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Review article

Corrosion of ECAPed magnesium alloys and its background: A Review

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Abstract

The aim of this review article is to provide a brief mechanistic overview of magnesium alloys, equal channel angular pressing and corrosion behavior of un-ECAPed and ECAPed Mg alloys. The considerate of the corrosion processes of ECAPed Mg alloys builds upon interpretation of the corrosion of fine-grain magnesium alloys. This provides an understanding of the effect of grain size on corrosion of Mg alloys. This deep understanding is essential as a foundation if we are to produce corrosion-resistant magnesium alloys. Considerable has previously been accomplished, but there is enormous scope for development. This present concise review can provide a foundation for further, much desirable research.

1. Introduction

The gradual destruction of metals or alloys leads to corrosion, due to the exploit of air, moisture or acids on the substrate materials [1]. The acids and other factors including temperature, relative humidity, carbon dioxide and chloride ion deposition rate on the substrate have a greater impact on the corrosion of metals. Ehteram et al. [2] reported that corrosion rate increases with increase in acid concentration also they made the statement that acid is highly corrosive to most of all metals and alloys. Mg alloys are one of the most reactive metals that have poor corrosion resistance and mechanical properties which limits its applications in industries. Therefore, enhancement of mechanical properties and corrosion resistance have led to greater interest in magnesium alloys because of its special applications. Magnesium alloy is alkaline earth metal having a density of 1.75 $g \cdot cm^{-3}$, high specific strength, and electromagnetic shielding, good damping, and recycling capacity make it more attractive towards industrial, aerospace, naval/ marine, materials handling, transportation, automotive and electronic industries [3,4]. Apart from above advantages it has few disadvantages like low formability, low strength, HCP structure with a minimum slip system, the deformation modes in hexagonal close-packed (HCP) Mg crystals at room temperature include three individual slip systems and one twin system, whose critical resolved shear stresses (CRSSs) have large differences: $\{0001\}\langle 11\bar{2}0\rangle$ basal slip, $\{10\bar{1}1\}\langle 11\bar{2}0\rangle$ prismatic slip, $\{11\bar{2}2\}\langle 11\bar{2}\bar{3}\rangle$ pyramidal slip and $\{10\bar{1}2\}\langle 10\bar{1}1\rangle$extension twin, this results in low ductility and workability [5-7], presently much effort is required for preparation of magnesium alloys with a grain size lower than 1 µm, i.e. ultrafine-grained (UFG) materials in order to improve the strength of Mg alloys, many researchers worked and finally developed a severe plastic deformation (SPD) process which greatly contributes towards grain refinement to enhance mechanical properties of the metal which leads to superelastic properties with respect to temperature [8,9]. Various SPD processes such as Equal channel angular pressing (ECAP), High pressure torsion (HPT), Accumulative roll bonding (ARB), Reciprocating extrusion-compression (REC), Repetitive corrugation and straightening (RCS) are employed to modify the microstructure to improve the strength, ductility and hardness of the magnesium alloys [6,10]. However, in SPD, ECAP is most developed and frequently used metalworking technique for significant materials hardening due to increasing dislocation density and considerable grain size reduction to sub-micron level [11]. Grain size reduction of metals or alloys increases the strength of the material by accumulating large strain into work-piece and without changing the shape of the material [4, 12, 13]. Muralidhar et al. (2016) observed the improvement in mechanical properties of AZ80 wrought Mg alloys after processing with ECAP, Similar observations were recorded on AZ31 and AZ61 [14,15]. Finally, ultra-fine grain structure in metallic materials and uniformly distributed second phase particles increases re-passivation tendency, which exhibits the corrosion resistance [16]. But, ECAPed Mg alloys are sensitive to corrosion. So it is worthwhile to investigate the corrosion behavior of Mg/ wrought Mg alloys and ECAPed Mg alloys. This paper reviews the corrosion behavior of Mg alloys and ECAPed Mg alloys. The boundary relationships of three different fields of selected components and the recent effort have been headed to the development of the relationship and correlating the refined grain size of ECAPed magnesium alloys and its corrosion response. The effect of grain size on corrosion behavior and corrosion resistance with grain refinement through ECAP have been reported in this review.

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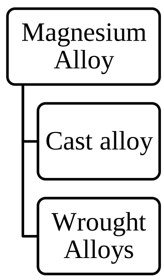
2. Magnesium alloys

Magnesium alloys was used since Sir Humphry Davy first produced pure Magnesium in 1808 [17, 18]. Mg is an alkaline earth metal (Group IIA) with hexagonal closed pack (HCP) crystal structure. Magnesium is the lightest metal among all categories of metals. Magnesium alloys have excellent material properties like strength-to-weight ratio, good fatigue and impact strengths, and large thermal and electrical conductivities and excellent biocompatibility [19, 20]. Its low density is one of the most promising property and a key material to increase fuel efficiency and to reduce environmental pollution. Extruded, forged or rolled sheets of magnesium alloys are considered as Wrought Mg alloys, these alloys have better mechanical properties than cast Mg alloys [21]. The available different Mg alloys are shown in Table 1. Indeed, alloying elements not only revise the mechanical properties and also it shows the significant impact on corrosion behavior because of alloying elements form secondary particles which are noble or active towards corrosion [22]. Therefore, in order to enhance the mechanical and corrosion properties of Magnesium alloys, Al, Zn, Sn, Ca, Sc, Si and rare earth (RE) are usually selected as strengthening elements. The addition of alloying elements is to promote the strengthening of base metal and it also shows better corrosion resistance [2, 23, 24]. RE addition improves the formability of wrought Mg alloys [25]. There are 17 rare earth (RE) elements which are identified through literature such as scandium (Sc), yttrium (Y), lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), lutetium (Lu) and promethium (Pm) [22,21]. Argade et al. have investigated the corrosion resistance of as-received Mg-Y-RE wrought alloys at 520°C for 4 h. Friction stir processing (FSP) was employed to achieve finer grain microstructures (70µm to 0.7µm), this UFG leads to increase in corrosion resistance of the Mg alloy [26] because the oxide film of rare earth elements is more stable than Mg $(OH)_2$ passive layer [27]. Considering that Aluminum has comparatively lower density and high solid solubility in magnesium, therefore firstly, Mg base metal combined with 2 to 10% Al and slight addition of Zinc 0.5 to 3%, manganese 0.1 to 0.4% formed AZ alloys, AM series magnesium alloys which are readily available. This poses good mechanical properties and corrosion resistance at a lower temperature but at elevated temperature mechanical properties of the materials reduces and material deterioration can be observed thus the inclusion of Rare Earth, Zinc, silver, thorium and zirconium content significantly improves the mechanical property es and corrosion resistance [28,29]. Indeed, the addition of zinc to AZ Mg alloys are limited to 1-3% because of its micro shrinkage characteristics, also above 3% of Zn accelerates corrosion and addition of zirconium act as a strong grain refiner for magnesium, Intensively Zr addition gives not only grain refinement also eutectic phase [30]. In addition, the aged solution treated and aged welded Mg alloys exhibited good corrosion resistance in the vigorous environment and avoids the failure due to stress corrosion cracking (SCC)[28, 31]. Li addition to Mg reduces the density by about 1.35 $g\cdot cm^{-3}$ which is much lower than other Mg alloys like AZ31, AZ61, AZ80, ZK60 etc and also improves the ductility [32]. The silicon addition to Mg alloys increase the fluidity of the molten metal and also forms Mg_2Si which shows a high melting point (1085°C), high hardness (460HV), high elastic modulus (120GPa) and low thermal expansion coefficient (7.510^{-6}/K), low density (1.9 $g\cdot cm^{-3}$). Also, Si addition improves the corrosion resistance of the Mg–Zn–Mn alloys. Mg_2Si intermetallic phase is very stable and can slow down grain boundary sliding at elevated temperatures [12]. The effect of adding alloying elements to magnesium are represented in Figure 1. Lightweight and good corrosion resistance, qualifies it as attractive structural material. Additionally, Mg alloys have major applications in automobile, aerospace and medical field are listed in Table 2. However, inadequate research towards the application of Mg and its alloys in the marine field was observed. Rossi et al. [14] investigated the use of Mg as a sacrificial anode for the protection of offshore steels and aluminum structures.

Table 1. Magnesium alloys. [19, 22, 27,52, 71, 72]



Mg Alloys	Elements
AZ Alloys	Mg-Al-Zn
AM Alloys	Mg-Al-Mn
ZK Alloys	Mg-Zn-Zr
ZM Alloys	Mg-Zn-Mn
WE Alloys	Mg-Nd-Y-Zr
AE Alloys	Mg-Al-RE
AX or AXJ Alloys	Mg-Al-Ca
AJ Alloys	Mg-Al-Sr
QE Alloys	Mg-Ag-Nd-Zr
ZE Alloys	Mg-Zn-RE
ZC alloys	Mg-Zn-Cu
HK Alloys	Mg-Th-Zr
HZ Alloys	Mg-Th-Zn
HM Alloys	Mg-Th-Mn
LZ Allots	Mg-Li-Zn

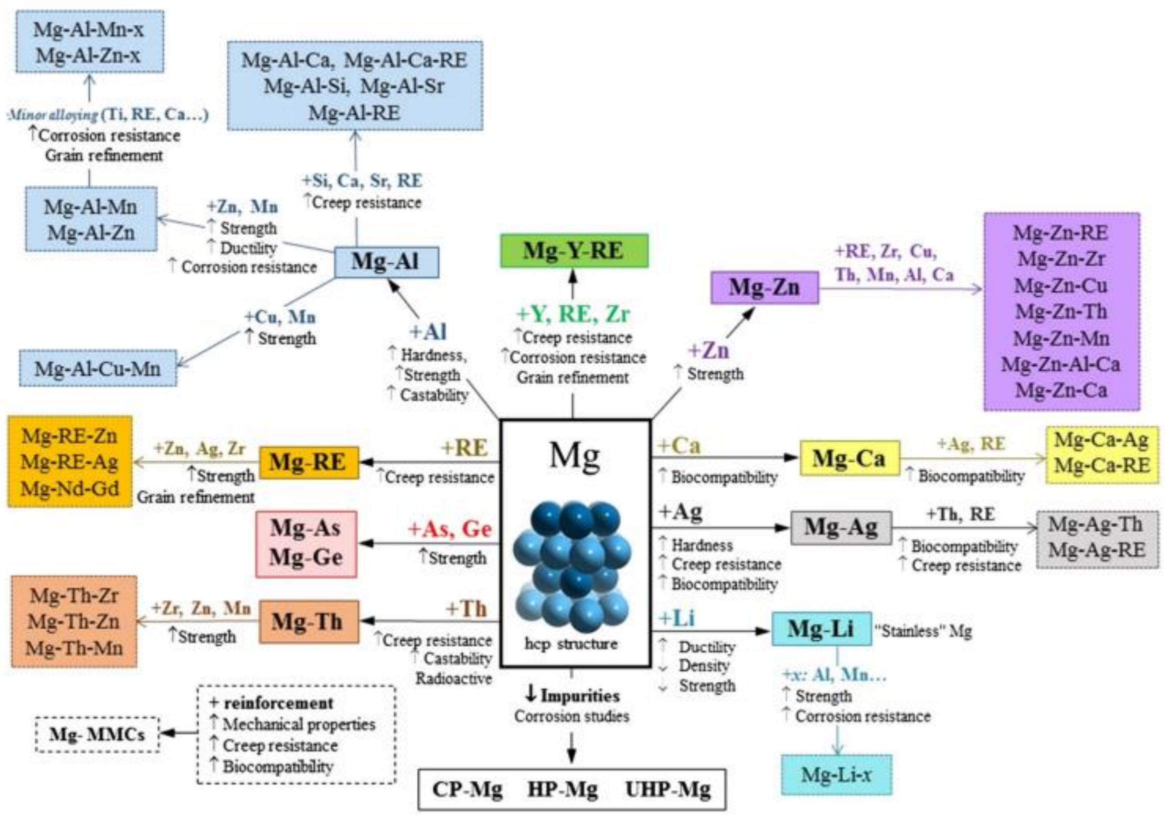


Figure 1 Development of magnesium alloys and its effects. [40]

Table 2. Applications of Mg alloys.

Applications	References
Aerospace applications – Gearbox housing, transmissions, intermediate compressors, Auxiliary gearboxes, generators, canopies and engine components.	[5], [48], [73]
Automotive application – Seat frames, steering wheels, airbag housing, instrument panels, transmission housing, Cylinder head cover, Intake manifold, Inner doorframe, tailgate inner door panel, lift gate, brackets and fans	[6], [8], [74], [75], [76]
Naval Application – Ship hull as sacrificial anode, Marine engine.	[14], [77]
Bio-medical application- Bone implants, cardiovascular stents, orthopedic implants	[34], [78], [109],
Nuclear applications- Reactors	[74]
Other applications include Electronics, Sporting goods, Office equipment, Flares, Sacrificial anodes, Hydrogen storage, Flash photography and tools.	[36], [71], [79], [80]

3. Equal channel angular press (ECAP)

Segal proposed this experimental technique in 1977 in Russia to improve the yield strength of materials through grain refinement [33, 34]. Figure 2 depicts, principle of ECAP and illustrates the schematic of equal channel angular press (ECAP) with its terminologies the die consisting of two equal channels intersecting at an channel angle (ϕ) and corner angle (Ψ) the material is pressed under load P, which induces intense plastic strain via simple shear without equivalent change in the cross sectional dimension of the work piece [35], It has unique qualities compared to the other methods of grain refinement, which is to build up plastic strain in the material at shear region, by increasing the number of passes which leads to reduction of the grain size in the material and it is more flexible compared to other SPD techniques. Moreover, the strain distribution in the process depends on the friction uniformity, die channel and corner angle [33]. In addition to that factors influencing the workability and microstructural characteristics of the as-pressed billets in ECAP are described in Table 3. Indeed the grain size of the polycrystalline materials generally plays a significant role, thus the strength of the all polycrystalline material depends on average grain size 'd'. The relationship between the yield strength and average grain size is clearly explained through Hall-Petch relation given in equation (1) explicitly materials yield strength is inversely proportional to the square root of the grain size [5, 6, 36].

$$\sigma_y = \sigma_0 + \frac{k_y}{\sqrt{d}} \quad (1)$$

Where σ_y is the yield strength, σ_0 (MPa) is the friction stress for dislocation movement, k_y (MPa-mm$^{1/2}$) is the strength coefficient for the normal stress and 'd' is the grain size. For AZ31B magnesium alloys the friction stress σ_0 ranges from 10 to 131MPa, the strength coefficient k_y ranges from 5.0 to 12MPa-mm$^{1/2}$[37]. The ECAP consists of two channel intersects at a particular angle called channel angle (ϕ) and the subtended intersection point of the channel is called corner angle (Ψ). Based on this geometry factor, the total strain developed in the ECAPed sample can be calculated, and is given by the Eq. (2). The total accumulated strain (ε_{eq}) is N*γ given in Eq. (3), [17,31,32]. Also it is reported that lower channel and corner angle gives larger accumulative strain to get ultra-fine grains in the materials [38]. Ultrafine microstructure with equiaxed grains which is separated by grain boundaries having high angles of misorientation, can be accomplished most easily when imparting a very intense plastic strain with a value of channel angle (ϕ) is very close to 90°, from eqn. (2) the strain imposed on a single pass through the die is very close to one (1) [35]. However, Muralidhar et al. [38] investigated the ECAPed AZ31 wrought magnesium alloy with channel angle and corner angle 120°, 30° respectively. From the study it was found that, dead zone was reduced with increased corner angle of curvature and the material flowed easily during ECAP process due to reduction in friction between the die channel and the work piece.

$$\gamma = 2\cot\left(\frac{\phi+\Psi}{2}\right) + \Psi \operatorname{cosec}\left(\frac{\phi+\Psi}{2}\right) \quad (2)$$

$$\varepsilon_{eq} = \frac{N}{\sqrt{3}}\left(2\cot\left(\frac{\phi+\Psi}{2}\right) + \Psi \operatorname{cosec}\left(\frac{\phi+\Psi}{2}\right)\right) \quad (3)$$

γ = shear strain

ε_{eq} = equivalent strain

In equal channel angular extrusion, the metal is pressed through the die using a plunger with a specific die and corner angle ϕ and Ψ respectively. The process has four basic processing routes in ECAP, such as Route A: here the samples are pressed without any rotations. Route B_A: the specimen is rotated by 90 degrees in a clockwise direction between consecutive passes. Route Bc: the specimen is rotated by 90 degrees in counterclockwise direction between consecutive passes. Route C: The specimen is rotated by 180 degrees between the passes, there is a provision to rotate the work-piece between the successive pressing in order to activate the shear planes and direction.

Table 3. Factors affecting ECAP.

Factor		Description	Reference
Die geometry	Channel angle (ϕ) Corner angle (Ψ)	The accumulation of effective strain magnitude in a single passage through the ECAP die is inversely proportional to the ϕ and Ψ channel angle and corner angles respectively. In other words, minimum channel and corner angle produce large strain towards the UFG structure in the material also it is most effective in grain refinement. It is found that for maximum strain homogeneity is possible corresponding to channel angle ϕ = 90°, corner angle ψ = 15° and friction coefficient μ= 0. 3.	[3],[5], [13],[17], [40],[81], [82]
Processing temperature		When ECAP processed at Lower temperature improves mechanical properties along with uniform microstructure can be obtained. Accordingly, by increasing processing temperature, it increases the grain size, also this reduces the dislocation density and strength of the material.	[4],[5],[13], [15],[83]
Back pressure		The backpressure in ECAP improves the plastic strain in the material which prevents cracking at lower temperatures, this leads to enhanced grain refinement in the ECAPed sample and results in considerable improvement in mechanical properties of difficult to deform materials.	[23],[84]
Ram speed		Increased ram speed can be employed to attain a homogeneous microstructure even at elevated temperatures. Typically, the ram speed (mm/s) in the range of 1-20mm/s prepared.	[13],[85]
Processing routes		There are four fundamental routes of ECAP, discussed in this paper; route Bc and route R are considered as optimum routes for getting UFG microstructure in the ECAPed materials.	[5],[35],[40] [38],[108], [115],[116]

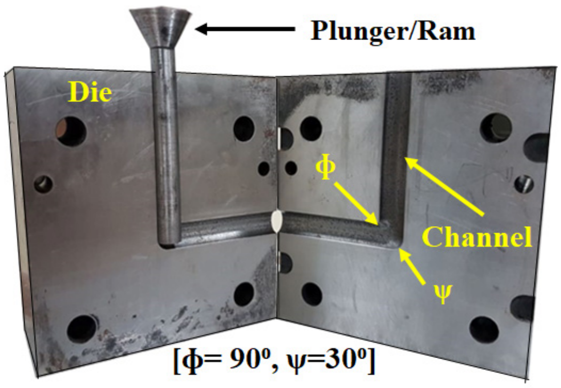


Figure 2. Schematic of Equal channel angular press (ECAP).

From the above-said routes, ultra-fine grains can be obtained [25,34,39]. The shear deformation of materials at different ECAP processing routes for two different channel angles ϕ =90 degrees and 120 degrees have reported in reference [40]. It was stated that the route Bc is most effective and route A is least effective in grain refinement. Also, the author summarized the effectiveness of ECAP processing routes that are in the order of route Bc> route C > routes A and B_A to facilitate the process. Authors [34, 36] also reported that grain refinement and microhardness is effective in route Bc compared to other ECAP routes. Muralidhar et al. [38] introduced the new ECAP route Route-R on wrought AZ61 magnesium alloys at 483K for grain refinement. Here the specimen is inverted to the original position in each ECAP passes, subsequently; the average grain size of the AZ61 alloy is reduced from 66µm to 16 µm, 14.1 µm and 10 µm for Route A, route Bc and route R respectively. Similarly, the microhardness of the alloy is increased from 60VHN to 71VHN, 72VHN and 74VHN for Route A, route Bc and route R respectively. It is clear that route-R ECAP processing produces enhanced ultra-fine grains (UFG) compare to route Bc. additionally, the hardness of the material also increases at route R.

4. Mg- Corrosion overview

According to the standard reduction potential of magnesium, which is appeared in active positions in both the electromotive force (emf) series and galvanic series for seawater, emf is about -2.37V. This reveals that the magnesium is active metal to all other engineering metals [10], however at open environment condition (air at room temperature) a gray oxide appears on Mg surface and moisture converts this oxide to magnesium hydroxide, $Mg(OH)_2$ provides corrosion protection in aqueous media having pH less than 12 [41]. Generally, metal surface consisting of bi-layer of MgO and $Mg(OH)_2$ or a single layer of $MgO_x(OH)_y{\cdot}nH_2O$ its thickness is approximately 5-40 nm [42]. The layers on the metal surface which act as passive protective film, henceforth passive film formed on unalloyed Mg surface do not protect for long term in the presence of chloride, bromide, sulfide, thus which is extremely prone to corrosion or leads to pitting corrosion, therefore unalloyed Mg are not used for structural applications [28,32]. Along with magnesium alloy failure is due to heavy-metal contamination, blast residues, flux inclusions, and galvanic attack furthermore the corrosion resistance of magnesium alloys is depends on the environment, composition, microstructure, properties of film developed, pH of the solution and chloride ion concentration [22]. In addition to chemical factors of Mg alloys chemical composition, structural aspects such as the amount and distribution of secondary phase particles (β-$Mg_{17}Al_{12}$), texture, dislocation density, and grain size significantly affect micro-galvanic corrosion [43,110]. The secondary phases play an important role in accelerating the corrosion of α-Mg matrix which increases with the extension of immersion time. During the corrosion process, α-Mg matrix act as anode and secondary phases collectively acts as strong cathode [18]. The presence of chloride ions in the solution led to the initiation and development of corrosion pits which gives the area corrosion. Raja et al. [44] have discussed the role of chloride ion and hydrogen embrittlement of hot-rolled Mg-Mn wrought Mg alloys in saturated 0.01M and 0.1M NaCl solution, which revealed that chloride ion found to damage the passive film, cause pitting, further initiates crack, that grows in a transgranular manner and increases the hydrogen embrittlement tendency in Mg alloys. In micro galvanic corrosion, distribution of secondary phase (β) decides the corrosion forms. When the β phase is distributed discontinuously along the grain boundaries, micro galvanic cell forms and material corrode in particle undercutting fashion which tends to increase the corrosion rate and β phase distributed semi-continuously along the grain boundaries which make the material to corrode. But after some time a continuous layer of β phase acts as a barrier between α phase and restricts corrosion, further when β phase distributed discontinuously in the eutectic region begins pitting corrosion [45]. In general rate of corrosion ($mm{\cdot}y^{-1}$) can be calculated by knowing the weight loss of corroded metals or alloys given in Equation (4) [46,47,114]. Schematic of general corrosion attack and magnesium reactions with the corrosive environment have been described in Figure 3. In this case, the lower corrosion rate of the ECAPed Mg alloy is correlated to its more refined microstructure. It is known that the α-phase acts as an anode and the β-phase as a cathode. The grain refinement causes a more uniform distribution of galvanic couples and a higher density of these per unit area, which favours faster nucleation of the corrosion products on the surface of the Mg alloys. The thin layer of corrosion products is more homogenous and less porous on the fine grained material, additionally it has better protective properties and can limit the corrosion rate. The different categories of Mg-corrosion are illustrated in Table 4.

$$\text{Corrosion rate (mm/y)} = \frac{87.6\ \Delta W}{\rho AT} \quad (4)$$

ΔW = Weight loss, mg

ρ = Density of the material, g·cm^{-3}

A = Area of specimen, sq. in.

T = Exposure time, h.

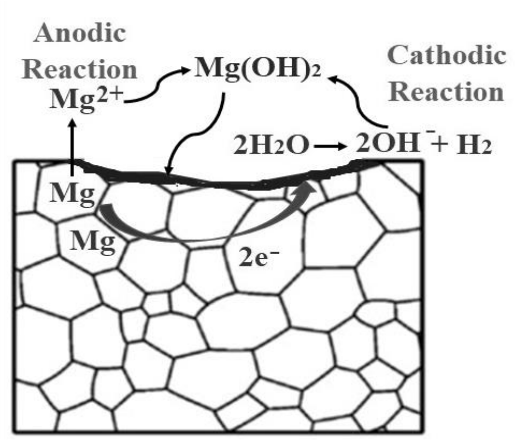


Figure 3. Schematic illustration of the corrosion mechanisms.

4.1 Corrosion behavior of Mg alloys:

Corrosion susceptibility limits the use of Mg alloys in engineering applications, therefore it is essential comprehend to improve the corrosion properties. The corrosion behavior of Mg and its alloys depends on the medium which they are exposed and also it is strongly influenced by microstructure, alloying composition and secondary β phases. In recent research's it is found that in Mg-Al alloys solid solution $Mg_{17}Al_{12}$ precipitates were found along the grain boundaries as continuous phase or laminar structure. Which shows a passive behavior over a wide pH range. Also it is found that distribution of $Mg_{17}Al_{12}$ estimates the corrosion resistance of Mg-Al alloys [22]. When unalloyed Mg gravimetric corrosion test of 3.5wt% NaCl was carried and it presented the highest mass loss about 196 m g·cm^2 after 16 h of immersion. On the other hand, addition of aluminium notably increases the corrosion resistance. Thus, 3 wt.% Al in AZ31 alloy reduced the mass loss up to 55.2 m g·cm^2 after 10 days of immersion. Nevertheless 8–9 wt.% Al in AZ80 and AZ91D alloys reduced the mass loss to 0.75 and 1.05 m g·cm^2 at the end of the test respectively. In early stages of corrosion for AZ31, AZ80 and AZ91D alloys when immersed in 3.5 wt.% NaCl revealed localized or pitting corrosion around $MnAl_2$ inclusions and β-phase interfaces due to a galvanic couple surrounded Mg matrix [22]. Ben-Hamu et al. [28] reported that grain size of the extruded Mg alloys are noticeably reduced by adding Ag to the Mg-6Zn and from the Potentiodynamic polarization (PD) measurements, linear polarization(LP) of DC polarization and EIS tests revealed that the addition of Ag to the Mg-6Zn reduces the corrosion resistance (galvanic corrosion), which is due to the formation of micro-galvanic corrosion between α-Mg and the precipitates of Mg–Ag ($Mg_{54}Ag_{17}$) of different electrochemical potentials. In another study, the addition of silicon to Mg–6Zn increased the corrosion resistance and [48] reported that the addition of silicon to Mg-Zn-Mn improved the surface oxidation, but addition of calcium to Mg–6Zn–5Si decreases the corrosion resistance. Addition of Si and Ca to Mg–6%Zn–1%Mn corrosion rate increases with increasing NaCl concentration due to presence of aggressive chloride ion. Singh et al. [49] compared the corrosion behavior of Mg, AZ31 and AZ91 in 3.5% NaCl solution using electrochemical polarization and impedance measurements. From the study it was observed that pure Mg has less corrosion rate compared to AZ91 and AZ31 alloys. Also, the AZ91 has less corrosion rate compared to AZ31 because of high aluminum contents.

Since majority of the magnesium alloys are produced by conventional casting process that results in casting defects, therefore, there is a strong reason to produce extruded Mg alloys [39]. Researchers have attempted to develop an improved mechanical and corrosion resistant extruded Mg-Zn and Mg-Zn-Ag alloy and the effect of Ag addition was investigated. Further they have studied double age hardening response (T5D) and found that grain refinement due to formation of precipitates the hardness was found to increase more rapidly in ZQ6X alloys with double aging treatment compared to those with single aging treatment.

The electrochemical impact of alloying elements is shown in Figure 4, which reveals that a large number of alloying additions enhance the cathodic and anodic kinetics of the Mg alloys. Therefore, during the development of new Mg alloys, the proper care should be taken for high purity Mg alloy, means percentage impurities such as Fe, Cu, Ni should be within the tolerance limit (Fe = 3.2%Mn max.; Ni = 50 ppm max.; and Cu = 400 ppm max.) results reduction in corrosion rates of Mg and its alloys. further Zn free AM60 Mg alloy has the lower tolerance limits of Fe, Ni, Cu this newly developed materials shows higher corrosion resistance than AZ91C [50]. Al percentage also plays a critical role in the improvement of resistance towards stress corrosion cracking of Mg alloys, where decrease in Al percentage in Mg alloys tendency towards stress corrosion cracking. Kelvii Wei Guo reports AZ31 shows greater resistance to stress corrosion cracking than AZ61 and AZ80. Furthermore, Mg alloys without Al or Zn has the good stress corrosion cracking resistance, such as ZE41, ZK60 [51].

Table 4. Categories of Mg-Corrosion.

Types of Corrosion	Description	Reference
General corrosion	General corrosion attack in salt-water exposures can be minimized through the selection of high-purity Mg alloys cast without introducing heavy metal contaminants and flux inclusions,	[86],[112], [113]
Galvanic corrosion (Bimetallic corrosion)	Magnesium alloys are prone to galvanic corrosion due to excessive levels of heavy metal contamination, poor design and assembly practices. The galvanic corrosion behavior of AZ91D, AM50 and AM60 cast magnesium alloys coupled with A3 steel, 316L stainless steel, H62 brass and LY12 aluminum alloy at atmospheric condition, yields increased Mg corrosion rates.	[87],[88]
Erosion corrosion	Erosion corrosion occurs from the wearing away of the metal surface or passive layer by the impact of wear debris.	[89]
Crevice corrosion	An attack that occurs at narrow gaps ("crevice"). Because the corrosion observed is caused by the retention of moisture in the crevice, which being unable to evaporate, promotes the corrosion of metal in the narrow recess over extended periods.	[87],[110]
Pitting corrosion	Pitting is a type of localized corrosion confined to a small area and associated with the breakdown of passivation layer in destructive environment. It is a very dangerous and highly corrosive compared to other forms of corrosion. Pitting corrosion in the Mg alloys due to galvanic differences in the materials.	[7],[88],[90]
Biological Corrosion	Biological corrosion is the interaction of Mg alloys and bio organisms in corrosion processes, this is due to metabolic activities of micro-organism. The biological corrosion occurring within the body environment with the influence of body fluid pH, concentration of ions, protein adsorption on the implant surface. Addition of alloying elements and surface modification techniques were used to overcome the effects of biological corrosion.	[89]
Stress corrosion cracking (SCC)	Extruded, rolled and Die-casted Mg alloys are more prone to stress corrosion cracking and alloys containing aluminium (A1) are believed to be particularly susceptible to SCC in air, distilled water and chloride-containing solutions.	[87],[111]
Intergranular corrosion(IGC)	IGC arises at the grain boundaries owing to the precipitation of secondary phase. The grain boundaries are always the preferred sites at which precipitation and segregation in alloys occur. It is generally regarded that alloys with intermetallic phases or compounds are highly susceptible to intergranular corrosion.	[87],[86]
Filiform corrosion	Filiform corrosion often occurs on the metals surface such as steel, A1 alloys and Mg alloys. It is caused by active galvanic cells across the metal surface. Its head is act as anodic, whereas the tail is act as cathodic. It is typically associated with metal surfaces having an applied protective coating also this corrosion tended to occur at lower chloride concentrations.	[7],[87], [58]
Hydrogen damage	Hydrogen embrittlement of Mg alloys become brittle leading to Mg fracture due to diffusion of hydrogen in to material. This results give the net contribution of hydrogen embrittlement to the stress corrosion cracking.	[91]
Fretting corrosion	Fretting corrosion is the result of damage produced by metal components in direct physical contact with each other in the presence of small vibratory surface motions. The micro-motions are produced by normal every day activities experienced by the human body which result in mechanical wear and metallic debris between the surfaces of metal components.	[89]

Moreover, distribution of secondary β phase ($Mg_{17}Al_{12}$) also plays a significant role in the corrosion of Mg alloys. Which act as initiation point for stress corrosion cracking, along with it act as cathode, which results an increase in the relative size of secondary β phase and surrounding α rich area leads an increased pitting corrosion [52]. In the material strengthening process of severe plastic deformation particularly ECAP can obtain the fine grained Mg alloys. Due to decrease in grain size and uniform distribution of second phase β particles leads to decrease of localized or pitting corrosion. ECAPed material has the higher corrosion resistance than conventional extrusion evidently discussed [53]. Furthermore, twins which occurs during casting or extrusion in microstructure, decreases the corrosion resistance therefore for new generation of alloys need to remove the twins in the microstructure [54]. Finally with a limited percentage of impurities in alloys, modifying the microstructure through ECAP can develop a new application oriented Mg alloys with higher corrosion resistance than conventional Mg alloys [51]. Corrosion behavior of Mg-10Gd-xZn (x= 2, 6 wt.%) alloys in 0.5 wt.% NaCl solution was tested, microstructure of both alloy consist of $(Mg,Zn)_3Gd$ phase and lamellar long period stacking ordered (LPSO) secondary phase. Electrochemical test confirmed that increase in Zinc (Zn) content from 2 to 6% in Mg-10Gd-xZn alloys, reduces the corrosion resistance due to presence of secondary phase at grain boundary. Which cause micro galvanic corrosion and also comments that chromic acid might have facilitated in the removal of the de-stabilized second phase during the cleaning process. [55]. Xue-Nan et al. [34] reported, the mechanical strength and degradation rate of as cast wrought and SPD/ECAPed processed Mg based alloys in their review. Based on the [34] it is concluded that the yield strength and % elongation of cast product is less compare to wrought product, which further increased by severe plastic deformation or ECAP technique. Furthermore, the cast Mg product is prone to corrosion, whereas wrought Mg alloys or SPD processed Mg alloys have shown resistance to corrosion. Therefore, it is necessary to review the corrosion behavior of the ECAPed Mg alloys. Hence an attempt is made to brief the corrosion information of ECAPed Mg alloys in the next section.

Further, Esmaily et al. [56] have investigated the contribution of Al content in Mg alloys at three temperatures. Which revealed that corrosion resistance of the alloys increased strongly with increasing Al content. The temperature effects on pure Mg have shown no clear correlation between the corrosion rate and temperature. In contrast, AM20 alloys exhibited, 15% decrease in corrosion rate by lowering the exposure temperature from 22 to−4°C, and decrease in temperature resulted in 92% decrease of corrosion rate in AZ91D alloy. Esmaily et al. [57] strongly described the corrosive nature of NaCl in the presence of CO_2 at 4°C. The corrosion evidence was identified with increase of salt (NaCl) addition.

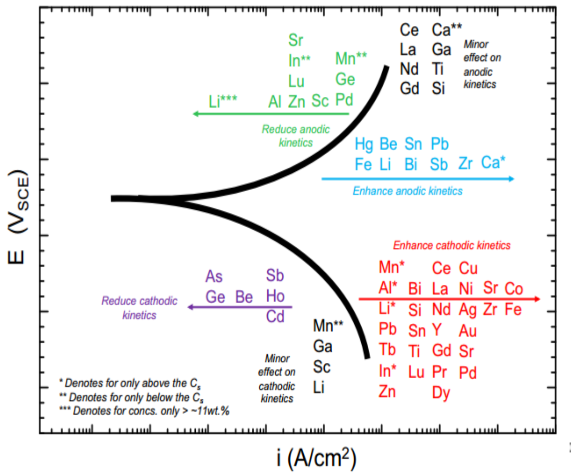


Figure 4. Schematic representation of the electrochemical impact of alloying elements in magnesium alloy. [70]

Pawar et al. [58] observed microscopic filiform-like corrosion in AZ31 Mg sheets with 3.5% NaCl solution, as a result, localized pits were identified initially at the cathodic-intermetallic sites and the surrounding Mg matrix. After 2 h of immersion, it was observed the dendrite arms, The dendrite arms consist Mg matrix preferentially corrode, this is anodic and highly prone to corrosion. Filiform-like corrosion reduced at the interdendritic, grain boundaries because these interdendritic and grain boundaries have quite high Aluminum(Al) and Zinc (Zn) contents compared to the dendrite arms concluded from the SEM and EDS study. This makes them relatively resistant towards corrosion. Also, author made an attempt to measure corrosion depth from the top surface, Type A and Type B grains showed a corrosion depth of ~35 µm and ~55 µm respectively. The study noticed that the corrosion depth varied significantly with immersion time.

In order to understand the microstructure, material deterioration, and stress corrosion cracking (SCC) susceptibility of Mg alloys Lianxi-Chen et al. [25] studied Mg-4Zn-0.6Zr-xSr, (ZK40xSr), they found size of grain boundaries precipitation in the ZK40xSr alloys and average degradation rate of ZK40xSr alloys were increased with increase of strontium (Sr) addition (i.e ZK40, the degradation rate was 2.2 mg cm^{-2} day^{-1}, which is lower than that of ZK40-1.6 Sr is 4.93 mg cm^{-2} day^{-1}). When ZK40xSr alloys were dipped in m-SBF, Sr-contained hydroxyapatite (HA) rod-like substance was noticed, also the fracture surfaces of the as-cast Mg-4Zn-0.6Zr-1.6Sr were shown intergranular stress corrosion cracking (IGSCC) patterns. Literature of IGSCC shows Zr containing Mg alloys had little SCC susceptibility [25] but study suggested that Sr could increase the SCC susceptibility in ZK40xSr alloys. The increase of SCC susceptibility of the higher Sr ZK40xSr alloys is attributed to the increase of micro-galvanic corrosion between the α-Mg and the grain boundaries precipitates. Some more literature on corrosion of Magnesium alloys has been summarized and presented in Table 5. From table 5, it has been observed that alloying elements typically increases the corrosion rate. Also, impact of each alloying elements on corrosion behavior were summarized in detail and its impact were resulted in table 5 (remark).

4.2 Corrosion behavior of ECAPed magnesium alloys

Few publications of corrosion behavior of UFG structured Mg alloys have shown that grain refinement reduces the corrosion resistance of pure Magnesium [20], AZ31 Mg alloy and AE21 Mg alloy in NaCl solution or corrosive media. But at same corrosive environment AE21, ZE41A [59] Mg alloy have shown improvements in the corrosion resistance [60]. Accordingly, corrosion results of ECAPed pure Mg alloys have discussed, Song et al. [20] refined the grain size of pure Mg of 800-1500 μm to 50-100 μm at 573 K after first, fourth and sixth passes of ECAP. Subsequently, studied the effect on corrosion of ECAPed pure Mg through electrochemical corrosion analyzer with 3.5 wt% NaCl solution. From the experimental results it was cleared that the ECAPed pure Mg has less corrosion resistance than as-cast pure Mg. Furthermore, the author had studied the EIS test to understand the electrochemical characteristics during 6h of immersion of ECAPed and unECAPed pure Mg. It is revealed that Nyquist plots of impedance spectra of as-cast and ECAPed pure Mg samples in 3.5 wt% NaCl the diameters of capacitance arcs of ECAPed pure Mg are much smaller than the as-cast pure Mg. Therefore, ECAPed pure Mg with more number of passes processed sample found smaller capacitance arcs, corresponds decreased corrosion resistance. Also found that the corrosion resistance of the samples was decreases with increasing the immersion time. The poor resistance of the ECAPed samples is due to the defects like energetic grain or sub grain boundaries and dislocations presents no protection which activates the drastic corrosion reaction. Therefore, the ECAPed pure Mg is erodible than as-cast Mg. Hence consequent annealing at below recrystallization temperature is useful to improve corrosion resistance of ECAPed Mg, attributed to the decrease of crystalline defects or dislocations. ECAPed pure Mg can be anticipated to obtain better corrosion resistance than coarse-grained or as-cast Mg with its excellent mechanical properties. Unfortunately, similar results of reduction in corrosion resistance of ECAPed ZK60 Mg alloys were observed in aqueous NaCl solution. In addition, internal stress at 4^{th} pass of ECAPed ZK60 samples after aging is −1.52 ± 0.23 MPa (normal stress) and the stress in the 16^{th} pass of ECAPed sample after aging was found −1.82 ± 0.23 MPa (normal stress). This result shows that the internal normal stress in the samples processed by equal channel angular press is compressive stress and also this proves the sample undergone more ECAP passes does accumulate a larger compressive stresses. The large compressive stress and secondary phases of the sample affects the corrosion resistance because which increases the activity of the Mg alloys likewise making it easier to corrode. Also this study demonstrates that aged samples have better corrosion resistance in comparison with the ECAP processed ZK60 alloys [60]. Similarly, Yang et al. [61] worked on ideal biodegradable implants of bone tissue engineering, here Mg-Zn alloys regarded as excellent biocompatibility materials based on its mechanical properties. But the corrosion resistance of Mg-xZn alloys was investigated by immersion and electrochemical tests in Ringer's solution, results revealed that by increasing Zn concentration increases the corrosion current, because micro-galvanic corrosion was caused by more large-size intermetallic phases. Although solid solution treatment possibly reduces the intermetallic phase quantity. Remarkably, aging treatment could reduce the isolation of Zn and support the compactness and uniformity of corrosion product layer on the surface. This leads to the improvement of corrosion resistance. Additionally, have shown as-extruded Mg-6%Zn alloy (wt%) aged for 72 h was harmless for biomedical applications. The corrosion resistance of ultrafine grained ECAPed ZE41A alloy increases in HCl aqueous solution but the same alloy has shown decreased corrosion resistance in NaOH aqueous solution [59]. Fortunately, some of the researchers have published the corrosion tendency of ECAPed Mg alloys in the noble side; which offers important step toward corrosion study of Mg alloys after ECAP. The ECAPed Mg alloy with more number of passes attains higher electrochemical activity and the increased corrosion tendency, thus more easily forms oxidation product in the various corrosive environment. This oxidation product with improved adhesion force can make ECAPed Mg alloy from SPD become more corrosion resistant [59]. The study on corrosion behavior of ECAPed AM 70 Mg alloys has shown better corrosion resistance properties, here ECAP 3^{rd} pass sample charge transfers resistance (R_t) values improved by ~5.28 and ~3.72 times in comparison to as-cast and homogenized specimens respectively. This is due to ultra-refined microstructure and formation of β phases [62], a similar observation was identified on AE42 Mg alloys after 8 ECAP passes due to more stable and thicker corrosion layer [46]. Qiang-Fan et al. [63] observed corrosion resistance of the fourth passed ECAPed Mg alloy was higher than the as-cast alloys but eighth passed ECAPed alloys have shown the poor result on Mg-12Al-0.7Si alloy, thus obtained result is rather contradictory to above discussions. Jiang et al. [64] also supports the above conflicting situation, here author investigates the corrosion behavior of ECAPed Mg–2Gd–1Y–1Zn–0·2Zr alloy with 3.5 wt% NaCl solution and ECAP passes went up to 12 passes. The study reveals, the corrosion rate of the ECAPed Magnesium alloy in a fine grained condition significantly decreased when it compared to the as cast alloy. This means that grain refinement can inhibit micro-galvanic reactions and hindrance the pitting corrosion.

Table 5. Summary of corrosion behavior of Magnesium alloys.

Reference	Mg-Based Alloys (x in wt%)	Media	Immersion time (hr)	Method /Test	Corrosion Temp.&pH	Corrosion Corrosion rate (mm/y)	Remark
[49]	Mg AZ31 AZ91	3.5 Wt% NaCl	3	Weight loss & Electrochemical	N/A	0.25 4.11 1.16	Weight loss measurement initially shows an increase in corrosion rate in order of Mg < AZ91 < AZ31 in 3.5% NaCl solution. After 3 h of immersion, the corrosion rate of AZ91 becomes much more than AZ31 alloy due to galvanic corrosion. Also from the Tafel plots, the corrosion resistance of the materials are given in order as AZ31 < AZ91 < Mg.
[39]	Mg–Zn–Ag	500 ml NaCl 3.5% saturated with $Mg(OH)_2$	72	Immersion Test	N/A	N/A	Addition of silver (Ag) leads to grain refinement due to the formation of precipitates, increases hardness and reduces corrosion resistance.
[9]	AZ61+Mn+RE	3.5 Wt% NaCl	1-96	Electrochemical	Room temp. &7 to 11	N/A	AZ61+Mn+RE have a significant effect on corrosion resistance.
	AZ61+Mn+RE	5 Wt% NaCl	72	Salt spray Test	N/A	N/A	
[19]	AZ91 AZ91+Ti	3.5 Wt% NaCl	150	Electrochemical	Room Temp. & N/A	0.77 0.75	Addition of Ti reduced the volume fraction of the β phases in AZ91. Also which shows corrosion resistance.
[18]	Mg-5Y-7Gd-1Nd-0.5Zr	5 Wt% NaCl	2, 24, 60,108	Electrochemical	22±1°C N/A	N/A	Corrosion rates increases with immersion time
[92]	Mg-2Zn-0.5Ca-Y	Hank's Solution 3.5 wt% NaCl	120 168 N/A	Electrochemical	Room Temp. & N/A	N/A N/A N/A	The addition of more Y in the alloy leads to the formation of a second phase MgY. The second phase MgY can form many of corrosion micro-batteries, which accelerate the corrosion rate of the alloy.
[42]	AZ31B AM60 AMX602 AZ91D	Urban and Marine Environment	3 Years	Weight loss	Env. Temp & N/A	N/A	AZ91D Mg alloy had superior corrosion resistance properties
[93]	Mg–Zn–Ca–x(0,0.5,1)Ce/La	3.5 Wt% NaCl	1 to 7 days	Electrochemical	Room Temp. & N/A	0.82 3.12 `1.73	Addition of Ce/La provides more fine secondary phase particles this makes more cathodic sites which accelerate the galvanic corrosion.
[94]	Mg−x(1,1,1,2,3)Sn−y(0.2,0.5,1.5,0.5,0.5)Ca	1 L Hank's salt solution	250	Electrochemical	37^{o}C & 7 to 10	0.31 0.27 0.40 0.30 0.31	The as-extruded Mg−1Sn−0.5Ca alloy has a homogenous microstructure, results in good mechanical properties and low corrosion rate, therefore this alloy might be potential for biomedical applications.

Table 5. (continue)

Reference	**Mg-Based Alloys (x in wt%)**	**Corrosion**					
		Media	**Immersion time (hr)**	**Method /Test**	**Temp.&pH**	**Corrosion rate (mm/y)**	**Remark**
[95]	Mg-x(0.5,1,1.5,2.5)Sr	Hank's solution	500	Immersion & Electrochemical	37ºC & N/A	0.29 0.33 0.40 0.52	As-extruded Mg-0.5Sr alloy had moderate mechanical properties and slow corrosion rate and good cytotoxicity
[61]	Mg-x(6,14.5,25.3,40.3)Zn	Ringer's solution	96	Immersion & Electrochemical	37ºC & N/A	0.72 2.47 3.66 6.03	Study revealed that by increasing Zinc (Zn) concentration reduced the corrosion potential but increased corrosion current.
[76]	Mg-x(2,4,6,8,4,4)Sb-x(0,0,0,0,2,4)Si	3.5 wt% NaCl solution	N/A	Electrochemical	Room Temp. &N/A	4.65 5.70 7.21 9.08 5.20 4.06	The electrochemical test reported that the corrosion resistance of Mg-Sb binary alloys reduced with an increase in Sb content. In contrast, Si additions improved the corrosion behavior of Mg-Sb-Si ternary alloys.
[97]	AZ31 AZ91 AZ111 AZ141	3.5 wt% NaCl solution	N/A	Electrochemical	Room Temp. & N/A	2.23 1.01 1.33 1.44	AZ91 magnesium alloys is resistant to corrosion
[96]	Mg-Zn-RE-x(0, 0.5, 1.5, 3 6) Ca	0.9 wt% NaCl solution	168	Electrochemical	Room Temp. & 7 to 12.5	9.71 7.13 14.41 15.46 22.30	The quaternary Mg-Zn-RE-0.5Ca alloy acquires a lower corrosion current density (i_{corr}) and higher charge transfer resistance (Rt) compared to the ternary Mg-Zn-RE alloy.
[98]	Mg-17Al-7Cu-3Zn-x(0,1,2,3)Gd	3 wt % potassium chloride (KCl) solution	0.5	Immersion & Electrochemical	25ºC & N/A	11.01 2.49 3.43 3.87	The degradation rate of Mg-17Al-7Cu-3Zn-1Gd alloy reduced compared with the base alloy
[99]	Mg–x(1.7,2.8,3.8)Y–y(1.3,2.1,3)Zn–z(0.18,0.18,0.18)Zr	3.5 wt% NaCl solution	24	Electrochemical	25ºC & N/A	0.60 0.55 0.51	As-extruded Mg-3.8Y-3Zn-0.18Zr alloy possess the maximum ultimate and yield strength of 420 MPa and 300 MPa, respectively, as well as it shown the best corrosion resistance
[47]	Mg–5Al–x(0,1,2,3,4)Zn	3.5 wt% NaCl solution	7	Electrochemical	Room Temp. & N/A	N/A	Mg-5Al alloys contain Zn shows lower corrosion and hydrogen evolution rate.

Table 6. Summary of the corrosion behavior of ECAPed Mg alloys.

Reference	Material	Equal Channel Angular Press (ECAP) of Mg alloys							Corrosion of ECAPed Mg alloy				
		Φ (deg)	**Ψ (deg)**	**Temp. (K)**	**Route**	**Speed (mm/min)**	**Number of pass**	**Grain size(μm)**	**Media**	**Immersion Time(hr)**	**Temp. (^{0}C) & pH**	**Corrosion Rate (mm/y)**	**Remark**
[20]	Pure Mg	90	N/A	573	N/A	30	6P	50-100	3.5 wt.% NaCl	6	Room Temp. & N/A	2.28	Pure Mg exhibits higher corrosion resistance than the ECAPed pure Mg.
[100]	AZ91D	90	N/A	523	C	60	1-12P	2-3	3.5 wt% NaCl	48	Room Temp. & N/A	6.35	The corrosion rate increased with the increase of ECAP passes. The sample of 12 ECAP passes had average corrosion rate nearly 38 times larger than the as-cast alloy.
[101]	AE21 and AE42	90	0	453	Bc	50	8P	2-3	0.1 M NaCl solution	168	Room Temp. & 7	N/A	Corrosion resistance of AE21 was reduced after 8 passes of ECAP. But in AE42, observed that the corrosion resistance significantly higher.
[102]	AZ91D	90	0	523	C	30	16P	1-2	3.5wt.% NaCl solution	168	Room Temp. & 10-11	N/A	The Micro-arc oxidation (MAO) coating on the ECAPed AZ91D Mg alloy presents lower corrosion rate and the larger Rf value than that on the coarse-grained as-cast alloys.
[62]	AM70	110	20	548	Bc	60	4P	8	0.1 M wt% NaCl	N/A	Room Temp. & 7.5	N/A	Showed better corrosion resistance properties of ECAP at 3 pass sample and Rt values improved by ~5.28 and~ 3.72 times in comparison to as-cast and homogenized samples
[43]	AE42	90	0	453-483	Bc	10 and 20	8P	8-10 & 3-4	0.1 M NaCl	168	Room Temp. & 7	N/A	The ECAPed AE42 Mg alloys showed substantially higher corrosion resistance.
[103]	Pure Mg	90	N/A	523	N/A	N/A	4P	2.35	0.1 M NaCl	N/A	Room Temp. & N/A	0.045	ECAP was shown the improved corrosion and mechanical properties of the pure Magnesium.

Table 6. (continue)

Reference	**Material**	**Equal Channel Angular Press (ECAP) of Mg alloys**							**Corrosion of ECAPed Mg alloy**				
		Φ (deg)	**Ψ (deg)**	**Temp. (K)**	**Route**	**Speed (mm/min)**	**Number of pass**	**Grain size(μm)**	**Media**	**Immersion Time(hr)**	**Temp. (^{0}C) & pH**	**Corrosion Rate (mm/y)**	**Remark**
[63]	Mg-12Al-0.7Si	90	20	573	Bc	1.5	2-8P	N/A	3.5% NaCl	0.055	Room Temp. & N/A	N/A	ECAP had a significant effect on corrosion for improving corrosion resistance of Mg-12Al-0.7Si magnesium alloy.
[104]	AZ31	120	60	423 & 573	Bc	240	8P	10-3	RPMI-1640	24	37 & 7.4	0.002	Immersion test results of AZ31 Magnesium alloy shows, Weight loss of ECAPed sample at 573K was smaller than the ECAPed sample at 473K.
[64]	Mg–2Gd–1Y–1Zn–0·2Zr	N/A	N/A	623	N/A	60	1-16P	N/A	3.5% NaCl	12	Room Temp. & N/A	N/A	Grain refinement through ECAP can inhibit general micro-galvanic reactions and hinder the pitting corrosion
[80]	ZK60	110	20	523	Bc	30	4P	0.7	Phosphate buffer solution (PBS)	96	37 & 7.4	N/A	ECAP technique decreases the size of the second phase particles thus improving microstructure homogeneity, thereby decreasing the pitting corrosion effects.
[24]	Pure Mg	90	N/A	523	Bc	N/A	8P	2.6	0.1M NaCl	N/A	N/A & <11	0.27	Smaller grain size had a lower current density
[60]	ZK60	N/A	N/A	518	C	N/A	16P	N/A	3.5 wt.% NaCl	0.5	Room Temp. & N/A	N/A	The corrosion behavior is improved after aging treatment. The improvement may be due to the reduction of stress and the better film Protection.
[65]	AZ31	120	60	473-573	B_A	20	4P	N/A	0.9% NaCl solution	24	37 & 10	N/A	Corrosion properties could be improved by better redistribution of the second phase particles through the post-ECAP aging treatment.

Table 6. (continue)

Reference	Material	Equal Channel Angular Press (ECAP) of Mg alloys							Corrosion of ECAPed Mg alloy				
		Φ (deg)	Ψ (deg)	Temp. (K)	Route	Speed (mm/min)	Number of pass	Grain size(µm)	Media	Immersion Time(hr)	Temp. (^{0}C) & pH	Corrosion Rate (mm/y)	Remark
[66]	AZ31	90	N/A	623	Bc	350	4P	10-30	3.5 wt.% NaCl	N/A	Room Temp. & 10.5	N/A	Corrosion resistance after conventional Extrusion was higher than after the ECAP process.
[68]	AZ31	N/A	N/A	573	N/A	24-30	4P	1.7	Hank's solution	480	37 ± 0.5 & N/A	0.73	ECAP with back pressure shows the improvement in mechanical properties without reducing the corrosion resistance.
[69]	ZE41A	N/A	N/A	603	N/A	N/A	8,16,60P	2.5	250ml Hank's solution	1, 96,192	Room Temp. & N/A	0.009	Observed decrement of corrosion current density for ultrafine-grained ZE41A Mg alloy immersed in Hank's solution.
[67]	AZ31	120	N/A	573	Bc	N/A	4P	1-5	saturated simulated body fluid (SBF 5×)	72	Room Temp. & N/A	0.22	ECAPed samples helped to reduce the degradation of AZ31 Mg alloy.
[105]	Mg-Gd-Nd-Zn-Zr	90	37	648	Bc	24	4P	2.5	simulated body fluid (SBF)	240	37 & N/A	0.36	The bio-corrosion resistance of ECAPed sample in simulated body fluid (SBF) was improved apparently.
[47]	AZ80	90	N/A	623	Bc	N/A	8P	300-3	0.1M NaCl	0-96	22 & N/A	N/A	Enhanced electrochemical properties were found in the ultrafine-grained ECAP specimen as compared to its coarse-grained.
[106]	AZ31	90	N/A	453	Bc	50	8P	1	0.1M NaCl	168	Room Temp. & N/A	1.32	After immersion time of 168 h the specimen after ECAP exhibits superior corrosion resistance to the specimen after extrusion.
[29]	AZ31	90	N/A	523	N/A	6	1P	4.5	phosphate-buffer solution (PBS)	2,24,48	N/A	N/A	The best corrosion behavior corresponds to the AZ31 alloy with the finest grain size in PBS.
[107]	AZ61	90	0	623,673	N/A	N/A	8,16P	10	Distilled water	N/A	N/A	N/A	The as-cast AZ61 Magnesium alloys with about 6% Aluminum content have a great tendency to stress corrosion cracking in distilled water and the ECAPed processing increased the susceptibility to SCC at room temperature.

The ECAPed alloy processed fourth pass showed lower corrosion current density and higher resistance to corrosion. But alloy processed twelfth pass shown lower corrosion resistance due to gradual loss of barrier effect of intergranular phases. Further, [60] had discussed the significance of ECAP-aged Mg alloys, primarily author investigates the corrosion behavior of ECAPed ZK60 Mg alloys by Electrochemical test, ECAP processed with more number of passes shown higher current density (i_{corr}) which shows, alloy is susceptible to corrosion. Subsequently aged ECAPed Mg samples was examined, which reveals that ECAP aging can slightly improves the corrosion resistance of the Mg alloys also enhance the performances due to the stress relief and uniform dispersion of secondary particles. Similar investigation is also observed on AZ31 alloy. Here the aging of ECAPed AZ31 was carried at 220°C and 260°C prior to electrochemical corrosion test, the corrosion study showed that aging at 220°C has most favorable corrosion resistance compared to aging at 260°C and also investigation revealed that there is no significant effect of aging time [65]. According to [66] fine grain size creates more number of grain boundaries which act as a corrosion barrier and also smaller grain size increases wettability and bioactivity of AZ31 Mg alloy. Hence the rapid bio-mineralization achieved in ECAPed samples helped to reduce the degradation of AZ31 Mg alloy [67]. Gu et al. [68] have checked the effect of back pressure in ECAP processing of AZ31 alloy on corrosion resistance. With or without back pressure, ECAP extruded sample exhibited closer corrosion rate between them. The ECAP with back pressure appeared to be an efficient method to improve the mechanical property of Mg alloy without a considerable reduction in corrosion resistance. Fan Zhang et al. [69] worked on ZE41A, rare earth-containing Mg alloys to study the charge transfer resistance after multi-pass of ECAP at 603K for 60 passes. This number of ECAP passes resulted in the association of corrosion potential toward the noble direction. Which show evidence of lower corrosion current density for ultra-fined ZE41A Magnesium alloy immersed in Hank's solution. The corrosion current density (i_{corr}) of the ECAPed sample is minimum, results low corrosion rate also from potentiodynamic polarization test obtained is 8.1 ± 1.1 $\mu A/cm^2$ for ECAPed, which is lower than that of the as-cast (14.5 ± 1.5 $\mu A/cm^2$) [100]. Further, detailed summary of corrosion behavior of ECAPed magnesium alloys and its effects are presented in Table 6. From table 6 it was observed that ECAPed Mg alloys significantly reduce the corrosion rates at higher ECAP passes, this is mainly due to grain refinement and distribution of secondary phase during ECAP. Also, it is noticed that corrosion rate is lower at higher processing temperature and vice versa. Along with this ECAP geometry has greater influence on grain refinement and its uniformity, which contributes to improving the corrosion resistance.

5. Conclusions

The current review presents the significant progress of grain refinement through equal channel angular pressing of Magnesium-based alloys and its corrosion performance in aqueous solution. The mechanical and corrosive behavior strongly depends on the microstructure of the Mg alloys. Based on the review process and subsequent discussions, the following conclusions were drawn:

- Improved mechanical and corrosion properties were documented for ECAP processed magnesium alloys when compared with as-cast magnesium alloys.
- ECAP is well-suited extrusion process for deforming Mg and its alloys because of its low plastic deformation ability; also by controlling the alloying chemistry overall microstructure of the Mg alloys can significantly reduce the rate of corrosion.
- Finer microstructure and more homogeneous secondary phase dispersion reduce the localized corrosion or pitting. It is possible to change the corrosion kinetics by changing microstructure without any changes in the composition of the alloy.
- The grain refinement by multi-ECAP passes significantly effects the corrosion behavior towards inhibition of Mg corrosion rate that is limited only up to certain number of ECAP passes.

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