Abstract

An anodizing process, based on environmental friendly electrolytes solutions that contains none of chromate, phosphate or fluoride has been studied by using three types of electrolytes: the first is based on sodium silicate, the second on sodium hydroxide- Boric acid- Borax and the third on sodium silicate- potassium hydroxide- sodium carbonate-sodium tetra borate. Two type of Pretreatment process commonly used in electroless processes and zinc immersion including fluoride activation has been applied before the anodizing process. Anodizing behaviors of AZ 91magnesium alloy are influenced by many factors, including the constituents of electrolyte solution, applied current density or voltage, and deposition time. It is found that the anodic film thickness increases as current density or anodizing voltage increases with deposition time until the deposition stops due to the formation of a thick anodic film. The increase in the film thickness is not always linear with increasing current density and deposition time. Optimization of the anodizing conditions - current density and deposition time - was made based on the maximum thickness obtained. Characterization of anodizing layer was achieved by determination of surface morphology, microstructure, phase analysis, coat thickness, adhesion and corrosion resistance.

For all electrolytes, excellent adhesion and corrosion resistance was obtained with a corrosion efficiency ranging from (94%-97%).

Key Words: Anodizing, Magnesium AZ91, Corrosion, Environmentally friendly.

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1.1 Introduction

Magnesium is the 8th most abundant element on the earth making up approximately 1.93% by mass of the earth's crust and 0.13% by mass of the oceans [1]. It also has some advantageous properties that make it an excellent choice for a number of applications. Magnesium has a high strength: weight ratio with a density that is only 2/3 that of aluminum and 1/4 that of iron. Magnesium also has high thermal conductivity, high dimensional stability, good electromagnetic shielding characteristics, high damping characteristics, good machinability and is easily recycled [1]. These properties make it valuable in a number of applications including automobile and computer parts, aerospace components, mobile phones, sporting goods, handheld tools and household equipment. Magnesium has even been suggested for use as an implant metal due to its low weight and inherent biocompatibility [2]. Due to limited fossil fuel stores and environmental problems associated with fuel emission products; there is a push in the automotive industry to make cars lighter in order to decrease fuel consumption. The use of magnesium alloys can significantly decrease the weight of automobiles without sacrificing structural strength. Unfortunately, magnesium has a number of undesirable properties including poor corrosion and wear resistance, poor creep resistance and high chemical reactivity that have hindered its widespread use in many applications. One of the main challenges in the use of magnesium, particularly for outdoor applications, is its poor corrosion resistance.

1.2 Identification of Magnesium Alloys [3]

Fig (1-1) and Table (1-1) shows that the identification of magnesium alloys is standardized worldwide in the ASTM norm; each alloy is marked with letters indicating the main alloy elements, followed by the rounded figures of each (usually two) weight in percentage terms. The last letter in each identification number indicates the stage of development of the alloy (A, B, C,--) as shown in table (1-2). In most cases, these letters show the degree of purity. The alloy AZ91, for example, is an alloy with a rated content of 9% aluminum (A) and 1% zinc (Z).

The corresponding DIN specification would be MgA19Znl. ASTM dictates the following composition (all values weight-%) Al 8.3-9.7; Zn 0.35-1.0; Si max. 0.10; Mn max. 0.15; Cu max. 0.30; Fe max. 0.005; Ni max. 0.002; others max. 0.02. Iron, nickel, and copper have tremendous negative effects on the corrosion resistance and hence these values are strictly limited.

Table (1-1) Equivalent British and American designation for Mg-alloys

Wrought alloys		**Cast alloys**	
British Designation	**American Designation (ASTM)**	**British Designation**	**American Designation (ASTM)**
ZW6	ZK60A	Z5Z	ZK51A
AM503	M1A	RZ5	ZE41A
AZM	AZ61A	TZ6	ZH62A
AZ855	AZ80A	MSR	QE22A
ZM21	ZM21	ZRE1	EZ33A
ZM61	ZM61	ZT1	HZ32A
AZ91X	AZ91	MTZ	HK31A
ZE63	ZE63	A8	AZ81A

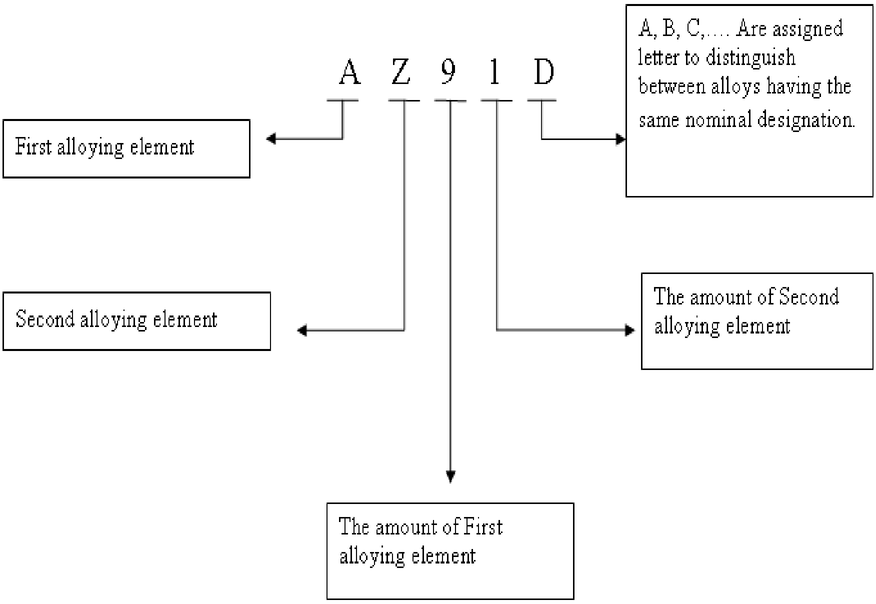


Fig (1-1) ASTM norm for magnesium alloys

Table (1-2) ASTM codes for magnesium alloying elements

Abbreviation letter	**Alloying element**	**Abbreviation letter**	**Alloying element**
A	Aluminium	N	Nickel
B	Bismuth	P	Lead
C	Copper	Q	Silver
D	Cadmium	R	Chromium
E	Rare earths	S	Silicon
F	Iron	T	Tin
H	Thorium	W	Yttrium
K	Zirconium	Y	Antimony
L	Lithium	Z	Zinc
M	Manganese		

1.3 Some applications of the Magnesium alloys [3]

1.3.1 Automotive Branch

Front frames, main frames, intermediate cases, bleed ducts, and other engine structures are all designed to be made as castings when weight and strength are important considerations.

- **Gearbox housing VW (AZ91)**
  - Weight reduction.
  - Vibration damping stiffness.

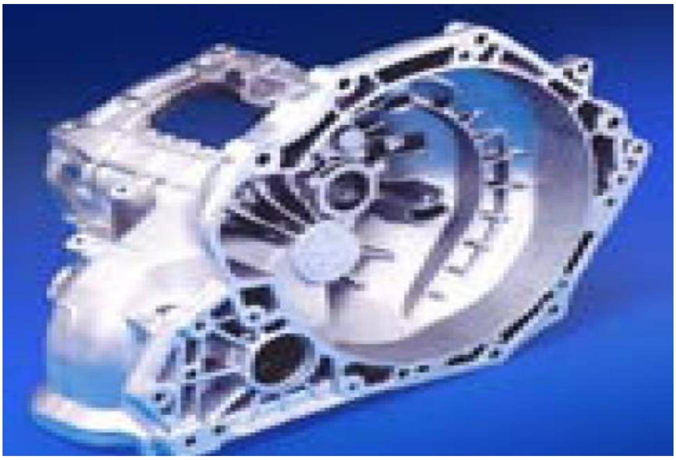


Fig (1-2) Gearbox housing VW

- **Fuel tank covering (AM60B)**
  - Weight: 3.2 kg; weight reduction approx. 4 kg .
  - Torsion resistance of the convertible frame.
- **Steering wheel**
- **Steering column holder and bracket Audi/Zitzmann (AZ91)**
  - Weight reduction (approx. 20 kg)
  - Dimensional accuracy

  - Environmental aspects

- **Seat frame - Alfa Romeo Meridian-MPI (AM60)**

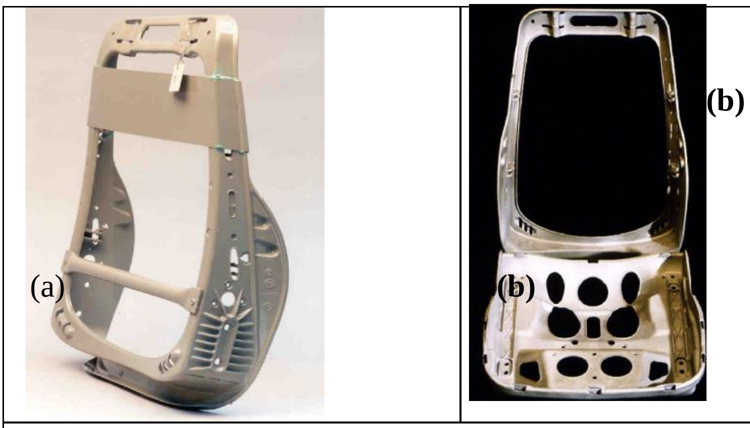
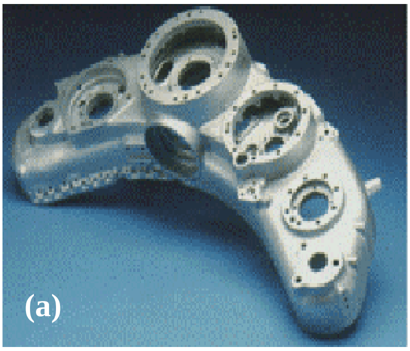


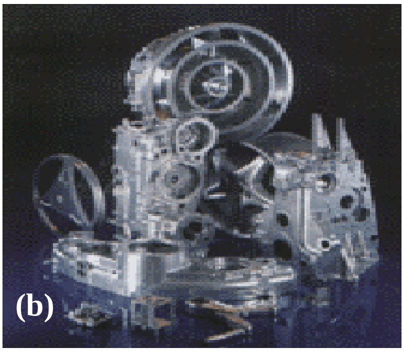
Fig (1-3) – a,b Seat frame made of Mg alloys

1.3.2 Aerospace.

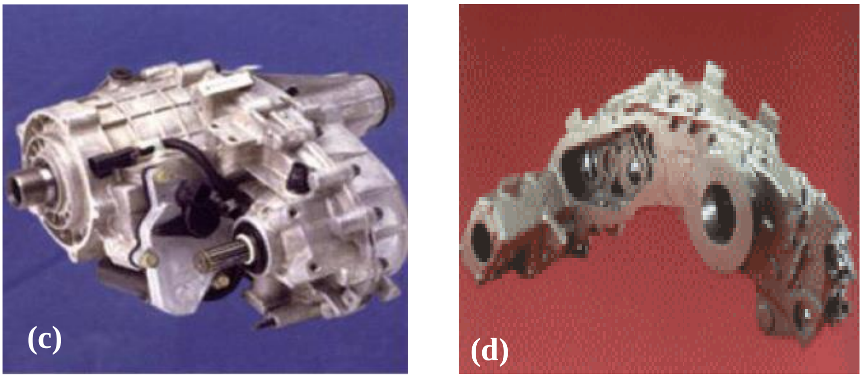
Magnesium alloys are extensively used for a range of helicopter transmission casings. ZE41 is an alloy specified for applications operating up to 150°C due to its excellent castability and good mechanical properties.



Brackets



Aircraft wheel discs



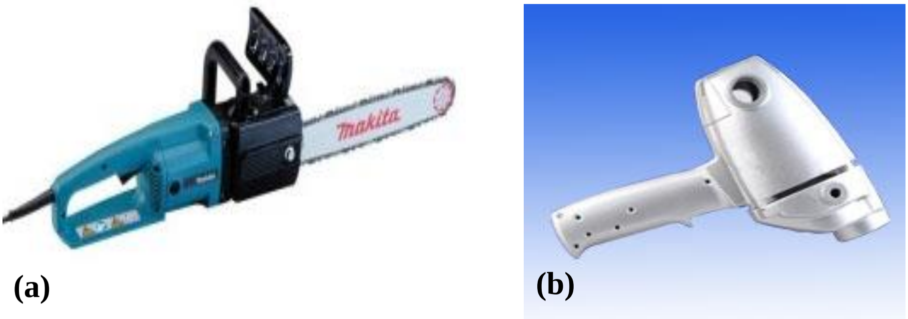
- Helicopter gear-box housings

- Various body components

Fig (1-4) (a,b,c,d) Applications of Magnesium alloys in Aerospace field

1.3.3 Tools

Magnesium castings of all types have found use in many commercial applications, especially where their lightness and rigidity are a major advantage, such as for chain saw , drills bodies.



-Electric Chain Saw (Makita)

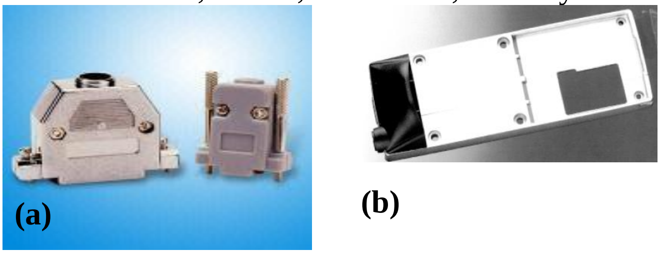
- Electric hummer drill (Makita - Bosh)

Fig (1-5) (a,b) applications of Magnesium alloys in workshop tools

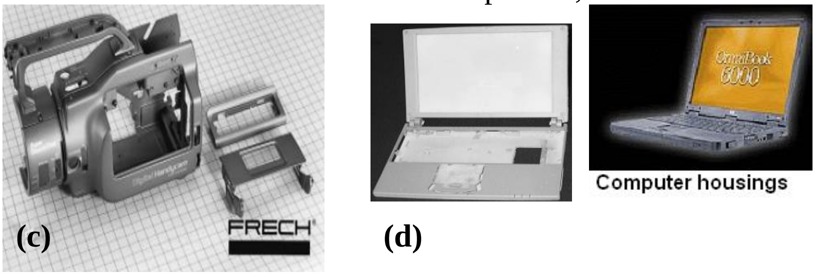
1.3.4 Electronics Industry

Magnesium alloys are now being extensively applied in computer components, camera bodies, communication micro electronics and optical instruments. Magnesium alloys can also be used in home appliances, mobile phones and electronic products.

Printed circuits, diodes, connectors, memory drums, etc



-Connectors -Cellular phones, Television



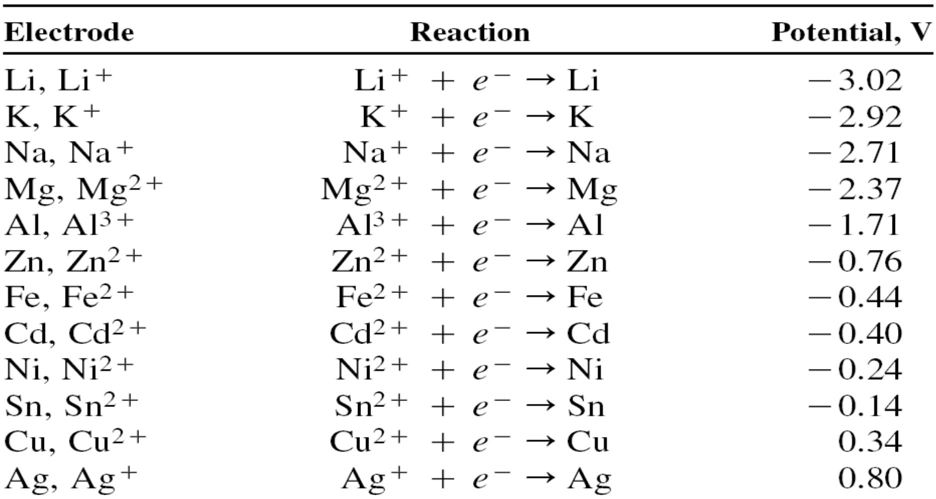
-Camera -Computer housing

Fig (1-6) applications of Magnesium alloys in Electronics Industry

1.4 Corrosion of Magnesium and its alloys

Magnesium and its alloys are extremely susceptible to galvanic corrosion, which can cause severe pitting in the metal resulting in decreased mechanical stability and an unattractive appearance. Magnesium and its alloys are often thought of as rapidly corroding metals because of their active positions in electromotive series Table (1-3).

Table (1-3) Standard reduction potentials



Electrode	Reaction	Potential, V
Li, Li^+	$Li^+ + e^- \rightarrow Li$	−3.02
K, K^+	$K^+ + e^- \rightarrow K$	−2.92
Na, Na^+	$Na^+ + e^- \rightarrow Na$	−2.71
Mg, Mg^{2+}	$Mg^{2+} + e^- \rightarrow Mg$	−2.37
Al, Al^{3+}	$Al^{3+} + e^- \rightarrow Al$	−1.71
Zn, Zn^{2+}	$Zn^{2+} + e^- \rightarrow Zn$	−0.76
Fe, Fe^{2+}	$Fe^{2+} + e^- \rightarrow Fe$	−0.44
Cd, Cd^{2+}	$Cd^{2+} + e^- \rightarrow Cd$	−0.40
Ni, Ni^{2+}	$Ni^{2+} + e^- \rightarrow Ni$	−0.24
Sn, Sn^{2+}	$Sn^{2+} + e^- \rightarrow Sn$	−0.14
Cu, Cu^{2+}	$Cu^{2+} + e^- \rightarrow Cu$	0.34
Ag, Ag^+	$Ag^+ + e^- \rightarrow Ag$	0.80

Unalloyed magnesium is not extensively used for structural purposes. Consequently fig (1-2), the corrosion resistance of magnesium alloys is of primary concern. Two major magnesium alloys systems are available: the first includes alloys containing 2 to 10% Al, combined with minor additions of zinc and magnesium. These alloys are widely available at moderate cost, and their room-temperature mechanical properties are maintained to 95 to 120ºC. Beyond this, elevated temperatures adversely affect mechanical properties sand corrosion properties deteriorate rapidly with increasing temperature.

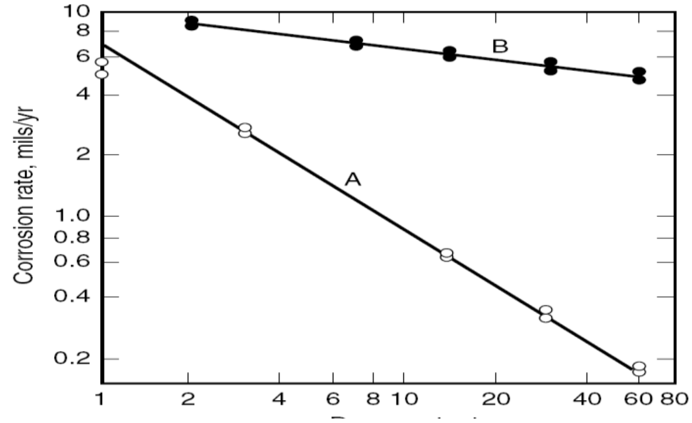


Fig (1-2) Corrosion rates as a function of time for commercially pure magnesium. Curve distilled water vented to air through a caustic trap; curve B, distilled water vented to atmospheric CO_2 Source

The second group consists of magnesium alloyed with various elements (rare earths, zinc, thorium, and silver) except aluminum, all containing a small but effective zirconium content that imparts a fine grain structure and thus improved mechanical properties. These alloys generally posses much better elevated-temperature properties, but the more costly elemental additions combined with the specialized manufacturing technology required result in significantly higher cost.

The corrosion resistance AZ91 magnesium alloy which is related to first group is influenced by the microstructural features of the alloy. The Mg-Al-Zn solid solution, called α phase, constitutes microstructure. However, thermal aging invariably and readily produces secondary β phase, which consists predominantly of $Mg_{17}Al_{12}$ .The β phase is considerably corrosion resistant and cathodic to α phase. Thus, the α and β phases when in contact will easily cause galvanic corrosion, Fig (1-3) [3, 4].

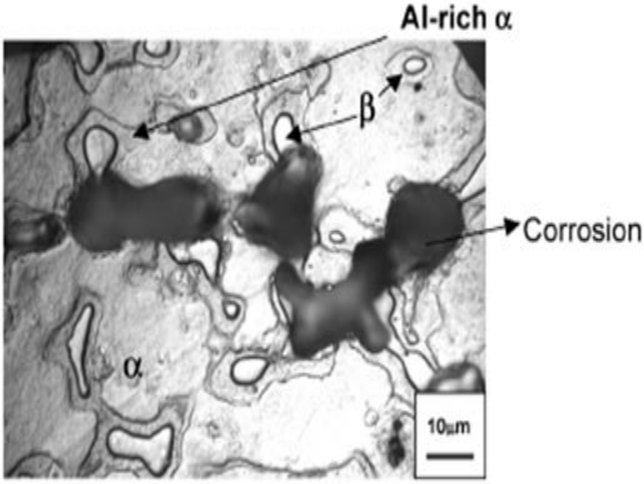


Fig. (1-3) Reflected light micrograph of the surface of the AZ91, after 100 h of immersion in 0.1 M NaCl solution

- The corrosion behavior of a WE43 Mg alloy, were studied by using AC/DC current density using a waveform involving a final period of current decay in an alkaline silicate solution and also the change of the oxide film morphology with immersion time was also examined using scanning electron microscopy. It was found that anodization of the WE43 alloy significantly improves its corrosion resistance and greatly increases the time to pitting in the NaCI solution, which for air-formed films is in the range 2-3 h. By fitting the impedance data to a two-time-constant equivalent circuit and by tracking the open-circuit potential, it is demonstrated that film hydration initially decreases the corrosion resistance, followed by an increase in the resistance due to the gradual conversion of MgO to Mg $(OH)_2$, which leads to partial blocking of the film pores. During this time period, the underlying barrier film is slowly thinned and/or penetrated by chloride ions, consistent with its increasing capacitance and decreasing resistance, ultimately leading to a loss in corrosion resistance. Overall, both the porous and barrier oxide layers contribute to the corrosion protection of WE43, and the higher the voltage and the longer the time of current decay in the latter stages of Anodization, the lower the alloy corrosion susceptibility.

- Electrochemical behaviors of magnesium alloys (AZ31 and AZ91) in NaOH alkaline solution [5]. Specimens were anodized for 10 min at 3, 10 and 80 V in 1 mol/dm^3 NaOH alkaline solution. The films anodized at 3 V Mg alloys had the best effective corrosion resistance and these films consisted of comparatively thick magnesium hydroxide. Anti-corrosion characteristics of AZ91 are better than those of AZ31 because of AZ91 has abundant Al content compared to AZ31. Al content largely affect corrosion resistance of Mg-Al alloys, so difference of corrosion resistance in AZ91 is larger than that in AZ31. Low Al content as in AZ31 does not affect pitting growth for specimen of non-anodizing, 10 and 80 V at 1*10^3 A/cm^2. AZ91 has a large (3 phase, Mg_7Al_2, because of rich Al content. Thus, the surface has (3 and a phases (Mg phase). In this case of anodizing for 10 min, current density was increased by pitting formed on p phase and reproduction of films, repeatedly. And the anodizing for 30 min, corrosion reaction was controlled by the phase because the film formed on the 3 phase by condensation is compact. So anodic polarization curve in anodizing for 30 min is the same shape those anodized at the other potentials. The films anodized for 10 min at 3 V had the most excellent corrosion resistance; these films consist of comparatively thick magnesium hydroxide. At comparison of potential corresponds to the current density of 0.1 mA/cm^2, corrosion resistances of the films anodized at 80 V on pure Mg and Mg alloys were higher than those at 10 V because the films anodized at 80 V consisted of magnesium oxide. Corrosion resistances of the films anodized at 80 V on Mg and Mg alloys were higher than those at 10 V and lower than those at 3 V.

- Protective composite coatings were prepared on magnesium alloy AZ91 by micro-arc oxidation (MAO) treatment plus a top coating with sealing agent using multi-immersion technique under low-pressure conditions [6]. The corrosion resistance of AZ91 alloy with composite coatings was superior evidently to that with merely MAO film. SEM observations revealed that the sealing agent was integrated with MAO film by physically interlocking; therewith covered uniformly the surface as well as penetrated into pores and micro-cracks of MAO film. The composite coatings can suppress the corrosion process by holding back the transfer or diffusion of electrolyte and corrosion products between the composite coatings and solution during immersion.

- the corrosion of anodized magnesium alloys, such as commercial purity magnesium (CP-Mg), high purity magnesium (HP-Mg) ingots, magnesium alloy ingots of MEZ, ZE41, AM 60 and AZ91 and die cast AM60 (AM60-DC) and AZ91 (AZ91-DC) plates by using salt spray and salt immersion testing**[7].** Anodized coating formation, during a constant-current anodizing process, Anodization can be divided into three stages according to different reactions involved in the anodizing process at different cell voltages. The initial stage includes deposition of Mg $(OH)_2$ and $MgSiO_3$ resulting from the electrochemical reaction $Mg + 2OH_2 = Mg(OH)_2 + 2e''$ and the chemical absorption of the silicate from the bath solution at cell voltages lower than about 12 V. in the second stage, apart from the deposition of Mg $(OH)_2$ and $MgSiO_3$, evolution the oxygen resulting from the deposition of the electrolyte occurs as the cell voltage increases up to 190V. When the cell voltage is over 190 up to 240 V and sparking occurs the anodizing process gets up into the third stage. It is generally accepted that sparking occurs when the cell voltage is above the dielectric breakdown voltage of the coating. The coating becomes thicker in the third stage through randomly breaking and rehearing of the coating formed in the previous stages at various areas. The corrosion resistance was in the sequential order: MEZ > AZ91-DC > AM60-DC > HP-Mg > ZE41 > CP-Mg.

1.5 Technologies available for coating magnesium and its alloys [8,9]

One of the most effective ways to prevent corrosion is to coat the base material. Coatings can protect a substrate by providing a barrier between the metal and its environment and/or through the presence of corrosion inhibiting chemicals in them. In order for a coating to provide adequate corrosion protection, the coating must be uniform, well adhered, pore free and self-healing for applications where physical damage to the coating may occur.