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A

S Y N O P S I S

On

Study the Electrochemical Behavior of Aluminium Sacrificial Anode by Adding Magnesium

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By

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1. TITLE OF THE THESIS AND ABSTRACT

Title of the Thesis: Study the Electrochemical Behaviour of Aluminium Sacrificial Anode by Adding Magnesium

Abstract:

Corrosion of steel and iron is a colossal issue faced by all global industries. According to the International Zinc Association (IZA), India loses around 5-7 per cent of its Gross Domestic Product (GDP) every year due to corrosion. One means of controlling corrosion is by the employment of cathodic protection. Aluminium (Al) is thoroughly used as a sacrificial metal for the cathodic protection of steel in seawater. It is most advantageous sacrificial metal for the cathodic protection of steel and other structural components as a consequence of light weight, high anode efficiency, current capacity, large electrochemical equivalent and used in various atmospheres like sea water, Freshwater and backish water. Sacrificial anodes are highly active metals but in case of Pure and unalloyed aluminium its highly activity turns into passivity because it is affiliated to passive group of metals whereas resist the further corrosion of aluminium by forming stable aluminium oxide on the surface that is the reason aluminium is rarely used as a sacrificial anode without being alloyed due to its built-in properties to get passivated. The reactivity of aluminium can be changed from passive to active state by removing the passive layer and break down of passive film to improve performance of aluminium sacrificial anode. The passive layer and the continuity of this layer depend on the chemical composition and microstructure. Several methods are deployed to depassivation of aluminium like alloy addition, Heat Treatment and Mechanical working.

This research deals with the alloying of magnesium in pure aluminium and cold working of developed alloy. Here, Aluminium-Magnesium (5xxx) system is considered because magnesium is more electronegative compare to aluminium and remarkably affects the chemical properties by changing the microstructure of Aluminium from a homogeneous solid solution to a complex structure with multiple intermetallic phases. Al-Mg sacrificial anode developed containing 2.5, 4.5, 6.5 and 8.5 weight percent magnesium. Developed Alloy are 10% and 20% cold worked by mechanical press because cold working also changed microstructure from coarse grain to fine grain and improve corrosion performance. Chemical Analysis is done with the help of spectroscopy to confirm the presence of magnesium and XRD is also carried out. Mechanical Testing like hardness, tensile strength and Grain size measurement is done to observe the outcome of magnesium addition. The microstructures of pure aluminium and developed alloys were studied with the help of optical microscopy, Scanning Electrons Microscopy (SEM) to understand the effect of the distribution of magnesium whether as a second phase particle, intermetallic compound or precipitates on the performance of aluminium sacrificial anode was discussed. To evaluate

corrosion behavior standard weight loss method and potentiodynamic study of all developed alloy and cold worked alloy was carried out.

The results show that as the magnesium content increases hardness and tensile strength increases and optimum result is found at 6.5% Magnesium containing alloy. Corrosion rate is also increased by increasing magnesium content due to formation of intermetallic compounds of Al-Mg at the grain boundary which have different electrochemical properties and micro galvanic cells are formed which will improve the corrosion of developed aluminium alloy. Cold working also improves the corrosion sites and grain refining so corrosion is increased as the percentage of cold working is increased. Optimum corrosion performance is achieved at 20% cold worked 6.5% containing magnesium alloy.

2. A Brief Description of the State of The Art of the Research Topic

The phenomenon of corrosion is as old as the history of metals; it is nothing but the degradation or oxidation of metals. Our human civilization is not possible without metals, so living with corrosion bay. Nowadays it is a large challenge for the industrial world. Several techniques have been developed to prevent corrosion like inhibitors, design modification, coating and anodic-cathodic protection from which Cathodic protection (C.P.) is being deployed by major industries. [1], [2]

Corrosion is initiated at the anode of the corrosion cell by generating electrons and these electrons are consumed at the cathode of the corrosion cell. This is the basic concept of cathodic protection converting anode into the cathode and restricting corrosion.

This can be achieved in two ways:

(1) Impress current method and

(2) Sacrificial anode method

Sacrificial anode method is most preferable due to ease of installation, no need for an external power source, and also suitable for localised protection. The main objective of this method is that the metal to be protected is coupled with more active metal (anodic metal) and makes it cathode. Hence, all the corrosion concentrated in active metals call a sacrificial anode. [3], [4]

Nowadays, Magnesium (Mg), Zinc (Zn) and Aluminium (Al) are the most preferable sacrificial metals for cathodic protection. From which, Aluminium is acquiring appreciable properties as a sacrificial metal like a light in weight and density, ease of availability, large electrochemical equivalent, thermal and electrical conductivity, high current capacity, and reasonable cost.[5], [6][7]

Aluminium belongs to a group of passive metals therefore when used in seawater aluminium forms a passive layer of aluminium oxide which will restrict further corrosion and decrease the efficiency of preventing steel structure. The existence of this film is the first time reported by Joseph W

Richards in 1896. There is just about the immediate formation of an oxide film having the general formula $Al_2O_3.nH_2O$ as given by the reaction a, b and c respectively, which is few nanometers thick and this film isolates the aluminium from direct contact with the environment.[9], [10]

Table 1. Comparison between sacrificial anode materials [8]

Properties	**Aluminium**	**Zinc**	**Magnesium**
Density (gm/cc)	2.70	7.13	1.74
Open circuit potential (SHE)	-1.66	-0.76	-2.38
Anode capacity (amp.hr/kg)	2500	780	1251
Consumption rate (kg/amp.yr)	3.4	11.5	7
Environment	Seawater Freshwater Backish water High and low resistive medium	Low resistive medium	High resistive medium Subsoil Freshwater

[a] Oxidation:

$Al \rightarrow Al^{+3} + 3e^-$

[b] Reduction:

$2H^+ \rightarrow 2e^- + 2H_2$ (Hydrogen reduction)

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (in alkaline or neutral media)

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ (in acidic media)

[c] Passivation:

$2Al^{+3} + 3O^{-2} \rightarrow Al_2O_3$

This passivating behavior of aluminium is subject to the stability of oxide film and this is express by their Pourbaix diagrams which give idea about the thermodynamic oxidising and reducing power of the major stable oxides, hydroxides, and oxyhydroxides of a various chemical compound. If we talk about aluminium oxide then it is a very stable oxide and also Rpb (Pilling-Bedworth ratio) for this oxide is 1.28 which concludes that this oxide film is denser than metal. This property of oxide film is enough for protecting the aluminium from further corrosion that's why aluminium has great atmospheric corrosion resistance. The parameter that affects the development of oxide is oxygen pressure, temperature, the surface of the metal and chemical substances present in the metal. [9, 10]

The breakdown of this passive film (Al_2O_3) improves the performance of the sacrificial aluminium anode.[11], [12]Breaking or weakening of the passive film moves the aluminium surface from the naturally passive state to the active state. Methods for this adjustment of aluminium surface by applying cathodic current, or by addition of alloying elements at a low quantity having a suitable negative potential which encourages depassivation and shifts the operating potential of the aluminium to the more electronegative direction.[13], [14]

In 1966, Reding and Newport carried out study to understand event of the addition of different metals on the performance of aluminium sacrificial anodes in seawater and found that many metals which improve the efficiency of the anode by forming intermetallic and other second phase particle depends on solubility limit of the solvent metal in Aluminium matrix (Table 2) and make more active aluminium electrode potentials. Generally, alloying elements are added into Aluminium are term as depassivators and modifiers.[10], [15]

Addition of alloy metal and impurities present in aluminium can pay-off degradation in passivating properties and it is basically governed by the nature and distribution of intermetallics compounds, the shape and particle size of the intermetallics. Beginning with the physical metallurgy of Al alloys clearly shows that all the alloying elements have negligible solubility at room temp and the addition of elements beyond this limit will give rise to the formation of another solid solution or compound. These compounds may be binary, ternary or even quaternary depending on the chemistry of the developed alloy. However, an alloying element can also form compounds with or without aluminium. This is possible in the system of Mg and Zn they will produce Mg_2Si and $MgZn_2$ in the 6XXX and 7XXX series respectively. These intermetallics compounds form in the liquid state by eutectic and peritectic reaction or in the solid state by precipitation process during the cooling or heat-treatment process [16], [18]

These intermetallics compounds take part in the galvanic corrosion process of the alloy, which may be anodic or cathodic to the aluminium matrix depending on their open circuit potential as listed in table 3. Therefore, this brings out development of galvanic corrosion cells between intermetallics and aluminium matrix and result is dealloying or localised corrosion. The Driving force for localised corrosion is the potential difference between intermetallics and aluminium matrix. These intermetallics lead to generalized surface corrosion like pitting; this will be initiated by an oxygen-reduction process on cathodic intermetallics. Pitting is usually starting when the oxide layer is breaking and it is the origin of localised corrosion. [16], [19]

The intermetallics may be Age-hardening precipitates, in the ageing process, the usual sequence is the formation of supersaturated solid solution (SSSS)-GP zones-metastable phases- stable phases. In GP zones [Guinier-preston zone], decomposition of SSSS of Al is producing precipitates (ppts) that may be fine or coarse. Fine ppts distributed throughout the matrix and coarse ppts concentrated on grain boundaries, and intergranular corrosion and stress corrosion will be initiated. The coarsening of ppts restricts the growth of the protective oxide layer and breaking in the oxide layer initiates corrosion. As suggested by several theories, at the breaking point where no oxide layer is present from that area pitting corrosion is started in presence of chlorides which leads to Al dissolution. [20], [21]

Table 2 Solubility of the elements in aluminium [16], [17]

Alloying element	Temp (^{o}C)	Solid solubility (wt%)	Liquid Solubility(wt%)	Type of system
Zn	380	82.8	95.0	Eutectic
Mg	450	14.9	35.0	-
Cu	550	5.67	33.15	Peritectic
Si	580	1.65	12.16	-
Sn	230	<0.01	99.5	Eutectic
Ti	665	1.0	0.15	Peritectic
Zr	660	0.28	0.11	Peritectic
Pb	660	0.15	1.52	-
Ga	30	20	98.9	-
Bi	660	0.87	<0.1	Monotectic

Magnesium is one of the two most soluble elements in aluminium (the other being zinc) in the solid-state, 14.9 wt.% at 451^{o}C and 1.7 wt.% at room temperature and forms a eutectic type of system. The excess magnesium beyond the solubility limit precipitated as Al3Mg2 (β-phase). This β-phase has mainly formed at the grain boundary and is incoherent with the matrix. The open-circuit potential of this β-phase is -1150 mV SCE which is very anodic compared to the Aluminium matrix (-760 mV SCE) leading to selective dissolution and improving the corrosion of Al-Mg alloy and if Mg exceeds 3.5 weight percent than the mass loss is observed due to sensitization.[16], [22]–[24]

Table 3 open circuit potential of intermetallic compounds (NaCl, H_2O_2 solution, ASTM G 69)[16]

Position	Intermetallic Compound	Open Circuit Potential (mV SCE)
Anodic	Cu	-110
	Si	-170
	Al_3Fe	-470
	Al_2Cu	-640
	1050A	**-750**
Cathodic	Al_6Mn	-760
	$MgZn_2$	-960
	Al_3Mg_2	-1150
	Mg_2Si	-1200

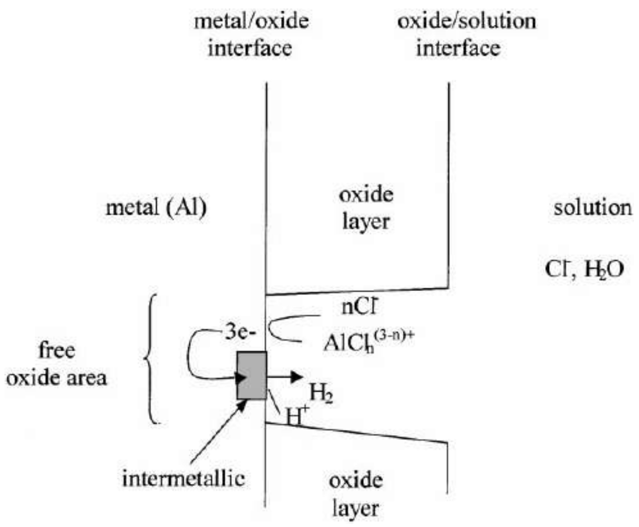


Figure 1 Formation of pit in oxide free area [7]

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 a precise relationship between grain size and corrosion rate. Change in grain size decreases or increases 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. [25]– [27]

3. Definition of the problem

The present research work addresses the following Problem:

It is known that the corrosion of metallic structures has a significant impact on the economy, including infrastructure, transportation, utilities, production and manufacturing, and government. There is no single figure for loss to the nation due to corrosion. It can be a minimum of 3.5% of the nation's GDP. Losses due to corrosion could be around Rs. 2.0 lack cr per annum in India. By using available corrosion protection practices, reduce the cost of corrosion 15-35% annually.

There are various methods adopted for corrosion control but the most widely accepted method is cathodic protection. Cathodic protection by sacrificial anode has gained general acceptance because it has the advantages of being simple to install, independent of a source of external electric power, suitable for localised protection and less liable to cause interaction on neighboring structures.

Aluminium and its alloy have been used as a sacrificial anode for several decades in corrosion protection of structural parts in sea water but aluminium gets passivated when it comes into exposure of oxygen and does not fulfill the function of sacrificial anode. For that purpose depassivation is necessary and that can be possible by adding another alloying element and mechanical working. By focusing on that area this research deals with the alloying of magnesium in pure aluminium and mechanical treatment like cold working (Height Reduction) is adopted for improving performance of pure Aluminium.

4. Objective and scope of the work

The present research work has been planned with the following objectives.

a) Main aim is looking at the possibility of alloying aluminium with Magnesium in order to enhance its performance as a sacrificial anode for the protection of steel in seawater.
b) Study the effect of Magnesium on the microstructure, mechanical Properties and electrochemical properties of developed alloy.
c) Study the Effect of Mechanical working (Cold Working) on the microstructure, mechanical Properties and Passivation behavior (electrochemical properties) of aluminium sacrificial anode.

Scope of Work

The Present work is carried out to achieve above objectives. Main concern of the research is to improve the performance of aluminium sacrificial anode. To achieve this goal two different methods are adopted. In the first method alloying element - Magnesium is added and in the second method cold working is used. In the first method Magnesium is added in pure aluminium in the range of 2.5%, 4.5%, 6.5% and 8.5% by weight. Then find out the recovery of magnesium in developed alloy. Hardness and Tensile Strength is compared with Pure aluminium to observe the effect of Magnesium on developed alloy. Grain size is measured to study the effect of magnesium as a grain refiner. Microstructural characterization is carried out with optical and scanning electron microscopy to understand Microstructural change after addition of magnesium and effect of these changes on the electrochemical properties of pure aluminium and developed alloy. XRD analysis is also carried out to identify phases .Potentiodynamic testing and standard weight loss methods is carried out to study corrosion behavior of developed alloy and pure aluminium than compare corrosion potential with pure aluminium and discussed how the magnesium improve the performance of pure aluminium sacrificial anode. In Second Method Mechanical working that is cold working carried by mechanical press at room temp. Hardness, tensile strength and grain size measurement is carried out to understand the effect of cold working and compare this result with exciting results of developed alloy (without cold work). Microstructural changes are studied with the help of optical microscopy and Scanning electron microscopy. Corrosion study of cold worked alloy is done with potentiodynamic test and standard weight loss method. Effect of mechanical working on corrosion behavior is discussed and compared with all the results and made conclusions.

5. Original contribution by the thesis

In the present research work, Effect of magnesium and Mechanical working on performance of Pure Aluminium Sacrificial Anode is studied to improve the performance of pure aluminium as a sacrificial anode. The Major research contributions are as follows:

a) Developed Al-Mg alloy through liquid metallurgy in the range of Mg 2.5 to 8.5 wt%.
b) The hardness and Tensile strength is measured and compared with pure aluminium also grain size measurement is done.
c) Determine corrosion potential and corrosion current of pure aluminium and develop Al-Mg Alloy.
d) Corrosion rate is 3.5% NaCl is measured for pure aluminium and developed Al-Mg Alloy. Polarization behavior is compared with pure aluminium.
e) Mechanical working that is cold working by 20% and 30% height reduction is given to pure aluminium and developed Al-Mg Alloy.
f) Comparison of mechanical properties and corrosion properties of as cast alloy and mechanically worked alloy.
g) Improve the performance of pure aluminium as a sacrificial anode by magnesium addition and cold working.

6. The methodology of research, results/comparisons

In this Research work two methods are adopted to improve performance of aluminium sacrificial anode. In the first method alloying element - Magnesium is added and in the second method cold working is used. In the first method Magnesium is added in pure aluminium in the range of 2.5%, 4.5%, 6.5% and 8.5% by weight. In Second Method Mechanical working that is cold working carried by mechanical press at room temp 20% and 30% height reduction given to pure aluminium and as cast developed alloy by first method. The Experimental procedure for Method-1 and Method-2 are shown in following fig.2 and 3 respectively.

6.1 Experimental Procedure and Materials

6.1.1 Raw Material

99.8% Pure Aluminium wire and 99.9% Magnesium Ribbon used for this study is obtained from Honest metal cast, Ahmedabad and Chemdyes corporation, Rajkot respectively. As received chemical composition given in Table 4

Table 4 Chemical Composition of raw material

Material	%Al	%Mg	%Zn
Aluminium Wire*	99.78	0.001	0.010
Magnesium Ribbon	--	99.5	0.005

* Aluminium wire containing impurities like Cr, Si, Fe, Cu and Mn less than 0.1%.

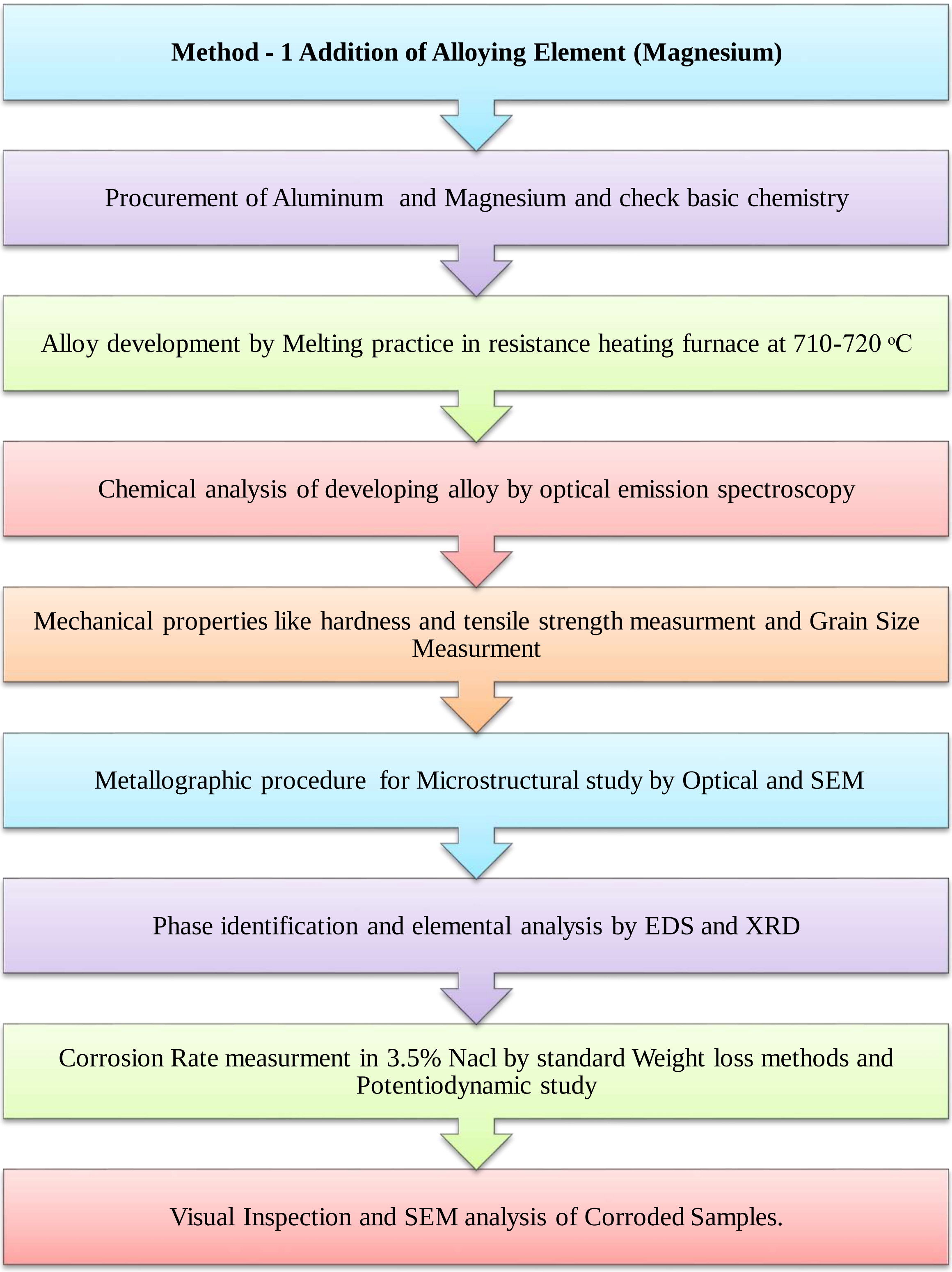


Figure 2 Flow chart for Experimental work (Method 1)

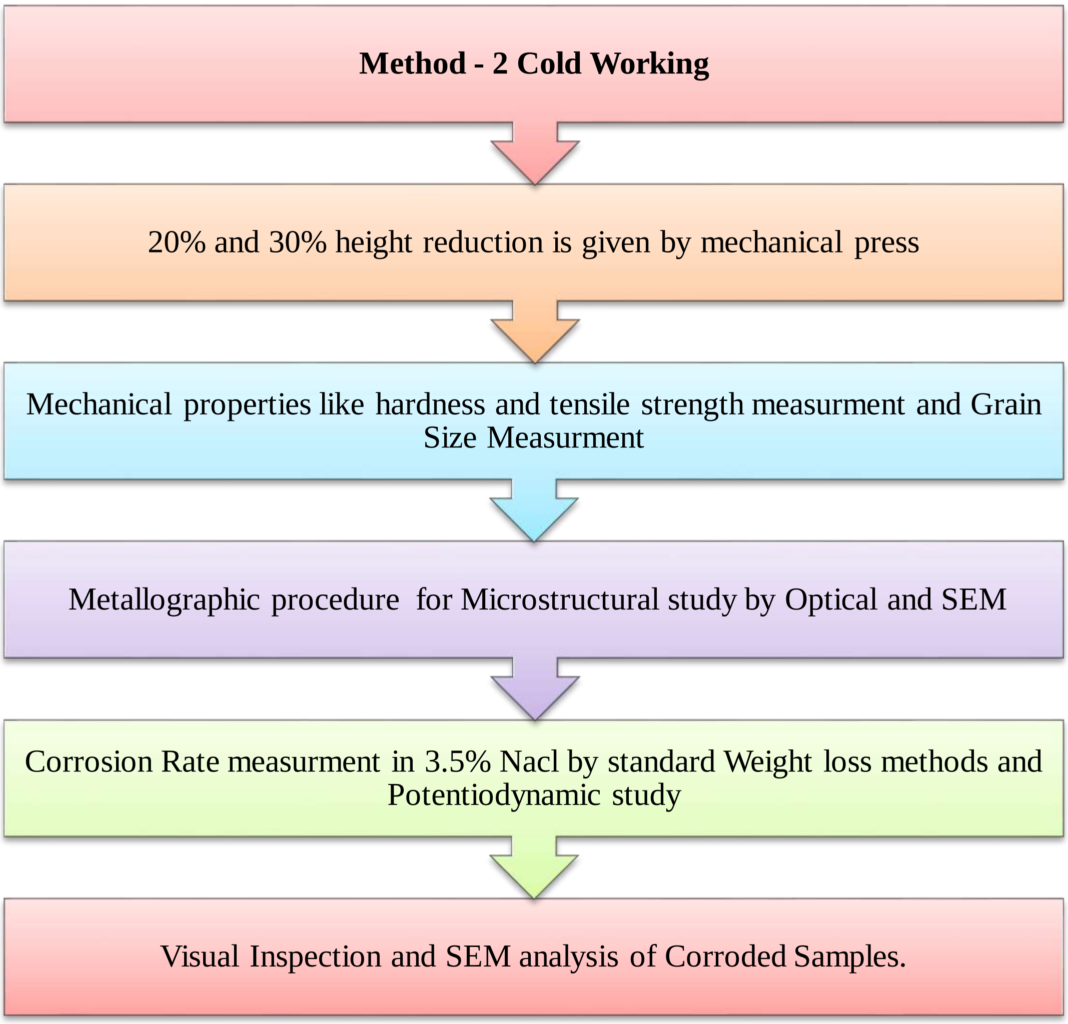


Figure 3 Flow chart for Experimental work (Method 2)

6.1.2 Casting and Charge Calculation

In this research work total 4 alloys of aluminium-magnesium are developed containing different amounts of magnesium that is 2.5wt%, 4.5wt%, 6.5wt% and 8.5wt% Magnesium through liquid metallurgy route. Total 5 casted systems is produced as shown in Table 5.

Table 5 List of System

Sr.no	System/Alloy	Composition
1	A	Pure Aluminium
2	B	Pure Aluminium + 2.5 weight percent Magnesium
3	C	Pure Aluminium + 4.5 weight percent Magnesium
4	D	Pure Aluminium + 6.5 weight percent Magnesium
5	E	Pure Aluminium + 8.5 weight percent Magnesium

Melting Practice is carried out in an electric resistance furnace as shown in Fig 4 with the help of Graphite crucible. In which raw material aluminium is charged as per the charged calculation (Given in table 6) and after getting processing temperature around 720-740^{o}C (Melting point of pure aluminium is 660°C) magnesium is charged calculation (Given in table 6). Stirring is done with the help of stainless steel rod for proper molten metal mixture. Drossing and Degassing were carried out for better melting practice. After that the molten mixture is poured into a permanent metallic die made-up of mild steel containing 5 cast rods having 15 cm height & 2.5 cm diameter of each as shown in fig 5. After that cooling & solidification of casting is done then casting of different systems is removed from the die as shown in fig 6. Sampling or cutting of casting was accomplished for various characterizations as per testing methods and requirements.

Charge Calculation for one heat is as follows:

- Volume of one rod (v) = πr2h = 73.60 cm^3
- Mass of one rod (m) = ρ (density). v = 199 gram(density of pure Aluminium is 2.7 gm/cc)
- Total Mass required for melting is 1.4 Kg (Including Runner & Riser)

For Design of alloy taking total mass 1.5 kg considering melting (Including melting losses) .Charge material for each system in furnace is given in Table 6.

Figure 4 Electric resistance furnaces with control unit.

Figure 5 Metallic Die **Figure 6 Casting after solidification**

Table 6 Charge calculation for Furnace

System	Composition	Aluminium (Grams)	Magnesium (Grams)	Total Mass (Grams)
A	Pure Aluminium	1500	-	1500
B	Pure Aluminium + 2.5 weight percent Magnesium	1462	38	1500
C	Pure Aluminium + 4.5 weight percent Magnesium	1432	68	1500
D	Pure Aluminium + 6.5 weight percent Magnesium	1400	100	1500
E	Pure Aluminium + 8.5 weight percent Magnesium	1370	130	1500

6.1.3 Chemical Analysis and Mechanical Properties Evaluation

Chemical analysis of develop alloy was carried out with Bruker Q4 TASMANA advance CCD based optical emission spectroscopy according to ASTM E1251:2017. This method describes the analysis of aluminium and their alloy by spark-atomic emission spectrometry .Hardness testing was carried out on Brinell hardness tester with ball indenter according to IS 1500 (Part 1): 2013 at 250 Kg load. Sample is cut from casting and polished with 1200 grit paper and after that hardness testing is carried out. Tensile testing was carried out on Universal Testing Machine at according to IS 1608 (Part 1) : 2018 at 250.

6.1.4 Microstructure and Phase analysis

Test specimens were prepared by conventional metallographic 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 using Olympus GX-41 optical microscope and JEOL 5610 LV Scanning Electron Microscope (SEM) with Energy Dispersive Spectroscopy (EDS) at different magnifications. X-Ray Diffraction (XRD) with Pan Analytical X'pert Pro Machine is carried out using Cu as the anode material with a k-alpha wavelength of 1.54060 Å for phase identification. Grain Size Measurement is accomplished by Optical microscope according to ASTM-112-13 practice.

6.1.5 Corrosion Analysis

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±0.5 cm height and 2.54 cm diameter were given the exposure of 3.5 weight percent NaCl solution. Corrosion solution was produced by dissolving 3.5±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 alloy and consider the average of that value. All the alloy samples were immersed in 3.5% NaCl solution upto 8 weeks. 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.

Corrosion Rate (MPY) = 534/DAT

Where, W = Weight loss (gm), D = Density (gm/cc), A = Area (inch2), T = Time (Hrs)

A potentiodynamic study is carried out to find out corrosion potential and corrosion current of developed alloy 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 (develop alloy), mild steel is a counter electrode and a standard calomel electrode is used as a reference electrode. Environment is 3.5% NaCl for testing and test sample were giving exposure of Environment on 1*1 cm window.

6.1.6 Cold Working

Casted rod of each alloy was cut in the same size and after that 20% and 30% height reduction is carried out by vertical mechanical press at 250 kg load and at room temp. Graphical representation of height reduction is shown in fig 7.

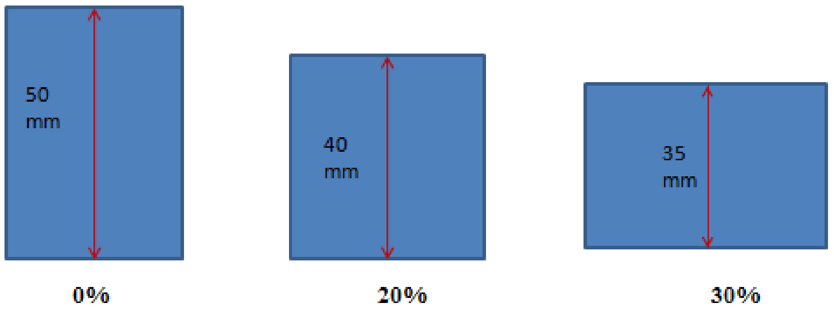


Figure 7 Graphical representation of height reduction

6.2 Result and Discussion

6.2.1 Chemical Analysis

The chemical composition of the developed alloy was listed in Table 7.

Table 7.Chemical Composition of Aluminium (Al) - Magnesium (Mg) Alloy

Elements (%)	Pure Al	Al + 2.5% Mg	Al + 4.5% Mg	Al + 6.5% Mg	Al + 8.5 %Mg
Mg	0.001	2.461	4.537	6.305	8.794
Si	0.056	0.090	0.084	0.086	0.082

Zn	0.010	0.047	0.054	0.009	0.070
Fe	0.127	0.128	0.182	0.149	0.154
Cu	0.006	0.017	0.003	0.006	0.007
Al	99.78	96.87	94.74	93.08	90.47

6.2.2 Hardness Measurement

Hardness testing was accomplished by a Brinell hardness tester at 250 Kg load for pure aluminium and aluminium containing 2.5 weight percent Magnesium, 4.5 weight percent Magnesium, 6.5 weight percent Magnesium and 8.5 weight percent Magnesium alloys without cold working and also for 20% and 30% cold worked alloys. BHN value of all developed alloy reported in Table 8. The result shows a continuously increasing hardness value compared to pure aluminium. This was observed due to precipitation hardening and formation of the secondary particles during solidification which promotes the hardening process and a remarkable change in hardness is observed. Cold worked samples showed more hardness compared to as cast alloy this is due to external strain applied during the working and grain structure of alloy got deformed and alloy became harder and stronger thereby as percentage of cold worked increase hardness value is increased.

Table 8 Hardness value of as cast and cold worked alloy

Sr .no	Developed alloy	As Cast BHN	20% Cold work BHN	30% Cold work BHN
1	Pure Aluminium	20	25	32
2	Al + 2.5% Mg	50	61	69
3	Al + 4.5% Mg	66	77	79
4	Al + 6.5% Mg	80	85	99
5	Al + 8.5% Mg	77	86	97

6.2.3 Tensile Testing

Tensile testing was accomplished by Universal Testing Machine at 250 kg load and observation is reported in Table 9. From the result and observation opines that as the amount of Magnesium increases, the tensile value increases.Magnesium gives rise to formation of intermetallics compounds and these phases improve the strength of the pure aluminium by solid solution strengthening. These phases are generally located at the grain boundary. As the concentration of Mg is increased grain boundary thickness is increased. This makes the grain boundary brittle and weakens so at higher levels of Mg a slight reduction in strength is observed. Also in case of cold worked alloy tensile strength is increased as the amount of cold worked increased; this is achieved due to work hardening. Grain structure became uniformed and equiaxed after working which will improve the strength of the alloy

Table 9 Tensile value of as cast and cold worked alloy

Sr .no	Developed alloy	As Cast UTS (N/mm^2)	20% Cold work UTS (N/mm^2)	30% Cold work UTS (N/mm^2)
1	Pure Aluminium	63	79	100
2	Al + 2.5% Mg	149	182	206
3	Al + 4.5% Mg	155	165	192
4	Al + 6.5% Mg	177	209	212
5	Al + 8.5% Mg	170	207	210

6.2.4 Grain Size Measurement

Average ASTM grain size number is measured with the help of an optical microscope; all results are reported in Table 10. From observation it has been noted that as the amount of Magnesium increases the grain size number increases. Generally Magnesium and its intermetallics is gathered 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. Grain Size is more reduced after the cold working.

Table 10 Average ASTM grain size number of as cast and cold worked alloy

Sr .no	Developed alloy	As Cast	20% Cold work	30% Cold work
1	Pure Aluminium	2-3	3-4	4-5
2	Al + 2.5 Mg	4-5	5-6	5-6
3	Al + 4.5 Mg	5-6	6-7	6-8
4	Al + 6.5 Mg	6-7	6-8	6-8
5	Al + 8.5 Mg	6-7	6-8	6-8

6.2.5 XRD Analysis

The XRD was carried out using Cu as the anode material with a k-alpha wavelength of 1.54060 Å to characterize various phases present in the alloy. The scan range was 10° to 110°. Phase analysis of pure aluminium (A), Aluminium with 2.5% Magnesium (B), Aluminium with 4.5% Magnesium. Aluminium with 6.5% Magnesium (D), Aluminium with 8.5% Magnesium (EE) shows in fig 8.

All the alloys show α-Aluminium phase but as the Mg content, increasing intensity of the α-Aluminium phase is changing as shown in table 11. The peak of all planes shifted towards the left as the Mg content increases and also the area and height of the peak is changed as compared to the pure aluminium pattern which confirms the presence of Mg. Here, no separate peak for magnesium or aluminium-magnesium intermetallic was observed. As discussed earlier in the introduction part of this magnesium have maximum solid solubility in aluminium is 14.9 wt. % at 451^{o}C. Magnesium is soluble in aluminium so when we are going to add magnesium, it goes into the solid solution of aluminium. That's why we don't observe a peak for magnesium due to the low amount of addition.

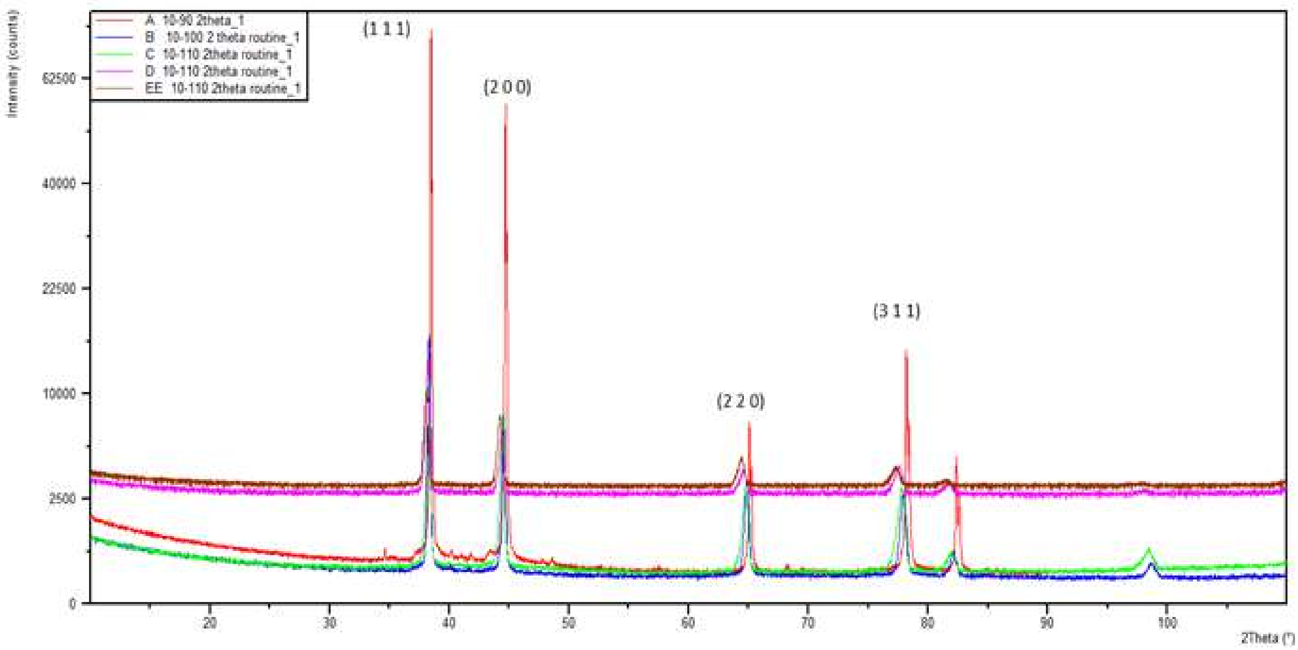


Figure 8 XRD pattern of (A) Pure Aluminium (B) Aluminium with 2.5% Magnesium (C) Aluminium with 4.5% Magnesium (D) Aluminium with 6.5% Magnesium (EE) Aluminium with 8.5% Magnesium

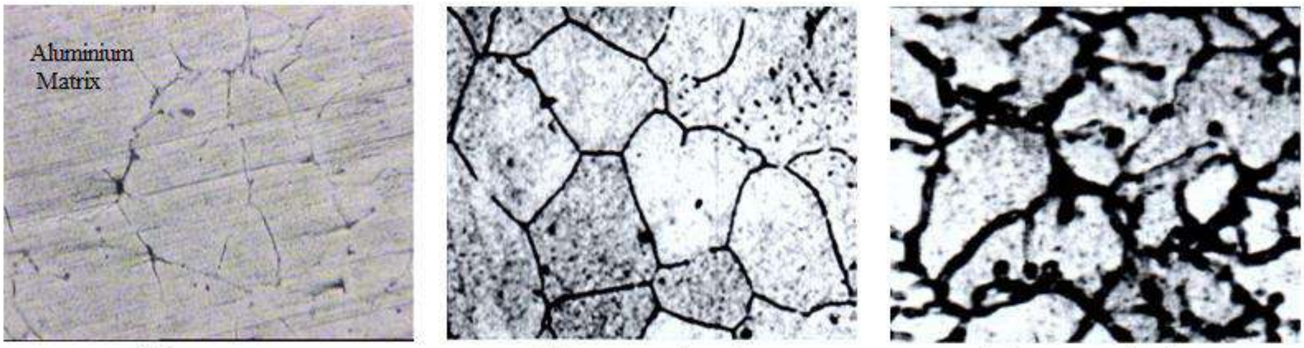
Table11. Values of 2θ and d-spacing for pure aluminium and aluminium containing 2.5 weight percent Magnesium, 4.5 weight percent Magnesium, 6.5 weight percent Magnesium and 8.5 weight percent Magnesium.

Plane	Pure Al		Al+ 2.5% Mg		Al+ 4.5% Mg		Al+ 6.5% Mg		Al+ 8.5% Mg	
	2θ	d	2θ	d	2θ	d	2θ	d	2θ	d
(1 1 1)	38.4460	2.33959	38.2897	2.34877	38.2499	2.35113	38.1844	2.35501	38.0183	2.36492
(2 0 0)	44.6903	2.02612	44.5261	2.03321	44.4432	2.03681	44.3792	2.03960	44.2102	2.04700
(2 2 0)	65.0656	1.43236	64.8209	1.43718	64.7691	1.43820	64.6503	1.44056	64.4436	1.44468
(3 1 1)	78.1835	1.22160	77.9498	1.22468	77.7216	1.22770	77.5438	1.23007	77.3834	1.23222

6.2.6 Microstructural Analysis

The typical Microstructure of pure aluminium and aluminium containing 2.5 weight percent Magnesium, 4.5 weight percent Magnesium, 6.5 weight percent Magnesium and 8.5 weight percent Magnesium with optical microscope and SEM with EDS Analysis are described below. Fig 9 shows typical Microstructure of pure aluminium which was taken by optical microscope at 100X. In which (a) shows as cast condition while correspondingly (b) and (c) shows 20% and 30% height reduction by Mechanical press. Fig 10 Shows EDS analysis of pure aluminium and Fig 11 shows SEM images at 100X. In which (a) shows as cast condition while correspondingly (b) and (c) shows 20% and 30% height reduction by Mechanical press.

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. α aluminium and another is an intermetallic compound of aluminium and magnesium i.e. β phase (Al3Mg2) which is form by eutectic reaction. This β phase is generally concentrated on the grain boundary. Fig 9 (a) Shows Microstructure of pure aluminium without the addition of magnesium containing only an aluminium matrix and fine insoluble particles. which is confirmed by EDS analysis as shown in fig 10. While fig 9(b) and 9(c) shows cold worked structure of pure aluminium which shows more refined and elongated aluminium grains compare to pure aluminium.



(a) As Cast (b) 20% Reduction (b) 30% Reduction

Figure 9 typical Microstructure of pure aluminium by optical microscope at 100X.

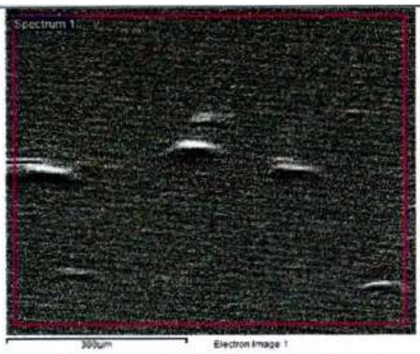
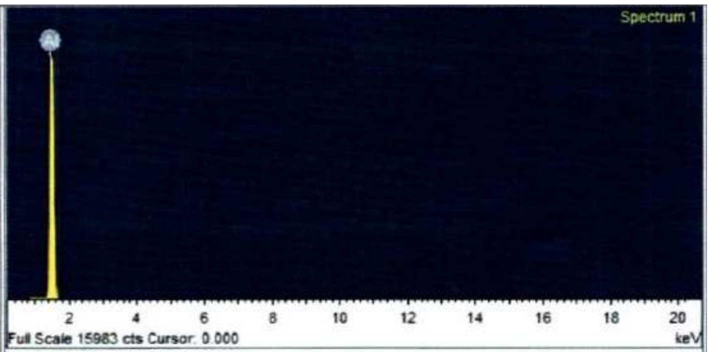
			
Secondary Electron Image		Energy Spectrum	
Element	**Wt. (%)**	**Element**	**Wt. (%)**
Aluminium	100.00		

Figure 10 EDS Analysis of pure aluminium

As shown in Fig 11 (a) the grey portion shows an α - aluminium matrix and fig 11(b) and 11(c) shows more refined structure due to cold working.

Fig 12 shows typical Microstructure of pure aluminium containing 2.5% Magnesium which was taken by optical microscope at 100X. In which (a) shows as cast condition while correspondingly (b) and (c) shows 20% and 30% height reduction by Mechanical press. Fig 13 Shows EDS analysis of pure aluminium containing 2.5% Magnesium and Fig 14 shows SEM images at 100X. In which (a) shows as cast condition while correspondingly (b) and (c) shows 20% and 30% height reduction by

Mechanical press. As shown in Fig 12 white portion shows α aluminium matrix and presence of Magnesium in a small dark circle which is unreacted Magnesium because solubility of Mg is limited to 1.4 weight% at room temp so Magnesium will remain in only solid solution and some Mg is react with Aluminium and form Intermetallic compound which is concentrated at the grain boundary. Fig 13 shows EDS analysis of the alloy which confirms the Magnesium presence at the grain boundary and possible phase formation is Al_6Mg or Al_3Mg_2 according to chemistry. SEM images also describe the Grey portion as an alpha aluminium matrix; black circle shows unreacted Magnesium and some intermetallic formation at the grain boundary as indicated by Fig 14. In Both Optical Microstructure and SEM images condition (b) and (c) shows small and refined grains due to mechanical working and grain size is also reduced which is confirmed by grain size measurement.

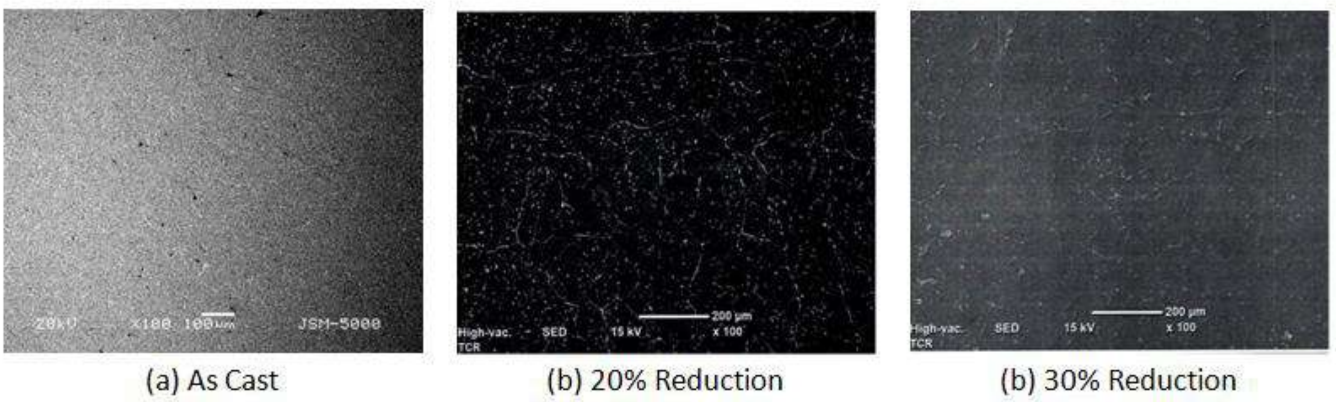


Figure 11 Microstructure of pure aluminium by SEM at 100X

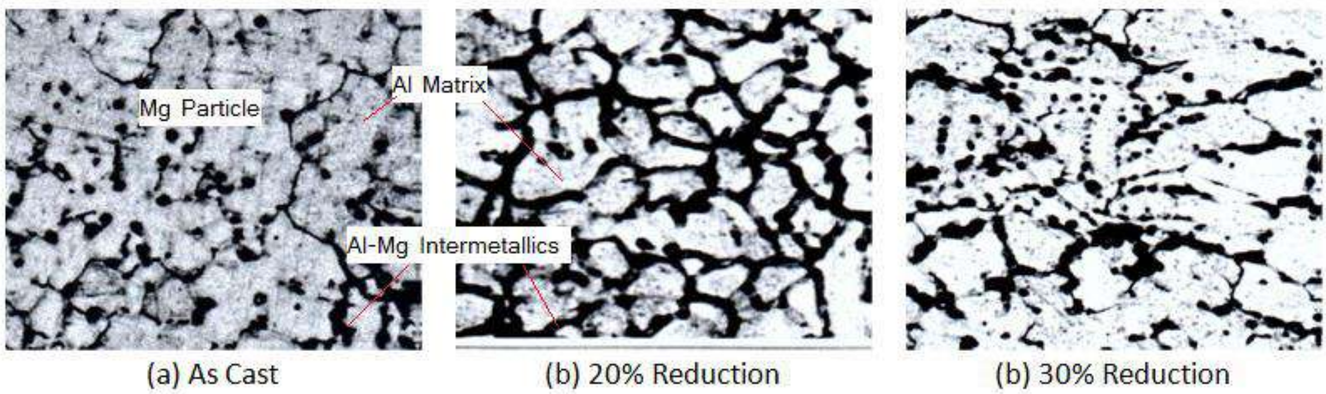
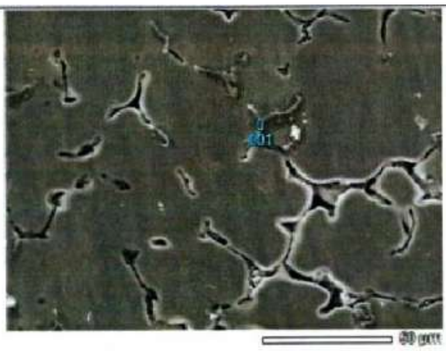


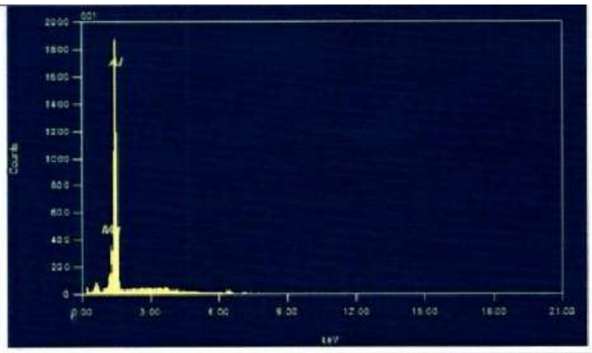
Figure 12 Microstructure of pure aluminium containing 2.5% Magnesium by optical microscope at 100X

Fig 15 shows typical Microstructure of pure aluminium containing 4.5% Magnesium which was taken by optical microscope at 100X. In which (a) shows as cast condition while correspondingly (b) and (c) shows 20% and 30% height reduction by Mechanical press. Fig 16 Shows EDS analysis of pure aluminium containing 4.5% Magnesium and Fig 17 shows SEM images at 100X. In which (a) shows as cast condition while correspondingly (b) and (c) shows 20% and 30% height reduction by Mechanical press.

As shown in Fig 15 white portion is an aluminium matrix and magnesium is present at the grain boundary which is in dark black colour. As the magnesium content is increasing grain boundary formation increasing as compare to microstructure of pure aluminium containing 2.5% Mg which is due to formation of intermetallics of aluminium and magnesium i.e Al_3Mg_2 this phase have a tendency to concentrate at the grain boundary. EDS analysis of pure aluminium containing 4.5% Magnesium confirms the presence of magnesium as shown in Fig 16 and SEM images of pure aluminium containing 4.5% Magnesium as shown in Fig 17 indicate the same thing as observed in optical microstructure. After the cold working grain boundary comes closer and refined structure is formed which is describe by SEM image also as shown in Fig 17.



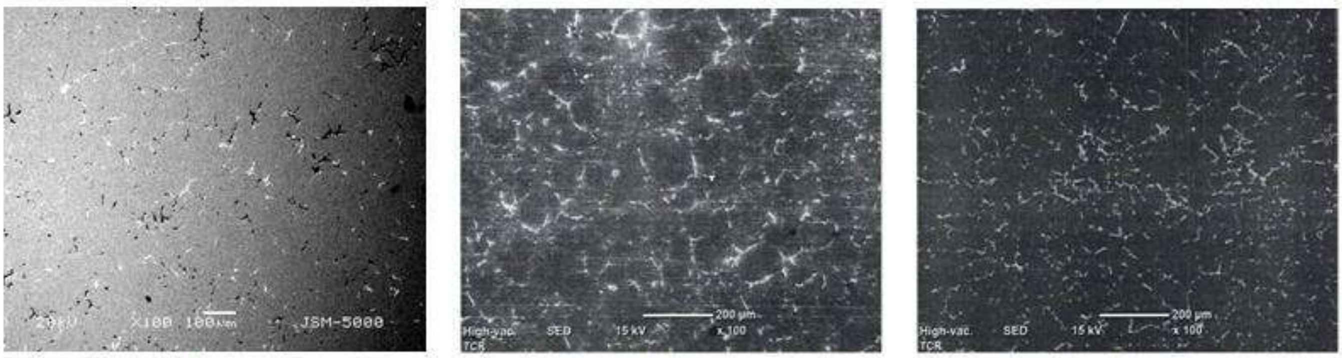
Secondary Electron Image



Energy Spectrum

Element	Wt. (%)	Element	Wt. (%)
Magnesium	3.84	Aluminium	96.16

Figure 13 EDS Analysis of pure aluminium containing 2.5% Magnesium



(a) As Cast (b) 20% Reduction (b) 30% Reduction

Figure 14 Microstructure of pure aluminium containing 2.5% Magnesium by SEM at 100X

Fig 18 shows typical Microstructure of pure aluminium containing 6.5% Magnesium which was taken by optical microscope at 100X. In which (a) shows as cast condition while correspondingly (b) and (c) shows 20% and 30% height reduction by Mechanical press. Fig 19 Shows EDS analysis of pure aluminium containing 4.5% Magnesium and Fig 20 shows SEM images at 100X. In which (a) shows as cast condition while correspondingly (b) and (c) shows 20% and 30% height reduction by Mechanical press. As shown in Fig 18 white portion is an α aluminium matrix and magnesium is present at the grain boundary which is in dark black colour. Here, Gathering and clustering of Al_3Mg_2 is increasing and the network of grain boundaries is also increasing. Presence of Al_3Mg_2 at the grain boundary which was confirmed by EDS analysis which is shown in Fig 19 and SEM images as shown in fig 20 also confirmed the same.

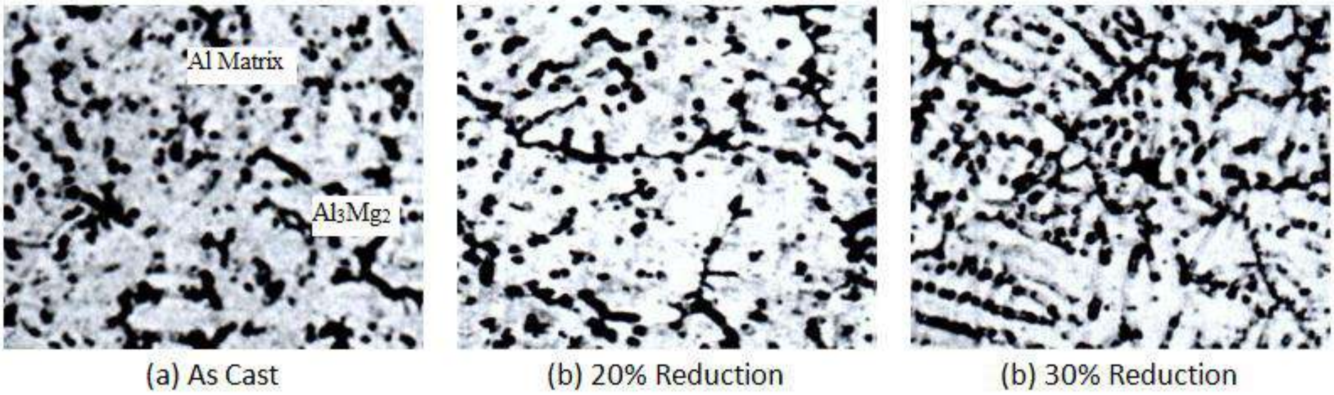
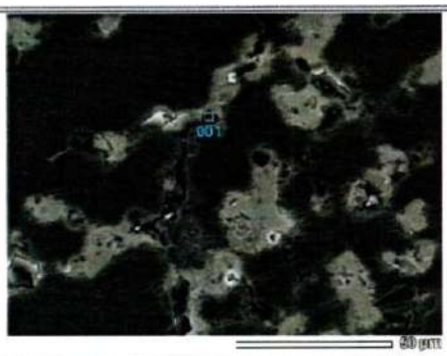
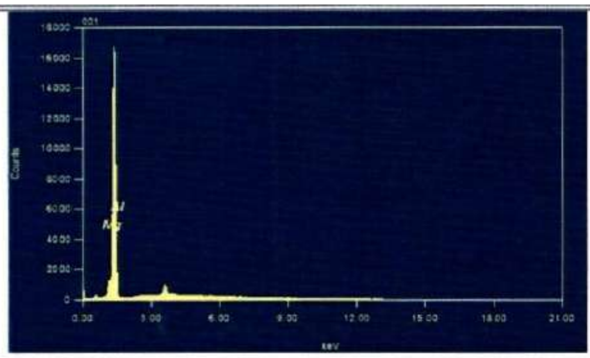


Figure 15 Microstructure of pure aluminium containing 4.5% Magnesium by optical microscope at 100X





Secondary Electron Image		Energy Spectrum	
Element	**Wt. (%)**	**Element**	**Wt. (%)**
Magnesium	5.68	Aluminium	94.32

Figure 16 EDS Analysis of pure aluminium containing 4.5% Magnesium

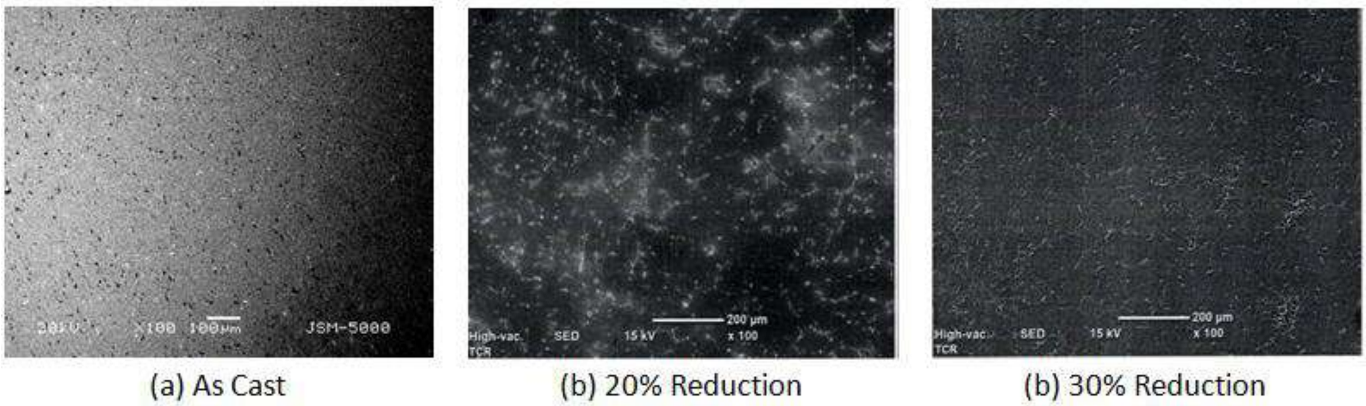
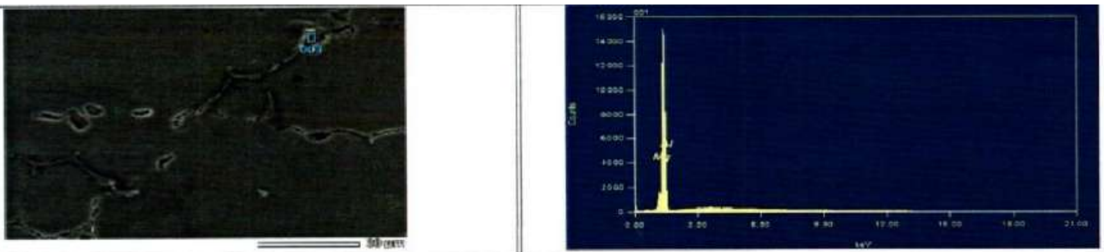


Figure 17 Microstructure of pure aluminium containing 4.5% Magnesium by SEM at 100X

Fig 21 shows typical Microstructure of pure aluminium containing 8.5% Magnesium which was taken by optical microscope at 100X. In which (a) shows as cast condition while correspondingly (b) and (c) shows 20% and 30% height reduction by Mechanical press. Fig 22 Shows EDS analysis of pure aluminium containing 4.5% Magnesium and Fig 23 shows SEM images at 100X. In which (a) shows as cast condition while correspondingly (b) and (c) shows 20% and 30% height reduction by Mechanical press. As shown in Fig 21 white portion is an α aluminium matrix and magnesium is present at the grain boundary which is in dark black colour. Here, Gathering and clustering if Al_3Mg_2 is increasing compare 6.5% Mg and Thickness of grain boundary is also increasing. Due to clustering at grain boundary mechanical properties decrease after more magnesium addition. Presence of Al_3Mg_2 at the grain boundary which was confirmed by EDS analysis which is shown in Fig 19 and SEM images as shown in fig 20 also confirmed the same. Reduction giving more compacted structure compared to as cast.

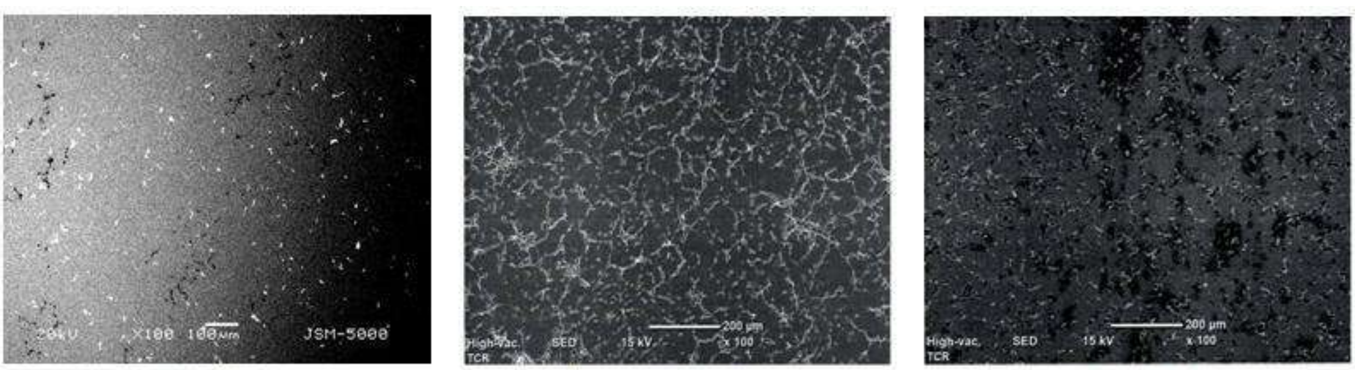
(a) As Cast (b) 20% Reduction (b) 30% Reduction

Figure 18 Microstructure of pure aluminium containing 6.5% Magnesium by optical microscope at 100X



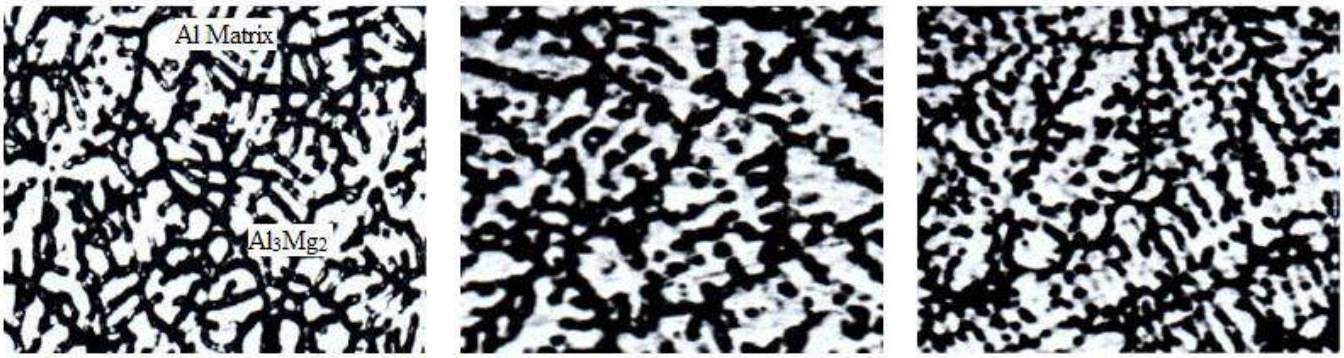
Element	Wt. (%)	Element	Wt. (%)
Magnesium	8.30	Aluminium	91.70

Figure 19 EDS Analysis of pure aluminium containing 6.5% Magnesium



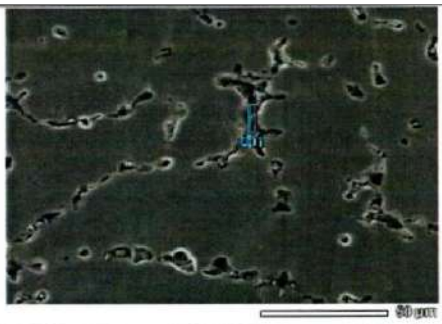
(a) As Cast (b) 20% Reduction (b) 30% Reduction

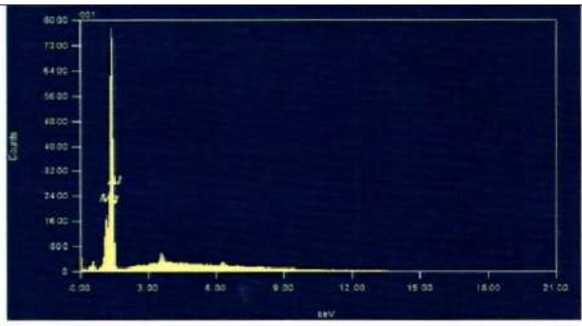
Figure 20 Microstructure of pure aluminium containing 6.5% Magnesium by SEM at 100X



(a) As Cast (b) 20% Reduction (b) 30% Reduction

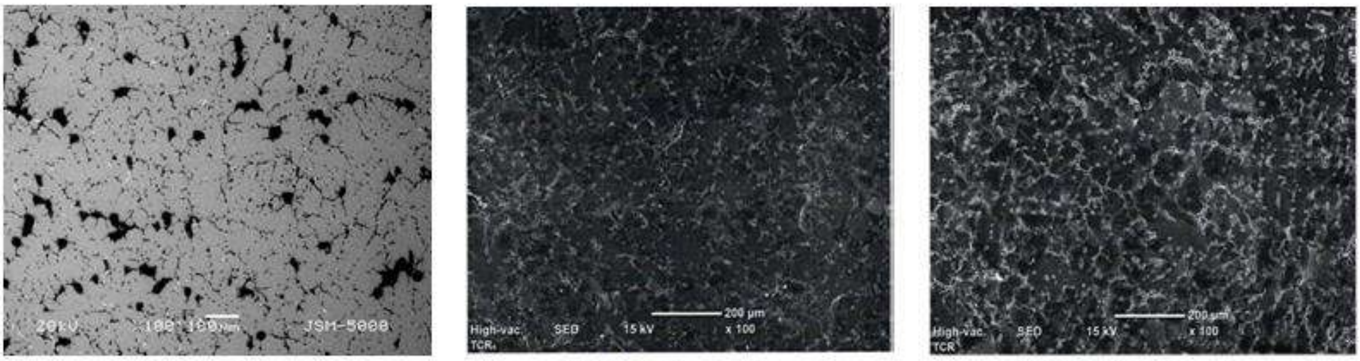
Figure 21 Microstructure of pure aluminium containing 8.5% Magnesium by optical microscope at 100X





Secondary Electron Image		Energy Spectrum	
Element	**Wt. (%)**	**Element**	**Wt. (%)**
Magnesium	14.52	Aluminium	85.48

Figure 22 EDS Analysis of pure aluminium containing 8.5% Magnesium



(a) As Cast (b) 20% Reduction (b) 30% Reduction

Figure 23 Microstructure of pure aluminium containing 8.5% Magnesium by SEM at 100X

6.2.7 Corrosion Analysis

The corrosion rate of pure aluminium (As cast, 20% Reduction, 30% Reduction), Aluminium with 2.5% Magnesium (As cast, 20% Reduction, 30% Reduction), Aluminium with 4.5% Magnesium(As cast, 20% Reduction, 30% Reduction), Aluminium with 6.5% Magnesium (As cast, 20% Reduction, 30% Reduction) & Aluminium with 8.5% Magnesium(As cast, 20% Reduction, 30% Reduction) by standard weight loss methods are shown in fig 24.

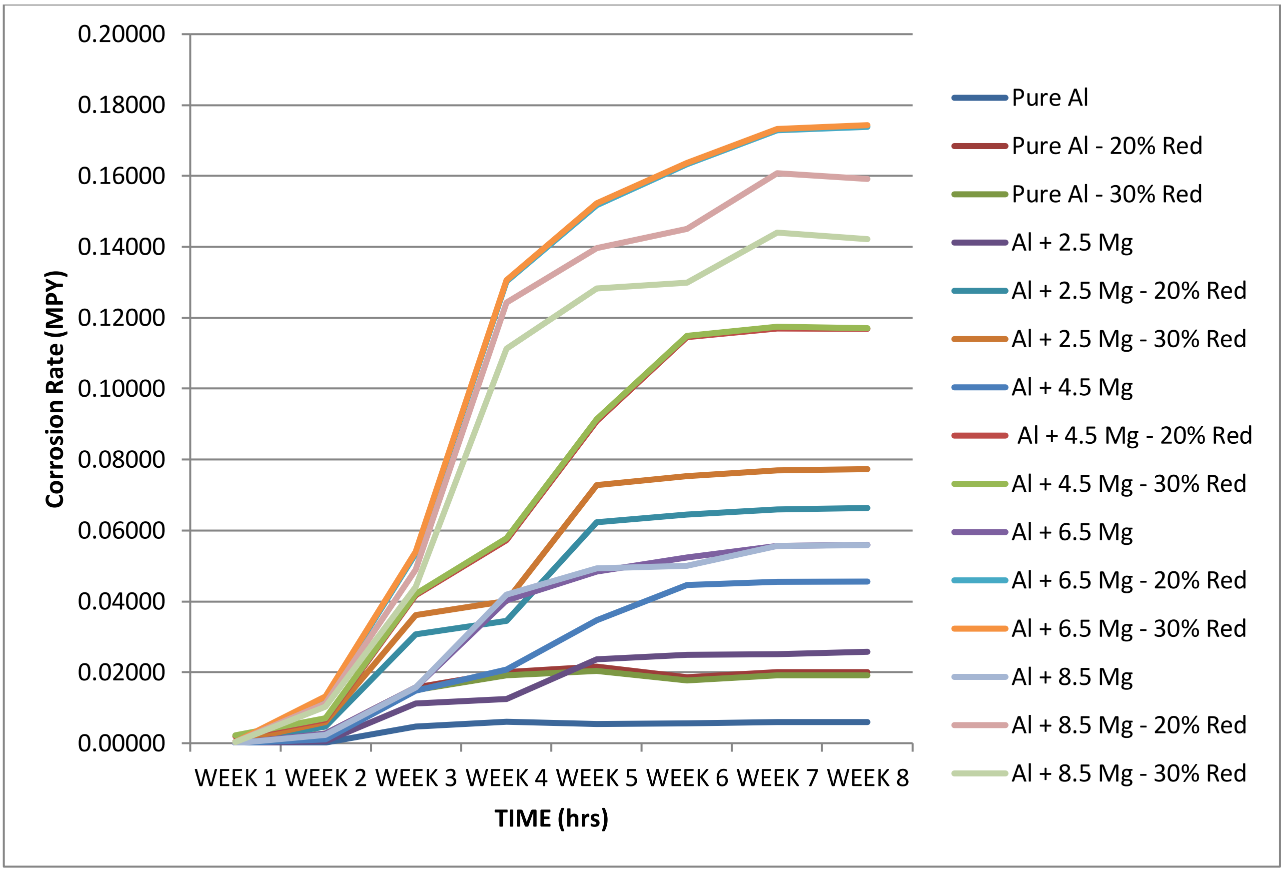
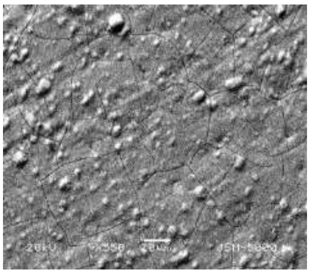
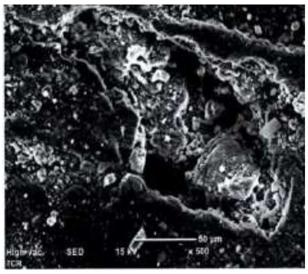
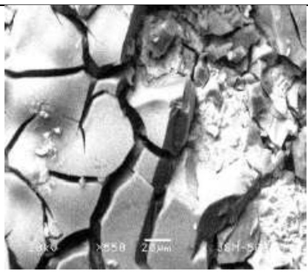
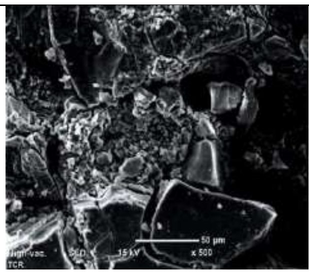
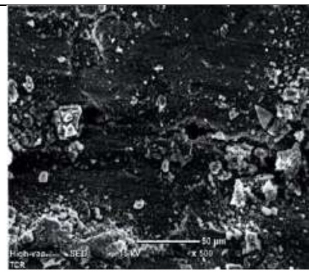
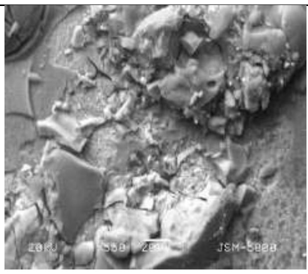
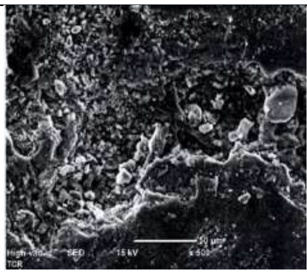
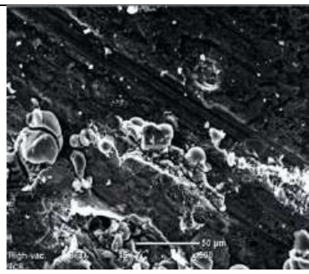


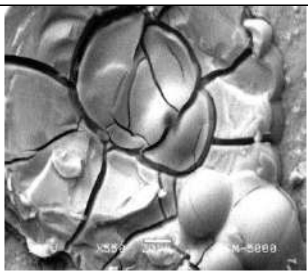
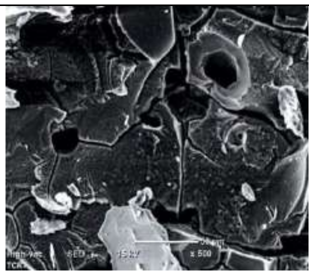
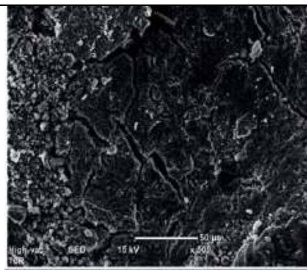
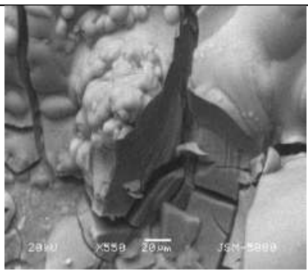
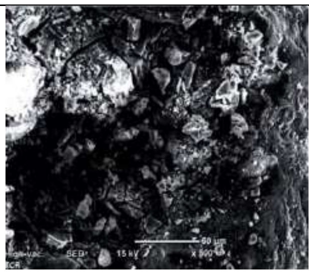
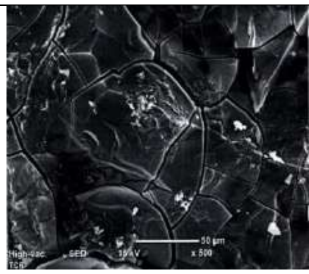
Figure 24 Corrosion Rate by Standard Weight Loss methods

As the observed plot of corrosion rate versus time is linearly communicated that the corrosion rate of pure aluminium and its alloy with different amounts of magnesium and with different amount of reduction is increased with time of exposure. Observation confirms as the amount of magnesium increasing the corrosion rate is increasing as well as the reduction increasing also increased corrosion rate. In the case of pure aluminium, the corrosion rate is almost at a steady value range because of the formation of the passive layer. Generally pitting is observed in chloride containing environments and formation of pits mainly start at manufacturing and mechanical defects, second phase particles are formed during solidification and mechanical treatments. These were observed in magnesium-containing alloys. Magnesium is going to form a second phase particle called β phase (Al_3Mg_2). This intermetallic compound or second phase particle has different electrochemical properties which form corrosion or galvanic cell between intermetallic compound (β phase) and aluminium solid solution (α-Al matrix). The difference in potential of intermetallic and matrix is the driving force for galvanic 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 β phase is act as an anode and the α-Al matrix act as a cathode in a galvanic cell. These lead to localised corrosion or dealloying. Under chemical attack, this anodic phase is dissolved leaving behind cavities or pits. This condition was observed at higher magnesium content because the volume fraction of the β phase is higher. This phase acts as an initiation site for corrosion. After reduction, the microstructure becomes more uniform so more grain boundary area is available for initiation of corrosion.

SEM Analysis is carried out after 8 weeks of 3.5% NaCl exposure and images are recorded in Table 13. All the alloys show general corrosion, Pitting Corrosion and grain boundary corrosion to different extent. In the case of pure aluminium general surface corrosion is observed and an oxide film is observed and this was more observed in cold work a sample which implies cold working improves the corrosion by breaking down the passive film. In the case of 2.5% Mg content alloy surface corrosion is observed as the magnesium content increases in alloy more corrosion is observed and in case of 20% and 30% reduction more corroded surface is observed. While in case of 4.5% Mg grain boundary corrosion is observed due to magnesium concentrated at grain boundary and it will increase in case of reduction because more grain boundary area is available to initiate corrosion. In Case of 6.5% Mg and 8.5% Mg grain boundary corrosion and pitting is also observed at various locations on the surface; this is due to high magnesium content. Alloys containing high intermetallic will possess more pits on the surface. More pit and surface roughness is observed in cold worked samples.

Table 12 Comparison of SEM Images at 500X

Pure Aluminium			
	(a) As Cast	(b) 20% Reduction	(b) 30% Reduction
Al + 2.5% Mg			
	(a) As Cast	(b) 20% Reduction	(b) 30% Reduction
Al + 4.5% Mg			
	(a) As Cast	(b) 20% Reduction	(b) 30% Reduction

Al + 6.5% Mg			
	(a) As Cast	(b) 20% Reduction	(b) 30% Reduction
Al + 8.5% Mg			
	(a) As Cast	(b) 20% Reduction	(b) 30% Reduction

The corrosion rate of pure aluminium (As cast, 20% Reduction, 30% Reduction), Aluminium with 2.5% Magnesium (As cast, 20% Reduction, 30% Reduction), Aluminium with 4.5% Magnesium(As cast, 20% Reduction, 30% Reduction), Aluminium with 6.5% Magnesium (As cast, 20% Reduction, 30% Reduction) & Aluminium with 8.5% Magnesium(As cast, 20% Reduction, 30% Reduction) by Potentio dynamic study are given in Table 13

Table 13 Corrosion Rate Measurement by Potentio dynamic study

Sr.No	Alloy	I corr (µA)	E corr (mV)	Corrosion rate (mpy)
1	Pure Al	14.6	-920	25.05
2	Pure Al - 20% Red	40.09	-750	70.27
3	Pure Al - 30% Red	38.3	-779	68.82
4	Al+2.5 Mg	19.3	-985	33.1
5	Al+2.5 Mg- 20% Red	21.7	-753	37.27
6	Al+2.5 Mg- 30% Red	24.6	-882	39.21
7	Al+4.5 Mg	28.2	-1170	48.42
8	Al+4.5 Mg- 20% Red	32	-800	64.01
9	Al+4.5 Mg- 30% Red	39	-804	67.01
10	Al+6.5 Mg	31.2	-1320	53.56
11	Al+6.5 Mg- 20% Red	113	-1050	194.4
12	Al+6.5 Mg- 30% Red	110	-1010	192.44
13	Al+8.5 Mg	33.9	-1320	58.16
14	Al+8.5 Mg- 20% Red	63	-856	102
15	Al+8.5 Mg- 30% Red	72	-891	123

Polarization curve of pure aluminium, Aluminium with 2.5% Magnesium, Aluminium with 4.5% Magnesium, Aluminium with 6.5% Magnesium and Aluminium with 8.5% Magnesium recorded in fig 25.

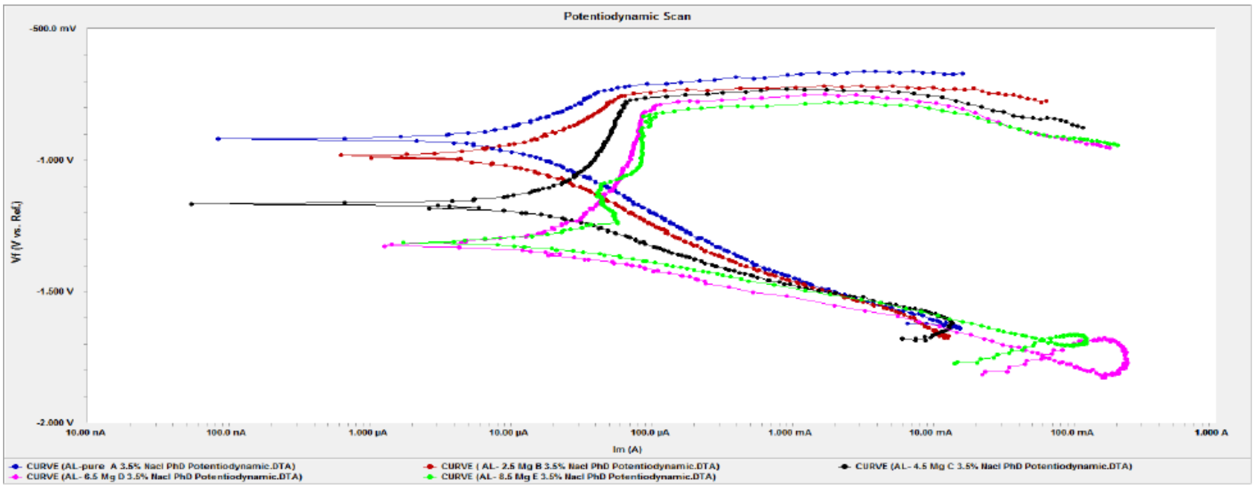


Figure 25 Polarization curve of pure aluminium, Aluminium with 2.5% Magnesium, Aluminium with 4.5% Magnesium, Aluminium with 6.5% Magnesium and Aluminium with 8.5% Magnesium

A comparison of corrosion behavior of pure aluminium and aluminium alloys with a variation of magnesium amount is done. Polarisation curves give the idea about dissolution reaction and reduction reaction. The addition of more negative potential alloying elements compared to pure aluminium typically increases the corrosion potential to more noble values. All the curves show active potential as indicated by Fig 25. The corrosion potential of pure Aluminium is -920mV which becomes more negative after the addition of magnesium and the corrosion current of aluminium 14.60 µA is also increasing by magnesium addition. As more anodic metal is added in more corrosion current and corrosion potential is increasing and also the passivation curve shifts towards a more negative direction. A same phenomenon is observed in cold work samples. Cold working reduces corrosion potential in a more negative direction. Comparatively study of cast and cold worked samples are indicated by following figures.

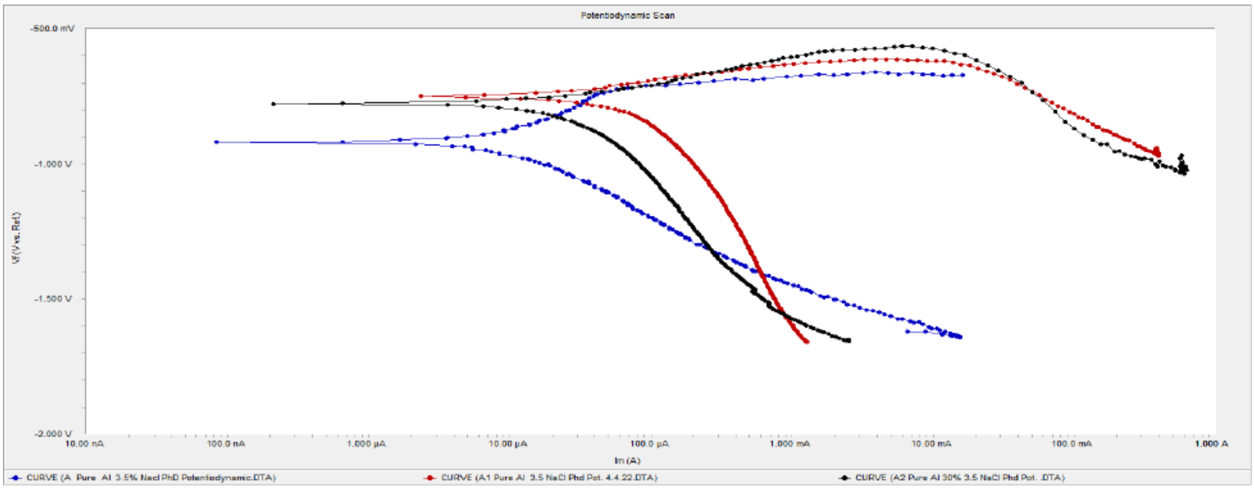


Figure 26 Polarization curve of Pure Aluminium, 20% Reduction pure aluminium and 30% Reduction pure Aluminium

Fig 26 describes corrosion behavior of pure aluminium in as cast condition and 20% and 30% cold worked condition. Cold worked samples show more negative corrosion potential compare to as cast condition which implies cold working induced the corrosion.

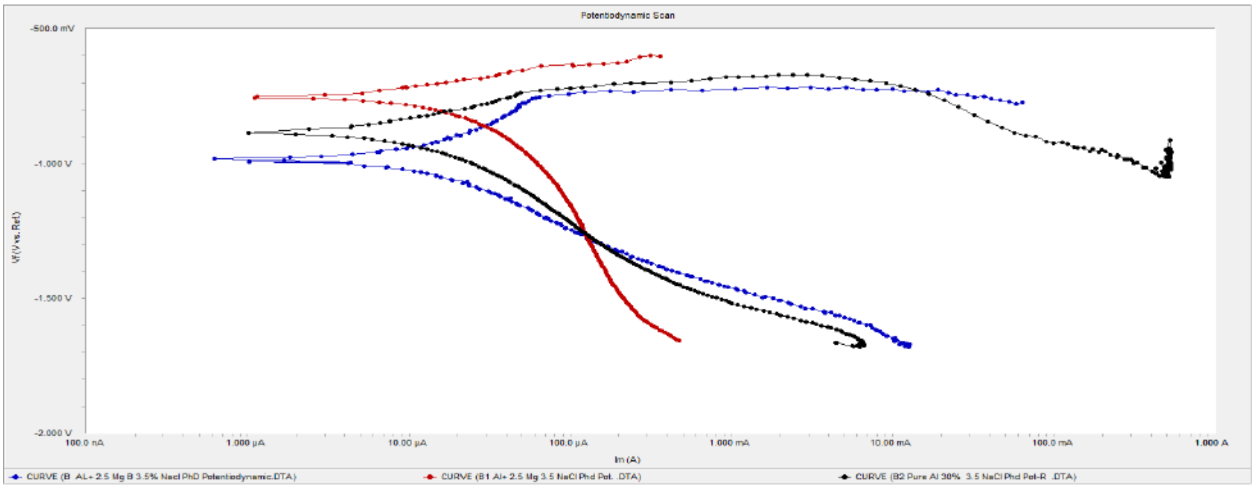


Figure 27 Polarization curve of Al+2.5% Mg, Al+2.5% Mg - 20% Reduction and Al+2.5% Mg - 30% Reduction

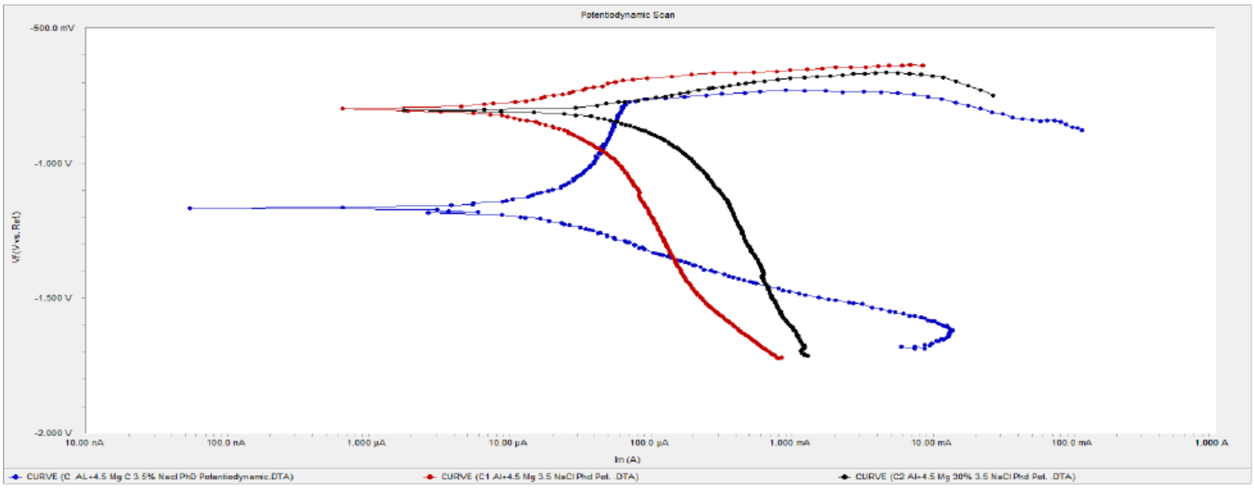


Figure 28 Polarization curve of Al+4.5% Mg, Al+4.5% Mg - 20% Reduction and Al+4.5% Mg - 30% Reduction

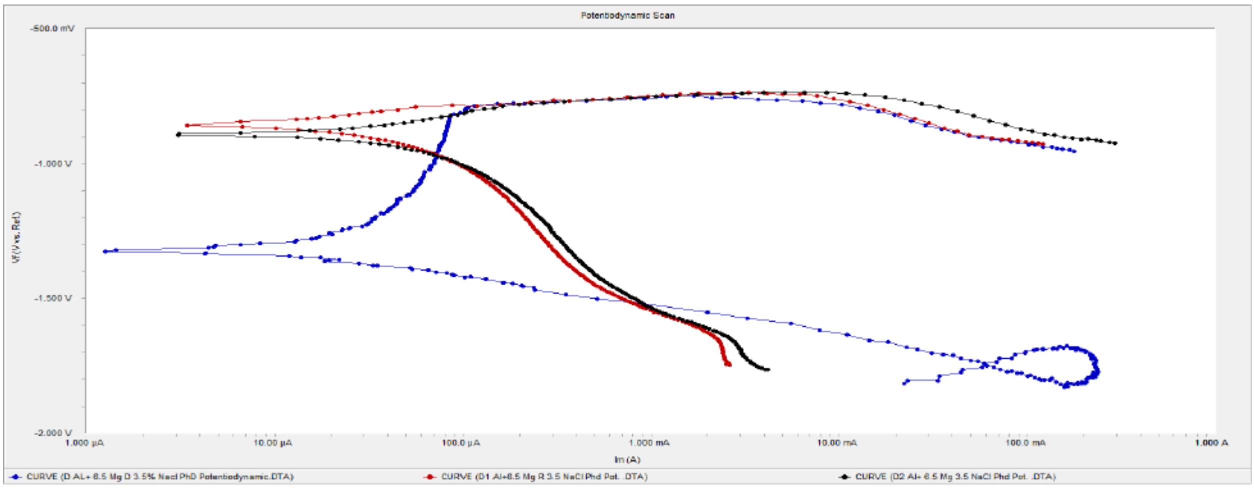


Figure 29 Polarization curve of Al+6.5% Mg, Al+6.5% Mg - 20% Reduction and Al+6.5% Mg - 30% Reduction

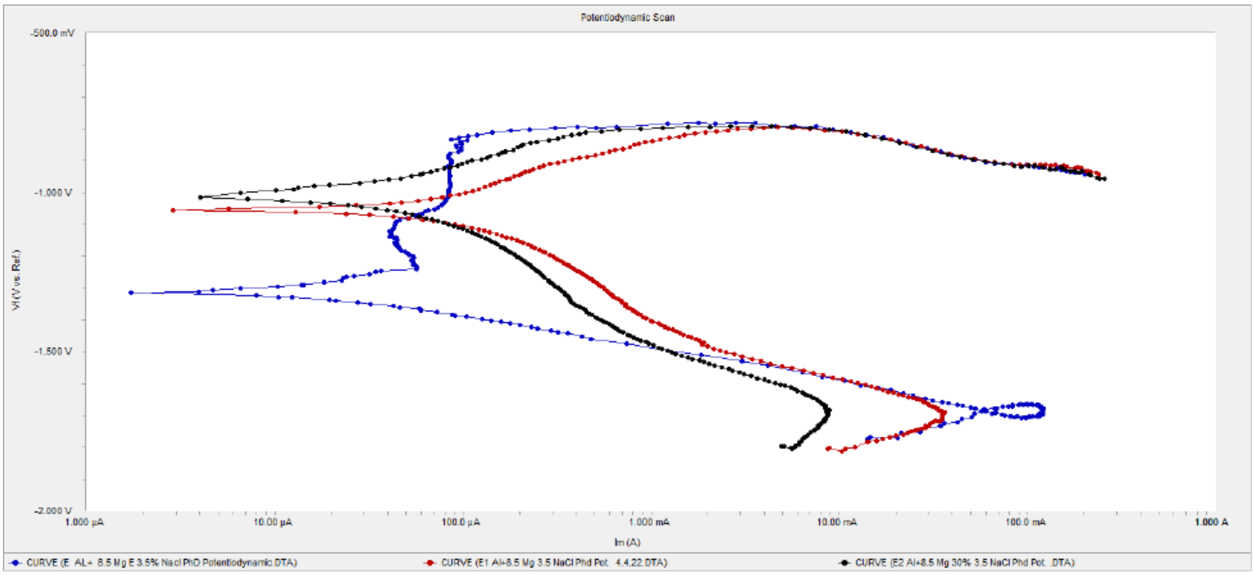


Figure 30 Polarization curve of Al+8.5% Mg, Al+8.5% Mg - 20% Reduction and Al+8.5% Mg - 30% Reduction

Similarly Fig 27, 28, 29 and 30 describe polarization curve for different Al alloys with variation of magnesium content in as cast and 20% & 30% cold worked sample. Which opines cold working improve the corrosion by reducing grain size. More uniform structure, more corrosion is observed in all cases.

7. Achievements with respect to objectives

The Main objective of this research is magnesium is alloyed with aluminium and improve the performance of aluminium sacrificial anode and effect of magnesium on mechanical properties and microstructure and electrochemical properties of aluminium and effect of cold working on mechanical properties and microstructure and electrochemical properties of aluminium.

- In the presence of a chloride-containing corrosive environment, the protective oxide layer of aluminium loses anti-corrosive properties.
- Magnesium successfully added by conventional melting practice in pure aluminium.
- Magnesium profoundly affects the properties of pure Aluminium and increases the hardness and tensile strength of pure aluminium.
- Magnesium also affects the passivation behavior of pure aluminium by changing the microstructure of pure aluminium.
- Cold working is also carried out successfully on pure aluminium and developed aluminium-magnesium alloy.
- Cold working is changing the microstructure and providing more corrosion sites to improve performance of aluminium sacrificial anode in sea water.

8. Conclusions

From all the observations and results, following conclusions are made.

- The addition of magnesium modifies microstructure with fine grain and ensures the uniform structure will also improve self corrosion of developed alloy.
- Magnesium damages the passive layer of aluminium by the formation of the β phase which prevents the formation of a homogeneous passive layer on the surface of the aluminium.
- Magnesium and its intermetallics uniformly distributed at the grain boundary upto 6.5% Magnesium after that clustering of intermetallics at the grain boundary was observed. For the reason the grain boundary was infirm and deteriorate the mechanical properties.
- Magnesium content increases hardness value 4 fold and optimum hardness observed at 6.5% Mg.
- Tensile strength increases 3 fold and optimum tensile strength is observed at 6.5% Mg.
- Aluminium 6.5 % mg shows a good combination of mechanical properties.
- The addition of magnesium reduced corrosion potential by -400mV 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.
- Cold working profoundly affects the corrosion properties of aluminium and aluminium magnesium alloy.
- Cold working increases strength and hardness of alloy by forming a more uniform structure.

9. List of publications arising from the thesis

Journal/ Conference	ISSN	Indexed	Paper title	Authors	Details
Dogo Rangsang Research Journal	2347-7180	UGC Care - 1	Performance Improvement of Aluminium sacrificial Anode by Magnesium Addition	1) Vidhi A Mistry 2) Dr Indravadan B Dave 3) Dr.Minal S Dani	Volume-12 Issue-01, January 2022
Compliance Engineering Jornal	0898-3577	UGC Care - 2	Influence of Magnesium on Mechanical Properties and Microstructure of Pure Aluminium	1) Vidhi A Mistry 2) Dr Indravadan B Dave 3) Dr.Minal S Dani 4) Dr V J Rao	Volume 13, Issue 1, January-2022

GIT-Journal of Engineering and Technology	2249 - 6157	National Journal	A Review on Effect of Alloying Element on Aluminium Anode	1) Vidhi A Mistry 2) Dr Indravadan B Dave 3) Dr.Minal S Dani	Special Edition 14th Volume-I, 2022
CORCON 2022		Asia's largest Corrosion conference in India	Improving Performance of Al-Mg Sacrificial Anode through Forging	1) Vidhi A Mistry 2) Dr Indravadan B Dave 3) Dr.Minal S Dani 4) Urvesh Vala	Presented on 15th -17th sept.
Jurnal Kejuruteraan (Journal of Engineering)	2289-7526	Worldwide Science & Goggle Scholar	Development of Al-Mg Alloy for the Protection of Steel Structure in 3.5% Nacl	1) Vidhi A Mistry 2) Dr Indravadan B Dave 3) Dr.Minal S Dani 4) Dr V J Rao	Volume – 35(5) September-2023 (Accepted on 24/03/2023)

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