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# Corrosion and Surface Treatment of Magnesium Alloys

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Additional information is available at the end of the chapter

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## 1. Introduction

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.

Magnesium is the 8<sup>th</sup> 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]. Other advantages of magnesium alloys have played an important role in a broad variety of structural applications in the automobile, aerospace, electronics, and consumer products industries. Magnesium has specific high strength to weight ratio, and it is 35% lighter than aluminium and 75% lighter than iron. Typical magnesium alloys weigh ~25% less than their aluminium counterparts at equal stiffness. Magnesium also has high thermal conductivity, good electromagnetic shielding characteristics, good ductility, excellent castability and better damping characteristics than aluminum, and Mg is easily recycled. The main use of magnesium by far is as an alloying addition to aluminum alloys. Other major uses of magnesium include desulphurization of steel and the production of ductile iron. As a structural material, it can be used in aerospace components, automobile and computer parts, mobile phones and sporting goods. Magnesium for structural applications is processed into castings (die, sand, permanent mold and investment), extrusions, forgings, impact extrusions and flat rolled products. Die castings account for 70% of the castings shipped. Magnesium can be joined by riveting, or any of the commonly used welding methods [2].

With the dramatically increased emphasis on weight reduction, magnesium is receiving a lot of attention as a material for use in the next generation automobiles. This is due to limited fossil

fuel supplies and arising environmental problems associated with fuel emission products. Magnesium alloys are a promising alternative to the aluminium alloys currently dominating the transportation industry. However, the limited use of magnesium in engineering applications results mainly from the shortcomings including high reactivity in the molten state, inferior fatigue and creep properties compared to aluminium, poor corrosion and wear resistance [22]. One of the main challenges in the use of magnesium, particularly for outdoor application, is to overcome its poor corrosion resistance. Magnesium and its alloys are extremely susceptible to galvanic corrosion, which can cause severe attack in the metal resulting in decreased mechanical stability and an unattractive appearance. Corrosion can be minimized by the use of high purity alloys in which the heavy metal impurities such as iron, nickel and copper are kept below a threshold value. The elimination of bad design, surface contamination, galvanic couples and inadequate or incorrectly applied surface protection schemes can also significantly decrease the corrosion rate of magnesium alloys in service [3].

In this chapter, the corrosion characteristic of Mg and Mg alloys are described. Fundamental aspects of magnesium corrosion such as general corrosion, galvanic corrosion, pitting, stress corrosion and corrosion fatigue are reviewed. The factors that control the corrosion behaviour of Mg and Mg alloys are discussed in some detail. Finally, the more recently developed corrosion science and engineering underpinning various surface treatment methods such as electrochemical plating, conversion coating, anodizing, gas-phase coating, organic coating, electrolytic plasma oxidation for magnesium alloys are described.

## 2. Corrosion characteristics of pure magnesium

Magnesium, like most metals and alloys, relies on a natural surface film to control its corrosion. However, the nature of this film is not thoroughly understood. Good passive films are those that restrict the outward flow of cations, resist the inward flow of damaging anions or oxidants, and rapidly repair themselves in the event of localized breakdown. The structure and composition of the surface films, which depends strongly on environmental and metallurgical factors, such as electrolyte species and impurities in the metal, determine the protective ability of a passive film.

### 2.1. Environmental effects

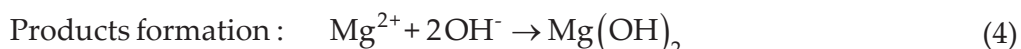
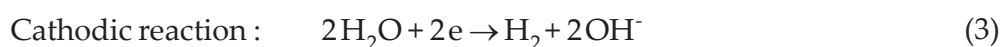
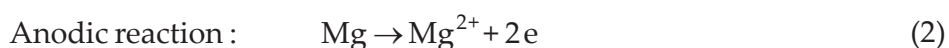
No material shows high corrosion resistance in all kinds of environments. The high corrosion resistance of materials always refers to some specific environments. Magnesium has its own preferred service environments. However, there are fewer media that are suitable for the magnesium and magnesium alloys compared with other materials, such as steels and aluminium alloys. For example, magnesium and magnesium alloys are usually stable in basic solutions, but in neutral and acidic media they dissolve at high rates [3]. This is quite different from aluminum alloys that are normally stable in neutral media but are unstable in both basic and acidic solutions.

### 2.1.1. General corrosion in aqueous solutions

With few exceptions, there is no appreciable corrosion of pure magnesium near room temperature unless water is present [4]. Magnesium dissolution in water or aqueous environments generally proceeds by an electrochemical reaction with water to produce magnesium hydroxide and hydrogen gas. Such a mechanism is relatively insensitive to the oxygen concentration, although the presence of oxygen is an important factor in atmospheric corrosion [5]. Reaction 1 describes the probable overall reaction:

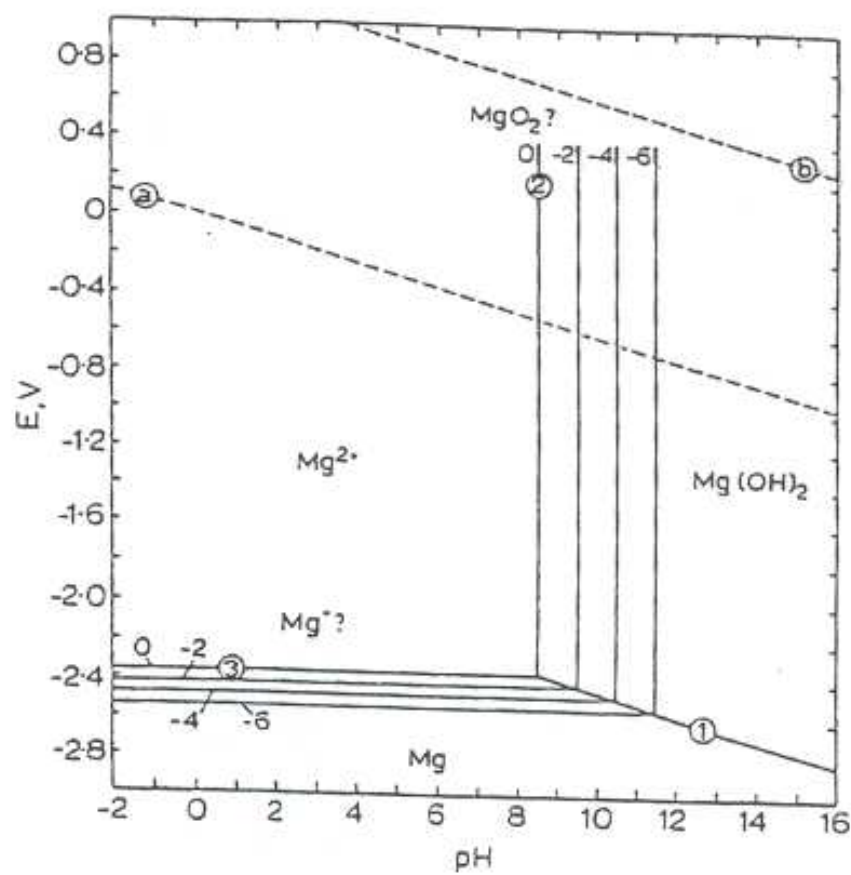
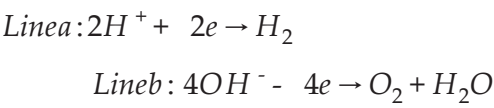


This net reaction can be expressed as the sum of the following partial reactions:



The reduction process of hydrogen ions and the hydrogen overvoltage of the cathode play an important role in the corrosion of Mg. Low overvoltage cathodes facilitate hydrogen evolution, causing a substantial corrosion rate [6].

Fig. 1 shows the corrosion domains of Mg in the Mg-H<sub>2</sub>O system. The region of water stability lies between the line a and line b. At a potential below line a, hydrogen is evolved; above line b, oxygen is evolved. The numbers identify the reactions that separate the different phases shown in reactions 5, 6, and 7. The horizontal and vertical parallel lines for reactions 5 and 6 give the concentration of Mg<sup>2+</sup> in mol l<sup>-1</sup> as a power of 10. As shown in Fig. 1, the ringed numbered lines separate the regions of corrosion (dissolved cations, e.g. Mg<sup>2+</sup>), immunity (unreacted metal, Mg), and passivation (corrosion products, Mg(OH)<sub>2</sub>) [5]. From Fig. 1, it can be seen that stable films would be expected to form depending on the values of the potential and pH. In neutral and alkaline environments, the magnesium hydroxide product can form a surface film that offers considerable corrosion protection to the pure magnesium or its common alloys, although this is not as effective as the oxide layer formed on aluminum. As corrosion proceeds, the metal surface experiences a local pH increase because of the formation of Mg(OH)<sub>2</sub>, whose equilibrium pH is about 11. The protection supplied by this film is therefore highly dependent on the condition of exposure. High purity magnesium is reported to have a corrosion rate of 10<sup>-2</sup>-10<sup>-3</sup> mils per year (mpy) when exposed to 2 normal KOH solutions at 25 °C [3].



**Figure 1.** Electrochemical potential-pH equilibrium diagram for the magnesium-water system at 25°C [5].

Magnesium’s corrosion performance in pure water is strongly dependent on temperature. At elevated temperatures, the resistance to corrosion in water decreases with increasing temperature, corrosion becoming particularly severe above 100°C [3].

Magnesium is subject to dissolution by most acids. Even in dilute solutions of strong and moderately weak acids, magnesium dissolves rapidly. There are a few exceptions, such as

chromic acid and hydrofluoric acid [6]. Very slow dissolution of magnesium in chromic acid is due to its becoming passive in this acid. An insoluble surface film of  $\text{MgF}_2$  is formed which protects against further attack, is the reason why magnesium is resistant to hydrofluoric acid [66].

The strong alkalinity of the natural hydroxide film on magnesium means there is little tendency for the compound to give up a proton to strong alkalis; consequently, the film provides excellent protection even in strong hot alkali solutions that would readily attack aluminum or zinc alloys [6, 7]. Magnesium's resistance to alkali attack combined with the metal's lightweight has made it the preferred material for cement finishing tools for many years [7].

### 2.1.2. Corrosion in the solutions containing specific ions

Salt solutions vary in their corrosivity to magnesium [7-9]: alkali metal or alkaline-earth metal (chromates, fluorides, phosphates, silicates, vanadates, or nitrates) cause little or no corrosion. Chromates, fluorides, phosphates, and silicates in particular are frequently used in the chemical treatment and anodize for magnesium surfaces due to their ability to form somewhat protective films. Chlorides, bromides, iodides and sulfates normally accelerate the corrosion of magnesium in aqueous solutions. Practically all heavy metal salts are likely to cause corrosion since magnesium normally displaces heavy metals from solution due to its high chemical activity, except iron phosphate solution.

Song et. al [10] investigated the electrochemical corrosion of pure magnesium in 1N NaCl and  $\text{Na}_2\text{SO}_4$  solutions. It was found that a partially protective surface film plays an important role in the electrochemical dissolution processes for magnesium in NaCl, and  $\text{Na}_2\text{SO}_4$  solutions. The presence of  $\text{Cl}^-$  made the surface films more active or increased the broken area of the naturally-formed protective film, and also accelerated the electrochemical reaction rate from magnesium to univalent ions according to the reactions 8 and 9, thus increasing the corrosion rates.  $\text{SO}_4^{2-}$  has less effect than  $\text{Cl}^-$ .



In a review given by Makar and Kruger [17], it is revealed that films on magnesium immersed in 3% sodium chloride consist of  $\text{Mg}(\text{OH})_2$ ,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Mg}_3(\text{OH})_5\text{Cl} \cdot 4\text{H}_2\text{O}$ , which were identified by infrared spectroscopy and X-ray diffractions. In addition, the stabilized film on magnesium also includes  $\text{MgH}_2$ .

Oxidizing anions, especially chromates, dichromates, and phosphates, which form protective films, can strongly increase the corrosion resistance of magnesium in water or aqueous salt solutions [6].



### 2.1.3. Corrosion caused by organic compounds

In a review [7], it was revealed that organic compounds, with a few exceptions, have little effect on magnesium and its alloys. It has been indicated in references 7 and 9 that magnesium is usable in contact with aromatic and aliphatic hydrocarbons, ketones, esters, ethers, glycols, phenols, amines, aldehydes, oils, and higher alcohols. Ethanol causes slight attack, but anhydrous methanol causes severe attack unless significant water content is introduced. Most dry chlorinated hydrocarbons cause little attack on magnesium up to their boiling points. In the presence of water, particularly at high temperatures, chlorinated hydrocarbons may hydrolyze to form hydrochloric acid, causing corrosive attack of the magnesium. Dry fluorinated hydrocarbons, for example, refrigerants, do not attack magnesium at room temperature. When water is present, however, hydrolysis may cause corrosive attack. In acidic food stuffs, such as fruit juices and carbonated beverages, attack of magnesium is slow but measurable. Milk causes attack, particularly when souring [7, 9].

A magnesium engine block has been targeted for reducing the weight of an automobile and corrosion is a major issue in the cooling system of an engine block. It was reported by Song et al [11] that some inhibitors in the traditional coolants, whose main compositions is 30-70 vol % ethylene glycol and molybdate, phosphate, borate, nitrite, tolyltriazole, benzoate and silicate inhibitors, fail to provide adequate corrosion protection to magnesium and magnesium alloys. Hence, some companies are developing coolants with new inhibitors for magnesium and magnesium alloys. Song et al. [11] studied the corrosion behaviour of pure magnesium in ethylene glycol containing various ions. It was found that the corrosion rate of magnesium in aqueous ethylene glycol depends on the concentration of the solution. A dilute ethylene glycol solution is more corrosive than a concentrated solution at room temperature. An ethylene glycol solution contaminated by individual contaminants NaCl,  $\text{NaHCO}_3$  and  $\text{Na}_2\text{SO}_4$  is more corrosive to pure magnesium. NaCl is the most detrimental contaminate, while in a NaCl contaminated ethylene glycol solution, a small amount of  $\text{NaHCO}_3$  or  $\text{Na}_2\text{SO}_4$  has some inhibition effect [11]. Fluorides in ethylene glycol can effectively reduce the corrosion of magnesium due to the formation of a protective fluoride-containing film on the magnesium surface. It has been observed [11] that a small amount of contaminants ( $\text{Na}_2\text{SO}_4$ ,  $\text{NaHCO}_3$ ) addition decreases the corrosion of magnesium in the chloride containing ethylene glycol solution.

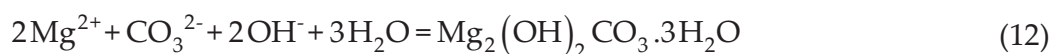
### 2.1.4. Corrosion in the air

Humidity plays a major role in the corrosion of magnesium [12]. Corrosion of magnesium increases with relative humidity. At 10% humidity, pure magnesium does not show evidence of surface corrosion after 18 months. However, at 30% humidity, a small amount of visible surface oxide haze and slight corrosion is evident, while at 80% humidity, an amorphous phase is clearly present over about 30% of the surface and the surface exhibits considerable corrosion. Crystalline magnesium hydroxide is formed only when relative humidity is at or above 93%. A theoretical explanation about less ordered films providing better protection was presented in reference 5 that a film without grain boundaries resists the movement of ions better than a crystalline film.

Furthermore, the presence of 300 ppm CO<sub>2</sub> and normally 1 ppm of SO<sub>2</sub> in the atmosphere also plays an important role in a formation of the surface films. In the atmosphere, an inhibitive effect of CO<sub>2</sub> in humid air has been reported [4]. Initially, the ambient levels of carbon dioxide enhance the corrosion attack, however, the rate of corrosion in the presence of CO<sub>2</sub> decreases with increased exposure time. It is suggested that the initial enhance of corrosion stems from the protolysis of carbonic acid, causing a pH decrease in the surface electrolyte as can be seen in reactions 10 and 11. The reduced pH in the surface electrolyte acts to increase the rate of dissolution of the air-formed film.



The hydroxide ions, generated in the cathodic reaction or dissolved from the film, can form carbonate with carbonic acid. In the presence of CO<sub>2</sub>, a magnesium hydroxyl carbonate is formed (reaction 12).



Magnesium hydroxyl carbonate may also form by reaction of solid magnesium hydroxide with CO<sub>2</sub> and water. The presence of the carbonate film, which is thicker than the magnesium hydroxide film, interferes with both the anodic and the cathodic reaction and thus reduces the corrosion rate. Further, the protolysis of CO<sub>2</sub> counteracts the development of pH gradients on the surface, impeding the development of macroscopic corrosion cells, resulting in inhibition of pitting corrosion. Hence, high purity magnesium and magnesium alloys have the potential to be extremely corrosion resistant, and perform better in the atmosphere than iron.

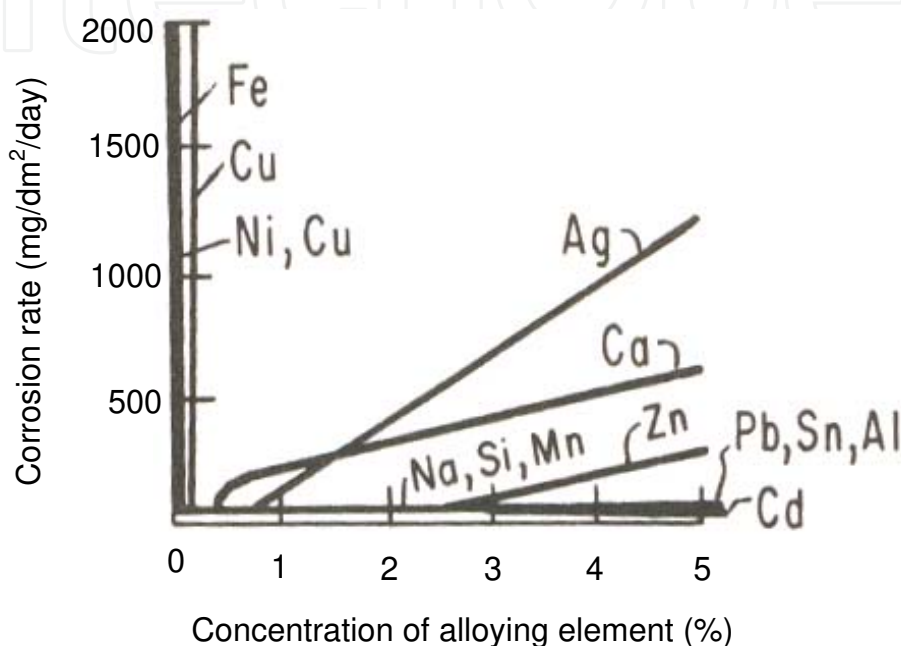
In urban/industrial locations MgSO<sub>4</sub>·6H<sub>2</sub>O and MgSO<sub>3</sub>·6H<sub>2</sub>O can predominate in the surface films. MgSO<sub>4</sub>·6H<sub>2</sub>O and MgSO<sub>3</sub>·6H<sub>2</sub>O are highly soluble and are easily washed away, re-exposing the surface. Hence, pure magnesium has a poor corrosion resistance in industrial atmospheres [3, 9].

## 2.2. Metallurgical effects

Magnesium becomes susceptible to accelerated corrosion if there are significant impurity levels present or it is in contact with other metals. Due to the lack of a nature surface film on the impurities, the more positive potential allows impurities to be efficient cathodes for hydrogen discharge, thereby providing significant microgalvanic acceleration of the corrosion rate [13]. Therefore even small amount of impurities in pure magnesium with metals having low hydrogen overvoltages, such as Fe, Ni, Co, or Cu, drastically reduces its corrosion resistance. Metals with higher hydrogen overvoltages, such as lead, zinc, and cadmium, and



also strongly electronegative metals, such as manganese and aluminum, are less dangerous in this respect [6]. Fig. 2 shows effect of impurity and alloying elements on the corrosion of magnesium in a 3% NaCl solution at room temperature. Fe, Cu, Ni can increase the corrosion rate, while Cd, Pb, Sn, and Al can drastically reduce the corrosion resistance of pure magnesium. The effect of various elements on the corrosion of magnesium alloys will be discussed in detail in section 3.2.



**Figure 2.** Effect of impurity and alloying elements on corrosion of magnesium (all alloys are formed by magnesium and the given element) in 3% NaCl solution at room temperature [6].

### 3. Corrosion characteristics of Mg alloys

Magnesium alloys in general can be divided into two main groups: (1) those containing aluminium as the primary alloying element; and (2) those free of aluminium and containing small additions of zirconium for the purpose of grain refinement. The most widely used magnesium alloys are those with aluminum (to 10%), zinc (to 3%), and manganese (to 2.5%). It is desirable that other metals, particularly Fe, Cu, Ni and Si be present in very small amounts not exceeding a total of 0.4% to 0.6% [13]. Mg alloys corrosion is governed by the characteristics of its surface film. The properties of film on Mg alloys depend on Mg alloys' metallurgy and environmental factors. Magnesium metallurgy includes alloying and impurity elements, phase components and microstructure. Metallurgical manipulation can provide an effective means to improve the corrosion resistance of magnesium alloys.

### 3.1. Influences of environment

#### 3.1.1. Corrosion by atmosphere and solutions

In general, atmospheric attack in damp conditions is largely superficial. The corrosion reactions of magnesium alloys are similar to those for pure magnesium, as shown in reactions 1–4. Generally, the corrosion resistance of magnesium alloy is better than that of pure magnesium, because other corrosion resistant phases exist. An analysis of the films formed when magnesium alloys containing Al, Mn, or Zn are exposed to the atmosphere, shows an enrichment of the secondary constituents. It was suggested that the air-formed oxide on Mg-Al alloys has a layered structure composed of MgO/Mg-Al-oxide/substrate, with the Mg-rich oxide becoming thinner with increasing Al content. It is likely that this benefit of Al is related to the strong tendency for Al to form a stable passive film [13].

Lindstrom et al [14] studied the influence of NaCl and CO<sub>2</sub> on the atmospheric corrosion of magnesium alloy AZ91. The combination of high humidity and NaCl is very corrosive towards AZ91. However, CO<sub>2</sub> inhibits atmospheric corrosion both in the presence of and in the absence of NaCl. In the absence of CO<sub>2</sub>, the NaCl-induced corrosion is localized and the main corrosion product is Mg(OH)<sub>2</sub>. Because of the cathodic reaction, high pH areas develop in the electrolyte adjacent to the AZ91 surface, resulting in the dissolution of alumina in the passive film. Due to the rapid hydrogen evolution, the metal disintegrates and pieces of un-reacted metal are embedded in the corrosion product. In the presence of CO<sub>2</sub>, AZ91 suffers general corrosion and carbonate-containing corrosion products were formed. In the presence of NaCl, Mg<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub> was detected by XRD. The inhibitive effect of CO<sub>2</sub> was suggested to be due to a combination of pH decrease in the surface electrolyte, stabilizing alumina in the passive film, and the formation of sparingly soluble carbonate-containing corrosion products that slow down the electrochemical reactions.

#### 3.1.2. Corrosion in coolants

A magnesium alloy engine block has the potential to significantly reduce the weight of an automobile, and studies on the corrosion of magnesium alloys in automotive coolants has received increasing attention. Song and StJohn [15] studied the corrosion of a new magnesium alloys AM-SC1 and magnesium alloy AZ91 in commercial engine coolants. AM-SC1 is a new alloy with rare earth elements, zinc and zirconium as the main alloying elements, which was developed as an engine block material. It was found that AZ91 is more corrosion resistant than AM-SC1 in existing coolants, because the existing commercial coolants are non-corrosive to aluminium alloys and they also have a certain degree of inhibitive effect on an aluminium-containing alloy. Potassium fluoride, KF, was an effective inhibitor for the magnesium alloys and can reduce the general and galvanic corrosion rates, while it had no detrimental effect on the other engine block materials (such as cast iron, aluminium alloy) in terms of their corrosion performance. Furthermore, Toyota and Ford long life coolant (Toyota long life coolant: 934 ml/L ethylene and 10ml/kg denatonium benzoate, 1:1 diluted with demineralised water; Ford long life coolant: 950 ml/l ethylene glycol and 10 ppm denatonium benzoate as a bittering agent, 1:1 diluted with demineralised water) [15] can be the most promising coolants for magnesium

alloys engine blocks, because the corrosion rates in them were acceptable. Slavcheva et.al [16] demonstrated that Lactobiono-tallowamide (a reaction product of lactobionic acid and tallowamine) had relatively high inhibition efficiency towards AZ91 alloy corrosion in ethylene glycol solution containing chloride ions at low as well as at high temperature. The inhibiting effect of lactobiono-tallowamide is a result of adsorption on the metal surface and formation of an adherent protective film. Hence, lactobiono-tallowamide can be considered as a promising inhibitor of magnesium alloy corrosion.

### 3.2. Metallurgical factors

Metallurgical factors include alloying and impurity elements, phase composition and micro-structure.

#### 3.2.1. Impurity elements

Studies [12, 17-20] have confirmed that the most critical factor in the corrosion behaviour of Mg and Mg alloys is the metal purity. Iron, nickel, and copper are extremely deleterious because they have low solid-solubility limits and provide active cathodic sites which lead to galvanic corrosion and increase corrosion rates. At the same concentration, the detrimental effect of these elements decreases as follows:  $Ni > Fe > Cu$ . When the impurity concentration exceeds the tolerance limit, the corrosion rate is greatly accelerated, whereas the corrosion rate is low when the impurity concentration is lower than the tolerance limit. The tolerance limits in magnesium alloys are influenced by the presence of other elements. For example, the iron tolerance limit for magnesium-aluminum alloys depends on the Mn or Zn concentration [5]. Furthermore, impurity limits are different depending on the method of manufacture. For example, die cast AZ91 has higher nickel tolerance than gravity cast AZ91. And the slower solidification rates significantly affect the nickel tolerance, but not Fe and Cu [17]. Different alloys have different tolerance limits as summarized in Table 1. In Table 1, the impurity tolerance limit of 0.032 Mn actually means that if there is manganese in a magnesium alloy, then the alloy would be able to tolerate an amount of the iron impurity equal to 0.032 of the manganese concentration (by weight).

Iron, nickel, copper, and cobalt are the four main elements so far found to have significant detrimental influence on the corrosion resistance of magnesium alloys [13]. Besides these detrimental elements, there is one special element, manganese, which is usually closely related to the detrimental effects of other elements and their tolerance limits.

#### Iron

The deleterious effect of iron in pure magnesium is shown in Fig. 3, and it is suspected to be due to the galvanic coupling between the magnesium matrix and the iron particles scattered in the matrix because Fe has a very low solid solubility in magnesium (about 9.9 ppm) [13], while Hawke and Olsen [18] thought that in the absence of Mn, virtually all the Fe precipitates in magnesium alloys as  $FeAl_3$  which has a high cathodic activity for corrosion, as shown in Fig. 4.

		Tolerance Limits*		
Specimen	Condition	Fe	Ni	Cu
Pure Mg		170 ppm	5 ppm	1000 ppm
Pure Mg		170 ppm	5 ppm	1300 ppm
AZ91		20 ppm	12 ppm	900 ppm
AZ91		0.032 Mn	50 ppm	400 ppm
AZ91	High pressure (F)	0.032 Mn	50 ppm	400 ppm
AZ91	Low pressure (F)	0.032 Mn	10 ppm	400 ppm
AZ91	Low pressure (T4)	0.035 Mn	10 ppm	100 ppm
AZ91	Low pressure (T6)	0.046 Mn	10 ppm	400 ppm
AZ91B			<100ppm	<2500 ppm
AS41	Die casting	0.032 Mn	50 ppm	400 ppm
AZ91	Die casting	50 ppm	50 ppm	700 ppm
AZ91	Die casting	0.032 Mn	50 ppm	700 ppm
AZ91	Gravity casting	0.032 Mn	10 ppm	400 ppm
AM60	Die casting	0.021 Mn	30 ppm	10 ppm
AE42		0.01 Mn	40 ppm	200 ppm

\* Variation of tolerance limits results from different manufacturing processes used by various alloy producers

Table 1. Tolerance limits for magnesium and magnesium alloys [113]

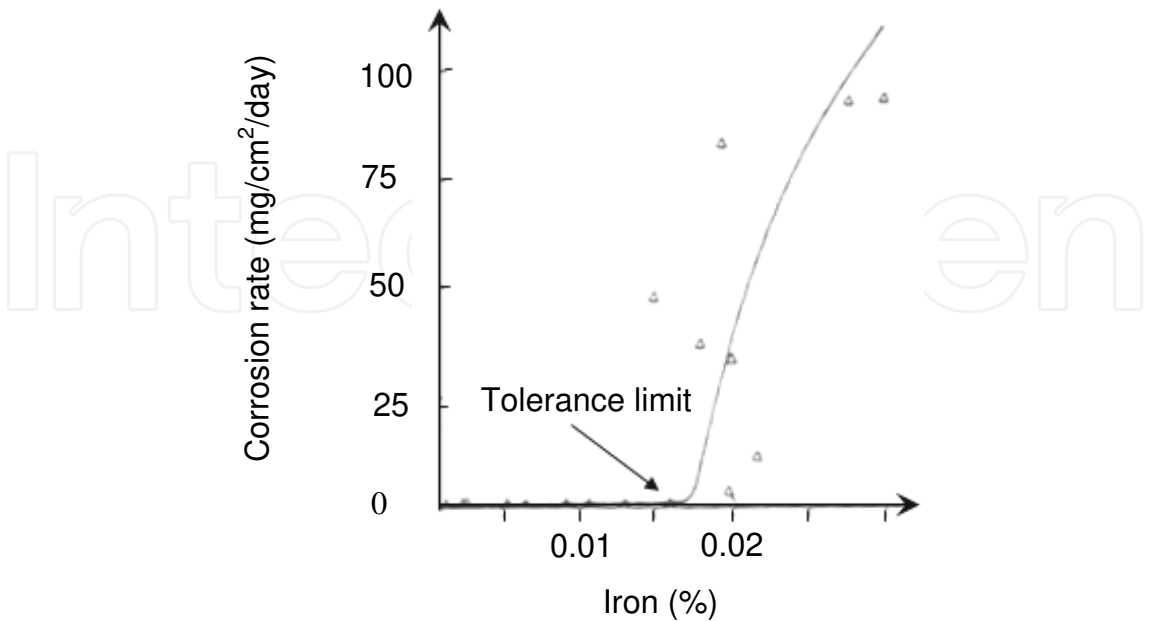
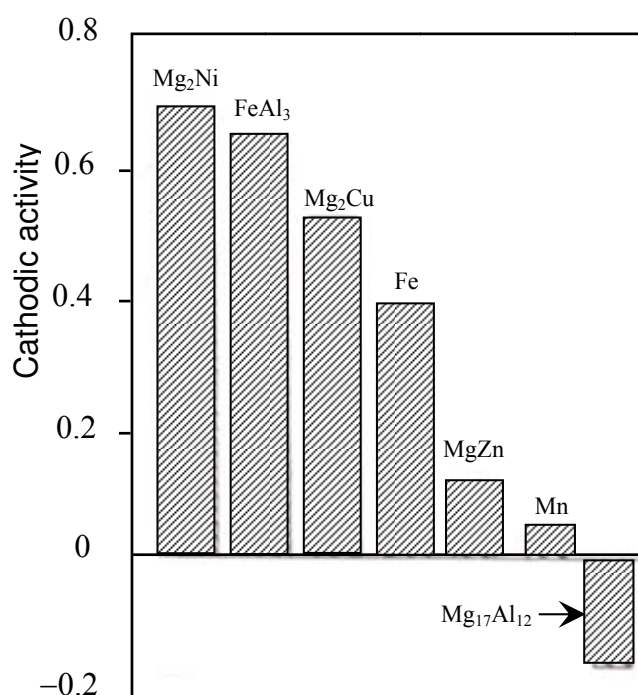


Figure 3. Effect of iron on the corrosion of pure magnesium immersed in 3% NaCl [13].

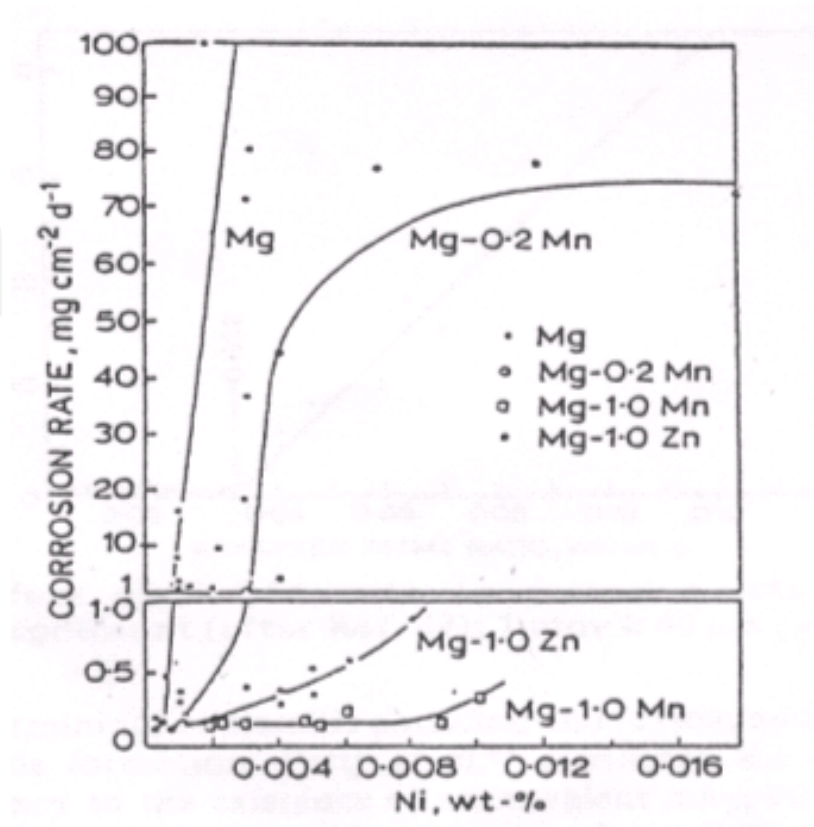
In Fig. 4, the effects of these phases are defined in terms of their electrode potential relative to the alloy matrix, and the overpotential values for the evolution of hydrogen gas. Within an appropriate medium,  $\text{FeAl}_3$  acts as an effective cathode, catalyzing the reduction reaction, hydrogen evolution, which is responsible for the corrosion process. Due to the low solubility of  $\text{FeAl}_3$  in Mg, increasing additions of Al result in increasingly smaller tolerance levels for Fe [17]. For example, when even as little as hundreds of ppm of aluminum is added to the magnesium, the tolerance limit for iron decreases from 170 wt.-ppm to a few wt.-ppm. With 7% Al, the tolerance is about 5 wt.-ppm Fe, while with 10% Al, the limit is too low to be determined [13].



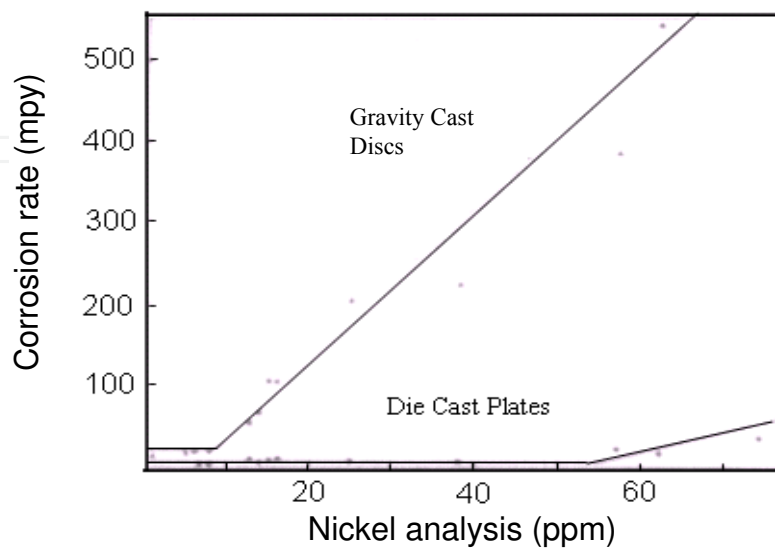
**Figure 4.** Cathodic activity of precipitated phases in Mg alloys in salt water relative to their alloy matrix [18].

### Nickel

Nickel is more harmful than iron both in pure magnesium and in magnesium alloys, because nickel precipitates in magnesium alloys as  $\text{Mg}_2\text{Ni}$  which is more cathodically active than  $\text{FeAl}_3$  and Fe, as shown in Fig. 4. Fig. 5 shows effect of nickel content on corrosion rates of pure Mg and Mg-Mn and Mg-Zn alloys using standard Dow immersion-emersion test in NaCl solution [5]. Furthermore, solidification rate changes the tolerance limit for Ni (higher tolerance limit for faster cooling, Fig. 6), but not for Fe, or Cu [17]. From Fig. 6, it was found that the nickel tolerance was significantly lower in the gravity cast (~10 ppm) than for the die cast (~55 ppm) [17].



**Figure 5.** Effect of nickel content on corrosion rates of pure Mg and Mg-Mn and Mg-Zn alloys using standard Dow immersion-emersion test in NaCl solution [5].



**Figure 6.** Salt spray corrosion performance vs nickel content for die cast and gravity cast samples [17].

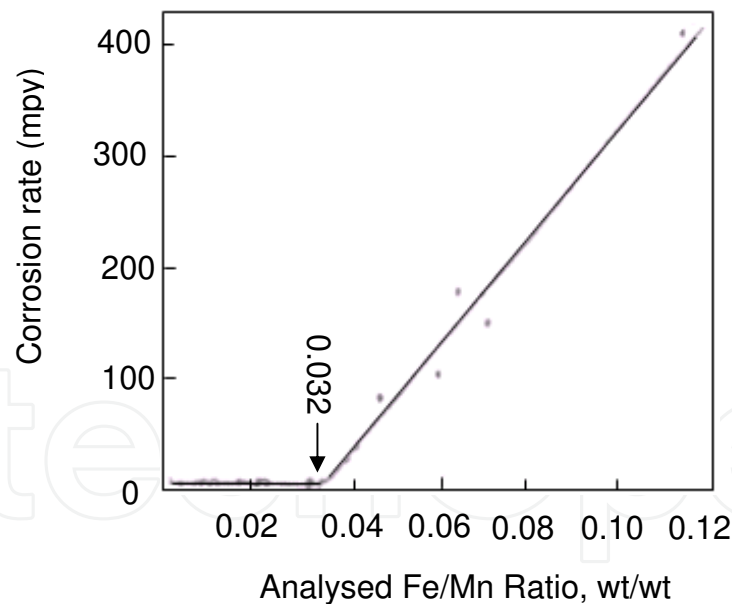


Copper

A small amount of copper has a beneficial effect on the creep strength of magnesium die castings, but strongly accelerates salt water corrosion [113]. Cu is less harmful than iron in magnesium, because copper precipitates in magnesium as  $Mg_2Cu$  which has a lower potential than  $FeAl_3$  [18].  $Mg_2Cu$  acts as an effective cathode, catalyzing the hydrogen evolution. The addition of copper to Mg-Al-Zn alloys has also been shown to have a detrimental effect on the corrosion resistance. This may be attributed to the incorporation of the copper in the eutectic phase as  $Mg(Cu, Zn)$ . The tolerance limit of copper has been set at 300 ppm, but it is known that higher levels can be tolerated if the zinc content is above the specification minimum of 0.4% [113].

Manganese

Manganese is added to many commercial alloys, particularly the Mg-Al-Zn alloys (AZ series) to improve corrosion resistance. Manganese itself does not improve the corrosion resistance, because it has a higher potential (see Fig. 4). However, it reduces the harmful effect of impurities. For example, manganese increased the Ni tolerance limit [17]. The Fe/Mn ratio seems to control the influence of iron upon the corrosion rate rather than the overall Fe content [17]. Fe tolerance limit was equal to 3.2% of the Mn content regardless of the melt temperature at the time of casting and the type of casting produced, as shown in Fig. 7.



**Figure 7.** Effect of Fe/Mn ratio on corrosion rate of magnesium, 1 mpy $\approx$  40  $\mu$ m/year [17].

Mn reduces the corrosion rate, probably by the following mechanisms [5]. Mn can reduce the corrosive effect of iron by wrapping the iron particles. A particle of iron embedded in a particle of manganese is less detrimental to magnesium because the galvanic activity between Mn and Mg is less than that between Mg and Fe [5]. Mn combines with the Fe and precipitates at the bottom of the crucible, where it reacts with the Fe left in suspension during solidification [19].

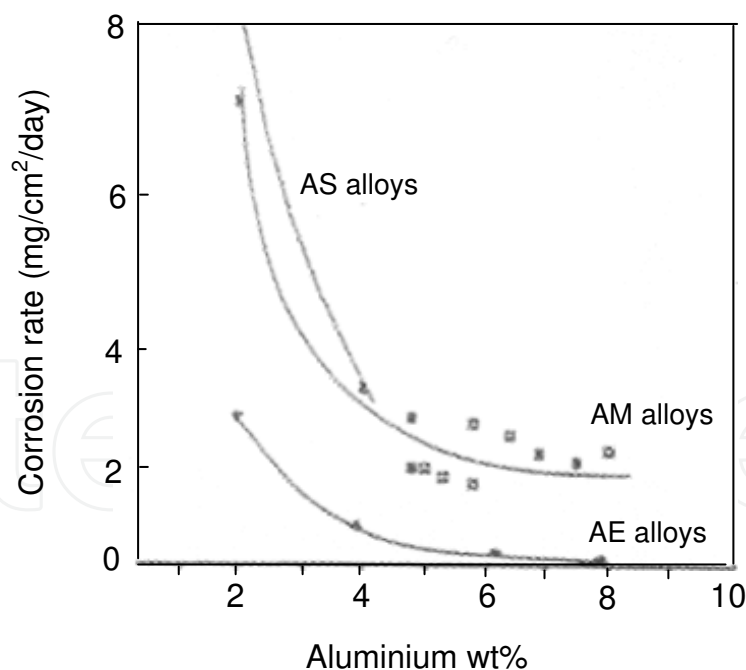
When Mn and Al are present together, the AlMnFe intermetallic compounds form preferentially relative to  $\text{FeAl}_3$ , which is known to be an active cathodic phase relative to the magnesium matrix [19]. Mn in excess of that needed to render to the Fe content ineffective could be detrimental to corrosion resistance. Low Mn binary AlMn particles:  $\text{Al}_4\text{Mn}$ ,  $\text{Al}_6\text{Mn}$ , show a decreasing cathodic current density, while high Mn content  $\text{Al}_8\text{Mn}_5$  particles show a continuously high cathodic current density. Thus, additions of Mn beyond that needed for the specified Fe/Mn ratio should be avoided [19].

### 3.2.2. Important alloying elements

Alloying elements not only enhance the mechanical properties of Mg but also have a significant impact on the corrosion behaviour of Mg-Al alloys. Alloying elements can form secondary particles which are noble to the Mg matrix thereby facilitating corrosion or enrich the corrosion product thereby possibly inhibiting corrosion [19].

#### Aluminium

Alloying magnesium with aluminium in general improves the corrosion resistance. Lunder et al reported [20] that there is a significant drop in the corrosion rate as the aluminium content is increased from 2 to 4%. Further aluminium additions up to 9% give only a modest further improvement, as shown in Fig. 8.



**Figure 8.** Corrosion rates of die cast Mg alloy immersed in 5% NaCl solution as a function of their Al content [19].

The aluminium is partly in solid solution, and partly precipitated in the form of  $\text{Mg}_{17}\text{Al}_{12}$ . Lefebvre and Nussbaum [21] discussed the role of Al in solid solution and role of  $\text{Mg}_{17}\text{Al}_{12}$  in the corrosion process. Both Al in solid solution and  $\text{Mg}_{17}\text{Al}_{12}$  can decrease corrosion rates. The

presence of Al in solid solution in the matrix decreases the corrosion rate of Mg alloys in 5% NaCl and  $\text{Mg}(\text{OH})_2$  solution, which is attributed to a change in the surface microstructures.

However, it has also been found that aluminum can have a negative influence on corrosion. Aluminium reduces the iron tolerance limit from 170 wt.-ppm to 20 wt.-ppm [17]. The tolerance limit of iron decreases almost linearly with increasing aluminium content. This trend in the iron tolerance limit appears to be consistent with the formation of a passive AlMnFe intermetallic phase on solidification [13].

### **Zinc**

The presence of Zinc can increase the tolerance limits and reduce the effect of impurities once the tolerance limit has been exceeded. Zinc is believed to improve the tolerance of Mg-Al alloys for all three impurities (Fe, Cu, Ni), but its amount is limited to 1-3%. The addition of 3% Zn raises the tolerance limit to 30 wt.-ppm Fe and greatly reduces the corrosion rate for iron concentrations of up to 180 wt.-ppm for Mg-Al-Mn alloys. For the Mg-Al-Mn-Ni alloys, 3% Zn shifts the tolerance limit from 10 to 20 wt.-ppm Ni and reduces the corrosion rate at higher concentration of nickel [13].

### **Zirconium**

Besides the improvement of mechanical properties, the zirconium containing magnesium alloys usually have a higher corrosion resistance than zirconium-free magnesium alloys. Zr reduces the corrosion rate, probably by the following mechanisms [22]: First, impurities combine with zirconium and form insoluble precipitates and purify the alloy. The second mechanism is that zirconium stabilizes the magnesium solid solution making it less soluble in aqueous solutions. The third mechanism is that zirconium combines with some intermetallic precipitates which were originally active cathodic sites, making them less active. Apart from the above mechanisms, the grain refining effect provided by zirconium could be another reason for the higher corrosion resistance of magnesium containing zirconium.

### **Silicon**

Si is intentionally added only to the Mg-Al-Si alloys (AS series) to combine with Mg and form  $\text{Mg}_2\text{Si}$  which precipitation strengthens the alloy and is relatively innocuous to the corrosion of Mg.  $\text{Mg}_2\text{Si}$  has a steady state corrosion potential of  $-1.65$  V similar to  $-1.66$  V for pure magnesium in 5% NaCl solution [19].

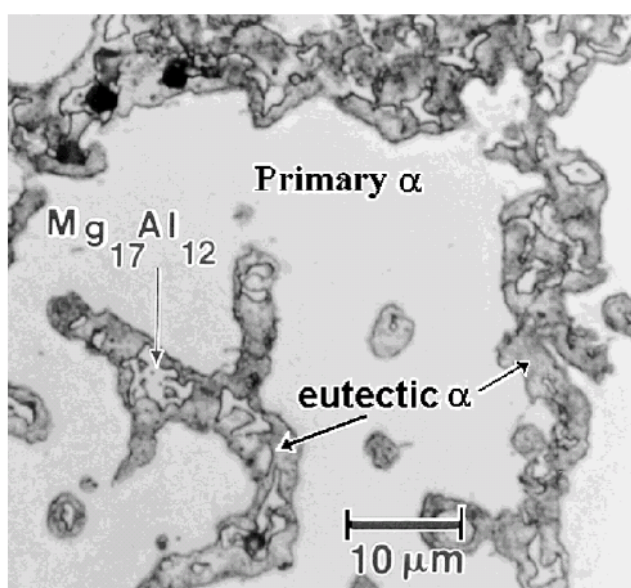
### **Rare earth additions**

It is well known that the addition of rare earth elements (RE) is an effective way to improve the mechanical properties of magnesium alloys at elevated temperatures. The improvement has mainly been attributed to the formation of a metastable RE-containing phase along the grain boundaries which significantly increases the creep resistance [23]. The beneficial effect of the RE could be similar in nature to that of the Mn additions i.e. the formation of an AlFeMn intermetallic phase which mitigates the harmful effects of Fe. However, no ternary phase was found to form in Mg-Al-RE alloys as the chemical stability of the  $\text{Al}_4\text{RE}$  intermetallic is quite high. Rather, it appeared to be more likely that the rare earths influenced the corrosion products, thereby affecting the corrosion behaviour of the Mg-Al alloys [19].

### 3.2.3. Role of $\beta$ phase

Phase contents have a pronounced influence on the corrosion of magnesium, because most elements only affect the corrosion resistance of magnesium alloys when they form second phases. For example, most impurities or alloying elements form second phases and either serve as effective cathodes during the corrosion processes, or eliminate the deleterious effect of impurities, as discussed in sections 3.2.2 and 3.2.1. In this section, the role of  $\beta$  phase ( $\text{Mg}_{17}\text{Al}_{12}$ ) is discussed.

The detailed microstructure is determined by the casting method, particularly the rate of solidification, and any subsequent heat treatment. Fig. 9 shows a typical microstructure of die cast AZ91D [24]. AZ91 alloy contains three main phases: a substitutional solid solution of aluminium in magnesium ( $\alpha$  phase) and two intermetallic phases:  $\beta$  ( $\text{Mg}_{17}\text{Al}_{12}$ ) present in a eutectic phase ( $\alpha+\beta$ ) and an intermetallic phase containing Mn, Fe and Al present at a minor level [25].



**Figure 9.** Microstructure of die cast AZ91D alloy [24].

In general, the  $\beta$  phase present in the alloy is considered more resistant to corrosion than the surrounding matrix alloy. Mathieu et al [25] studied the corrosion resistance of the different constituents of an AZ91 alloy in ASTM D1384 water, pH 8.3. It was found that Al contributed to the enhancement of the protection of the  $\alpha$  phase through a superficial layer of a carbonate hydroxide of magnesium and aluminium. Song et al. [26] suggested that the role of the  $\beta$  phase in corrosion may be twofold: (1) The  $\beta$ -phase could have a barrier influence because it is very stable in a NaCl solution; (2) The  $\beta$ -phase is an efficient cathode for hydrogen evolution. First, when the  $\beta$ -phase is present in an alloy, it reduces the reactive surface area, so less area of the alloy is available to be corroded. Moreover, when corrosion is developing, a continuous  $\beta$ -phase along the  $\alpha$ -grain boundaries might be able to prevent corrosion from spreading from one  $\alpha$ -grain to another  $\alpha$ -grain directly across the  $\beta$ -phase. Then corrosion might be stopped

after the top layer  $\alpha$ -grains have been dissolved and a continuous  $\beta$ -phase is exposed to solution. In this manner, the  $\beta$ -phase might improve the corrosion resistance of the alloy. Its barrier role is however limited to stopping the corrosion from either spreading laterally or from progressing deeper into the  $\alpha$ -matrix. Unfortunately, in most cases the  $\beta$ -phase is discontinuous and then it does not stop corrosion completely. Second, the cathodic reaction of hydrogen evolution on the  $\beta$ -phase is much easier than on the  $\alpha$ -phase. Consequently, if the  $\beta$ -phase is present in an alloy, it acts as an effective cathodic phase to the  $\alpha$ -matrix. It causes significant acceleration of the  $\alpha$ -phase corrosion by galvanic coupling. However, the role of  $\beta$ -phase strongly depends on the volume fraction. If the  $\beta$ -phase is present in the  $\alpha$ -matrix as intergranular precipitates with a small volume fraction, then the  $\beta$ -phase mainly acts as a galvanic cathode, and accelerates the corrosion of the  $\alpha$  matrix. If the  $\beta$  fraction is high, then the  $\beta$ -phase mainly acts as an anodic barrier to inhibit the overall corrosion performance.

### 3.2.4. Microstructure

Microstructural parameters such as composition, porosity, grain size, and amount and distribution of  $\beta$ -phase also play a role in determining the corrosion behaviour. For example, reduction of grain size increases the overall grain boundary area thereby optimizing the distribution and minimizing the size of any possible detrimental intermetallics such as  $\text{FeAl}_3$ . The microstructure can be controlled by the cooling rate, with more rapid cooling leading to a smaller grain size, more  $\beta$ -phase and a more finely distributed  $\beta$ -phase. For example, Mathieu et al [27] found that the casting method strongly influences the corrosion performance through control of the microstructure. The corrosion resistance of semi-solid cast AZ91D alloy is 35% higher than that of the same alloy processed by high pressure die-casting with the impurity level (Cu, Fe) being the same, and the difference in corrosion behaviour is attributed to the distribution, composition and volume fraction of the constituent phases (mainly  $\alpha$  and  $\beta$ ). Even for the same material, the corrosion resistance is different depending on the location of the material in the casting. For example, Song et al [24] found that the skin of die cast AZ91D shows a corrosion resistance significantly better (by nearly a factor of 10) than its interior in 1 N NaCl at pH 11. This is attributed to a higher  $\beta$ -fraction, and more continuous  $\beta$ -phase around finer  $\alpha$ -grains and low porosity. The corrosion behaviour of the  $\alpha$ -phases in AZ91 depends on both their aluminium contents and the local current density (which in turn depends on the details of the microstructure and the details of the environmental conditions). For high current densities, the eutectic- $\alpha$  at the grain boundaries tends to be corroded first. For low current densities, the primary- $\alpha$ , in the grain interior, would be preferentially corroded.

## 4. Forms of corrosion suffered by magnesium alloys


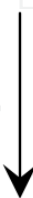
### 4.1. Galvanic corrosion

When two dissimilar metals are placed in contact in a corrosive or conductive solution, a potential difference produces electron flow between them. The more active metal then becomes anodic and is corroded, and the less active metal becomes cathodic and is protected. This kind



of corrosion is called galvanic corrosion, or two-metal corrosion. Magnesium and its alloys are highly susceptible to galvanic corrosion, because magnesium has the lowest standard potential of all the engineering metals as illustrated in Table 2 [288].

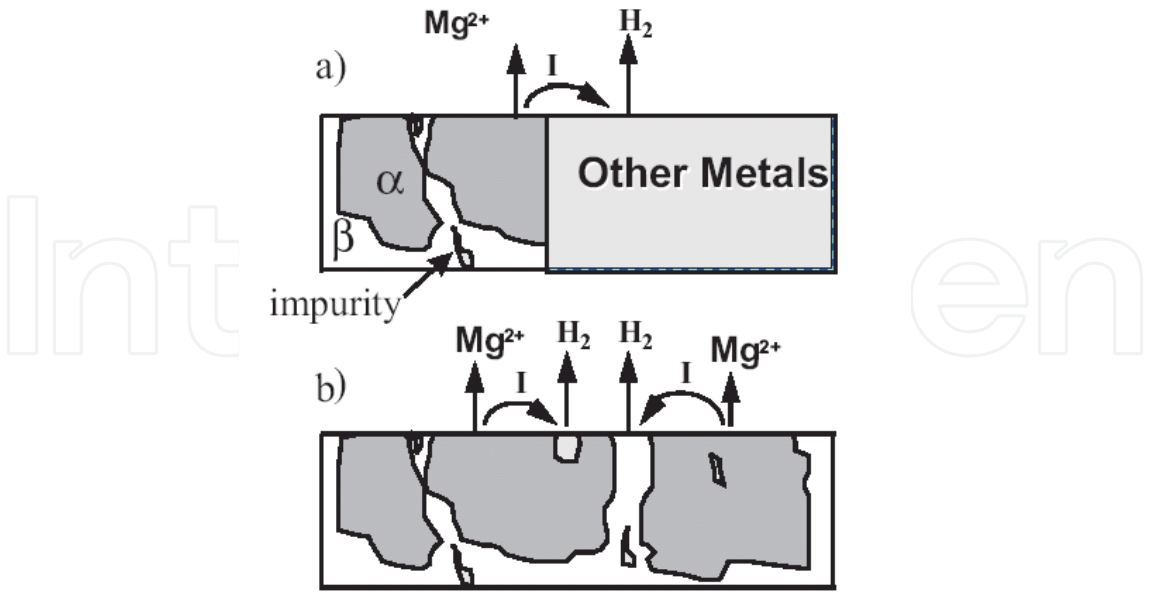
Galvanic corrosion can also occur between two different phases. Fig. 10 illustrated those kinds of galvanic corrosion, external and internal [13]. When magnesium and its alloys are placed contact with other metals, magnesium and magnesium alloys are corroded, while hydrogen gas is evolved on the other metals. When magnesium and magnesium alloys contain second phases because of impurities or alloying elements, the matrix  $\alpha$ -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 [29].

	Metal – metal ion equilibrium (unit activity)	Electrode potential vs normal hydrogen electrode 25 °C, volts
 Noble or cathodic	Au – Au <sup>3+</sup>	1.498
	Pt – Pt <sup>2+</sup>	1.2
	Pd – Pd <sup>2+</sup>	0.987
	Ag – Ag <sup>+</sup>	0.799
	Hg – Hg <sub>2</sub> <sup>2+</sup>	0.788
	Cu – Cu <sup>2+</sup>	0.337
	H <sub>2</sub> – H <sup>+</sup>	0.000
	Pb – Pb <sup>2+</sup>	– 0.126
	Sn – Sn <sup>2+</sup>	– 0.136
	Ni – Ni <sup>2+</sup>	– 0.250
Active or anodic 	Co – Co <sup>2+</sup>	– 0.277
	Cd – Cd <sup>2+</sup>	– 0.403
	Fe – Fe <sup>2+</sup>	– 0.440
	Cr – Cr <sup>3+</sup>	– 0.744
	Zn – Zn <sup>2+</sup>	– 0.763
	Al – Al <sup>3+</sup>	– 1.662
	Mg – Mg <sup>2+</sup>	– 2.363
	Na – Na <sup>+</sup>	– 2.714
	K – K <sup>+</sup>	– 2.925

**Table 2.** Standard EMF series of metals [28]

From Table 3, it was found that the most potent cathodes in Mg-Al alloy are iron-rich phases, in particular the iron-aluminum intermetallic phase FeAl<sub>3</sub>. FeAl<sub>3</sub> is one of the most detrimental cathodic phases present in Mg-Al alloys on the basis of its potential and its low hydrogen overvoltage. Al-Mn phases are also detrimental, while Mg<sub>2</sub>Si seems to have no influence.





**Figure 10.** a) External galvanic corrosion. b) Internal galvanic corrosion [13].

Metal	$E_{corr} V_{SCE}$
Mg	−1.65
$Mg_2Si$	−1.65
$Al_6Mn$	−1.52
$Al_4Mn$	−1.45
$Al_8Mn_5$ – 1.25	
$Mg_{17}Al_{12}$ – 1.20	
$Al_8Mn_5(Fe)$	−1.20
Beta–Mn	−1.17
$Al_4Mn$	−1.15
$Al_6Mn(Fe)$	−1.10
$Al_6(MnFe)$	−1.00
$Al_3Fe(Mn)$	−0.95
$Al_3Fe$	−0.74

**Table 3.** Typical 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)) [29]

The matrix  $\alpha$ -phase in Mg alloys is normally anodic to the second phases and is usually preferentially corroded. Song and coworkers [24, 26] have suggested that the primary  $\alpha$  and eutectic  $\alpha$  phases, which have different aluminum contents, have different electrochemical behaviour. Both the primary and eutectic  $\alpha$  can form galvanic corrosion cells with the  $\beta$  phase.

The galvanic corrosion rate is increased by the following factors: high conductivity of the medium, large potential difference between anode and cathode, large area ratio of cathode to anode, and small distance from anode to cathode [288]. Song et al [30] investigated the corrosion behaviour of AZ91D when it is in contact with 380 aluminium alloy, 4150 high strength steel and pure zinc. It was found that even though the galvanic effect offers some degree of cathodic protection for aluminium and zinc cathodes, the dissolution of these metals in the salt solution is still unavoidable, particularly in the region far away from the anode/cathode junction. The dissolved  $Zn^{2+}$  or  $Al^{3+}$  ions flushed to the surface of the AZ91D anode could react to form zinc or aluminium oxides or hydroxides and finally deposit on the AZ91D surface. These products can provide a certain degree of protection for the AZ91D surface.

#### 4.2. Stress corrosion cracking (SCC)

Stress-corrosion cracking refers to cracking caused by the simultaneously presence of tensile stress and a specific corrosive medium [288]. Pure magnesium can be considered immune to stress corrosion cracking in both atmospheric and aqueous environments, with no reported failures occurring when loaded to its yield strength [7]. Aluminum containing alloys of magnesium are generally considered the most susceptible to SCC, with the tendency increasing with the aluminum content [7]. The alloys AZ61, AZ80, and AZ91 with 6, 8, and 9% aluminum, respectively, can show high susceptibility to SCC in laboratory and atmospheric exposures, while AZ31, a 3% aluminum alloy used in wrought product applications, is considered to show good corrosion resistance [7]. Magnesium-zinc alloys such as ZK60 and ZE41 that are alloyed with zirconium, or zirconium and rare earth elements, are typically considered only mildly susceptible, while magnesium alloys containing no aluminum or zinc are the most SCC-resistant. For example, M1 alloy, a 1% manganese alloy, like unalloyed Mg itself, shows no evidence of SCC when placed under tensile stresses as high as its yield strength [13].

SCC in 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 [13].

#### 4.3. Corrosion fatigue

There is very little research on the corrosion fatigue of magnesium alloys. It has been indicated in reference 7 that corrosion fatigue has a close relationship with humidity. For example, AZ31 subjected to an axial load cycle at  $10^5$  cycles per hour in air and then subjected to increasing levels of humidity showed a slow decrease in the fatigue strength once the humidity exceeded 50%. At 93% relative humidity, the measured fatigue strength had declined to about 75% of that in dry air. It has also been found [13] 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. And the corrosion fatigue resistance of AZ91-T6 was significantly reduced in 3.5% salt water relative to that in air.

#### 4.4. Pitting corrosion

Few studies have addressed these forms of localised attack of Mg and Mg alloys because other forms of corrosion such as general, galvanic, or stress corrosion have been the cause of more serious failure of these materials. The studies of pitting of Mg and Mg alloys have been concerned with comparing the pitting behaviour of cast to that of rapidly solidified Mg alloys. Makar and Kruger [31] showed that rapidly solidified AZ61 exhibited better resistance to pitting than cast AZ61 in a buffered carbonate solution containing various levels of  $\text{Cl}^-$ . Pit initiation of rapidly solidified AZ61 is found to take place at a higher potential and the pit growth rate was apparently lower than cast AZ61. In a review given by Makar and Kruger [5], it is reviewed that the difference between rapidly solidified and cast Mg. A metallic glass  $\text{Mg}_{70}\text{Zn}_{30}$  exhibited a better resistance to pitting. Also, the film on the metallic glass was more protective against pitting attack than the pure Mg. The glassy Mg alloy is found to exhibit a more stable passive film than pure Mg, Zn or several other crystalline Mg-based alloys. Heavy metal contamination promotes general pitting attack. In Mg-Al alloys, pits are often formed due to selective attack along  $\text{Mg}_{17}\text{Al}_{12}$  network that is followed by the undercutting and falling out of grains [13].

Crevice corrosion does not occur with the Mg alloys because corrosion is relatively insensitive to oxygen concentration difference [3, 6].

#### 4.5. Filiform corrosion

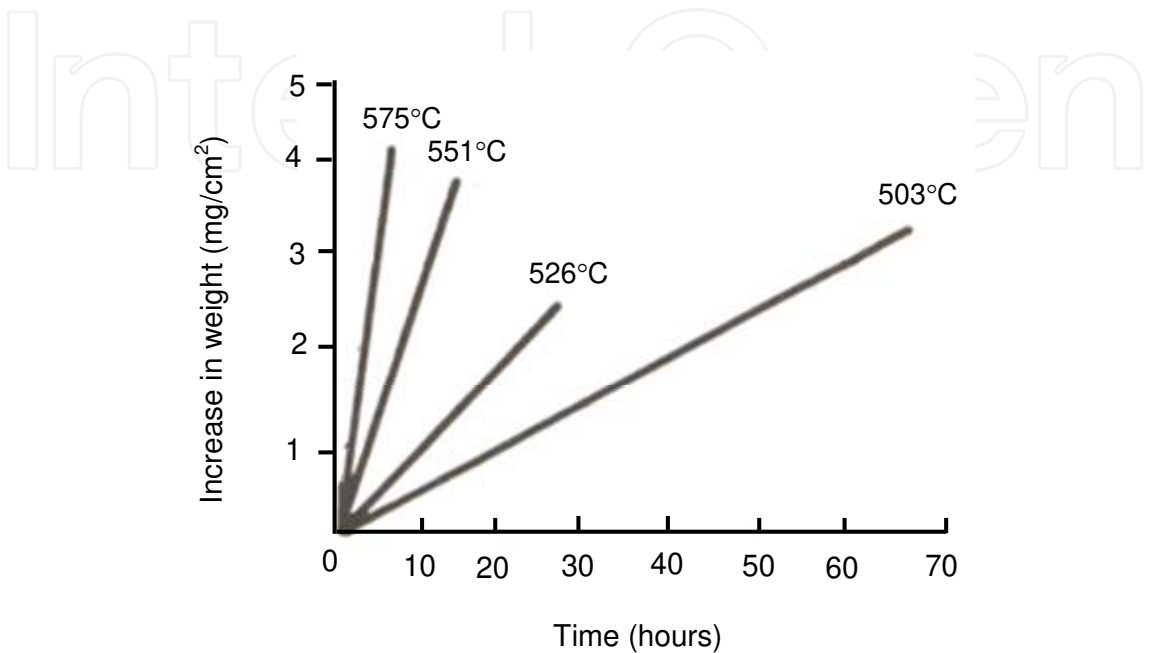
Filiform corrosion is caused by an active corrosion cell which moves across a metal surface. The head is the anode and the tail the cathode. Filiform corrosion occurs under protective coatings and anodized layers. Uncoated pure magnesium does not undergo filiform corrosion. However, filiform corrosion can occur on uncoated AZ91 and this indicates that a relatively resistant oxide film can naturally be formed on this alloy [13].

#### 4.6. Oxidation at elevated temperatures

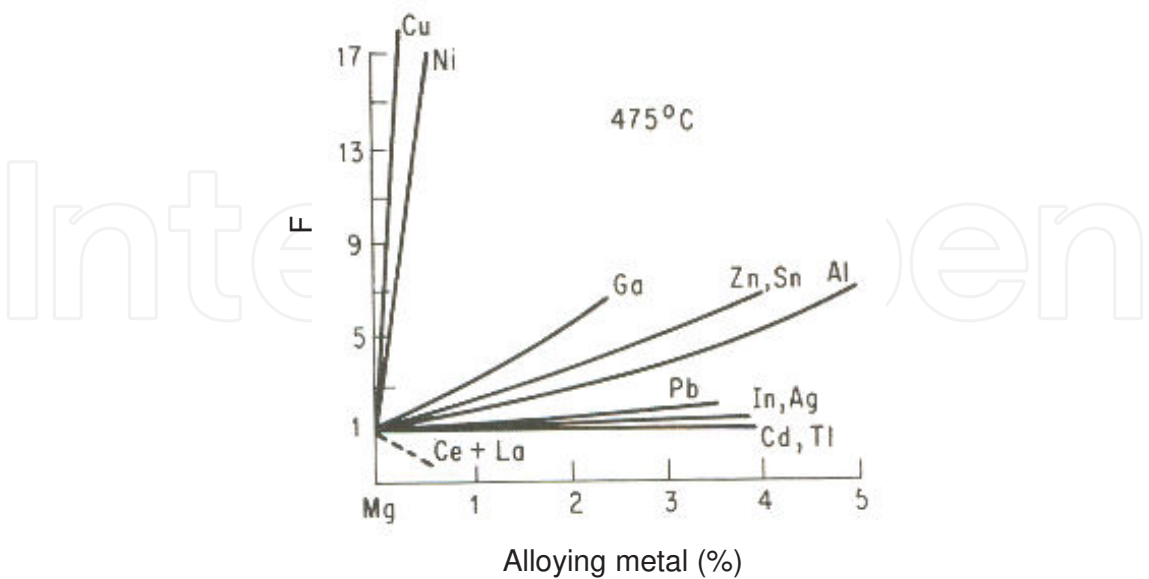
The research on oxidation at elevated temperatures is very limited. Magnesium corrosion resistance is typically considered to be good in dry air to about  $400^\circ\text{C}$  and to about  $350^\circ\text{C}$  in moist air [7]. At elevated temperatures, magnesium oxidizes easily in air according to a linear, kinetic oxidation curve (see Fig. 11) [6], which demonstrates the insufficient protective character of the magnesium oxides. Fig. 12 shows the effects of various elements on the oxidation rate of magnesium alloys in air at  $475^\circ\text{C}$ . Additions of Pb, In, Ag, Cd, or Ti have little effect on the rate of oxidation. The additions of rare earths (Ce+La) somewhat retard the oxidation process of magnesium in air on heating. Additions of Cu, Ni, Ca, An, Sn, or even Al accelerate the oxidation rate of magnesium alloys in the air at elevated temperatures [6].

Czerwinski investigated the early stage oxidation and evaporation of AZ91D alloy [32]. Thermogravimetric technique was used to determine the oxidation and evaporation behaviour of AZ91D magnesium alloys with 5 and 10 ppm of beryllium at temperatures between 200 and  $500^\circ\text{C}$ . The oxidation mechanism of AZ91D changes from protective to non-protective with linear or accelerated kinetics depending on the temperature and time of exposures. During

reaction in an oxidizing environment, the beryllium addition delays the onset of non-protective oxidation. It does not affect, however, the oxidation kinetics during the initial stages. During reaction in an inert atmosphere of argon, beryllium suppresses the magnesium evaporation [32]. Fig. 12 shows the effects of various alloying elements on the oxidation rate of Mg alloys in air at 475 °C.



**Figure 11.** Pure Mg oxidation in an oxygen atmosphere under one atmospheric pressure at various temperatures [6].



**Figure 12.** Effect of various alloying elements on the oxidation rate of magnesium alloys in air at 475 °C [6]. F – ratio of oxidation rate of the alloy to oxidation rate of pure magnesium.

## 5. Corrosion prevention

There are a number of approaches to overcoming the corrosion problems of Mg alloys [5]: (1) High purity or new alloys: Decrease impurities to below their tolerance limits and develop new alloys with new elements, phases, and microstructure distributions; (2) Surface modification: this includes ion implantation and laser annealing; (3) Refinement of the grain size and intermetallic particles: corrosion resistance can be affected through the microstructure; and (4) Protective films and coatings.

### 5.1. High purity or new alloys

Improving corrosion resistance by producing Mg alloys with low concentration of deleterious elements is an often-used strategy. This ensures the highest possible degree of uniform corrosion resistance of the starting material [5].

### 5.2. Surface modification

There are two main surface modification techniques which are discussed below.

**Ion implantation** is the technique whereby almost any elemental ions may be implanted into the surface of any solid using a beam of energetic ions accelerated into a target under vacuum conditions. This homogenization is the primary benefit of ion implantation in terms of corrosion resistance. Additional benefits include the ability to alter the surface while retaining the bulk properties, the creation of novel surface alloys, and the elimination of surface adhesion problems associated with coatings. The primary disadvantages are that it is a line-of-sight technique and it modifies only a thin film [33]. Akvipat and co-workers [34] examined the effects of iron implanted Mg and AZ91C in boric acid and borate buffer solution with 1000 ppm NaCl. It was known that iron degrades the corrosion resistance of magnesium alloys when introduced during conventional processing, and the goal of their work was to evaluate the effects of iron introduced by implantation. The implanted iron changed the nature of the attack on the AZ91. In the un-implanted case,  $Mg_{17}Al_{12}$  islands acted as local cathodes, causing accelerated corrosion of the surrounding matrix to form a deep channel around these islands. The implanted iron shifted the attack to the  $Mg_{17}Al_{12}$  particles themselves, which resulted in a more uniform attack without the rapid channelling suffered by the magnesium matrix in the un-implanted case. The results of these ion implantation studies are encouraging, but improvements in the economics and versatility of the implantation process are necessary for increasing the practical importance of this approach.

#### Laser annealing

Laser annealing technique involves the formation of metastable solid solutions as promoted at metal surfaces by laser annealing, where cooling rates as high as 1010 K/s are achievable using lasers pulsed in the nanosecond range [33]. It is, therefore, another form of rapid solidification processing, but involves the melting and solidification of surface layers only. Besides the advantages of ion implantation, the advantages include the ability of lasers to treat more complex geometries, the greater depth of treatment, inexpensive operation costs, and

greater control of the concentration of the modified layer [33]. The main disadvantage is the extra machining necessary because of dimensional changes during treatment. Akvipat and co-workers [34] examined the effects of thin layers of about 100nm of Al, Cr, Cu, Fe, and Ni on the pitting resistance of AZ91C in boric acid-borate solution with 1000 ppm NaCl. The role played by these elements after laser treatment is certainly different from that when they are present in conventional processing, especially Cu, Fe, and Ni, which are detrimental, even in small concentrations under equilibrium conditions. This improvement is probably related to the structure and composition of the near-surface region [34].

### 5.3. Microstructure refinement

Corrosion resistance can be affected through modification of the microstructure. Recent studies [19, 35, 36] have centered on the refinement of the grain size and intermetallic particles and on developing a more homogeneous microstructure.

#### Grain Refinement

Reduction of grain size increases the overall grain boundary area thereby optimizing the distribution of detrimental intermetallics and minimizing the size of any possible detrimental intermetallics such as  $\text{FeAl}_3$ . The traditional grain refinement method in sand casting is to add an inoculant which facilitates heterogeneous nucleation during solidification. Indeed, additions of strontium to Mg-Al alloys have shown a marked reduction in grain size but also have pointed to a possible alteration of both the oxide layer structure and composition and the electrochemical properties of the phases present [19].

#### Effect of Rapid Solidification Processing

Rapidly solidified materials show improved corrosion resistance because of a refined microstructure which translates to a more homogeneous composition thereby minimizing the potential of any microgalvanic corrosion cell.

Govind et al [35] claimed that technology of making rapid solidification ribbon of highly reactive Mg-9%Al-1%Zn-0.2%Mn alloy was established successfully. Grain sizes of 1-3  $\mu\text{m}$  could be achieved in as-spun ribbons in contrast to a 250-300  $\mu\text{m}$  grain size normally attained in sand cast structure. Below a temperature of 200 °C no grain growth was observed in RS ribbons of Mg alloy as the precipitates of intermetallic compound  $\text{Mg}_{17}\text{Al}_{12}$  pin the grain boundaries.

#### Effect of Heat-Treatment

Heat-treatment can drastically alter the size, amount and distribution of the precipitated  $\beta$  phase,  $\text{Mg}_{17}\text{Al}_{12}$ , which in turn, alters the corrosion behaviour of Mg-Al alloys. Aung and Zhou [36] studied an AZ91D ingot in the as-cast condition that was homogenized by solution treatment and then aged for various periods of time. The homogenization treatment of an AZ91D ingot at 420 °C for 24h was found to be effective in dissolving the  $\beta$ -precipitates. Artificial ageing at 200°C caused precipitation of the  $\beta$ -phase mainly along the grain boundaries. The volume fraction of the  $\beta$ -phase was observed to increase with ageing time. A homogenization treatment improved the corrosion resistance of the AZ91D ingot, but ageing



for 8 h, 16 h or 26 h lowered the corrosion resistance. These results support the suggestion that microgalvanic coupling exists between the cathodic  $\beta$ -phase and the anodic  $\alpha$ -matrix. The inhibiting effect of the  $\beta$ -phase in the artificially aged alloy predominated during the short interval of electrochemical testing but the accelerating effect of the decrease in aluminium content in the matrix predominated in the long period immersion testing. During immersion testing, the  $\beta$  phase may dissolve into the chemical solution and this also tends to accelerate the corrosion rate.

#### 5.4. Protective coatings and films

There are a number of technologies available for coating magnesium and its alloys. These include electrochemical plating, conversion coatings, anodizing, hydride coatings, organic coatings and vapour-phase processes.

##### 5.4.1. Electrochemical plating

One of the most cost effective and simple techniques for introducing a metallic coating to a substrate is by electrochemical plating. The electrochemical plating can be subdivided into two types: electroplating and electroless plating. In both cases a metal salt in solution is reduced to its metallic form on the surface of the substrates. In electroplating the electrons for reduction are supplied from an external source. In electroless or chemical plating the reducing electrons are supplied by a chemical reducing agent in solution or, in the case of immersion plating, the substrate itself.

#### Electroplating:

Besides some traditional disadvantages of electroplating such as non-uniform coatings and difficulties in coating complex shapes, there are some challenges to be met for electroplating on magnesium. The pre-treatment processes are complicated due to the fact that, in the presence of air, magnesium very quickly forms a passive oxide layer. Cu-Ni-Cr plating has been shown to have good corrosion resistance in interior and mild exterior environments [37]. Also, it is necessary to develop non-traditional plating baths since magnesium reacts violently with most acids and dissolves in acidic media. Furthermore, magnesium and its alloys are prone to galvanic corrosion, so the metal coating must be pore free otherwise the corrosion rate will increase. Usually, the coating is at least 40-50  $\mu\text{m}$  thick to ensure pore-free coatings. Furthermore, the alloys are difficult to plate because intermetallic species such as  $\text{Mg}_x\text{Al}_y$  are formed at the grain boundaries, resulting in a non-uniform surface potential across the substrate, and therefore further complicating the plating process. Recently, Jiang et al [388] studied Zn-Ni alloy coatings pulsed-plated on magnesium alloy AZ91. Before deposition, the substrate surfaces were processed in a standard industrial way: polishing with alumina sand paper, alkaline degreasing, chemical pickling, activation, zinc immersion and Zn-Cu alloy plating. A Zn layer and a Zn-Cu layer under the Zn-Ni coating were applied to improve the adhesion and to protect the substrate using the small electrode potential difference between Zn-Cu and Zn-Ni layer. Zn-Ni coatings were deposited in an alkaline bath with a composition as ZnO 10g/l, NaOH 150 g/l,  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  g/l, triethanolamine 50 g/l, and at 10-40°C, 500-4000

Hz, 0.04-0.1 A/cm<sup>2</sup>. The bonding strength can be as high as 14.8 MPa. The corrosion life of the Zn-Ni coating can reach over 200 h in a salt spray test conducted according to ASTM B1117. However, no detailed data were given on the porosity of the coatings, which may increase the corrosion rate due to the galvanic corrosion effect.

### **Electroless plating:**

Electroless plating has good throwing power and can produce a uniform coating thickness on complex objects. It also involves a simple pre-treatment and is suitable for magnesium alloys with high aluminium contents [1]. However, electroless deposited coatings cannot be too thick, the bath life is limited, and deposition rates are slow. In particular, electroless plating requires the use of hydrofluoric acid during the pre-treatment, which increases the danger of the operation and is not environmentally friendly [1]. Research on increasing the bath life and eliminating toxic chemicals is necessary in order to create a green-plating process for coating magnesium. Sharma et al. [39] studied the properties of an electroless nickel coating on magnesium alloy ZM21. The solution contains nickel carbonate, sodium hypophosphite (metal-reducing agent), citric acid and bifluoride (act as accelerators, complexing agent, and accelerators), thiourea (solution stabilizer and brightening agent) and ammonia solution. The paper put forward some reactions, and suggested that the autocatalytic reaction for nickel deposition is initiated by catalytic dehydrogenation of the reducing agent with release of hydride ion, which then supplies electrons for the reduction of nickel ions.

The coated samples were immersed in a 5% solution of sodium chloride at pH 7.0. No corrosion spots on the coatings were noticed after 96 hrs of immersion. The formation of corrosion spots initiated only after the fifth day of immersion. Recently, Huo et al.[40] developed an environmental-friendly combined technique of chemical conversion treatment followed by electroless nickel plating for AZ91D alloy to improve corrosion resistance. The presence of the conversion coating, which was mainly  $\text{MgSnO}_3 \cdot \text{H}_2\text{O}$ , between the nickel coating and the substrate reduced the potential difference and avoided any catastrophic galvanic corrosion between nickel and magnesium. The electroless nickel coating containing about 10 wt% phosphorus greatly enhanced the corrosion potential of AZ91D from -1.50 V to -0.60 V.

#### *5.4.2. Conversion coatings*

Conversion coatings are produced by chemical or electrochemical treatment of a metal surface to produce a superficial layer of substrate metal oxides, chromates, phosphates or other compounds that are chemically bonded to the surface. On magnesium, these coatings are typically used to enhance paint adhesion to the coatings and provide improved corrosion protection to the metal. There are a number of different types of conversion coatings including chromate, permanganate, phosphate, phosphate-permanganate and fluorozirconate treatments. The conventional conversion coatings are based on chromium compounds that have been shown to be highly toxic carcinogens. The development of an environmentally friendly process is a necessity due to the more stringent environmental protection laws currently in effect, or being proposed. The coatings on alloys also represent a significant challenge due to their non-uniform surface composition.

### Phosphate–permanganate conversion coatings

Phosphate–permanganate treatments are being explored as an alternative to conventional chromate conversion coatings. These treatments are more environmentally friendly and have been shown to have corrosion resistance comparable to chromate treatments [1].

Chong and Shih [41] reported that a conversion coating on magnesium alloys AZ61A, AZ80A and AZ91D prepared from a solution containing permanganate ( $\text{KMnO}_4$  20g/l) and phosphate ( $\text{MnHPO}_4$  60g/l) showed an equivalent or slightly better passive capability than a conventional chromate-based conversion treatment, but an inferior passive capability for the pure Mg specimen. Hawke and Albright [42] studied a phosphate–permanganate treatment for the conversion coating of AM60B. The coating is based on magnesium phosphate, but contains significant amounts of aluminum compounds generated from the alloy's aluminum content, and manganese compounds formed by reduction of the permanganate ion. The manganese is considered to contribute manganese to the coating, and acts as an accelerator without depositing metallic manganese on the magnesium surface. The coatings were shown to have good corrosion resistance and paint adhesion.

It was found that the most important factor in producing the best quality conversion coatings was the control of the pH [1]. Since pH is the most important factor determining conversion coating quality, the research on stabilizing the pH of solutions has gained increasing attention. Umehara et al. [43] claimed that a pH-stabilizing solution was developed for the conversion coating on AZ91D. The surface film formed was composed of magnesium oxide, and manganese oxide, and contained boron oxide. The pH change was insignificant with increasing the surface area of the magnesium treated. After cleaning and surface activation, the samples were immersed in a solution containing potassium permanganate and either nitric or hydrofluoric acid. The coatings formed in the bath containing nitric acid were substantially thicker and crystalline manganese oxide was observed. The corrosion resistance of these coatings was equivalent to the protection afforded by a standard chromate treatment.

### Stannate conversion coatings

A study on stannate treatment of ZC 71 and a metal matrix composite of ZC71+12% SiC particles has been undertaken by Gonzalez-Nunez et al [44]. After mechanical finishing and pickling, the samples were immersed in a stannate bath for selected periods of time. The treatment resulted in the formation of a 2–3  $\mu\text{m}$  thick, continuous and adherent, crystalline coating of  $\text{MgSnO}_3$  on both materials. The nucleation and growth of the coating was completed in about 20 min. The initial nucleation was found to occur at cathodic sites on the surface with crystal growth to a grain size of about 2–5  $\mu\text{m}$  until they coalesced. There was an increase in the corrosion potential of the magnesium surfaces as the film formation proceeded indicating that the coating does have a passivating effect on the surface.

### Rare earth process

The corrosion protection of cerium, lanthanum and praseodymium conversion coatings on magnesium and magnesium alloy WE 43 has been investigated by Rudd et al [45]. The samples were polished, cleaned in water and methanol and dried prior to immersion in a  $\text{Ce}(\text{NO}_3)_3$ ,

$\text{La}(\text{NO}_3)_3$  or  $\text{Pr}(\text{NO}_3)_3$  solution. A visible, adherent but easily removed coating was produced on the surface. It has been demonstrated that these coatings provide an increase in corrosion resistance for magnesium and its alloys. However, the coatings deteriorated on prolonged immersion in the test buffer solution so their protective effect is short term.

Conversion coatings have been known for some time, but it should be mentioned that a great deal of the work done on conversion coating of magnesium substrate is proprietary in nature. Thus, there is still a great deal of research to be done to better understand the surface reactions between magnesium based substrates and coatings [1].

#### 5.4.3. Anodizing

Anodizing is an electrolytic process for producing a thick, stable oxide film on metals and alloys. These films may be used to improve paint adhesion to the metal, as a key for dyeing or as a passivation treatment. The stages for processing include [1]: (1) mechanical pre-treatment, (2) degreasing, cleaning, and pickling, (3) electrobrightening or polishing, (4) anodizing using AC or DC current, (5) dyeing or post-treatment and (6) sealing. Sealing of the anodized film is necessary in order to achieve an abrasion and corrosion resistant film. This can be accomplished by boiling in hot water, steam treatment, dischromate sealing and lacquer sealing [1]. One of the main challenges for producing adherent, corrosion resistant, anodic coatings on magnesium results from the electrochemical inhomogeneity due to the phase separation in the alloy. Another disadvantage of this technique is that the fatigue strength of the base metal can be affected by localized heating at the surface during the treatment.

**Dow 17 process:** Chemical treatment no.17, developed by Dow Chemicals, can be applied to all forms and alloys of magnesium [46]. The anodizing bath employed in this treatment is a strongly alkaline bath consisting of an alkali metal hydroxide and a fluoride or iron salt or a mixture of the two. This process produces a two-phase, two-layer coating. The first layer is deposited at a lower voltage and results in a thin, approximately 5  $\mu\text{m}$ , light green coating. The over layer is formed at a higher voltage. It is a thick dark green, 30.4  $\mu\text{m}$ , layer that has good abrasion resistance, paint base properties and corrosion resistance [46].

**HAE process:** named after its discoverer, H.A. Evangelides [47]. This treatment can be applied to all magnesium alloys including the rare-earth magnesium alloys [47]. The HAE bath is a strongly alkaline and oxidizing solution, consisting of potassium-hydroxide-aluminate-fluoride-manganate and tribasic sodium phosphate [48]. The treatment produces a two phase coating as in the DOW 17 process [46]. At a lower voltage a 5  $\mu\text{m}$  thick, light tan subcoating is produced. At a higher voltage a dark brown, thicker (30  $\mu\text{m}$ ) film is produced. Upon sealing the HAE treatment provides excellent corrosion resistance. The corrosion resistance of AZ91D treated with this technique has been tested by a 3-year atmospheric exposure experiment. Superior corrosion resistance compared to conversion coating was observed [49].

**Other processes:** Mizutani et al. [50] studied the electrochemical behaviours of pure magnesium, AZ31 and AZ91 in 1 mol/dm<sup>3</sup> NaOH during the anodizing process. The anodizing films on Mg alloys at 3 V had the best effective corrosion resistance and these films consist of



magnesium hydroxide. However, the coatings were really thin and the film thickness of anodized AZ91 at 3, 10 and 80 V was approximately 4, 1, and 0.5  $\mu\text{m}$ , respectively.

#### 5.4.4. Gas-phase deposition processes

Protective coatings can also be produced from the gas phase. These are typically metallic coatings but can include organic coatings such as thermal spray polymer coatings and diamond like coatings. All of these processes have the advantage that they have little negative environmental impact. However, the capital costs associated with these techniques are usually high [1].

#### **Chemical vapour deposition (CVD)**

Chemical vapour deposition can be defined as the deposition of a solid on a heated surface via a chemical reaction from the gas phase. Advantages of this technique include deposition of refractory materials well below their melting points, achievement of near theoretical density, control over grain size, processing at atmospheric pressure and good adhesion [51]. However, CVD is limited to substrates that are thermally stable at  $\geq 600\text{ }^{\circ}\text{C}$ . Efforts are underway to reduce the high temperature requirements and plasma and organometallic CVD processes offset this problem somewhat. A further disadvantage of this process is high-energy cost due to the need for high deposition temperatures and sometimes low efficiency of the process.

A plasma-assisted CVD technique has been successfully used to deposit  $\text{SiO}_x$  thin films on magnesium alloy WE43 [52]. The coatings were deposited at low temperature ( $T < 60\text{ }^{\circ}\text{C}$ ) and 100 mTorr of pressure. Pre-treatments were performed immediately before the application of the  $\text{SiO}_x$  coating, in plasma fed with oxygen, hydrogen or  $\text{CF}_4\text{-O}_2$  (20%). The  $\text{SiO}_x$  coatings exhibited better corrosion resistance in 0.1 M NaCl with the pre-treatment in  $\text{H}_2$  plasma than in  $\text{CF}_4\text{-O}_2$  (20%) plasma. When the magnesium surface is treated in  $\text{H}_2$  plasma, a preferential removal of OH groups occurs, resulting in a clean surface. The improvement of corrosion resistance of pre-treated magnesium alloy in  $\text{CF}_4\text{-O}_2$  (20%) plasma has been attributed to the formation of  $\text{MgF}_2$  [52].

#### **Diamond-like carbon films (DLC)**

Diamond like carbon films can be produced using a number of different processes such as physical vapour deposition (PVD), CVD and ion implantation. These coatings are desirable for many applications due to their high hardness, low friction coefficient, electrical insulation, thermal conductivity and inertness. Yamauchi et al. [53] reported that DLC films were deposited on the magnesium alloy substrate (Al 2.4 wt%, Zn 0.87 wt %, Si 0.001 wt%, Mn, Cu, Ni, Fe non-detected) by the plasma CVD method using radio frequency. The DLC coating was confirmed to be effective in decreasing the friction coefficient and improving the corrosion resistance in 3 wt% NaCl and 0.05 N NaOH solutions. However, DLC films showed poor corrosion wear resistance in 0.05 N HCl due to the existence of pits in the films.

#### **Physical vapour deposition processes**

PVD involves the deposition of atoms or molecules from the vapour phase onto a substrate. There are a few challenges to overcome in the PVD coating of magnesium substrates. The

deposition temperature must be below the temperature stability of magnesium alloys (180 °C) and good adhesion must be obtained despite this low temperature. Hollstein et al [54] compared the mechanical and chemical properties of various PVD coatings on a high purity AZ31 magnesium alloy, including single layer TiN, CrN, double layer TiAlN, NbN-(TiAl)N, CrN-TiCN, the multi-layer composite AlN/TiN, and superlattices CrN/NbN. The difference between the (TiAl)N layers and the TiN/AlN multilayers is that the (TiAl)N layers were produced using a Ti-50%–Al-50% target compound, whereas the TiN/AlN multilayers are produced by power switching between a titanium target and an aluminium target. NbN/CrN superlattices are characterised by a repeating layer structure of the two materials with a nanometric scale dimension. The best results in corrosion resistance, adhesion and hardness were obtained from the CrN and (TiAl)N coatings. The classical TiN monolayer coating with a thickness that is typical for decorative purposes (about 1 µm) is not suitable to protect Mg alloys against corrosion effectively. It seems that a minimum thickness of about 4 µm or more is necessary for industrial applications. Hoche et. al [55] developed a new method of plasma anodisation to ensure acceptable corrosion resistance, besides excellent wear protection on Mg alloy. The anodizing and PVD-coating can be done in one process. The 0.5 µm plasma anodisation layer and 1.5 µm PVD-Al<sub>2</sub>O<sub>3</sub> coating was subjected to 120 hours salt spray.

#### 5.4.5. Organic/ polymer coatings

Organic finishing is typically used in the final stages of a coating process. These coatings can be applied to enhance corrosion resistance, abrasion and wear properties, or for decorative purpose. An appropriate pre-treatment process is required in order to produce coatings with superior adhesion, corrosion resistance and appearance [1]. Many coating processes can be applied to magnesium and magnesium alloys, including painting, powder coating, e-coat, sol-gel process, and polymer plating. In the following section, we discuss the sol-gel process.

#### Sol-gel process

Synthesis of gels by the sol-gel process involves the hydrolysis and condensation polymerization of metal alkoxides. One of primary advantages of this technique is the excellent adhesion obtained with a minimum of sample pre-treatment [1]. The metal surfaces are simply degreased, rinsed and dried prior to dip-coating in the sol-gel mixture. A significant advantage is that irregular shapes and larger integral structures can also be coated. However, sol-gel coatings tend to fail if the film thickness exceeds 5 µm because of shrinkage strains during drying, and densification of the as-deposited xerogel film. Phani et al [56] reported that sol-gel coatings consisting of ZrO<sub>2</sub> as well as 15 wt% of CeO<sub>2</sub> could be deposited on magnesium alloys AZ91D and AZ31 by the dip coating technique. Adhesion measurements on the coatings showed good adhesion with critical loads of up to 25 N. Depth-sensing nanoindentation tests of the coatings showed a hardness of around 4.5 GPa and an elastic modulus of 98 GPa. Coatings deposited on AZ91D and AZ31 substrates exhibited good corrosion resistance in the salt spray test performed for 96 hr.



#### 5.4.6. Electrolytic plasma oxidation

Electrolytic Plasma oxidation (EPO), also called plasma anodising or micro arcing, is a promising surface treatment for hexavalent chromium replacement in anti-corrosion protection or in the improvement of the tribological properties of lightweight metal structures. This electrolytic plasma oxidation can be distinguished from classical anodising by the use of voltages above the dielectric breakdown potential of the anodic oxide being formed. This leads to the local formation of plasmas, as indicated by the presence of sparks that are accompanied by a release of gas [57].

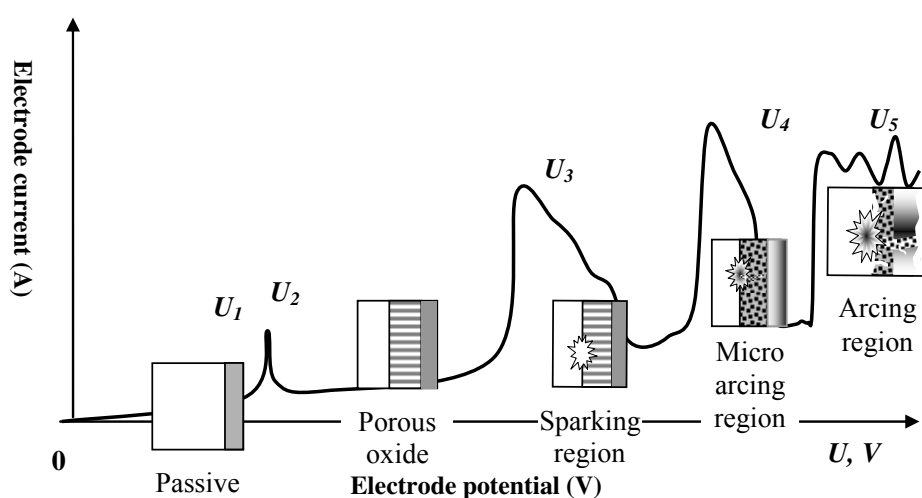
Some interesting historical comments are presented in a review by Yerokhin et al. [57]. Plasma anodizing dates back at least to 1932. At that time it was studied by two German scientists, Gunterschulze and Betz, while working on electrolytic capacitors using aluminium foil. During the 1970s oxide deposition on an aluminium anode under an arc discharge condition was also developed and studied. In the 1980s, the possibilities of utilising surface discharges in oxide deposition onto various metals were studied in more detail. Early applications were introduced in the textile and aerospace industries. Electrolytic plasma oxidation (EPO) is recently considered to be a promising technique to deposit ceramic coatings on magnesium alloys for corrosion protection.

The EPO process involves anode electrochemical dissolution, the combination of metal ions with anions to form ceramic compounds, and sintering on the substrate under the action of the sparks. Yerokhin et al [58] described three main steps leading to ceramic coating formation. First, a number of discrete discharge channels are formed in the oxide layer as a result of loss in its dielectric stability in a region of low conductivity. The material in the channel is heated-up to temperatures of  $10^4$  K by the generated electron avalanches. Due to the strong electric field, the anionic components are drawn into the channel. Owing to the high temperature, the elements are melted out of the substrate, enter the channel and are oxidized. Second, these oxidized metals are ejected from the channels into the coating surface in contact with the electrolyte, thereby increasing the coating thickness in that location. In the last step, the discharge channels are cooled and the reaction products are deposited on to its walls. The above process repeats itself at a number of discrete locations over the entire coating surface, leading to an overall increase in the coating thickness. However, there is no support experimentation to confirm the above interpretation.

Yerokhin et. al. [57] also described current –voltage characteristics during the EPO process. Fig. 13 is the current-voltage diagram for the process of plasma electrolytic oxidation. First, the previously formed passive film begins to dissolve at point  $U_1$ , which, in practice, corresponds to the corrosion potential of the material. Then, in the region of re-passivation,  $U_1$ - $U_2$ , a porous oxide film grows, and it is across this film that most of the voltage drops now occurs. At point  $U_2$ , the electric field strength in the oxide film reaches a critical value beyond which the film is broken through due to impact or tunnelling ionisation. In this case, small luminescent sparks are observed to move rapidly across the surface of the oxide film, facilitating its continued growth. At point  $U_3$ , the mechanism of impact ionisation is supported by the onset of thermal ionisation processes and slower, larger arc discharges arise. In the region  $U_3$ - $U_4$ , thermal ionisation is partially blocked by negative charge build-up in the bulk of the thickening

oxide film, resulting in discharge-decay shorting of the substrate. This effect determines the relatively low power and duration of the resultant arc discharges, i.e. micro-discharges, which are termed “micro arcs”. Owing to the ‘micro-arcing’, the film is gradually fused and alloyed with elements contained in the electrolyte. Above the  $U_4$ , the arc micro-discharges occurring throughout the film penetrate through to the substrate and transform into powerful arcs, which may cause destructive effects such as thermal cracking of the film.

Recently, Wang et al. [59] reported different characteristics of oxidized coatings at different voltages on AZ91D in an alkali-silicate solution. Three types of oxide coatings, passive film, micro-spark ceramic coating and spark ceramic coating, were prepared at 100 V, 195 V, and 235 V, respectively. The passive films are thin and cannot provide effective protection to the substrate. The micro-spark ceramic coatings are homogeneous with compact internal layer and exhibit the highest resistance owing to the highest effective thickness. The spark ceramic coatings are thickest, but due to the large pores in the oxide layer, they are loose and defective.



**Figure 13.** Current-voltage diagram for the process of plasma electrolysis: discharge phenomena are developed in the dielectric film on the electrode surface [57].

Electrolytic plasma oxidation (EPO) technology has been used for depositing ceramic coatings on magnesium alloys for corrosion protection [60-63]. The coatings can be as thick as a few hundreds of micrometers and their corrosion behaviour strongly depends on the process parameters employed, the chemical compositions of the materials studied, and the electrolytes used. The effect of electrolyte composition on properties of EPO oxide coatings on Mg and Mg alloys has also been an interesting subject of investigation to the automobile industry. The electrolytes consisted of potassium hydroxide and some other passive agents that can modify the characteristics of the oxide coatings. Hsiao and Tsai [62] studied the characteristics of anodic films formed on solutions containing 3M KOH, 0.21M  $\text{NaPO}_4$ , 0.6 MKF, with and without  $\text{Al}(\text{NO}_3)_3$ . It was found that the addition of  $\text{Al}(\text{NO}_3)_3$  into 3 M KOH+0.21 M  $\text{Na}_3\text{PO}_4$ +0.6 M KF base electrolyte assisted uniform sparking on AZ91D magnesium alloy in anodizing. Either with or without a low concentration of  $\text{Al}(\text{NO}_3)_3$ , a porous and non-uniform anodic was formed. The presence of  $\text{Al}(\text{NO}_3)_3$  in the base electrolyte resulted in the formation of  $\text{Al}_2\text{O}_3$  and

$\text{Al}(\text{OH})_3$  in the anodic film. The presence of  $\text{Al}_2\text{O}_3$  in the films is beneficial to the corrosion resistance of films in 3.5 wt% NaCl solution.

The process parameters employed also play an important role in the characteristics of oxide coatings. Zhang et al. [61] found that the properties of oxide coatings were strongly influenced by the process parameters employed. With an increase of solution temperature, the film thickness decreased. On the other hand, the film thickness increased with an increase in treatment time and current density. The voltages rise during the EPO process is always accompanied by the increase of film thickness. Higher voltage indicates thicker film. Khaselev et al [60] investigated the characteristics of the oxide coatings on binary Mg-Al alloys in a solution containing 3 M KOH, 0.6 M KF, and 0.21 M  $\text{Na}_3\text{PO}_4$  with 1.1 M aluminate. The breakdown voltages increased with an increase in Al content in the alloys. The growth of oxide films was non-uniform. The growth started on  $\alpha$ -Mg and continued on the  $\beta$ -phase ( $\text{Mg}_{17}\text{Al}_{12}$ ) when the voltage exceeded 80 V, and a uniform anodic film was formed on the alloy substrate when the voltages reached 120 V. Al was incorporated into oxide coatings from both the substrate and the electrolyte. The EPO coatings exhibited better corrosion resistance than the coatings treated by anodizing. Zhang et al [61] compared the oxide coatings produced by the EPO process with the anodic coatings prepared by the HAE and Dow 17 process. It was found that the EPO coatings were smooth, uniform, in contrast to rough, patchy film produced by HAE and relatively rough, even, partly powdery film produced by DOW17. Furthermore, the films produced by the EPO process are much more corrosion protective than those produced by HAE and DOW17.

Now studies on the effects of power supply modes on EPO coating properties have been paid more and more attention. Researchers [64] tried to modify the morphologies and structures of oxide coatings by altering the sparks during the EPO process. Originally, DC or amplitude-modulated AC was used in the EPO process, which allowed coating growth rates of only  $1\text{--}2\ \mu\text{m min}^{-1}$ . Yerokhin et al [64] utilized a pulsed bipolar current to make oxide ceramic layers dense and uniform with a fine-grained microstructure on a Mg alloy (2% Al, 1% Zn, 0.2% Mn, Mg-balance) and the coating growth rates was up to  $10\ \mu\text{m min}^{-1}$ . The pulsed bipolar current was also beneficial to elimination of the fatigue cracks by strain distortion of the metal subsurface layers induced during the oxidation process. The phase was mainly  $\text{MgAl}_2\text{O}_4$  using pulsed bipolar power, while MgO and  $\text{Al}_2\text{O}_3$  are mainly in the films using DC power.

Other methods have also been applied to the EPO process to improve the properties of coatings. Guo et al [65] demonstrated that ultrasonic power can play an important role in the coating formation and enhance the coating growth. The anodic coatings consisted of two layers when the ultrasound field was applied and the acoustic power value increased to 400W at a constant frequency of 25 kHz in 0.1 M potassium hydroxide, 0.15 M potassium fluoride, 0.30 M sodium aluminate, 0.004 M sodium pyrophosphate and 0.5-1.0 M additives. This was different from the situation without an ultrasonic field where the anodic coatings consisted of only one layer. For the two layer anodic coatings, the inner layer was compact and enriched in aluminum and fluorine, and had a uniform thickness. In contrast, the aluminum and fluorine contents in the external layer were very low and the thickness was non-uniform. Also, studies [66-73] demonstrate that Plasma Electrolytic Oxidation (PEO) is a relatively cost-effective and

environmentally friendly technique to improve the corrosion and wear resistance of magnesium and its alloys. The PEO method can be used to form a thin or thick, hard and adherent ceramic-like coating on the surface of Mg alloys for automotive applications.

It has been indicated [74-77] that magnesium is a good candidate as an implant material due to its bioabsorbability and high specific strength. To avoid the rapid degradation of the magnesium in the human body, techniques of surface treatment can be applied to improve magnesium corrosion resistance and consequently mitigate its degradation. Very recently, Hu and Nie [78] applied the plasma electrolytic oxidation (PEO) treatment to pure magnesium in an effort to develop an implant material with controllable degradation. This is because the PEO process is inexpensive and environmentally friendly and capable of producing a coating that is non-harmful to the human body. Magnesium is a strong candidate as due to its bioabsorbability and high specific strength. In their study, Potentiodynamic polarization corrosion tests, performed in a simulated body fluid (Hanks' Balanced Salt Solution) were carried out on coated and uncoated magnesium samples. The results of the testing showed that the coated magnesium exhibited higher corrosion resistance than the substrate. With the PEO coating thicknesses of 6.3 and 18.6 microns, the corrosion current density was decreased by  $1.330 \times 10^{-3}$  and  $1.341 \times 10^{-3}$  mA/cm<sup>2</sup> from the uncoated magnesium respectively, indicating a significant reduction in the degradation rate between pure magnesium and coated magnesium from  $6.17 \times 10^{-1}$  to  $1.91 \times 10^{-2}$  and  $1.42 \times 10^{-2}$  g/year respectively. A pin-on-disc tribometer was employed to measure the coefficient of friction (COF) for the coated and uncoated magnesium samples, lubricated with and without Hanks' solution. The measured COFs of the coated samples were very low. They were averaged to be 0.198 and 0.256 for the thick and thin coatings respectively, while the substrate exhibited an averaged COF of 0.203 under the lubricated condition. The COF measurements indicated the coatings had very comparable COFs to the substrate. By maintaining the low level of the COFs, the developed PEO coating on the Mg substrate could cause almost no irritation or harm to the surrounding tissue during the implant insertion operation.

## 6. Summary of the literature review

The examples described in the previous section demonstrate that it is possible to develop appropriate coating schemes for the protection of magnesium for use in automotive components. However, no single coating technology has been developed which functions to adequately protect magnesium from corrosion in harsh service conditions. For example, in winter, the mixture of deicing salt and sand often attacks Mg chassis components of automobiles, such as transfer cases. Also, coolants can cause corrosion on Mg alloy engine blocks.

One of the most effective ways to prevent corrosion is to coat the base material. In order for a coating to provide adequate corrosion protection for Mg and Mg alloys, the coating must be uniform, pore free, well adhered, and self-healing in case that physical damage to the coating may occur.

In the case of electrochemical plating, the capital investment is relatively small. Electroplating process is extremely difficult to achieve uniform coatings on complex shapes due to uneven throwing power. Electroless plating can obtain uniform coatings. However, there are some serious concerns over waste disposal.

Conversion coatings also represent a minimum capital investment, however the most widely used type of conversion coatings are chromate conversion coatings. These represent a serious environmental risk due to the presence of leachable hexavalent chromium in the coatings. A number of chromate free conversion coatings are under development but this technology is still in its infancy. Conversion coatings do not provide adequate corrosion and wear protection from harsh service conditions when used alone. However, they can act as a good base for producing adherent organic coatings and act to enhance corrosion resistance of a combined coating system by protecting the substrate at the defect sites in overlying layers.

Anodizing is the most widely commercially used coating technology for magnesium and its alloys. This process is technologically more complex than electroplating or conversion coating but is less sensitive to the type of alloy being coated. It does involve more capital investment due to the need for cooling systems and high power consumption but this may be balanced by the decreased cost of waste disposal. The coatings produced by anodizing are porous ceramic-like coatings. These properties impart good paint-adhesion characteristics and excellent wear and abrasion resistance to the coating. However, without further sealing, they are not adequate for use in applications where corrosion resistance is of primary importance.

The use of gas-phase coating processes and laser surface melting to modify the surface or create coatings is an excellent alternative for corrosion protection of Mg alloys with little environmental impact. However, the capital investment of equipment is really high.

Organic coatings such as sol-gel coatings on magnesium alloys require a minimum of pre-treatment steps prior to deposition. But, their thicknesses might be limited.

It is evident that there is limited information comparing erosion and corrosion properties of the ceramic coatings prepared from different electrolytes. The relative significance of the EPO process parameters on effects of the corrosion resistance of magnesium alloys, in particular for bio-applications, needs to be fully investigated.

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