

## Improving Performance of Al-Mg Sacrificial Anode Through Forging

V.A.Mistry<sup>1</sup>, Dr I B Dave<sup>2</sup>, Dr M D Dani<sup>2</sup>, Urvesh Vala<sup>1</sup>

<sup>1</sup>Phd Scholar, Gujrat Technological University, Ahemdabad, Gujarat, India

<sup>2</sup>Metallurgy Dept., Government Engineering College, Gandhinagar, Gujarat

### Abstract:

Aluminium is most advantageous sacrificial material for the cathodic protection of steel in sea water but pure Aluminium cannot be used directly due to its quirky properties to get passivates. The reactivity of aluminium can be change from passive to active state by adding alloying elements and mechanical treatments. In these research Al+4.5% Mg alloy is developed and than 20% and 30% height reduction given by forging process. here, performance and corrosion rate is improved due to formation of in homogeneity in microstructure by magnesium addition and forging process. Addition of Mg give rise to formation of secondary phase having different electrochemical properties so micro galvanic cell is formed hence, corrosion is initiated by difference in electrode potential. Forging Process will increase corrosion sites in then microstructure thus improve the corrosion rate of Al-Mg sacrificial anode, corrosion potential shifted in negative direction by 250 volt and corrosion rate is almost double.

**key words:** *Aluminium anode, Cathodic protection, Passivation, Al-Mg Alloy.*

### 1.Introduction:

Corrosion of metal is one of the most serious destructive agent that has ever challenged in the industrial world. Several techniques have exhibited the ability for protecting corrosion like inhibitors, design modification, coating and anodic-cathodic protection from which Cathodic protection (C.P.) being deployed by major industries. Sacrificial anode cathodic protection is greatly employed to protect oil pipelines, marine and some domestic structures. This is because it has the advantages of being simple to install, independent of a source of external electric power, suitable for localized protection and less liable to cause interaction on neighboring structures. This is achieved by changing the electrode potential of the metallic structure so that it lies in the immunity region, within this region, the metal is in the stable form of the element and corrosion reactions are therefore impossible[1], [2].

Generally, Aluminum and its alloys, Zinc and its alloys and Magnesium and its alloys are most widely used as sacrificial anode materials. Among which Aluminium alloys are most preferable because of having high current efficiency, high capacity, light weight and low price compare to rest of two materials [3]–[6].

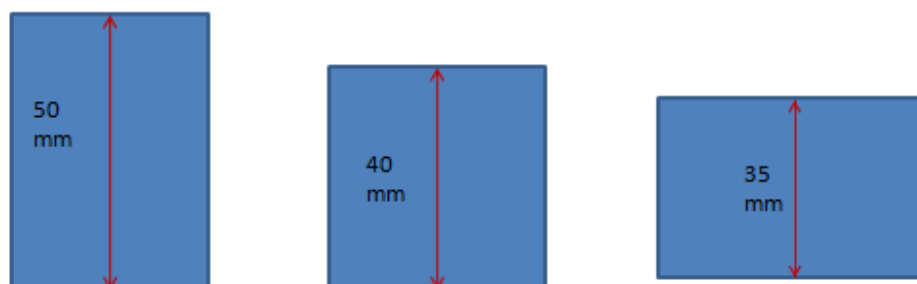
Pure aluminum is not used as a sacrificial anode because it has tendency to passivate and form an impervious  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> film on the surface and this surface will act as barrier for self corrosion of anode. In order to promote surface activation (break down of passive film), aluminum is usually alloyed with small quantities of one or more elements. The alloying elements used to accomplish this are referred to as depassivators and modifiers. Modifiers that have been used include zinc (Zn), magnesium (Mg), barium (Ba), and cadmium (Cd). The depassivators commonly used are indium (In), mercury (Hg), and tin (Sn) and also rarely used are gallium (Ga), titanium (Ti) and thallium (Tl)[1], [7].

The distribution of alloying element and formation of precipitates in the aluminium matrix improves self corrosion of anode by forming micro galvanic cell within the matrix. From physical metallurgy and phase diagram of Al-Alloys it shows that at room temp all the alloying element have negligible solubility and at eutectic temp or peritectic temp maximum solubility. The addition of alloying element (solute) more than their solubility limit will give rise to formation of another solid solution or intermetallic compound that has a different composition, even distribution of such phases will breakdown the network of passive film. It is important to obtain a microstructure of  $\alpha$ -Al with a good distribution of fine intermetallic compounds in the as cast or heat treated condition. A finer and more uniform structure is expected which can enhance surface activation anode and also self corrosion [7]–[10].

Another method for activating Aluminium is mechanical working or cold working of aluminium. Cold working changes the microstructure from coarse grain to fine grain and there is precise relationship between grain size and corrosion rate. Change in grain size decrease or increase the corrosion rate and more grain boundary area is available for chemical attack. Formation of intermetallic during solidification is concentrated at the grain boundary which is leading to dealloying of the alloy. In brief cold working increase galvanic site for the corrosion.[11]–[13] In these research paper focus on optimum corrosion rate of the aluminium-magnesium sacrificial anode in 3.5% NaCl for the protection of steel in chemical and fertilizer industries and marine structure.

## 2.Experimental Details

Aluminium containing 4.5 weight percent Magnesium is develop using 99.8% Pure aluminium wire and 99.9% Pure magnesium ribbon through liquid metallurgy route using electric resistance furnace. 20% and 30% Height reduction is carried out by Forging of aluminium and Al+4.5%Mg by vertical mechanical press at 250 kg load. Graphical representation of height reduction is shown in Figure 1.



**Figure 1 Graphical Representation of Height Reduction**

Chemical analysis of aluminium and Al+4.5%Mg was carried out with Bruker Q4 TASMAN advanced CCD based optical emission spectroscopy according to ASTM E1251:2017. The microstructure is developed by conventional metallography practice according to ASTM E407-07(2015) and was observed using Olympus GX-41 optical microscope and JEOL 5610 LV Scanning Electron Microscope with Energy Dispersive Spectroscopy (EDS) at different magnifications on 0.5%HF etched Surface. Grain Size Measurement is accomplished by Optical microscope according to ASTM-112-13 practice.

The standard weight-loss method is carried out to find out corrosion rate according to ASTM standard G1-03 (2017). Test samples having  $1.5 \pm 0.5$  cm height and 2.54 cm diameter were given the exposure of 3.5 weight per cent NaCl solution. Corrosion solution was produced by dissolving  $3.5 \pm 0.5$  grams of NaCl powder into 100 ml demineralised water. Samples are finely ground with the help of 1000 grit emery paper. The four-digit accurate weight pan balance has been used to measure the initial weight of samples. Take three samples for each consider the average of that value. All the samples were immersed in 3.5% NaCl solution for 8 weeks and corrosion rate is measured. After every week a test sample is taken out from the corrosion media and rinsed with water, cleaned with acetone and air-dried after that final weight is measured and calculates corrosion rate by using the mpy formula.

$$\text{Corrosion Rate (MPY)} = 534/\text{DAT}$$

where, W = Weight loss (gm), D = Density (gm/cc), A = Area (inch<sup>2</sup>), T = Time (Hrs)

A potentiodynamic study is carried out to find out corrosion potential and corrosion current of aluminium and Al+4.5%Mg using potentiostat gamry reference 600 according to ASTM G-5 standard. Test sample having the size of 5 cm height and 1-inch dia. This study is carried out by using three-electrode systems in which the working electrode is our test sample, mild steel is a counter electrode and a standard calomel electrode is used as a reference electrode. Line diagram of the experimental set-up is shown in Figure 2. Environment for the test is 3.5% NaCl.

### 3. Result & Discussion

#### 3.1 Chemical Analysis

The chemical composition of the cast Aluminium and Aluminium + 4.5% Magnesium was listed in Table 1.

**Table 1 Chemical Analysis of Developed Alloy**

	%Si	% Mn	%Cr	%Cu	%Zn	%Mg	%Fe	%Al
Aluminium	0.056	-	-	0.006	0.010	0.001	0.127	99.78
Al + 4.5% Mg	0.084	0.003	0.002	0.003	0.054	4.537	0.0182	94.74

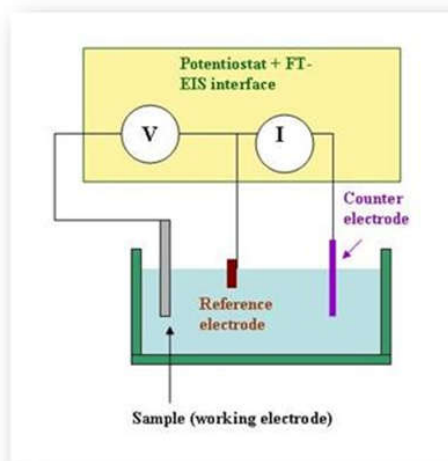


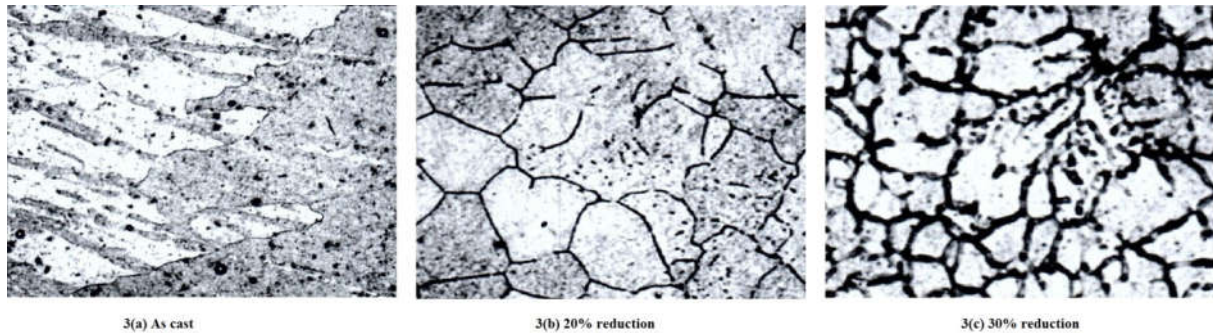
Figure 2 Line Diagram of Potentiodynamic Study

### 3.2 Microstructure analysis

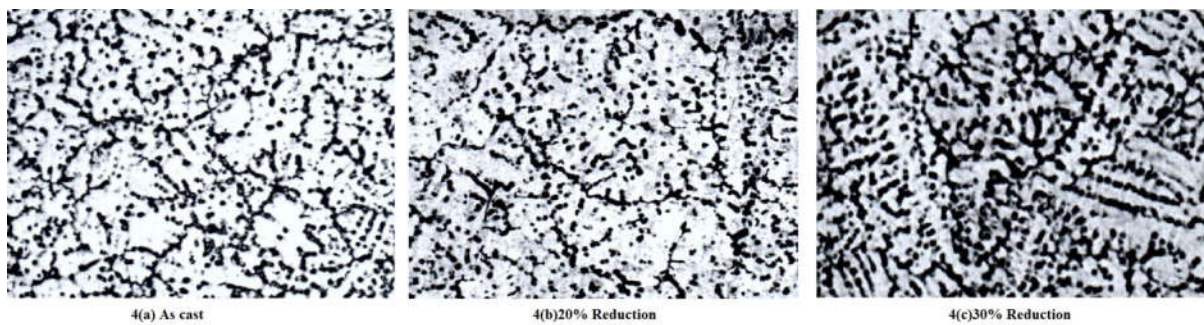
Test specimens were prepared by conventional metallography practice according to ASTM E407-07(2015) including rough and fine grinding up to 1200 number Sic emery paper using kerosene as a coolant. The ground surface is polished with the alumina paste on velvet cloth to obtain a surface having mirror polish. The polished surface is etched by 0.5% HF solution for 10 seconds. The etched sample was carefully handled and washed with water and air dry for 30 seconds after that image was observed in optical microscope and JEOL 5610 LV Scanning Electron Microscope (SEM) with Energy Dispersive Spectroscopy (EDS) at different magnifications.

The typical Microstructure of pure aluminium and aluminium containing 4.5 weight per cent Magnesium are shown in Fig.3 and Fig.4 respectively which was taken by optical microscope. In which fig 3(a) shows as cast condition while correspondingly fig 3(b) and fig 3(c) shows 20% and 30% height reduction by forging. Similarly fig 4(a) shows as cast condition while correspondingly fig 4(b) and fig 4(c) shows 20% and 30% height reduction by forging and Fig.5 and Fig.6 respectively which was taken by scanning electron microscope (SEM) along with Energy Dispersive Spectroscopy (EDS) Analysis.

According to binary phase diagram of Aluminium Magnesium system, in the microstructure two phases will presence one is a solid solution of Aluminium i.e.  $\alpha$  aluminium and another is an intermetallic compound of aluminium and magnesium i.e.  $\beta$  phase ( $Al_3Mg_2$ ) which is form by eutectic reaction. Fig 3 Shows Microstructure of pure aluminium without the addition of magnesium containing only an aluminium matrix and some impurities like Fe and Si. Microstructure shows distributed  $Mg_2Si$  (dark) along with  $Fe_3SiAl_{12}$  particles in the matrix of aluminium grains. Fig 3(a) describing as cast microstructure of pure aluminium and fig 3(b) define 20% forging, in that case grain boundary get closer as compare to as cast condition in same way microstructure become fine in case of 30% forging which is define by fig 3(c).



**Figure 3 Microstructure of Pure Aluminium (a) As cast condition (b) 20% Height reduction (c) 30% Height reduction at 100X**



**Figure 4 Microstructure of Aluminium + 4.5% Magnesium (a) As cast condition (b) 20% Height reduction (c) 30% Height reduction at 100X**

Fig 4 represent microstructure of aluminium containing 4.5% magnesium describe by fig 4(a) in the as cast condition consist of three phases: The aluminium matrix (bright matrix),  $Al_3Mg_2$  (dark precipitation) and  $Mg_2Si$  (grey precipitation) which form near grain boundaries. In fig 4(b) and 4(c) increases the clustering and gathering of Mg and the formation of Al-Mg Intermetallics increases at the grain boundary and microstructure changes from coarse grain to fine grain.

SEM images in backscattered mode at 100X also indicate the presence of magnesium and  $\alpha$ - aluminium matrix. EDS analysis confirms the presence of magnesium. The dark black portion shows the presence of magnesium and the grey portion was  $\alpha$  - aluminium matrix. Fig 5 noted only aluminium matrix and some impurities present in raw material. Fig 6 represent aluminium matrix contain intermetallic compound of aluminium magnesium i.e  $Al_3Mg_2$

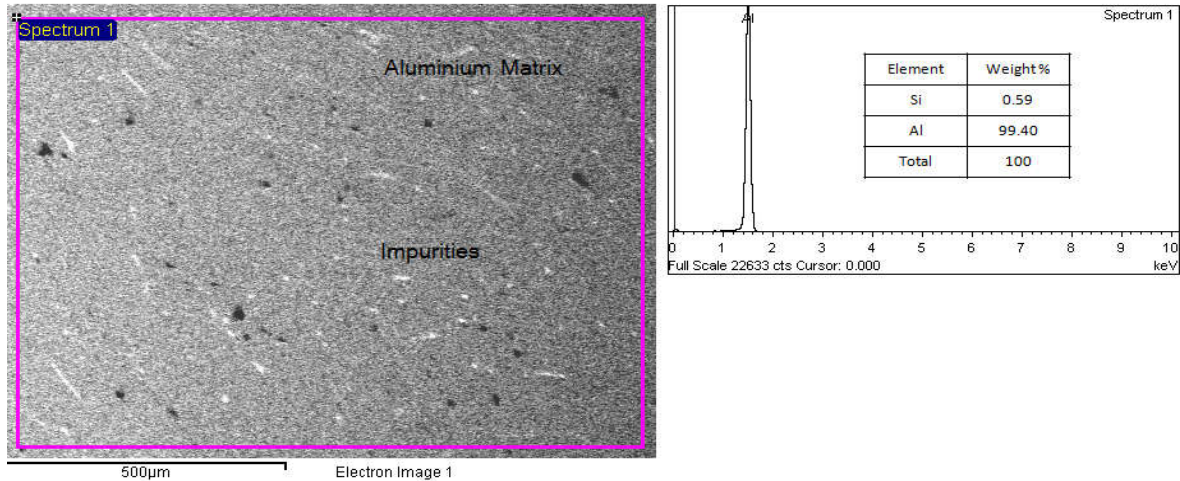


Figure 5 SEM-EDS Analysis of Pure Aluminium at 100X

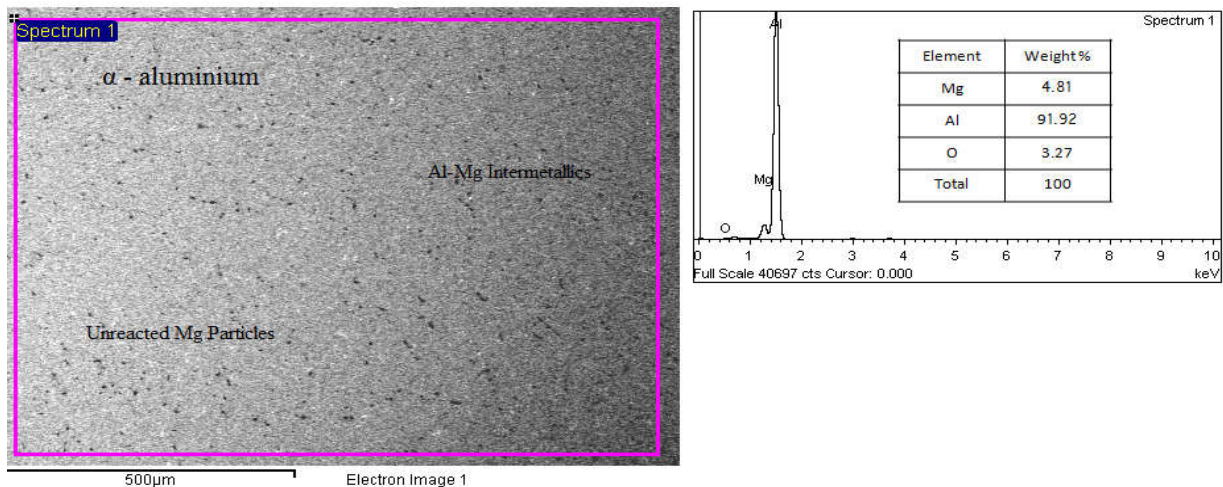


Figure 6 SEM-EDS of Aluminium + 4.5 Weight percent Mg at 100X

### 3.3 Grain Size Measurement

Average ASTM grain size number is measured with the help of optical microscope, all result are reported in Table 2. From observation it has been noted that grain size in case of pure aluminium is higher which can be reduced by forging. Aluminium containing 4.5% magnesium have smaller grain size as compare to pure aluminium which indicate magnesium act as grain refiner for aluminium. Generally Magnesium and its intermetallics is gathering next to the grain boundaries or on the grain boundary and act as network former and reduce grain size. Mg acts as a grain

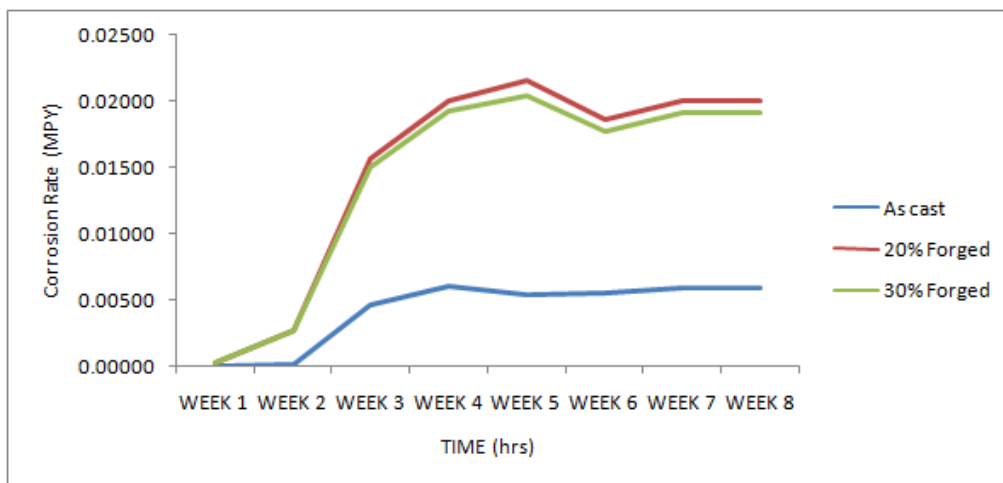
refiner and after addition of magnesium Microstructure of pure aluminium changes non uniform to uniform with equiaxed grain. After forging grain size no decreases more smaller value as compare to as cast Al+4.5% Mg.

**Table 2 Average Grain Size Number**

Sr .no	Developed alloy	As Cast	20% Cold work	30% Cold work
1	Pure Aluminium	1	3-4	4-5
2	Al + 4.5 Mg	5-6	4	4

### 3.4 Corrosion Rate Measurement by the standard weight-loss method.

Corrosion rate by standard weight loss method for pure aluminium and Aluminium containing 4.5% Magnesium are recorded in fig.7 and fig.8 respectively.

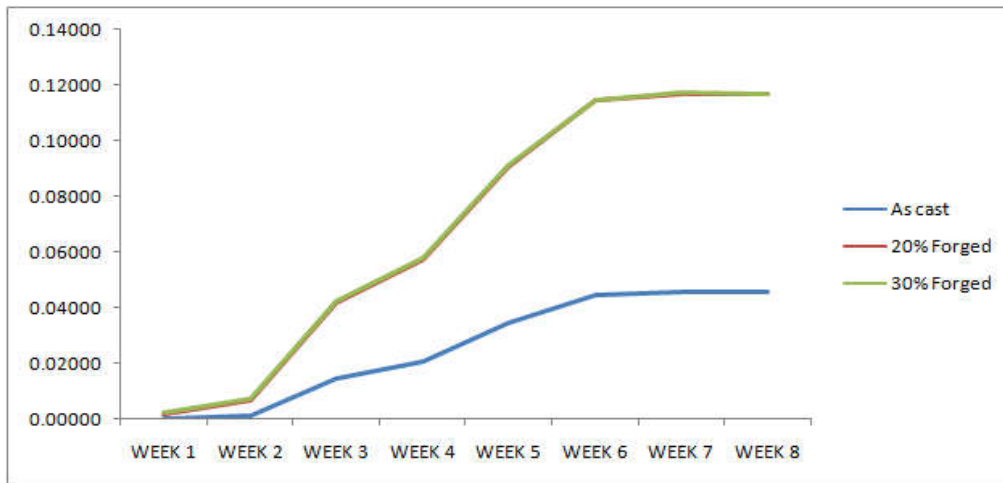


**Figure 7 Corrosion rate of pure aluminium by standard weight loss method**

As observed in the plot of corrosion rate versus time is linearly communicated that the corrosion rate of pure aluminium increased with time of exposure. In as cast condition the corrosion rate is almost at a steady value range because of the formation of the passive layer. while in case of 20% forged and 30% forged condition corrosion rate is increased with time which opines that forging condition will break the passive layer or after forging stability of oxide layer is week due to cold working operation. corrosion rate directly proposal to loading or deformation level given to the metal.

In the case of Aluminium - 4.5% Magnesium corrosion rate is increased as exposure time is increased. This is because of the presence of magnesium. Here, magnesium goes into the solid solution of aluminium and decreases the possibility of passivation and corrosion is observed with time. the corrosion rate is almost thrice compared to pure aluminium. Here, in this case, some magnesium will remain in a

solid solution of aluminium and some magnesium react with aluminium and form an intermetallic compound of aluminium and magnesium which was moving towards the grain boundary and near the grain boundary area, as confirmed from the microstructure. The grain boundary is electrochemically different compared to the alloy microstructure. This causes an electrochemical potential set up between the two and an exchange of electrons takes place. This situation leads to intergranular corrosion. This phase has an electrode potential of -1,150 mV ESC and the aluminium matrix has an electrode potential of -780 mV ESC. While comparing these values Al-Mg intermetallics act as an anode and the Al matrix act as a cathode in a galvanic cell. These lead to localized corrosion or dealloying. Under chemical attack, this anodic phase is dissolved leaving behind cavities or pits. This phase is concentrated at the grain boundaries which restrict the formation of a passive oxide layer. Mark out in case of 20% and 30% forged condition. grain boundary area is increase after forging process so more corrosion rate is observed in rest of the cases.



**Figure 8 Corrosion rate of Al+4.5% Mg by standard weight loss method**

### 3.5 Potentiodynamic Study

Polarization curve of pure aluminium, Al+4.5%Mg are recorded correspondingly in fig 9 and fig 10 ,electrochemical properties of pure aluminium and Al+4.5%Mg are listed in Table 3.



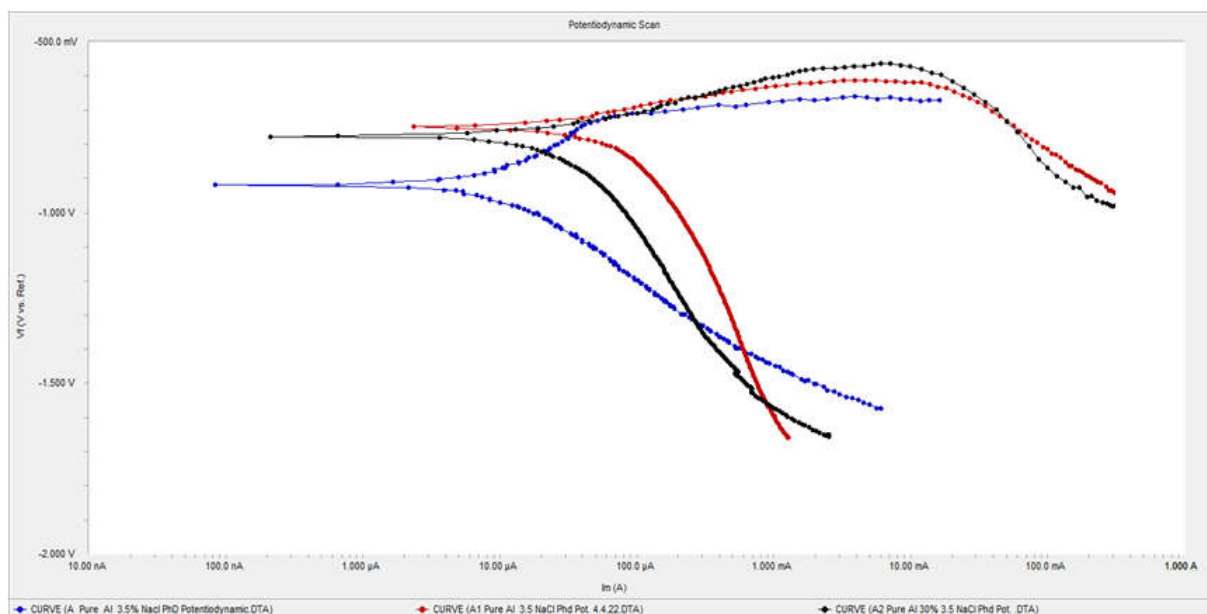


Figure 9 Polarization curve of pure aluminium

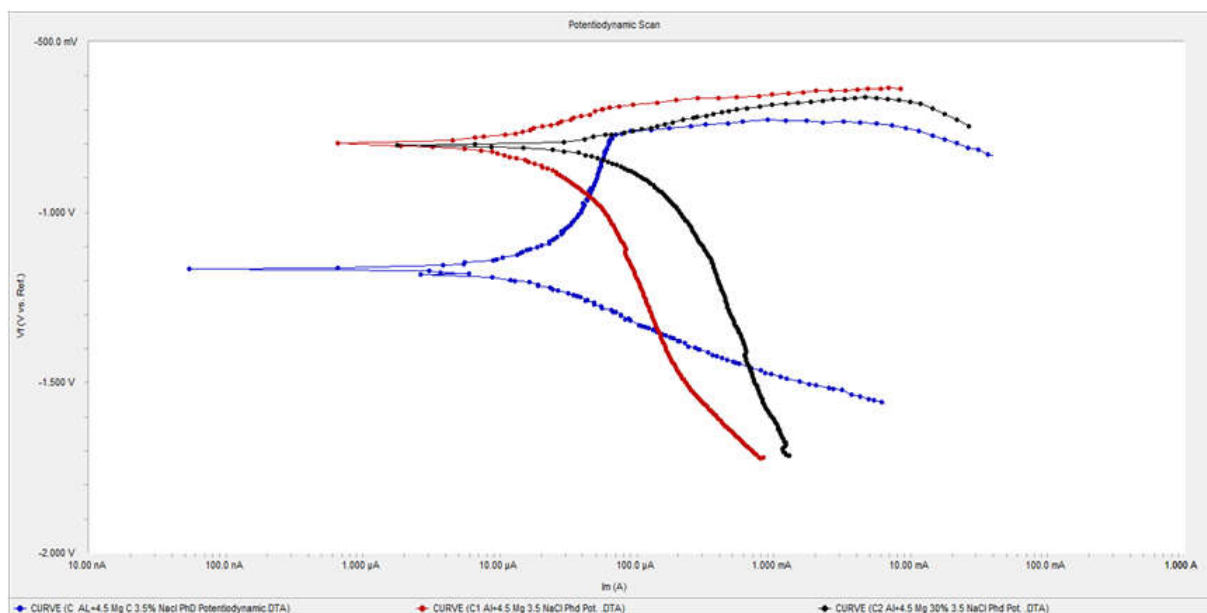


Figure 10 Polarization curve of Al+4.5%Mg

Table 3 Corrosion properties of Pure Al and Al+4.5%Mg

Alloy	E corr (mV)	I corr ( $\mu$ A)	Corrosion rate (mpy)
Pure Aluminium	-920.00	14.60	25.05
Pure Aluminium - 20% forged	-750.00	40.09	70.27
Pure Aluminium - 30% forged	-779.00	38.00	68.82
Aluminium + 4.5% Magnesium	-1170	28.20	48.42
Aluminium + 4.5% Magnesium - 20% forged	-800.00	32.00	64.01
Aluminium + 4.5% Magnesium - 30% forged	-804.00	39.00	67.01

Polarization curves give the idea about dissolution reaction and reduction reaction. The addition alloying elements having more negative potential compared to pure aluminium typically increases the corrosion potential to more noble values. As pure Al have corrosion potential -920 mV which will decrease to more negative value after the addition of magnesium that is -1120 mV this is achieved due to formation of  $Al_2Mg_3$  particles at the grain boundary which leading to the grain boundary corrosion or dealloying. As suggested in case of forging condition for pure aluminium corrosion rate and corrosion current is increase as compare to pure aluminium and passivation range is decrease so there is less chance to passivates and hence corrosion rate is improved. Accordingly in case of Al+4.5Mg more clustering and gathering of grain boundary observed will improve corrosion rate by grain boundary corrosion.

#### 4. Conclusion

The experimental work made the following conclusions.

- In the presence of a chloride-containing corrosive environment, the protective oxide layer of aluminium loses anti-corrosive properties.
- The addition of magnesium modifies microstructure with fine grain and ensure the uniform structure act as a grain refiner.
- Magnesium damages the passive layer of aluminium by the formation of the Al-Mg intermetallics which prevents the formation of a homogeneous passive layer on the surface of the aluminium.
- The addition of magnesium reduced corrosion potential by -250mV and shifted to the more active region.
- The corrosion current is increased almost two folds by the addition of magnesium and the corrosion rate is almost double compared to pure aluminium.
- Forging process profoundly affect the corrosion properties of aluminium and aluminium magnesium alloy.
- Optimum corrosion rate is observed in case of Al+4.5%Mg-20% forged alloy.

## 5 Acknowledgment

- I am very thankful to the Management and Metallurgy dept. of Government Engineering College, Gandhinagar for providing an Experimental setup for melting and weight loss analysis.
- I would like to thank Dr V.J.Rao ( Associate Professor), Metallurgical & Materials Engineering Dept, M.S.U, Baroda for helping during S.E.M, EDS and XRD analysis.
- I would thank Dr Sunil Kahar ( Assistant Professor), Metallurgical & Materials Engineering Dept, M.S.U, Baroda for helping during the Potentiodynamic study.

## 6.References

- [1] L. E. Umoru and O. O. Ige, "Effects of Tin on Aluminum-Zinc-Magnesium Alloy as Sacrificial Anode in Seawater," 2007.
- [2] A. Muazu and Yaro, "Effects of Zinc Addition on the Performance of Aluminium as Sacrificial Anode in Seawater," 2011.
- [3] D. jizhou and Z. jie, "Effect of Ti on microstructure and properties of aluminum sacrificial anode containing rare earth elements," 2015.
- [4] S. Lameche-Djeghaba, A. Benchettara, F. Kellou, and V. Ji, "Electrochemical Behaviour of Pure Aluminium and Al-5%Zn Alloy in 3% NaCl Solution," *Arab. J. Sci. Eng.*, vol. 39, no. 1, pp. 113–122, 2014.
- [5] J. Wen, J. He, and X. Lu, "Influence of silicon on the corrosion behaviour of Al-Zn-In-Mg-Ti sacrificial anode," *Corros. Sci.*, vol. 53, no. 11, pp. 3861–3865, Nov. 2011.
- [6] J. G. He, J. B. Wen, X. D. Li, G. W. Wang, and C. H. Xu, "Influence of Ga and Bi on electrochemical performance of Al-Zn-Sn sacrificial anodes," *Trans. Nonferrous Met. Soc. China (English Ed.)*, vol. 21, no. 7, pp. 1580–1586, Jul. 2011.
- [7] F. J. Garcia-Garcia, T. Y. Chiu, P. Skeldon, and G. E. Thompson, "Effect of magnesium and titanium on the cathodic behaviour of aluminium in nitric acid," *Surf. Interface Anal.*, vol. 47, no. 1, pp. 30–36, Jan. 2015.
- [8] Oluwole O O, "International Journal of Science and Technology Aluminium Anode Activation Research-A Review," vol. 2, no. 8, 2012.
- [9] S. Vuelvas, S. Valdez, and J. G. Gonzalez-Rodriguez, "Effect of Mg and Sn Addition on the Corrosion Behavior of an Al-Mn Alloy in 0.5 M H<sub>2</sub>SO<sub>4</sub>," 2012.
- [10] A. Barbucci, P. L. Cabot, G. Bruzzone, and G. Cerisola, "Role of intermetallics in the activation of Al-Mg-Zn alloys," *J. Alloys Compd.*, vol. 268, no. 1–2, pp. 295–301, 1998.
- [11] V. K. Beura, C. Kale, S. Srinivasan, C. L. Williams, and K. N. Solanki, "Corrosion behavior of a dynamically deformed Al-Mg alloy," *Electrochim. Acta*, vol. 354, p. 136695, 2020.
- [12] B. Wang, L. Zhang, Y. Su, Y. Xiao, and J. Liu, "Corrosion behavior of 5A05 aluminum alloy in nacl solution," *Acta Metall. Sin. (English Lett.)*, vol. 26, no. 5, pp. 581–587, 2013.
- [13] K. A. Unocic, M. J. Mills, G. S. Daehn, and P. Kobe, "Microstructural Analysis of 5XXX Series Aluminum Alloys Modified for Optimal Strength and Corrosion Resistance," vol. 11, no. Suppl 2, pp. 700–701, 2021.