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A Review on Corrosion behaviour of Mn added Magnesium and its alloys

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Abstract: This research proposal provides corrosion behaviour of Manganese added Magnesium and its alloys. Magnesium is lightest of all Engineering metals and therefore it is attractive alternatives for Steels and aluminium. The corrosion of Mg and its alloys continues to be a major technological issue preventing wider usage of such alloys. Different corrosion like Galvanic corrosion, pitting corrosion, intergranular corrosion (IGC), filiform corrosion, crevice corrosion, stress corrosion cracking (SCC), and corrosion fatigue (CF) were already discussed for Mg alloys by different researchers[13]. In Magnesium- Aluminium (Mg-Al) alloys, the formation of intermetallic $Al_8(Mn,Fe)_5$ phase improves the corrosion resistance by removing elemental iron particles from the Mg and its alloy[10]. The corrosion rate examined via electrochemical and Weight loss method (Immersion test). It was seen that samples with Mn additions exhibited an increased Fe impurity tolerance level. This indicates that the Mn addition was able to moderate the effect of the Fe impurity on the corrosion of the Mg alloy. In addition, influencing factor of corrosion behaviour of Mg alloys like effect of allying element, Microstructure and secondary phases, grain size, effect of welding and heat treatment were discussed.

Keywords: Magnesium alloy; Manganese, Aluminium, Alloying Elements, Intermetallic phase; corrosion

I. INTRODUCTION

Magnesium is lightest of all engineering metals and therefore is attractive alternatives for Steels and Aluminium in areas of automobiles, electronic production and aerospace[7]. However, it is well recognized that the corrosion of Mg and its alloys continues to be a major technological issue preventing wider usage of such alloys. There is an overwhelming demand to develop magnesium alloys with an improved corrosion resistance, with a necessary precursor being a detailed and fundamental understanding of the role of key alloying elements and impurities.

Manganese is a common addition in Magnesium alloys. While Manganese containing Mg alloys can also show some improvements in corrosion resistance and ductility, Manganese additions have little effect on tensile properties. The addition of manganese is usually strategic and aimed at lowering the effect of the iron (Fe) impurity content in order to control the overall corrosion of Mg-Al alloys. In the presence of Al and Fe, additions of Mn produce an $Al_8(Mn,Fe)_5$ phase that can moderate the corrosion rates caused by the impurity Fe. This is important, when present in Mg, any Fe is nominally insoluble and forms a pure-Fe (BCC) phase in the Mg matrix. This pure Fe has a large potential difference compared to the Mg and is able to support cathodic reactions efficiently and hence accelerates the corrosion rate dramatically [21].

Mn also is sparingly soluble in Mg, and in isolation it causes a major corrosion risk. The exact levels of Mn addition necessary to counter-act the detrimental effect of the Fe impurity are still unknown.

Main target of research work is to modify Magnesium metal or Mg alloy with better corrosion resistance property which can be use as alternative of Aluminium alloys.

II. LITERATURE REVIEW

Manganese is a common addition in Magnesium alloys. While Manganese containing Mg alloys can also show some improvements. The purpose of this review is to provide an understanding of useful research directions for producing Mg and its alloys with lower corrosion rates [8].

The need for fuel efficiency and increased performance in transportation systems continually places new demands on the materials used. The design criteria which automobile and aerospace industries are primarily concerned with are density, strength, stiffness, and corrosion resistance. Low-density materials may reduce fuel costs, increase range, and allow larger payloads. High strength and stiffness are necessary for adequate performance and safety characteristics, while corrosion resistance helps to ensure that design lifetime is achieved.

A. *Magnesium[2]:*

It is the 3rd most abundant metallic element in the earth's crust. Dolomite ($CaMgCO_3$), Magnesite ($MgCO_3$), Karnellite ($KMgCl_3.6H_2O$) and Seawater (0.13% of the element in the form of $MgCl_2$.) are sources of Mg. Production of Mg are done with Electrolytic method, Thermal-reduction method and Pidgeon method.

Mg has a good ductility, better noise and vibration dampening characteristics than Aluminum and excellent castability.

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TABLE I: COMPARISONS OF PHYSICAL PROPERTIES OF METALS

	Magnesium	Aluminum	Iron
Crystal Structure	FCC	BCC	HCP
Density	1.74	2.70	7.86
Coefficient of thermal expansion	25.2	23.6	11.7
Melting Point (°C)	650	660	1539

Advantages of Mg[2]:

- Lowest density of all commercial casting alloys.
- Magnesium alloys have a comparable strength to weight ratio to Aluminum.
- Magnesium and its alloys also have a high vibration damping capacity.
- Electromagnetic interference reduction
- Full recyclability

Limitations of Mg[2]:

- Low strength and toughness
- Low corrosion resistance
- Easily flammable

B. *Mg Alloys[1]:*

- ***Resources of Mg Alloys Manufacturing :***
  - Sand Casting
  - Die casting
  - Squeeze casting
  - Semi solid metal casting
  - Spray forming/ Spray casting
  - Melt infiltration methods

Available Forms of Mg Alloys

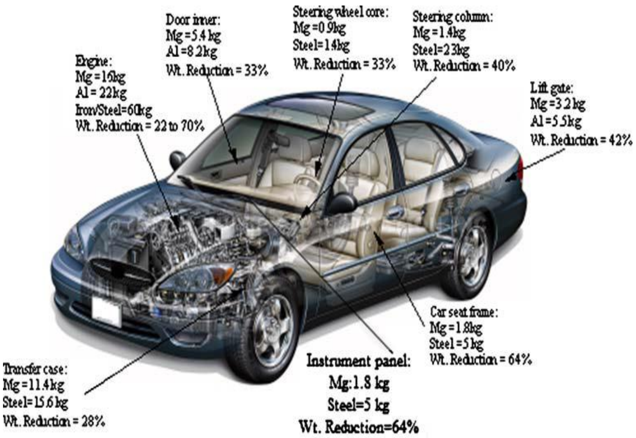
- **Wrought products**

Magnesium alloys are available as both castings and as wrought products. As castings, alloys can be cast in a variety of ways into near net shape products. In the wrought form, they can be obtained as extruded bars and shapes, forgings and rolled plates and sheets. Automobile application over Al alloys.

- ***Most common Cast alloys are***

AZ63, AZ81, AZ91, AM50, AM60, ZK51, ZK61, ZE41, ZC63, HK31, HZ32, QE22, QH21, WE54, WE43, Elektron 2

Fig. 1. Some automotive components made of Mg alloy and obtained weight reduction[14]



Property	Unit	AZ91	AM60	AM50	AM20	AE42
Ultimate Tensile	MPa	240	230	210	240	220
Tensile YS	MPa	160	130	125	90	140
Compressive YS	MPa	148	-	113	74	106
Fracture Elong.	%	7	13	15	20	15
Elastic Modulus,	GPa	45	45	45	45	45
Brinell hardness	HBS	70	65	60	45	60
Impact strength	J	9	18	18	18	16

TABLE II TYPICAL MECHANICAL PROPERTIES OF MG ALLOYS AT ROOM TEMPERATURE

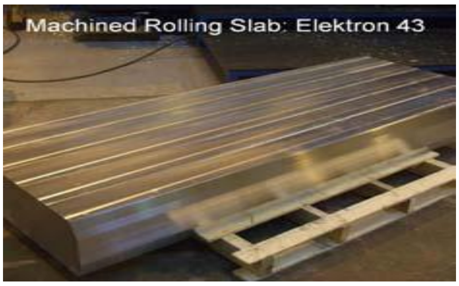
Some Developments of Mg alloys[1]:

Magnesium forged alloy wheels:

Fig:2This is ZK30 with Zn and Zr is lighter than Aluminum forged wheel which is used in Audi A8 series.

Machining Rolling slab:

Fig:3Made from Electron 43,High strength Mg alloys which used in Aircraft seat. Mg alloy with Yitrium,rare earth and Zr.



Handrails for city bus made byAZ31B:

Fig:4The curved, extruded magnesium tubing forms handrails that are lighter, thinner and stronger than Aluminum handrails.

***Magnesium Engine Front Covers Lighten the Load*:**

Fig:5Compared to Aluminum, the area tension pulley is strengthened in the magnesium cover, due to a high bending moment and compaction behavior. As engines

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become ever-lighter with magnesium, improved fuel economy and durability compare with Aluminum alloys.

Effect of alloying elements on Magnesium:

Many alloying elements can be useful in a variety of different applications whereas others are only ideal for very specific applications due to the change in properties.

1.Aluminum

- The maximum solubility is 11.5 at % (12.7 mass %) and alloys in excess of 6 mass % can be heat treated.
- Aluminum improves strength, the optimum combination of strength and ductility being observed at about 6%.
- Alloys are readily castable.
- The creep resistance is limited due to the poor thermal stability of the $Mg_{17}Al_{12}$ phase.

2. Calcium:

- Alloying with calcium is becoming more common in the development of cheap creep resistant alloys essentially replacing $Mg_{17}Al_{12}$ with $Al_{12}Ca$.
- Ca can act as a deoxidant in the melt or in subsequent heat treatment.
- It improves the roll ability of sheet but > 0.3 mass % can reduce the weld ability.

3. Cerium:

- Improves corrosion resistance.
- Increases plastic deformation capability, magnesium elongation, and work hardening rates.

4. Manganese:

- Increases saltwater corrosion resistance within some Aluminum containing alloys.
- reduces the adverse effects of iron, usually present in .2-.4 weight percent.
- Binary alloys (M1A) are used in forgings or extruded bars. The maximum amount of manganese is 1.5–2 mass %.

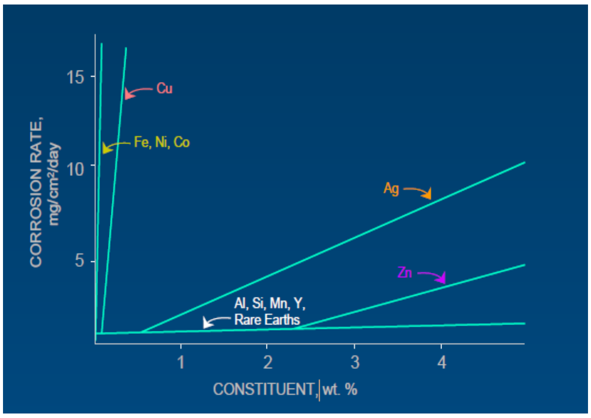
5. Silicon:

- It can increase molten alloys' fluidity
- Improves elevated temperature properties, especially creep resistance
- Only used in pressure die casting.

6. Rare Earth Metals:

- Increase in high temperature creep and corrosion resistance and strength
- Allows lower casting porosity and weld cracking in processing.

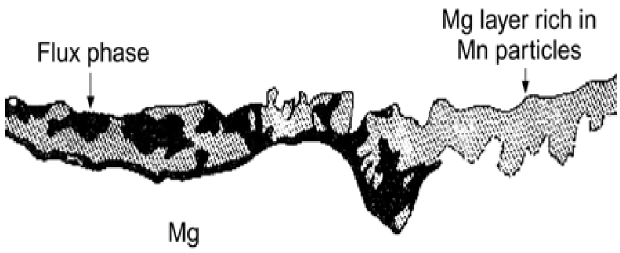
Fig 6 : Effect of alloying elements on corrosion rate of Mg alloy



Mn Addition in Mg Alloys[2]:

Manganese is added mainly for corrosion resistance. In Mg-Al alloys, Manganese combines with the detrimental impurity iron and precipitates it to the bottom of the melt as $Al_5(Mn,Fe)_2$[10]. In addition to reducing the soluble iron content in the alloy melt, the manganese, addition also passivates the residual iron that remains in solution provided the content is less than a critical limit for the alloy, referred to as the critical Fe/Mn ratio. Manganese additions can be problematic since the melting point of manganese is high and the solubility of manganese is reduced with Aluminum in the melt. Various manganese additives and addition techniques can be used. Mn can be added as anhydrous $MnCl_2$ flake, or as electrolytic manganese in the form of flake or briquettes[2]. While manganese containing Mg alloys can also show some improvements in corrosion resistance and ductility, Mn additions have little effect on tensile properties.

Fig:7Effect of addition of Mn in Mg-Al alloy



Corrosion behavior of Mg metal and Mg alloys

Magnesium alloys are corroding metals because of their active positions in both the electromotive force (EMF) series and the galvanic series for seawater. Depending on the environment and certain design considerations, the corrosion of magnesium can be well within acceptable design limits. (it is between steel and Aluminum). Knowledge of environmental factors that influence degradation, types of corrosion to which magnesium alloys are most susceptible, protection schemes, and design considerations can significantly minimize corrosion and increase use of this family of lightweight structural metals[2].

Pure magnesium is exposed to the air at RT, a gray oxide forms on its surface. Moisture converts this oxide to magnesium hydroxide, which is stable in the basic range of pH values, but is not in the neutral or acid ranges. As a

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result, in neutral and low pH environments magnesium dissolution is accompanied by hydrogen evolution. In basic environments, passivation is possible as a result of the formation of a $Mg(OH)_2$ layer on the metal surface[5].

Metal − metal ion equilibrium and Electrodepotential

Au − Au+3	1.498
Ag − Ag+	0.799
H2 − H +	0.0
Pb − Pb+2	− 0.126
Sn − Sn+2	− 0.136
Ni − Ni+2	− 0.250
Co − Co+2	− 0.277
Cd − Cd+2	− 0.403
Fe − Fe+2	− 0.440
Cr − Cr+3	− 0.744
Zn − Zn+2	− 0.763
Al − Al+3	− 1.662
Mg − Mg+2	− 2.363
Na − Na+	− 2.714

TABLE:III METAL ION ELECTRODE POTENTIAL

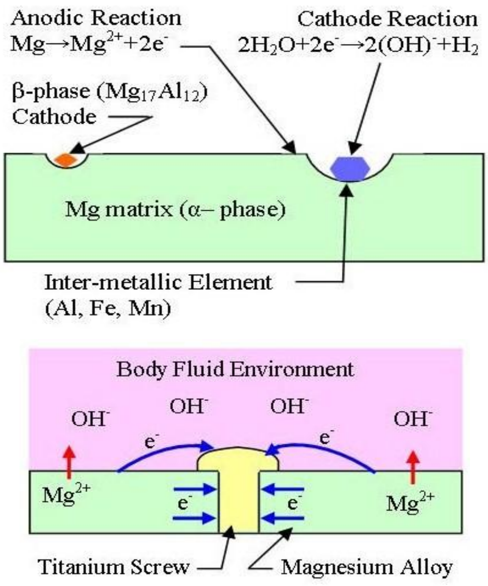
Types of Corrosion observed in Mg and its alloy

Galvanic corrosion[10]

Magnesium alloys are highly at risk to galvanic corrosion as anodic behavior to the metals. Galvanic corrosion forming by placing two dissimilar metals in corrosive conductive solution. In this process electron flow produce from corroded (Anodic) to protected metal (Cathodic)(fig:9). Magnesium and its alloys are highly susceptible to galvanic corrosion due to it has lowest standard potential in EMF series. From the table3, we can say that Mg can corrode by the contact of other metal andby H_2 evolution.

When magnesium and magnesium alloys contain second phases because of impurities or alloying elements, the matrix α−phase is corroded, while the hydrogen gas is evolved on the second phases. Table 3 shows typical corrosion potential values for magnesium and common magnesium alloy second phases.

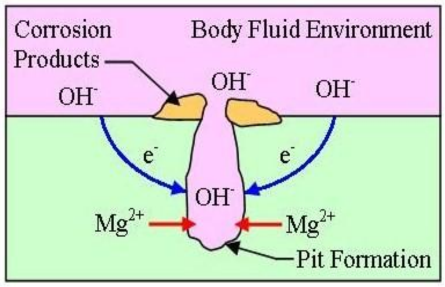
Fig:8,9 Galvanic Corrosion



Pitting corrosion[10]

In Mg alloys, Pitting corrosion occur at free corrosion potential of magnesium, when exposed to chloride ions in a non-oxidizing medium. The as-extruded magnesium alloy AM60 was immersed in natural 3.5% NaCl solution, and the corrosion pits occurred on the surrounding of AlMn particles. The alloy has a protective oxide film in air. The potential of MgO (+1V),.when it is immersed in a sodium chloride aqueous solution, C1- ions will absorb on the *α-Mn* areas bordering on Al-Mn particles.

Fog:10Pitting morphology of extruded AM60 in 3.5%NaC1 aqueous solution



Anodic reaction: $Mg = Mg^{2+}+2e$ (1)

Cathodic reaction: $2H_20+2e = 2\ H_2 +20H^-$ (2)

Total reaction: $Mg+2H_20=Mg(OH)_2+2H_2$

Mg hydroxide precipitates on the bottoms of pits and surfaces of samples.

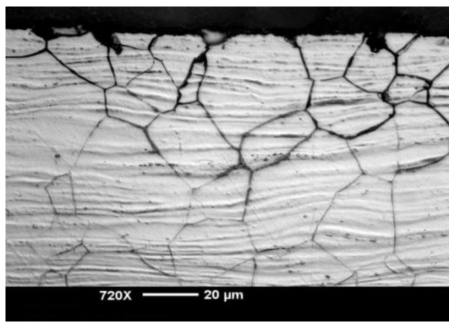
Metal E_{corr}	**VSCE**	**Metal E_{corr}**	**VSCE**
Mg	−1.65	Al8Mn5(Fe)	−1.20
Mg2Si	−1.65	Beta−Mn	−1.17
Al6Mn	−1.52	Al6Mn(Fe)	−1.10
Al4Mn	−1.45	Al3Fe(Mn)	−0.95
Al8Mn5	−1.25	Al3Fe	−0.74
Mg17Al12	−1.20		

TABLE:IV CORROSION POTENTIAL VALUES FOR MAGNESIUM AND FOR COMMON MAGNESIUM SECOND PHASES (AFTER 2 H IN DEAERATED 5% NACL SOLUTION SATURATED WITH $MG(OH)_2$ (PH 10.5).

- ***Intergranular corrosion[10]***

Intergranular corrosion (IGC) occurs at the grainboundaries due to the precipitation of secondary phase. However, recent studies show that IGC can occur on Mg alloys. VALENTE noticed of IGC occurred in WE43 in 3.5% NaCl aqueous solution. In early stages of immersion, a localized attack of Mg and its alloy can form grain boundaries at interface of cathodic precipitation in mild corrosive media which considered as IGC.

Fog:11Intergranular corrosion morphology of AZ80-T5 in 3.5%NaCI aqueous solution after 1 h.



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Filiform corrosion

Filiform corrosion is caused by an active corrosion cell which moves across a metal surface. The head is the anode and the tail the cathode. Filiform corrosion occurs under protective coatings and anodized layers. Uncoated pure magnesium does not undergo filiform corrosion[13].

Crevice corrosion

It is reported that crevice corrosion does not occur with the magnesium Alloys[13].

Stress corrosion cracking(SCC):[10]

Stress corrosion cracking means cracking due to the effect of tensile stress and corrosive. Pure megnesium has good resistance to SSC in both atmospheric and aquaousenvirnonment. But; Aluminium is susceptible to sscsi so it making alloys asAZ61,AZ80, and AZ91 with 6,8, and 9% aluminium respectively. Magnesium is mainly transgranular. Sometimes intergranular SCC occurs as a result of $Mg_{17}Al_{12}$ precipitation along grain boundaries in Mg-Al-Zn alloys[11].

- ***Corrosion fatigue[10]***

Corrosion fatigue directly relates humidity. Fatigue strength and Humidity have inversely proportional relation.It has also been found that corrosion fatigue cracks propagate in a mixed transgranular-intergranular mode and that the corrosion fatigue crack growth rate was accelerated by the same environments that accelerate stress corrosion crack growth. AZ91-T6 has resistance to corrosion fatigue *reduced in 3.5% salt water relative to that in air.*

Influencing factors of corrosion behavior of Mg Alloys

- ***Metallurgical influence:[8]***

1.*Alloying elements:* Alloying elements like Fe, Co, Ni and Cu are detrimental for the corrosion of magnesium alloys. Corrosion resistance improves with the A1 content. The corrosion rate of AZ91, AZ61 and AZ31 in 5%NaCl solution increasedwith the decrease of A1 content.Mn can improve the corrosion resistance of magnesium alloys. Binary Al-Mn phase with lower AlMn ratio has higher cathode potential. Therefore, the corrosion rate increases when Mn is added into Mg-A1 magnesium alloys to form A1-Mn and intermetallic phase Al-Mn-Fe [22].For example, salt fog corrosion tests for Mn-containing Mg-A1 magnesium alloys such as AM50 and AM20, showed corrosion that pits initiated at low A1 areas, the matrix was attacked in the form of fissures. The fissures started from pitting locations and usually stopped in front of areas of high A1 segregation [22]. The continuous high Al segregation seemed to contribute much more in stopping the propagaijon of corrosion fissures than the discontinuous, more or less isolated, p-MgI7All2p articles [22]. Mn can improve the corrosion resistance of magnesium alloys, but this is not always the case. The corrosion rate of magnesium alloys is related to iron content and Fe/Mn ratio. Binary Al-Mn phase with lower AVMn ratio has higher cathode potential. Therefore, the corrosion rate increases when Mn is added into Mg-A1 magnesium alloys to form A1-Mn and intermetallic phase Al-Mn-Fe [22].

Zr can stabilize the magnesium matrix phase and reduce its corrosion rate. The beneficial effect of Zr cannot be extended to an alloy with too much Zr. The excess addition of Zr can lead to precipitation of Zr in the matrix, which is detrimental to the corrosion [23].

In addition, rare earth improves also the corrosion resistance of magnesium alloys, but is affected by medium and pH value[21].

2.***Microstructure and secondary phases[10]:***

Table V shows that the corrosion potential of AlMn is higher than that of Mgl7AIl2T.Thus, AlMn is more detrimental than $Mg_{17}Al_{12}$.

Sr.No.	Phase	φ corr/V
1	Mg	-1.55
2	AlMn	-1.28
3	***B*** (Mg17A112)	-1.31

TABLE :V CORROSION POTENTIAL OF PURE PHASES AFTER 3 H IMMERSION IN ASTM D1384 WATER (INITIAL PH= 8.3)

3.GRAIN SIZE[10]:

The rapid solidification process can refine the microstructure which is beneficial to the corrosion properties. It can change the mechanism of corrosion turning pitting corrosion of Mg-Al magnesium alloys into overall corrosion . The surface or skin layer of die-cast Mg-A1 magnesium alloys with very fine grains, high β volume fraction and continuous distribution of β phase along grain boundaries has a higher corrosion resistance than its core **.** It is the same that die castings of magnesium alloy AZ91D have better corrosion resistance than ingots.

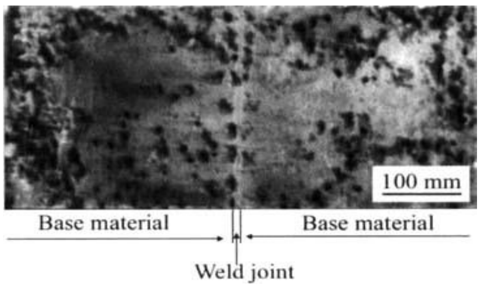
4.Effects of post processing : Heat treatment[10]

Heat treatment can change the microstructure of magnesium alloys. Aging makes A1 atoms diffuse towards grain boundaries and form precipitation of the β phase, thus, reducing the Aluminum concentration in the α-Mg matrix.

5.Effects of welding [10]:

HAFERKAMP et a1made some investigations on the corrosion behavior of laser welded AZ91D in synthetic seawater. Fig 12 shows the corrosion morphology of the weld zone of AZ91D weld with gas tungsten arc (GTA) welding after 48 h salt fog test. The corrosion morphology of the weld zone of AZ31 with laser beam welding after 24 h salt **frog** test is shown in Fig.12. It is visible that the corrosion does not attack the weld zone.

Fig 12:Corrosion morphology **of** weld zone of AZ31 with laser beam welding



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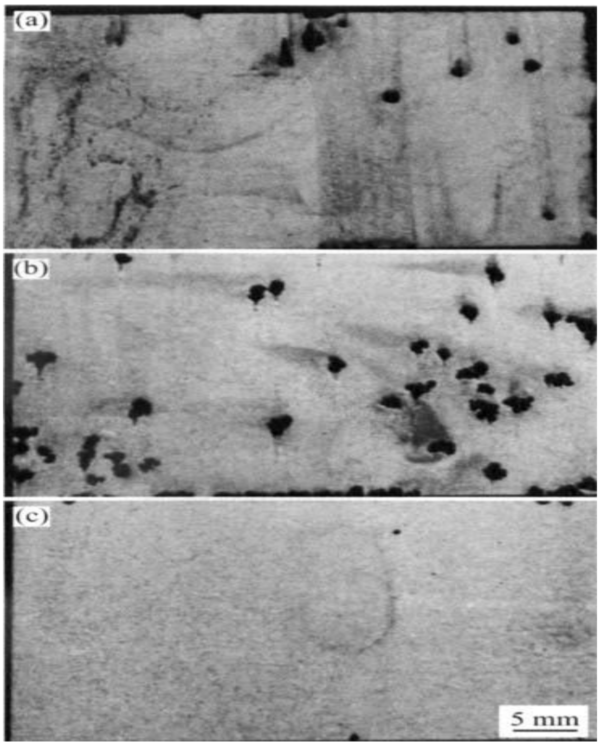
Environmental influence:
Corrosion of magnesium alloys increases with the increase of relative humidity (RH)[23]. High humidity accelerates SCC during atmospheric exposure [13]. The fatigue life is reduced, and the FCP rate is enhanced by the increasing environmental temperature and relative humidity (RH).

1.**Electrolyte pH value:**
The pH value of the medium has an important impact on the corrosion morphology and the number of pits. As a result, the corrosion of magnesium alloys in neutral or alkaline salt solutions typically takes the form of pitting [23].

Fig 13: Corrosion morphologies of AM60 as extruded in 3.5%NaC1 aqueous solution at pH=3(a), pH=7(b) and pH=l2(c), respectively



2.**Chloride ion concentration[23]:**
Extruded Magnesium alloys with 3% to 8% A1 and 0.5%-0.8% Zn are susceptible to filiform corrosion and pitting corrosion in aqueous chloride solutions depending
on chloride concentration

Corrosion rate measurement techniques for Mg metal and Alloys[17]:
Different corrosion tests are carried out on Mg metal and Mg alloys as follows:

Weight loss method (Immersion test)
Here samples were cut in regular size of 15 X 15 dia mm and polished with 80,220,400,600 grit emery papers. They were polished with 0.25 μ m diamond paste and cleaned with acetone. Exact weight of samples were taken and they were immersed into the solution of 3.5% Nacl in beaker for 100 hrs. After immersion test the samples were cleaned with 200gms/l CrO3+ 19 gm/l AgNo3 solution for 10 min to remove the corrosion products. It was again wash with distilled water and weighted. The difference between initial and final weight gives the corrosion weight loss.Thus Immersion test will give Corrosion rate for 100 hr in 3.5NaCl solutions for mg metal and different Mg alloys.

Electro chemical tests :
It is carried out using Potentiodynamic anodic polarization method in ASTM D 1384 solution. The ASTM D 1384 solution contain 148 mg/l of Na2SO4, 138 mg/l of NaHCO3 and 165 mg/l Nacl(Ph=8.3). All corrosion test were carried out at RT using I lit five neck ASTM electrochemical cellconsisting of three working electrodes, reference electrod(Ag/AgCl-sat), counter electrode(pt), and working electrodes(W). Solartron 1287 electrochemical interface was used for the polarization experiments. During electrochemical corrosion test, the electrode potential was anodically scanned at a scan rate of 10 mV/min from -1400mV towards anodic potential. All the electrode potential was measured against Ag/AgCl(in saturated KCl) reference electrode.

Outlook:
Magnesium and its alloys producers usually add more manganese to reduce the iron content in the melting. Mn, reacting with Al, forms Al5(Mn,Fe)2 phase, which has a highest noble potential and at the same time it decreases the formation of α phase. A review of the current research on Magnesium and its alloys corrosion and its corresponding mechanisms in the industry such as galvanic corrosion, pitting, stress corrosion, intergrannular corrosion and corrosion fatigue has been expressed. The corrosion mechanisms of magnesium alloys are still not well understood. Therefore, it is definitely necessary to continue this investigation. There is a challenge for corrosion scientists to create a Mg alloy with better corrosion resistance.

Because of the well-known characteristics of magnesium and its alloys with high susceptible to corrosion, new Mg alloys including cast and wrought alloys with better properties such as finer grain, new phases should be developed, more feasible, reliable, maintainable and cheaper protection systems and higher techniques must be investigated to match with the practical applications. Moreover, according to the eco-friendly requirements, more considerations on recycling should be given both in industrial environment and bioenvironment.

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