elements On Aluminum Anodes In Seawater, Dow Chemical Co.
- [2]. H.P. Godard, (1981); An Insight Into the corrosion Behaviour of Aluminum. Plenary Lecture. National Association of Corrosion Engineers. Material Performance. 9-15.
- [3]. C.B.Breslin, W.M.Carroll. (1993); The Activation of Aluminum by Activator elements. *Science*. Vol. **35**, 197-203.
- [4]. Christian Vargel. (2004); Corrosion of Aluminum. Elsevier Ltd, UK. 26
- [5]. Francis L.Laque. (1975); Marine Corrosion Causes And Prevention. John wiley & Sons, Inc. 191
- [6]. S.L. Wolfson. (1994); Operating Performance Of Aluminum Anodes – Results From Lab And Field Tests. *Materials Performance*, 22.
- [7]. A.G. Munoz, S.B.Saidman, J.B. Bessone. (2001); Influence Of In On The Corrosion Of Zn-In Alloys. *Corrosion Science* **43**, 1245-1265.
- [8]. C.B.Breslin, L.P.Friery, W.M.Carroll. (1994); *Corrosion Science* **36**, 85.
- [9]. A.Barbucci, G. Cerisola, G. Bruzzone and A.Saccone. (1997); *Electro. Acta*. Vol.42.