EFFECT OF ZINC ADDITIONS AND HEAT TREATMENT ON THE MICROSTRUCTURE AND CORROSION PROPERTIES OF THE MAGNESIUM ZINC ALLOYS

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FOZI MUSTAFA SALEM MAKHLOF

EFFECT OF ZINC ADDITIONS AND HEAT TREATMENT ON THE MICROSTRUCTURE AND CORROSION PROPERTIES OF THE MAGNESIUM ZINC ALLOYS

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I certify that in my opinion the thesis submitted by Fozi Mustafa Salem MAKHLOF titled "EFFECT OF ZINC ADDITIONS AND HEAT TREATMENT ON THE MICROSTRUCTURE AND CORROSION PROPERTIES OF THE MAGNESIUM ZINC ALLOYS" is fully adequate in scope and in quality as a thesis for the degree of Master of Science.

Dr. Erkan KOÇ

Thesis Advisor, Department of Metallurgical and Materials Engineering

This thesis is accepted by the examining committee with a unanimous vote in the Department of Metallurgical and Materials Engineering as a master thesis. 23/03/2018.

Examining Committee Members (Institutions)   Signature

Chairman: Prof. Dr. Hayrettin AHLATÇI (KBU)   ....

Member : Dr. Erkan KOÇ (KBU)   ....

Member : Dr. Abdullah Cahit KARAOĞLANLI (BU)   ....

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The degree of Master of Science by the thesis submitted is approved by the Administrative Board of the Graduate School of Natural and Applied Sciences, Karabük University.

Prof. Dr. Filiz ERSÖZ

Head of Graduate School of Natural and Applied Sciences

ii

"I declare that all the information within this thesis has been gathered and presented in accordance with academic regulations and ethical principles and I have according to the requirements of these regulations and principles cited all those which do not originate in this work as well."

Fozi Mustafa Salem MAKHLOF

ABSTRACT

M. Sc. Thesis

EFFECT OF ZINC ADDITIONS AND HEAT TREATMENT ON THE MICROSTRUCTURE AND CORROSION PROPERTIES OF THE MAGNESIUM ZINC ALLOYS

Fozi Mustafa Salem MAKHLOF

Karabük University
Graduate School of Natural and Applied Sciences
Metallurgical and Materials Engineering Department

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The purpose of this study is; effects of zinc (0,5-1-2-3 wt.%) additions and heat treatment parameters on the microstructure, hardness and corrosion properties of magnesium zinc alloys. After the solution heat treatment at 400ºC, the samples subjected to 8 and 16 hour aging heat treatment. Microstructures were examined in optical and SEM microscopes, and potentiodynamic polarization values were obtained in the electrochemical corrosion test, compared to the casting structure.

As a result of the microstructure studies, it was observed that the grain size decreased with the increase of Zn content and the MgZn intermetallic phase was formed by the addition of 3% Zn.

As a result of the hardness test, an increase of hardness by 36% was observed with increase of Zn content. The increase in hardness value of the samples subjected to 8 hours of heat treatment was 39%, while the values of 16 hours of heat treated samples increased to 58%.

For the as-cast samples, as the amount of Zn increased, I_{corr} and CR increased at around 5.7 fold, in other words, the corrosion resistant decreases as the Zn ratio increases. It can be suggested that in the galvanic couple of AZ03, MgZn intermetallic phase behaves as an anode and α-Mg matrix phase behaves as a cathode. As the amount of Zn increased, I_{corr} and CR values decreased by 50% and 35% after 8 hours and 16 hours of heat treatment respectively. In other words, the corrosion resistant increases as the Zn ratio increases both after 8 hours heat treated and 16 hours heat treated samples. It can also be suggested that in the galvanic couple of AZ03, α-Mg matrix phase behaves as an anode and MgZn intermetallic phase behaves as a cathode.

ÖZET

Yüksek Lisans Tezi

MAGNEZYUM ÇİNKO ALAŞIMLARININ MİKROYAPI VE KOROZYON ÖZELLİKLERİNE ÇİNKO İLAVELERİ VE ISIL İŞLEMİN ETKİSİ

Fozi Mustafa Salem MAKHLOF

Karabük Üniversitesi
Fen Bilimleri Enstitüsü
Metalurji ve Malzeme Mühendisliği Bölümü

Tez Danışmanı:
Dr. Öğr. Ü. Erkan KOÇ
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Bu çalışmanın amacı; çinko (%0,5-1-2-3 oranlarında) ilavesinin ve ısıl işlem parametrelerinin, magnezyum çinko alaşımlarının mikroyapı, sertlik ve korozyon özelliklerine etkisini incelemektir. 400ºC'de çözeltiye alma ısıl işleminden sonra 8 ve 16 saatlik yaşlanma ısıl işlemine tabi tutulan numunelerin, döküm yapı ile karşılaştırmalı olarak, mikroyapıları optik ve SEM mikroskoplarında incelenirken, elektrokimyasal korozyon testinde ise potansiyodinamik polarizasyon değerleri elde edilmiştir.

Yapılan çalışmalarda; mikroyapı incelemeleri sonucunda Zn miktarının artışıyla tane boyutunun küçüldüğü ve %3 Zn ilavesiyle MgZn intermetalik fazının oluştuğu gözlenmiştir. Sertlik deneyi sonucunda, Zn miktarının artmasıyla sertlikte %36'ya varan artış gözlenmiştir. Bu oran 8 saat ısıl işleme maruz kalmış numunelerde %39 iken, 16 saat ısıl işleme maruz kalmış numunelerde %58'lere kadar yükselmektedir.

Elektrokimyasal korozyon testlerinde ise; döküm halde olarak alınan numuneler için, Zn miktarı arttıkça, I_{corr} ve CR, yaklaşık 5.7 kat artmıştır, diğer bir ifadeyle, Zn oranı arttıkça korozyona direnç azalmıştır. AZ03'ün galvanik çiftinde MgZn intermetalik fazının anot gibi davrandığı ve α-Mg matris fazının bir katot gibi davrandığı öne sürülebilir. Zn miktarı arttıkça, 8 saatlik ve 16 saatlik ısıl işlem sonrasında sırasıyla I_{corr} ve CR değerleri% 50 ve% 35 oranında azalmıştır. Diğer bir ifadeyle, 8 ve 16 saatlik ısıl işlemden sonra Zn oranı arttıkça korozyona direncin arttığı gözlenmiştir. AZ03'ün galvanik çiftinde α-Mg matris fazının bir anot görevi görmesi ve MgZn intermetalik fazının bir katod olarak davranması da bu durumu açıklayabilir.

Anahtar Kelimeler : Magnezyum, magnezyum alaşımları, ısıl işlem, mikroyapı, vickers sertlik, korozyon.

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CONTENTS

LIST OF FIGURES

LIST OF TABLES

SYMBOLS AND ABBREVIATIONS

SYMBOLS

Mg   : Magnesium

Al   : Aluminum

Zn   : Zinc

Pt   : Platinum

Ta   : Tantalum

Li   : Lithium

Mn   : Manganese

Ni   : Nickel

$Mg(OH)_2$: Magnesium hydroxide

NaCl   : Sodium chloride

HV   : Vickers hardness unit

CO_2 : Carbon dioxide

ABBREVIATIONS

μm : Micrometer

XRD   : X-Ray Diffraction

MPs   : Mega Pascal

SEM   : Scanning Electron Microscope

E_{corr} : Corrosion Potential

EDS   : Energy Dispersive X-Ray Spectroscopy

I_{corr} : Corrosion Current Density

μA : Microamper

CR   : Corrosion Rate

GRF   : Growth Limiting Factor

CHAPTER 1

INTRODUCTION

Magnesium and magnesium alloys are typically used as building materials in lightweight applications as in various transport industries, because of their fast machinability, low weight and high specific strength [1]. In addition to this, magnesium is considered a good convene choice for biodegradable osteosynthesis or other temporary medical applications because of the following reasons:

1. It is physiologically compatible.
2. It stimulates bone formation.
3. It is biodegradable in the human body.

In contrast to the applications of magnesium and its alloys in the transport industry, where corrosion is unwanted, it is particularly advantageous in medical applications. However, a significant matter to be considered is the commonly high corrosion rate of Mg alloys and it can be changed by selecting convenient alloying elements or by surface adjustments. Therefore, care should be taken to identify only elements, which are not harmful [2-4].

Magnesium is an attractive material for many uses and applications owing to the fact that it has many unique advantages including low density, stiffness, high specific strength, good electrical conductivity, absorption of vibration and heat dissipation when combined with forming, recycling, easy machining and casting. Magnesium has witnessed significant development and growth in recent years on a large scale, prompting industrial companies and research centers to discover more efficient ways to manufacture primary metals as well as research and discovery of new alloys and expanding the fields of their applications [2].

Magnesium, through above information is useful when the elements to be selected are important. So the high corrosion rate of Mg alloys is a significant issue in transportation industry in which corrosion is not desired. Additionally, accounts for the reasons why magnesium is advantageous by making mention of its unique low density, stiffness, high specific strength, good electrical conductivity, absorption of vibration and heat dissipation. Thanks to these characteristics, the importance given to magnesium alloys has significantly increased and urged researchers to study on magnesium with new alloys and application fields.

Structural applications of magnesium alloys are growing due to general interest. For automotive applications, this is largely because of an attractive array of advantages including low density, high specific strength, and acceptable ductility and, most importantly, low cost handling and assembly across die casting components of complex form.

Several studies have shown that alloying is a beneficial way to improve the performance of magnesium alloys where refining structures have been widely recognized, enhanced solid solution and enhanced dispersion [1, 2].

Heat treatment is also an active way to improve performance. If it is possible to combine the alloying and aging treatment correctly, thus, the performance of magnesium alloys can be more developed.

The magnesium production market faces several technical problems that limit the expansion of this market. The first of these problems is the low production rates of wrought magnesium. From 5 to 10 times Typical magnesium alloy must be extruded slower than typical aluminum alloy [1, 2].

Researchers are looking for reasons and possible solutions for this fact. Temperature window is one of the core causes where the material is applicable, but do not suffer from hot tightness (initial melting), is very narrow to traditional extrusion alloys such as AZ61 and ZK60 [2].

Some recent research has been conducted on magnesium alloys for low alloy content in order to significantly increase production rates while it has been taken into consideration maintaining sufficient strength, obtained from either the thermal or electrolytic route with different levels of purity, is not used for structural applications.

The alloys are created in engineering applications by adding a number of different elements such as Al, Zn, Mn, Si, Zr, Ca, Ag, Li, Cu, alkaline or rare earth elements. The main purpose of alloying additions to magnesium is to improve the strength and other properties of magnesium.

Although alloys change some properties of magnesium alloys are not affected much and remain similar to the properties of pure magnesium [4,5]. For example, zinc improves room temperature strength of Magnesium alloy and zinc also improves fluidity of the melt.

CHAPTER 2

MAGNESIUM AND MAGNESIUM ALLOYS

2.1. GENERAL PROPERTIES

The discovery of magnesium is due to Joseph Black in 1755. Magnesium accounts for about 2.7% of the earth's crust and 0.13% of the ocean's water in the earth, making magnesium a relatively abundant element [4]. Magnesium has been used for many different applications throughout history including fireworks, chemicals as well as structural materials.

Magnesium was used on a wide scale in World Wars but interest later diminished. apart from its use in specialized applications such as in military aircraft, metallurgy, and nuclear industry. The most important application was its use by Volkswagen Company in a VW beetle car but even this pitted out when high performance was required.

Renewed interest in magnesium, especially in transportation, to reduce vehicle weight and introduce legislation to reduce emissions. In 1944, consumption amounted to 228 thousand tons, but fell after the war to 10.000 tons per year. In 1998 renewed interest rose to 360 000 tons per year at $ 3.6 per kilogram. The growth rate over the next 10 years is expected to be 7% annually [5].

The number of major producers has increased, and it is hoped that magnesium will increase at reasonable prices when demand increases. Figures 2.1 and 2.2 show magnesium divided into metal applications.
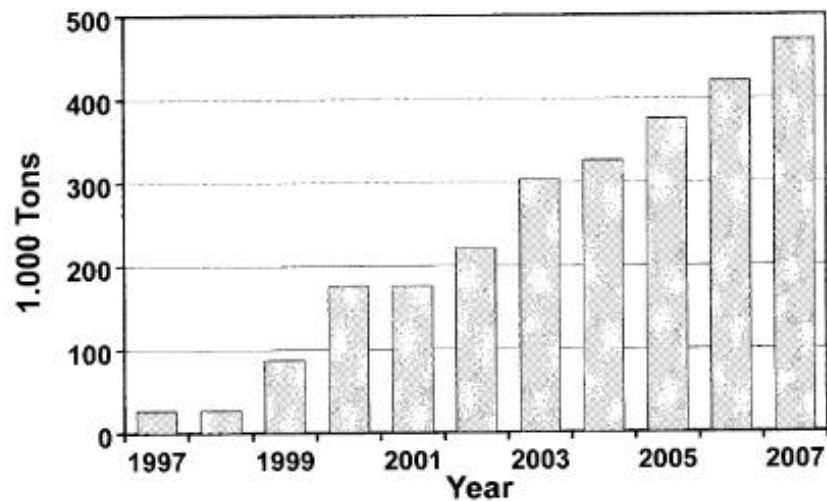
Figure 2.1. Capacity of primary magnesium [6].
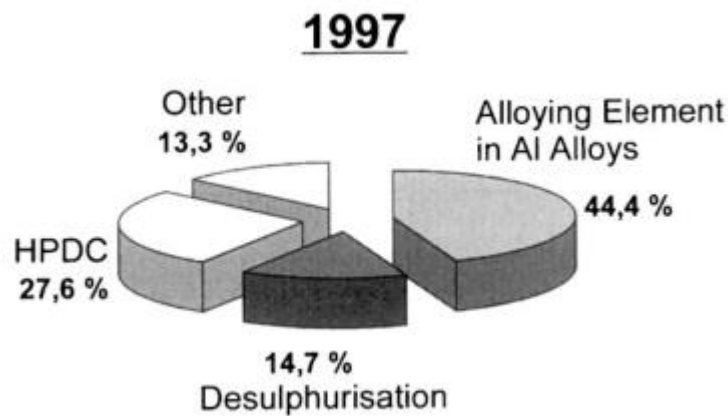
Figure 2.2. Metallurgical applications areas of magnesium [6].

Hexagonal structure of the magnesium limits the ductility of the alloy. The only alloy component, which causes a phase change useful for bcc, in this regard, is lithium. One of the advantages for Magnesium is its large availability. Magnesium is the 8th element of abundance on earth and it can be extracted from its sources like magnesite, dolomite, bischofite, carnallite, and sea waters. Another advantage is high strength/weight ratio, which is attractive to the transportation industry [2]. Other qualities like good machinability and recyclability make it ideal for many other applications. However, magnesium also has high electrochemical activity, which its use in some certain applications that required proper corrosion resistance. For corrosion sensitive applications, the current use of magnesium is far less than

aluminum and steel. Both Song et al., found that one of the reasons for corrosion of magnesium alloys is internal galvanic attack [3]. This internal galvanic attack can happen between the matrix phase and the secondary phase or inclusions. Another reason is the fluctuation of the Mg $(OH)_2$ film which formed on the surfaces of magnesium alloy. This hydroxide film is only stable at pH values above 10.5 which is very alkaline. Knowing these causes, the corrosion resistance can be improved by alloying the base metal and applying a surface treatment [7].

Magnesium has a very low density value (1.738 g/cm^3). Hexagonal dimensions of its crystal structure are; a =0.320 nm, c = 0.520 nm, c/a = 1.624. It has a close-packed basal plane and an axial ratio which is slightly higher than the theoretical value for incompressible spheres [7].

The atomic diameter of magnesium is 0.320 nm, so there is a favorable size factor with a diverse range of the solute elements zinc (Zn), aluminum (Al), thorium (Th), zirconium (Zr), yttrium (Y), cerium (Ce) and silver (Ag) [8]. Magnesium has found a wide variety of applications and the general properties of magnesium are given in Table 2.1

Table 2.1. Physical properties of magnesium.

Atomic Number	12
Density	1.738 g/cm^3 (20 °C)
Melting Point	650°C
Boiling Point	1090°C
Thermal conductivity	156 W/m.K. (27 °C)
Specific Heat	1.025 kJ/K.kg (27 °C)
Elasticity Module	45 GPa
Hardness	30-47 HB
Crystal Structure	Hexagonal Close Pack

The advantages of magnesium and magnesium alloys include the following,

1. High specific strength;
2. Characterized by a lower density of all metallic materials;
3. Good for casting, especially for high pressure die-casting;
4. Good weldability under controlled atmosphere;
5. Can be easily recycled: milled at high speed;
6. Corrosion resistance much improved using Magnesium high purity;
7. Easily available;
8. Compared with polymeric materials:
   - Electrical and thermal conductivity better,
   - Resistant to aging,
   - Mechanical properties better,
   - Easily recycled.

The reason for the limited use of magnesium is some weaknesses that worsen due to the inefficient of development work. The disadvantages of magnesium are listed based on the following:

1. Elastic modulus is lower,
2. Limited high strength and creep resistance at high temperatures,
3. High chemical reactivity,
4. Cold workability and toughness are limited,
5. Limited corrosion resistance insome applications,
6. Shrinkage on solidification a high degree.

Use conventional alloying techniques is not possible to improve certain properties such as flexible constants. The melting of alloy elements in magnesium is limited and limiting the possibility of improving the mechanical properties and chemical behavior. Magnesium alloys have entirely uncommon properties which prompt to particular applications. Specifically, their high strength to weight proportion makes magnesium alloys to a great degree alluring for applications requiring light weight,

for example, transport, aviation, and so forth. All in all, these light alloys have a promising future.

The corrosion mechanisms of magnesium alloys try to give an establishment to comprehension the corrosion mechanisms of magnesium alloys. This principal comprehension of the corrosion mechanisms is imperative as it gives the premise to the plan of new alloys with enhanced corrosion properties. Magnesium alloys have high stiffness/weight ratios, high damping capacity and good castability. Mg is alloyed with many other elements to garner selected characteristics and the common alloying elements, and the reason for their use, are shown in Table 2.2 [9].

Table 2.2. List of some alloying elements and their effect in Mg alloy systems [9].

Element	Alloy Designation	Properties
Ag	Q	Improve elevated temperature properties and creep when present with rare earths
Al	A	Improve castability, precipitation hardeners produced, corrosion protection
Ca	X	Grain refinement, improves creep resistance, improve high temperature properties
Rate Earths (Ce, La, Nd)	E	Improve creep resistance, castability, grain refining, age hardening
Si	S	Improves creep resistance
Sr	J	Improves creep resistance
Mn	M	Purification
Y	W	Improve tensile properties, grain refining
Zn	Z	Ductility and castability
Zr	K	Grain refiner, purification

Magnesium alloy casting is better than aluminum alloy casting in terms of their strength/weight ratio. Magnesium and magnesium alloys have a non-magnetic, high thermal conductivity, high electrical conductivity, reliable vibration, good shock absorption capability. Magnesium is nontoxic and can be formed and worked by all

known methods. Moreover, more than half of the annual production of magnesium is used in addition to the irreplaceable alloys in aluminum alloy and nodular cast iron. It is mainly used as castings in the aviation industry and public transportation with some wrought products in specialized applications. In these engineering applications, magnesium is hardly used as unalloyed.

2.2. MECHANICAL PROPERTIES OF MAGNESIUM AND ITS ALLOYS

Due to properties of magnesium it has made it attractive to a wide range of applications. Especially for the large growth in the field of die casting components in recent years, great interest has been observed in magnesium and magnesium alloys, as in automotive applications, The reason for this is an attractive array of characteristics including acceptable ductility, high specific strength low cost handling and most importantly low density and assembly across die casting components of complex form. Several studies have shown that alloying is a useful way to improve the performance of magnesium alloys, where refining structures have been widely recognized, enhanced solid solution and enhanced dispersion by adding REE [10, 11].

2.2.1. Specific Strength

The most of magnesium applications cover AZ91 alloys, die-casting alloy. These alloys (AZ91) have enough creep resistance for the most applications wanted at temperatures above (130°C). The aluminum system forms the basis. Though much less from specific high-strength wrought alloys. The perfect combination of strength and ductility It can be obtained from the double alloy of Al 6 wt.%. Further development of Mg-Al alloys for die-casting Mg–Al–Mn and for sand casting alloys with Mg–Si, Mg–Al–Ca and for wrought alloys, Mg–Al–Zn.

Magnesium alloys have a higher specific strength than steels and aluminum alloys. Some properties such as specific toughness and specific strength of materials and structures are important for the design of weight-saving components. As energy consumption and restrictions have become a major concern, especially in the

automotive industry, the provision of weight is particularly important in car structures, components and other products [12]. When comparing the specific strength and specific hardness of magnesium with aluminum and iron as in Figure 2.3. There was little difference in these properties which makes magnesium and its alloys more demanding and specific to light weight.

The specific stiffness of iron and aluminum is higher than magnesium only in the ratio of 3.752% and 0.69% respectively. On the other hand, the specific strength of magnesium is considerably higher than that of iron and aluminum in the ratio of 67.716% and 14.075% respectively, as shown in Figure 2.3.
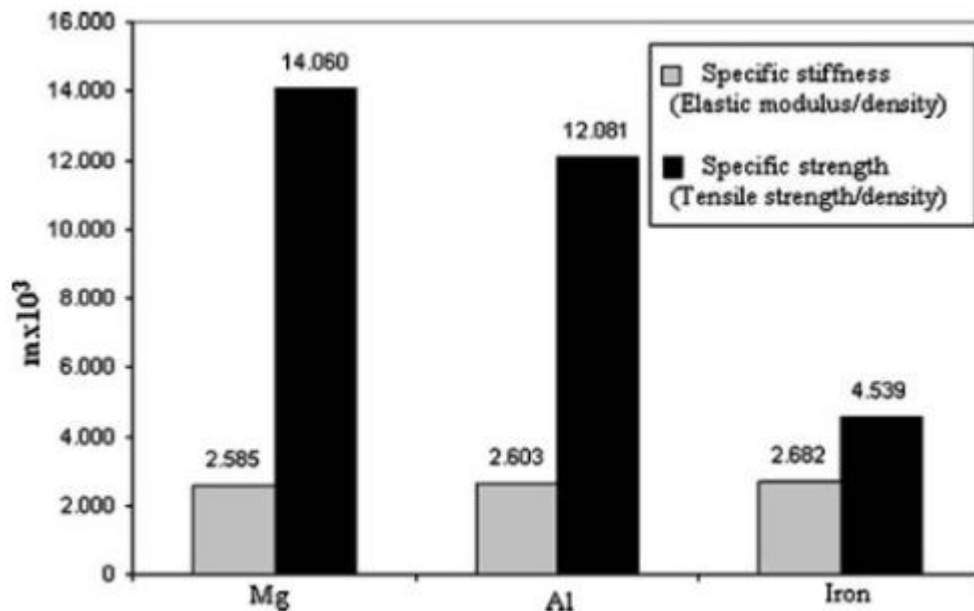
Figure 2.3. Basic structural properties of magnesium compared with Al and Fe [14].

Property features are claimed by cars and other potential large-scale users of its magnesium revealed the need to develop the alloy. Respectively the transfer of "high-performance" aircraft alloys is not possible not only for economic reasons but also property features do not coincide. Figure 2.4 shows different trends in alloy development depending on the main condition.
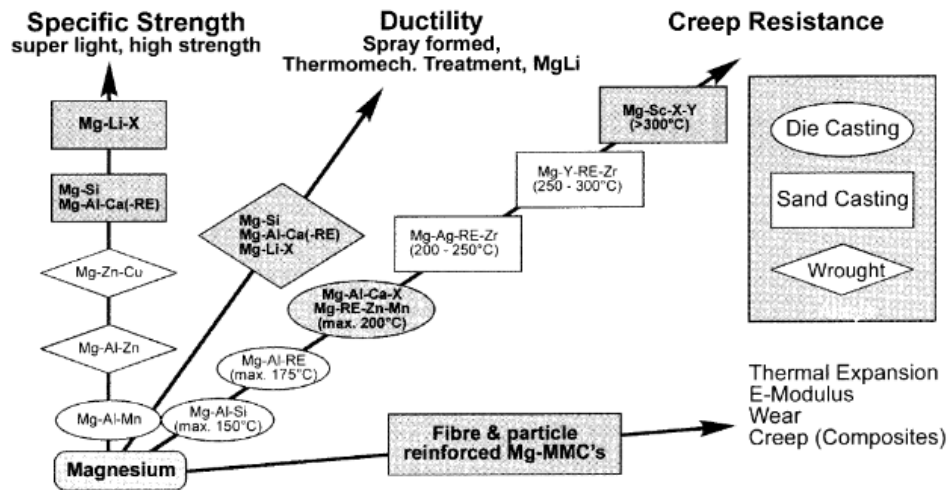
Figure 2.4. Directions of alloy development.

For good and improved properties such as increased mechanical strength. Magnesium should be poured with other elements such as zinc and aluminum which give improved properties. Some magnesium properties such as heat resistance and creeping can be improved by alloys. By adding some elements, for example, AZ series magnesium alloys consist primarily of adding an element aluminum (Al) and a component zinc (Zn) to pure magnesium.

In order to obtain alloys with improved properties such as weldability, workability, castability, corrosion resistance and high specific strength. The added quantities must be correct of these alloys in a well-balanced way. For room temperature applications Aluminum, zinc, and manganese are the most common alloying elements and using, while zirconium, cerium and thorium are used at high temperature [13]. Cerium or thorium is added to improve strength at the temperatures of 260 °C to 370 °C.

Magnesium components are mostly in the form of Mg alloys. The addition of other alloying elements can be harden and strengthen Mg as well as change its chemical reactivity. Magnesium alloys are the most candidates for applications because of their high specific strength, where weight reduction and therefore the energy saving is required.

However, often the mechanical properties of magnesium are inadequate, especially when compared to other elements, the absolute specific strength is low and the plastic deformability is limited due to magnesium's hexagonal close-packed crystal structure (hcp), However, prismatic slip is activated and ductility increases at higher temperatures. Under these conditions it is difficult to form magnesium alloys due to inadequate number of independent slipping systems, preferential orientation of the crystals during forming occurs and thus a textured material is generated. During the extrusion process and since the wrought magnesium has mechanical properties of a very different nature. And, since the activation of deformation modes in magnesium depends on the direction of stress applied, i.e. winning is more pronounced in compression than in tension, a tension-compression yield stress asymmetry due to twinning arises. To overcome these problems and to improve the strength and ductility of magnesium alloys a fine microstructure is used as an efficient way (of the extrusions and castings). The chemical and structural homogeneity across the billet diameter improve by grain improvement during casting. Moreover, extrusion is facilitated because of reducing of the hot tearing susceptibility. Furthermore, in a small-grained microstructure twinning is restricted due to geometric causes.

Prefer magnesium alloys for preference reasons:

1- Magnesium is preferred especially in aircraft industry due to its light weight.
2- If it is desired that the alloy is hard and durable, it can be alloyed with hard metals.
3- Because it is a bright and white metal, it has visual beauty in use on the outer surface.
4- It is preferred because of its high strength / density value even though its strength is very low.

Magnesium is the most used alloy of magnesium-aluminum alloy. Magnesium-aluminum alloy gives magnesium aluminum hardness. If this alloy is added to zinc, the hardness is slightly increased. If the zinc mixture is about 0.75%, a castable alloy is obtained. If the amount of zinc increases, the situation is reversed. If 0.25%

manganese is added to the magnesium alloy, it becomes resistant to corrosion [4, 12, 14].

2.2.2. Ductility

It is necessary to be available in the magnesium alloys mix that combines high strength with appropriate ductility so as to improve the ductility of these alloys. So that there is a need for many alloys with high ductility having the ability to be formed by thermal treatment. The ductility can be determined by a number of effective slip systems. In addition to the development of new alloys based on Mg and other elements which offer the possibility of having a phase mixture of hcp and bcc phases, there has been punch work into the development of fine grain material. A proven technique for copper and aluminum based alloys and steels, is fine grain material and spray forming [15].

2.2.3. Creep Resistance

As the magnesium dissolves at a temperature of 650°C. Therefore, problems are expected to be prevented creep in stressed components. These problems can be decreased by obtaining creep resistance without ambient temperature strength and ductility at an acceptable price and without making fabrication difficult. The castability (fluidity) of die-casting alloys, for instance, is impaired by using rare earth (RE) elements to enhance the creep resistance.

2.2.4. Fiber and Particle Reinforced Magnesium

The practice of traditional alloys cannot guarantee certain properties; these fibers and reinforcing particles must be used to achieve a better elastic modulus and perhaps wear and creep resistance values. Thermal expansion can also be modified. Problems arise from the interaction of magnesium - the reinforcement can be attacked - which can weaken the booster. An appropriate matrix alloy can be determined to obtain better manufacturing results.

2.3. APPLICATION OF MAGNESIUM ALLOYS

Magnesium alloys have become attractive as environmentally friendly materials that are lightweight and highly efficient for high-performance applications such as automotive and electronics components. Because of low density, high specific strength, relatively excellent dent resistance, damping ability and shielding capacity of electromagnetic waves as compared to plastic and aluminum alloy. Magnesium alloys have a weak plastic workability due to limited slip systems available only in a hexagonal close-packed (hcp) crystal structure, limiting extended applications. Therefore, most components of magnesium alloys have been fabricated by the casting method. If poor plastic operation is improved, more applications can be expected from magnesium alloys. Plastic workability of Mg alloys can be improved by changing the crystal structure by adding Li element [16,17].

Magnesium alloys are light metal alloys with a vast spectrum of applications. These alloys are used, among others, in the aircraft, automotive, armaments, electronic, textile, sports, medical and building industries.

2.3.1. Magnesium in Aviation

The most important characteristics of metals used in the aviation industry are; lightness, durability, shock, vibration, and corrosion resistance. Lightness can be achieved by reducing density. Metal materials such as aluminum, steel, titanium, magnesium, and copper are mostly used in production and it is almost impossible to meet the special needs of flying reasons with low strength properties of pure minerals.

The core of contemporary research and development studies; new and previously untested alloys for more useful materials. An example of the use of magnesium in aviation is given in Figure 2.5. The aircraft industry uses a wide range of magnesium alloy parts, from gearbox and engine components, castor gearbox, wings, fuselage skin, door, wheels and wheels, dashboard panels and seat components [14,19].

Figure 2.5. Examples of application for magnesium alloys in Boeing 747.
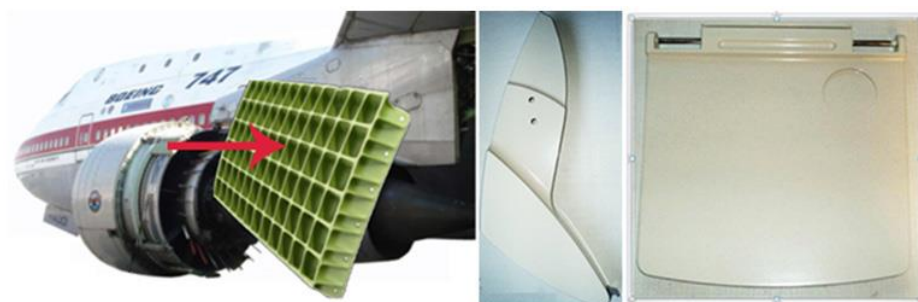
Figure 2.6. Examples of application for magnesium alloys: wing and seat components.

The characteristics improved by the sector are significantly improved are;

1) They must not be flammable,

2) If no protective coating is applied to the surface, it should undergo corrosion in the form of white clusters or dots in a corrosive environment,

3) The oxide-carbonate film in informed on the surfaces of alloys does not provide adequate corrosion protection even in non-corrosive environments. When the appropriate protective coating is applied, corrosion can be reduced considerably.

The use of lightweight parts serves to reduce fuel consumption. Due to the increase in speed and power requirements, it's also obvious that the use of more durable materials is also necessary. It is actively used in air vehicles for parts not loaded on Mg alloys (hydraulic deposits, fuel deposits, etc.). The quadrant, the tail, gives the movement and does not load on it. Hydraulic tank and quadrant AZ91 casting. The tank feeds the hydraulic system; there are 1-3 units by air according to the models. Dipolar tanks are used to store and prepare the hydraulic fluid in accordance with the working conditions. The heated hydraulic fluid must be able to cool down easily. These properties make AZ91 alloy very good. AZ31, AZM and AZ61 forging alloys are widely used in many helicopter gearboxes such as MD500, Eurocopter EC120, NH90 and Sikorsky S92, and ZE41 alloys for satellite parts. The B-36 bomber aircraft weighs a total of 8.6 tons and is made up of about 3.4 tons of Mg alloys. If Al was used instead of Mg, a weight of 4.5 tons would have formed. In addition to these, about 115 kg ZW3 alloy was used in S55 helicopter.

New alloying studies increase the known parameters of Mg and thus the number of magnesium alloys that can be used today in air tools. Another advantage is the reduction of noise and vibration. Wendt et al. compared to AZ91D, they obtained new alloys with better strength properties. Although weight reduction is a fundamental issue, Mg alloys do not have a wide range of applications due to the poor resistance to corrosion. Alloys to be used in the space industry must meet the high-performance requirements associated with both mechanical properties and corrosion resistance. Despite the fact that there are currently 20 standards Mg casting alloys, the abundance of these alloys that meet the requirements of the modern aviation industry is a major obstacle [4, 18].

2.3.2. Magnesium in the Automotive Sector

As for the auto industry, one can notice more and more vehicle parts are being made of magnesium alloys. The application of magnesium alloys in automotive design enables weight reduction of the entire vehicle, and thus reduced fuel consumption. The following parts are made of magnesium alloys in the automotive sector: engine and body components, cylinder head covers, seat frames and roof openings, pedals and steering wheels, as in Figure 2.7. Automobile manufacturers have also begun to produce magnesium alloy parts due to their superior and favorable properties. The BMW Company has produced an AZ91 alloy motor block and has begun commercial use. In the motive of the R6, the crankcase is made of aluminum alloy magnesium with cam lid and provides 10 kg lighter than the comparative motor. An example of the use of magnesium in the automotive industry is given in Figure 2.8. Volkswagen has a variety of processes that different automobile parts use for manufacturing. Firman's vehicles are intended to use parts manufactured using various methods such as hot metal forming and thixocasting. The use of such alloys is generally divided into three compartments. The primary short-term is to upgrade the available technologies of magnesium alloys and casting. The development of special casting techniques such as medium term, semi-solid casting and extrusion. The long term is the development phase of forging alloys, which can be called new alloys and new manufacturing techniques [5, 21].
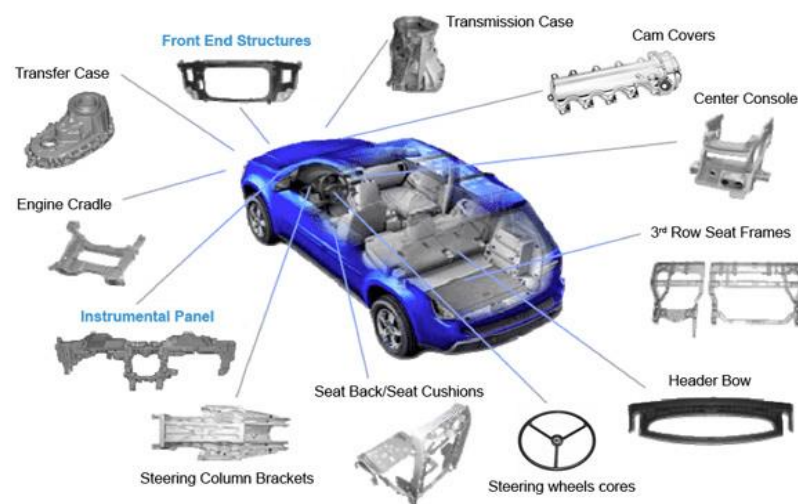
Figure 2.7. Examples of applications for magnesium alloys in the automotive industry [21].

Automotive parts die casting market, By Raw material type
Mordor Intelligence Analysis
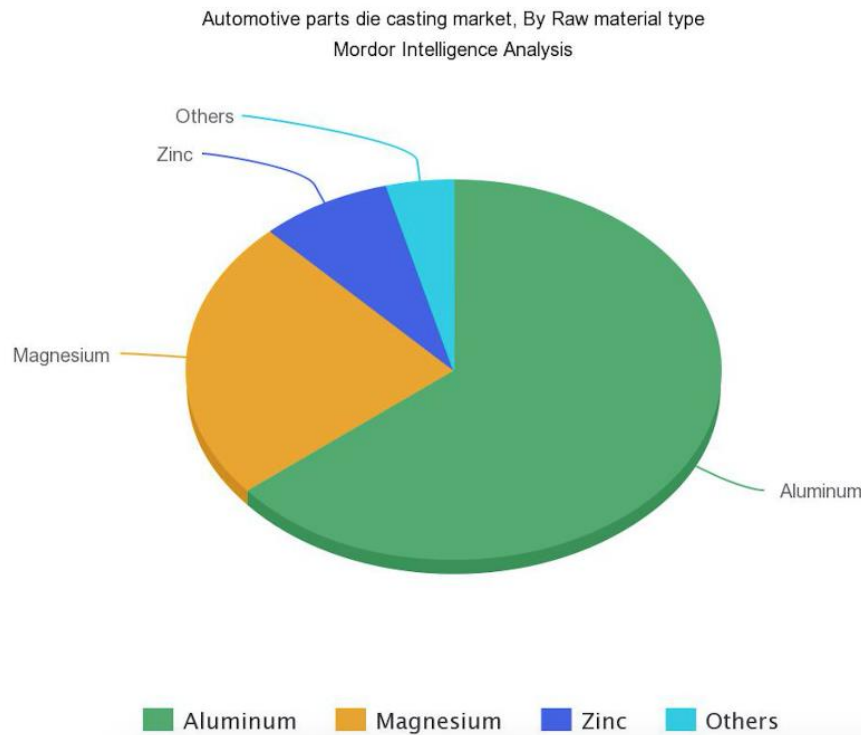
Figure 2.8. Mordor intelligence analysis of automotive parts die casting market, by raw material type.

2.3.3. Magnesium in Defense Industry

In machining, only low ductility Mg is suitable for machining, but it is dangerous due to its easy flammability. With these properties, magnesium also has important and critical usage areas in the defense industry. It is used for firearms in ammunition with large destructive power, radar equipment, portable ground equipment and Stingray torpedoes. The rod-shaped extruded magnesium is used as anti-tank ammunition. The standard 120 mm or 100 mm firing ignition also incorporates magnesium as an aid for ammunition. For this purpose, AZ80, AZ61 and AZM alloy powders are used. In addition, Mg emits white light and intense heat when it is lit. First, atomized dust is used as a firearm and army equipment material, especially for danger marking and lighting purposes. Mg-based devices are used to defeat military helicopters and aircraft in order to mislead the target. An example of the use of magnesium in the defense industry is given in Figure 2.3. It is also benefited from these illuminations when visualizing the scene during parachute jumps [5].

2.3.4. Applications for Magnesium Die Castings

Magnesium alloys are used in several different industries by die casting to produce many parts that are important to human life. The parts which can be produced by magnesium die casting are: (cell phones, covers tools, housings, portable saws, transmission casing, drills, engine blocks, grinders cameras, structural castings for power train components, bicycle parts, interior trim parts, lawn mower, luggage, computers, equipment housings, cases brackets, wheels, bakery racks, steering wheel, chain saw body). The following Figure 2.9 illustrates these products mentioned above.

Figure 2.9. Applications for magnesium die castings.

The added quantities for a particular alloy may vary for the purpose of reaching the desired application. Much work has been done in the development of magnesium alloys and new compositions are constantly being developed to fill the basic knowledge deficit of magnesium alloys [19]. Recent developments have included the

19

introduction of magnesium alloys. These alloys can join the list of commonly used magnesium alloys, as shown in Table 2.3 [20].

Table 2.3. The list of commonly used magnesium alloys [20].

Name	Composition (Balance Mg.wt%)	Example Uses
AZ31	3 %Al – 1 %Zn – 0.20 %Mn	Aircraft fuselage, Cell phones Laptops
AZ91	9 %Al- 0.70 %Zn- 0.13% Mn	Valves, door mirror brackets, die casting, cam covers
AM50	5%Al – 0.13 % Mn trace Si	Steering wheel arm, seats
AM60	6% Al – 0.13 % Mn	Car seat frames, steering wheel, inlet manifolds
ZE41	4% Zn – 1% Nd	Ballistics, aircraft parts
QE22	2%Ag – 2% Nd	Aerospace
ZK60	6%Zn - <1% Zr	Military components, tent, poles, sports equipment
WE43	4.3%Y – 3% RE – 0.4%Zr	Helicopter transmission, race car

2.4. CORROSION OF MAGNESIUM AND MAGNESIUM ALLOYS

One of the major problems associated with the magnesium component and its alloys is the problem of corrosion. This is because the metal is the most active and active because of several factors, including the low level of potential electrode. It will readily form galvanic corrosion system with another metal and even a micro-galvanic corrosion system with some secondary phases (such as α-phase and/or β-phase) and impurity grains in an aqueous environment. Consider the density and potential increase in the potential of small galvanic corrosion systems, which is particularly important. Especially, the different from most other metals such as Fe and Cu, magnesium and its alloys exhibit the negative difference effect [21]. Magnesium dissolution in the aquatic environment is usually done by electrochemically. This occurs through chemical reactions that are accompanied by magnesium hydroxide and hydrogen formed a mechanism that is highly insensitive to the oxygen concentration [22].

$$Mg(s) + 2H_2O(aq) \rightarrow Mg(OH)_{2(s)} + H_{2\,(g)} \qquad\qquad (2.1)$$

The protection is extremely dependent on their environmental conditions and magnesium generally turns into the opposite of other general metals such as aluminum, which has a resistant tendency to alkalis but not to acids, although aluminum can be attacked by strong alkalis but not by weak acids.

Magnesium materials go through both general and localized corrosion in general. The characteristic of magnesium electronegative potential makes its alloys very vulnerable to its galvanic corrosion. The galvanic corrosion can be internal corrosion due to micro-structural components that has less active potential.

2.4.1. Corrosion Mechanism for Magnesium Alloys

Corrosion resistance of magnesium and its alloys in aqueous solutions is generally rather low [21, 23]. Thereby reducing its use in engineering applications, However, it is considered degradable and this is an important aspect [24].

Magnesium corrosion in water solutions begin according to the following reactions (2.1-2.4) shown below resulting in the formation of gaseous hydrogen and magnesium hydroxide which are the primary electrochemical reactions on magnesium surface [21, 23] $C^{-2}O_2$

$$Mg(s) + 2H_2O(aq) \rightarrow Mg(OH)_{2(s)} + H_{2\,(g)} \text{ (overall reaction)} \qquad (2.1)$$

$$Mg \rightarrow Mg^{2+} + 2e^- \qquad\qquad \text{(anodic reaction)} \qquad\qquad (2.2)$$

$$2\,H_2O + 2e^- \rightarrow H_{2(g)} + 2OH^- \text{ (cathodic reaction)} \qquad\qquad (2.3)$$

$$Mg^{2+} + 2(OH)^- \rightarrow Mg(OH)_2 \text{ (product formation)} \qquad\qquad (2.4)$$
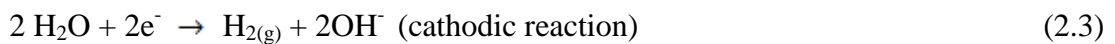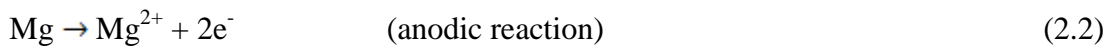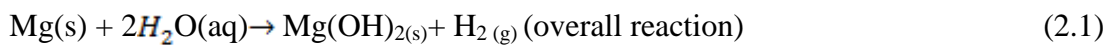
The corrosion rate of magnesium in aqueous solutions depends on the pH. As magnesium dissolves below the pH value of about 11.5, it forms a negative $Mg(OH)_2$

film at the highest pH values, as shown in the (Figure 2.10) dependence is based on pH [29].
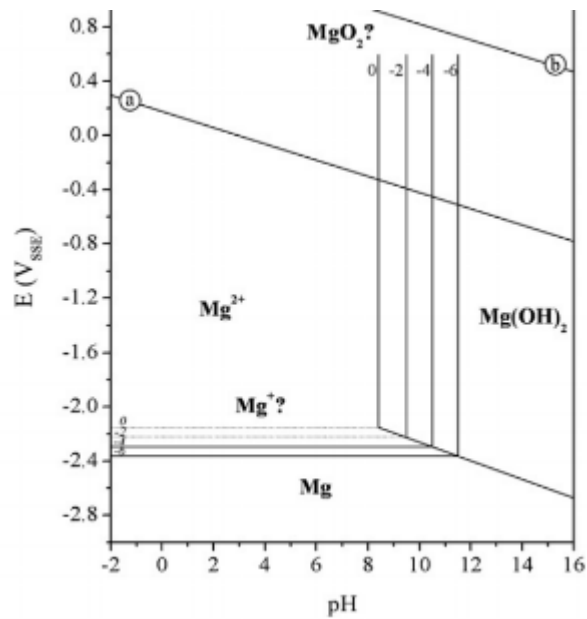
Figure 2.10. Pourbaix-diagram magnesium showing the range of corrosion [29].

Magnesium has a very low standard electrode potential; with the value of -2.37 V with respect to the potential of the hydrogen electrode taken zero and 25°C so it is less noble than most metals and makes the anodic mg matrix. This results in a high-molecular magnesium and its corrosive galvanic corrosion, which is dangerous to magnesium technology [23].

2.4.2. The Types of Magnesium Corrosion

Due to the effects of air pollutants and the presence of salts, magnesium and its alloys have various types of corrosion.

2.4.2.1. Galvanic Corrosion (Contact Corrosion)

When two different metals or alloys that have different corrosion potential are met in a corrosive environment, one of them is mostly corroded as other metals are protected from corrosion. Galvanic corrosion is also known as contact corrosion.

There are four basic conditions for active galvanic corrosion:

A cathode (a dissimilar metal), an anode (the magnesium), an electrolyte and direct electrical contact.

Between the cathode and anode [1-5], magnesium alloys will lose as the sacrificial anode and wear away in such active environments. The schematic representation of these corrosion mechanisms, which can be separated externally or internally, is shown in Figure 2.11 [25].
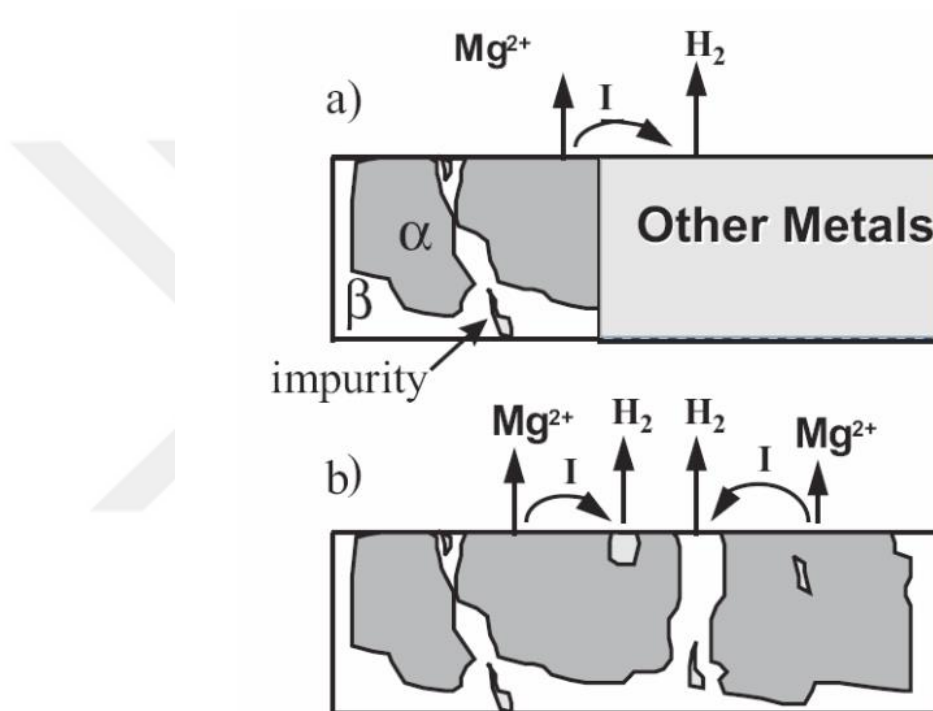
Figure 2.11. Galvanic corrosion mechanism of magnesium and its alloys [25].

Galvanic internal corrosion is an important issue to consider, and structural properties may bring galvanic corrosion. In pure magnesium, elements of iron impurity, Ni or copper act a large role; they have a detrimental effect on the corrosion performance of magnesium even when they are present in small amounts only [26]. Since these elements have a low level of solubility in Mg and hydrogen overvoltage, micro-galvanic cells can be formed which leads to internal galvanic corrosion. Therefore high-purity material should be used during the melting process to stay below the impurity tolerance limit for Mg alloys.

There are two ways to protect magnesium and their alloys from galvanic corrosion.

1. Reduce the chemical potential difference between magnesium and magnesium alloys and asymmetric substances.

In order to minimize the potential differences, some metals exhibit significant cathodic polarization in their coupling with magnesium and its alloys in salt water environments. Tin, cadmium and zinc also polarize and show good compatibility as well as aluminum [22]. These metals are commonly used coatings on steel fasteners to minimize the galvanic corrosion. Otherwise, magnesium and its alloys will be corroded if the steel fasteners were used in an uncoated state. However, for maximizing the resistance in the galvanic circuit, the options are relatively few.

2. Maximize circuit resistance.

The rate of galvanic corrosion is basically determined by the galvanic current I_c and its distribution.

2.4.2.2. Intergranular Corrosion

Magnesium and its alloys are almost resistant to internal attack between their crystals (intercrystalline attack). Corrosion does not penetrate inwards along the grain boundaries because the grain-boundary phases are invariably cathodic to the grain interior. Corrosion concentrates on the field adjacent to the grain boundary, and as a result, grain might be cut and fallen.

2.4.2.3. Localized Corrosion

Magnesium is a passive metal for pitting corrosion due to free corrosion potential. However, if the oxides are exposed to chlorine in a closed environment, they may form a structure similar to the pitting corrosion. The presence of heavy metals is a factor that increases the overall pitting effect.

Magnesium alloys show no gap corrosion mechanism because magnesium is sensitive to oxygen concentration differences.

For worm corrosion, it leads to an active cell that is constantly displaced on the metal surface. Due to this cell, called the anode at the head and the cathode at the tail, the corrosion mechanism occurs under the coatings or in the anodized layers. Uncoated pure magnesium does not suffer this kind of corrosion.

2.4.2.4. Stress Corrosion Cracking (SCC)

Stress corrosion cracking in magnesium alloys is usually intergranular. It can also be seen as an intragranular fracture in Mg - Al - Zn alloys. The presence of MgH_2 may trigger hydrogen brittleness. This corrosion mechanism rarely occurs in cast alloys exposed to a maximum of 0.2% displacement stress.

Al and Zn alloys are the factors that cause stress corrosion cracking. Zirconium-doped alloys almost eliminate this fracture. Breaking does not occur until near the flow limit [22]. pure magnesium, its impervious to stress corrosion cracking in atmospheric and aqueous environments [18]. For magnesium alloys, there are two kinds of mechanisms of stress corrosion cracking. The first one is discontinuous crack propagation at the crack tip under the effect of mechanical fractures and the second one is continuous crack propagation at the crack tip under the effect of anodic dissolution.

2.4.2.5. Corrosion Fatigue

There are a number of research on corrosion fatigue of Mg alloys. Speidel et al. [35] found that corrosion fatigue cracks propagate in a mixed intergranular and trans granular mode that the corrosion fatigue cracks growth rate were accelerated by the same environments that accelerate stress corrosion crack growth. Stephens et al. [36] found that the corrosion fatigue resistance of AZ91-T6 was significantly reduced in 3.5 wt.% salt water relative to that in air.

2.4.2.6. Corrosion at High Temperatures

Oxygen at high temperatures brings about a unprotective oxide layer on the magnesium surface within a linear time required for the oxidation of magnesium (Figure 2.12). It also increases in proportion to the increasing heat. The presence of Al and Zn alloys is an element that accelerates oxidation. Small amounts of cerium, lanthanum added alloys were found to have lower oxidation values than pure magnesium [22].
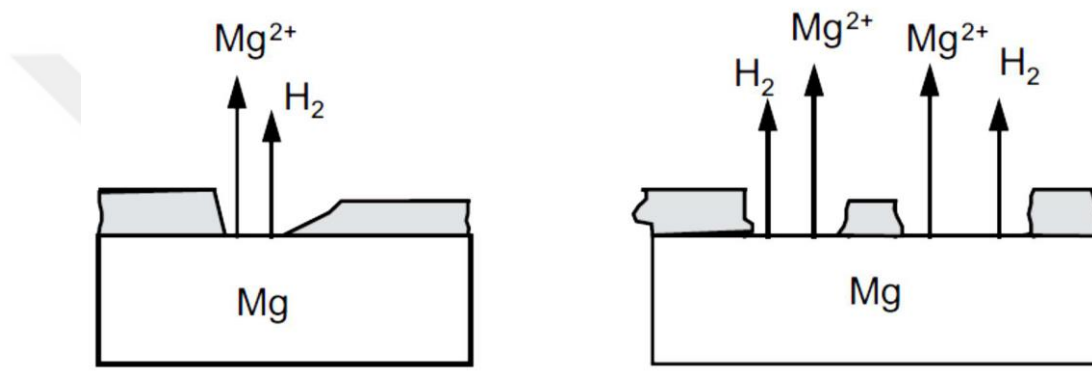
Figure 2.12. Semi passive surface film model on magnesium surface.

2.5. THE CORROSION PERFORMANCE OF MAGNESIUM ALLOYS

The corrosion performance of magnesium alloys broadly depends on the alloying elements and impurity elements. With suitable metallurgical manipulation, the corrosion resistance can be improved [24]. In general, alloying elements useful for corrosion resistance should be added and impure elements which are detrimental to corrosion resistance should also be removed.

The corrosion of Mg alloys can be studied using a variety of techniques such as mass loss, hydrogen collection, and various electrochemical techniques including electro chemical impedance spectroscopy, all of which should provide corrosion rates in agreement with one another. Mg alloys are susceptible to galvanic corrosion when coupled to a second material which is more noble in the galvanic series of material as well as micro galvanic corrosion within the alloy itself.

26

2.5.1. Impurity Elements

Some tests which performed with 14 elements alloyed with pure magnesium and measured the corrosion rate with immersion tests in 3 wt.% sodium chloride solution NaCl [27]. As shown in (Figure 2.13), they found that elements such as Fe, Ni, Cu and Co have the greatest effect of accelerating corrosion rate even at very low concentration. Ag, Ca and Zn have the lower effect of accelerating corrosion rate, while Al, Sn, Cd, Mn, Si, and Na have little or no effect on the concentration below 5%. Therefore, it is important to improve the purity of the alloy, as elements such as of Cu, Ni or Fe at 0.2% can increase corrosion rate by 100 times. The reason is that the solid solubility for these alloys is low and they become active cathodic sites. For each magnesium alloy, there are tolerance limits for Cu, Ni and Fe. Below these limits, there is little or no effect on the corrosion rate [7].
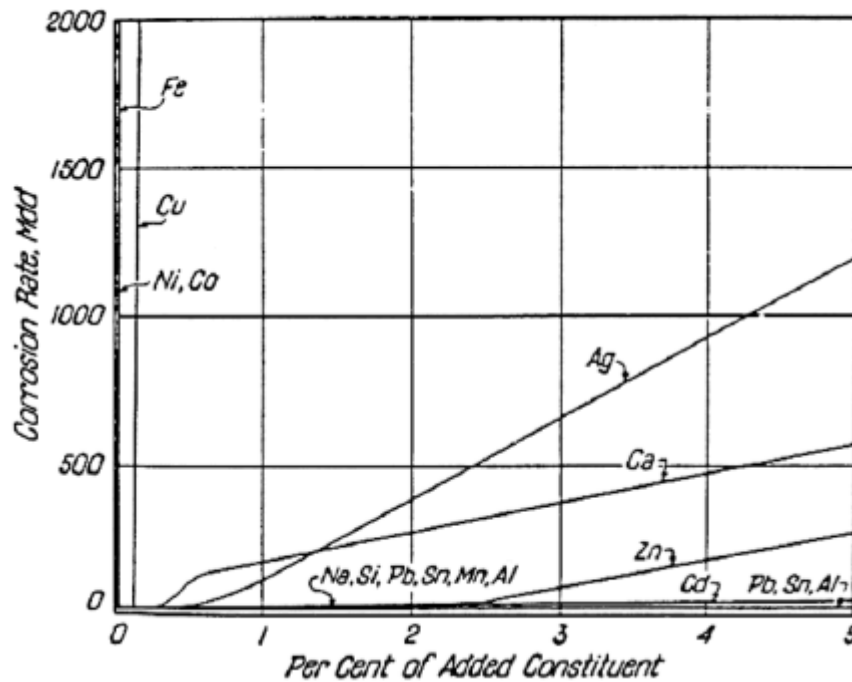
Figure 2.13. Elements affecting the magnesium corrosion rate [7].

2.5.2. Alloying Elements

Some elements are added intentionally such as zirconium, zinc, aluminum, yttrium and silicon are beneficial to corrosion resistance and considered to be alloying

elements. Commonly manganese is added to most the commercial magnesium alloys. Manganese has no direct effect to improve or reduce the corrosion resistance of magnesium alloys, but it can reduce the harmful effects of impurities when their concentration exceeds the permissible limits [28]. For example, loose found that when magnesium alloy contains Cu and Fe impurities with a concentration above their tolerance limit, adding 1% of Mn would definitely reduce the corrosion rate [29].

2.5.3. Effects of Alloying Elements on Properties of Magnesium Alloys

Casting products are obtained by adding alloy elements to enhance the properties of Mg. Mg has a hexagonal lattice structure, and its particle diameter permits solid solubility with a large number of elements. The main principle in alloying is to provide certain improvements in the strength properties of the material. When Mg is used as a structural material, elements like Mn, Al, Th, Ce, Zn, Zr are added by alloying. Alloys usually have a high strength / weight ratio when alloying with one or more of these elements. The most commonly used alloy element in Mg alloys is Al. These alloying elements alter the microstructure of magnesium, and therefore its mechanical properties. Solid solution hardening and precipitation hardening are the most important mechanisms in order to increase the mechanical performance of magnesium based materials [30, 31]. The effect of different alloying elements used in commercial Mg alloys is briefly explained.

2.5.3.1. Aluminum (Al)

In Mg alloys, Al improves the solid precipitation strength, the melt castability of Mg and reduces the micropores of cast alloys. Al additives increase the hardness, stiffness and solidification time of the alloy, but reduce ductility. Mg17Al12 intermetallics formed by solid solution hardening and precipitation hardening are formed at low temperatures (≤ 120 ºC) to improve the strength of the alloy. However, alloys containing too much Al tend to be micropores [31].

2.5.3.2. Lithium (Li)

The metal has a relatively high solid solubility in magnesium. (Atomically 17%, 5.5% by weight) Low density reduces the density of magnesium caused by other alloying elements. Fall in resilience; causing an increase in ductility [8].

2.5.3.3. Lead (Pb)

Since the Pb added to the alloy has a good solubility, Pb dissolves up to 40% at elevated temperatures (about 460 ºC) and does not emerge as a separate phase. The $Mg_2Pb + \alpha$ phase is formed as the alloy temperature decreases. Since Pb is an element with a good solubility, the $Mg_{17}Al_{12}$ intermetallic phase is reduced [32].

2.5.3.4. Zinc (Zn)

Zn decreases the solidification temperature of the alloy by increasing the amount of eutectic in the grain boundary. Zn is added to eliminate the adverse effect of Cu on corrosion properties. Zn is limited to 2% due to precipitation hardening, resistance to ambient temperatures, and at the same time increasing the flow of the melt, due to precipitation into grain boundaries and hot rupture. When the material is deformed at temperatures near the melting temperature of the segregated region, it differs along grain boundaries [33]. Figure 2.14 shows the Mg-Zn balance diagram.
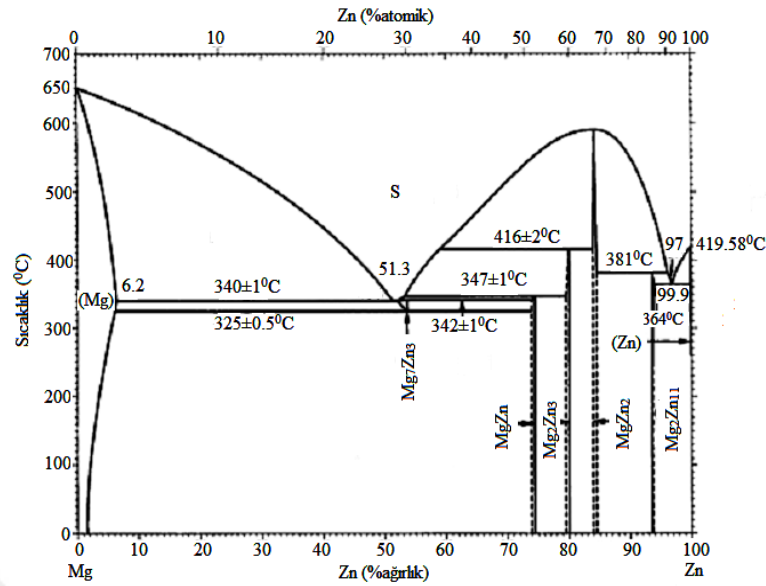
Figure 2.14. Mg-Zn balance diagram [5].

2.5.3.5. Manganese (Mn)

Melt added Mn is used to increase corrosion resistance. In the Mg alloys of Mn, the effect of corrosion resistance is high. In Fe-Mn precipitates, Mn is used to control Fe. Mn improves the creep resistance of Mg alloys and inhibits corrosion as it reduces the effect of Fe. However, the effect of Mn on the strength of Mg alloys is small [31]. According to the Mg-Mn equilibrium diagram Mn can form solid solution depending on the temperature up to 3.4% in Mg.

2.5.3.6. Strontium (Sr)

Strontium (Sr) has an effect on the dispersion of micropores and reduces the porosity tendency of Mg alloys. Creep increases resistance. The effect of corrosion of Sr alloys on Mg alloys is very small [31].

2.5.3.7. Nickel (Ni)

It has a limited solubility in magnesium. It improves in yield and tensile strength, it causes decrease in ductility. Even a very low amount of incorporation adversely affects corrosion properties [29].

2.5.3.8. Copper (Cu)

It has a limited solubility within the magnesium. Copper reacts with magnesium to form Mg_2Cu intermetallic compound. Copper also increases strength both at ambient temperature and at high temperatures. It affects the ductility and corrosion properties badly [29].

2.6. CASTING METHODS OF MAGNESIUM ALLOYS

Magnesium alloys are usually produced by various casting processes. The main problem in the casting of Mg alloys is the loss of oxidation and burning. Contraction of Mg from liquid to solid is 3.9% to 4.2% and from liquid at melting temperature to a solid at room temperature is 9.7% [30, 31]. Considering that a high percentage of Mg-based parts used in aerospace are produced by casting, the solution of casting problems in part production is one of the main priorities [34].

Magnesium casting alloys are generally melted in an extruded carbon steel (<0.10% C) from the outside. Steel is widely used because the magnesium reacts very slowly with steel at normal casting temperatures (magnesium is molten at 650°C). A common application for the molten magnesium process is melting and spilling the metal at the same time. Because the matrix iron is less soluble in the liquid magnesium alloy, the tendency of the alloy to stick to the die is less than in aluminum alloys. Accordingly, the die life is 2-3 times longer than aluminum parts. However, molten magnesium and its alloys tend to oxidize and burn in the air, and therefore, their melted magnesium surfaces must be protected from oxidation by air. Today, most modern foundries use an unsealed process of air-sulfur hexafluoride gas mixture (SF6) [34]. Mg casting techniques are grouped into 4 groups:

1. Sand mold casting.
2. Die casting mold.
3. Pressure casting.
4. Semi-solid casting.

The selection of one of the casting processes is based on the size, the required tolerance and the amount of production, similar to other casting materials. In recent years, the use of pressure die casting alloys has increased rapidly [34] .

2.6.1. Sand Casting

Sand casting is the most common casting method. Almost all alloys can be cast. Metal with high melting temperature can cast. The molding can be made up to tons of grade GR. Production speed is generally low. Suitable series for production, sand mold casting is a conventional casting method. In this method, sand will get air from them and measures against the danger of burning Mg should be taken. The mold cavity must be protected by protective gas. The best-known sand casting method in Mg alloys is shell molding. As this layer forms a layer of resin between the sand, the risk of burning Mg in the mold will be reduced. The casting mold template appears in Figure 2.15.

Although Mg-Al and Mg-Al-Zn alloys are usually easy to cast, there are limitations in certain cases. Sand molds show micro-shrinkage when poured and are not suitable for applications at temperatures above 95 °C [35] .
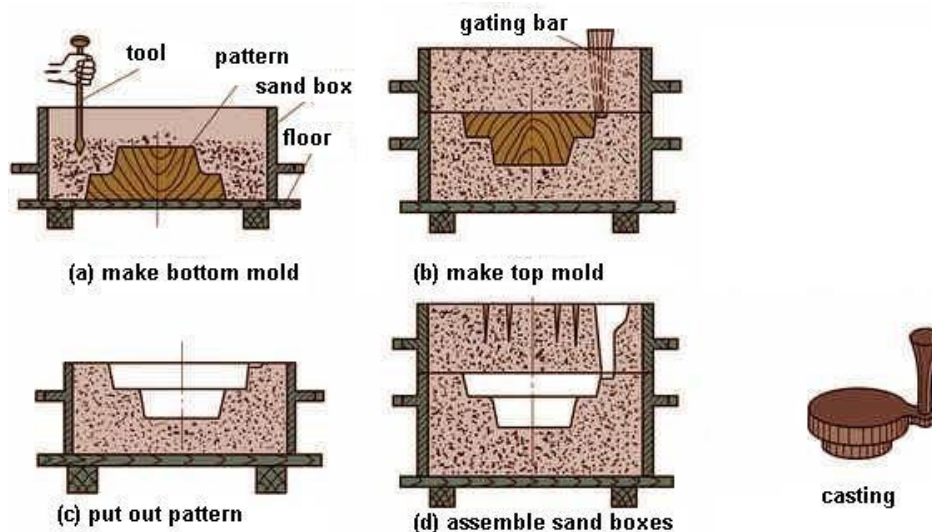
Figure 2.15. Graphical presentation of sand casting method.

2.6.2. Die Casting Mold

Core mold casting is a metal die casting technology consisting of two or more parts. Many parts of the same shape can be cast quickly. Liquid metal enters the cavity under the effect of gravity. Grease casting is especially suitable for high-density parts production. The superiority of casting molds when compared to sand casting; Due to dimensional tolerances and surface quality, more uniform cast parts are produced. With the duration of the casting process, the molten metal mold enters with a sharp turbulence and splash. In order to prevent the molten metal from falling for a long time, oblique casting machines are frequently used in production [34] . In the oblique casting process, the mold is placed in the mold with vertically oriented pieces.

Mg-Al-Zn type metals are alloys produced by the casting method. In this method, Mg alloys are poured much faster than Al alloys. Mold life is longer than aluminium alloys. Because Mg is more sticky on mold surface and less on Al. The Mg molds last two more times than the Al molds. When properly used and protected, the life of the mold can be further increased by protective coating methods. The different physical and chemical properties of the Mg alloy are compared to Al and different ladle materials are used. Molten Mg does not react with Fe as in molten Al, so Mg and its alloys can be melted and retained in Fe and steel pots [35] .

2.6.3. Pressure Casting

Mg alloys are usually produced by gravity or pressure casting. Pressure casting is the process of filling the molten metal into the metal mold at high speed by means of the hydraulic system. There are two main operations: pressure casting with cold chamber and hot chamber. Materials with low melting point are used in the hot-chamber process. During the transfer of liquid metal in the hydraulic system in the hot chamber process, turbulence in the molten metal leads to heat loss and oxidation. In this process, metal is injected into the mold to advance the process [31].

From the casting methods of Mg alloys, low-pressure casting technique provides the production of high quality clean alloy in the completely closed system. Figure 2.16 shows a schematic picture of a cold and hot chamber pressure casting system.
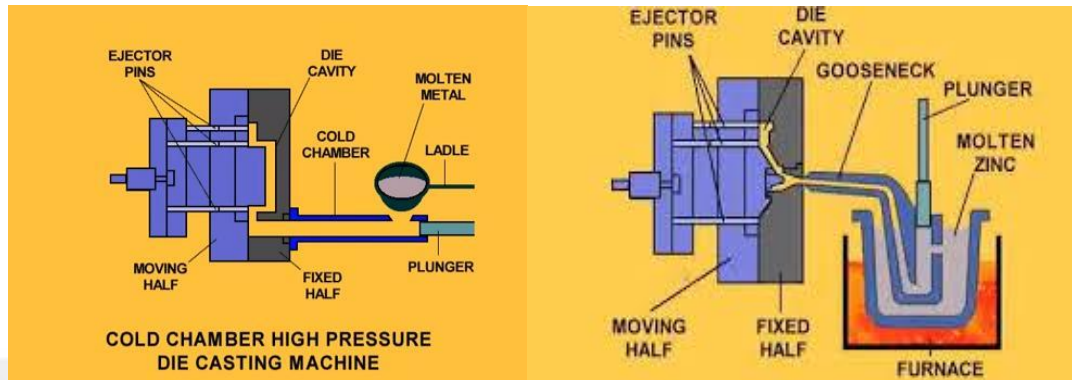
Figure 2.16. Cold and hot chamber pressure casting system.

2.6.4. Semi-Solid Casting Method

The use of Mg alloys is mainly dependent on casting technology and semi-rigid shaping. Automobile manufacturers are working on the suitability of semi-solid Mg alloys instead of steel and Al for the production of automotive steel sheets When the alloy is cooled from the liquid state and a stirring action is applied at a temperature between liquid-solid temperatures, the normal dendritic growth is stopped and coarse, spherical, and different dendrite particles are formed [36]. Figure 2.17 shows the semi-solid state casting.
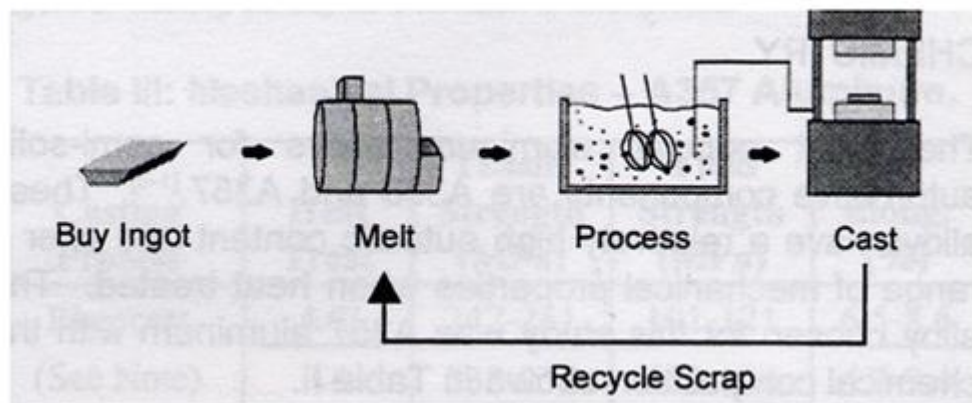
Figure 2.17. Semi-solid state casting process.

It is used in many applications of magnesium alloys. The main reasons for this are high production efficiency, high production volume, and low production costs. In spite of all these, production mistakes occur in the parts produced by this method.

The pores are formed in the casting parts of the mold which cannot be evacuated during the filling of the mold with the liquid metal. In addition, hot rupture occurs during solidification in the mold [10]. These faults not only weaken the mechanical properties of the material but also prevent the heat treatment applied to improve the mechanical properties of the alloy. Some advantages of this method are [37];

1. Reduction of the voids from the casting to the minimum in the produced part.
2. Produced parts show consistent mechanical properties (isotropic behavior).
3. Production of complex shaped parts.
4. Extension of mold life.

2.7. HEAT TREATMENT OF MAGNESIUM ALLOYS

In general terms, heat treatment is defined as controlled heating and cooling processes applied in a solid state in order to give desired properties to metals or alloys [38]. The purpose of heat treatment applied to magnesium alloys is to improve the mechanical properties or to regulate the micro structural and mechanical properties required in the production steps. The most common heat treatments applied to magnesium alloys are annealing, stress relieving, and aging. Most of the equilibrium diagrams corresponding to industrial ultra-light alloys contain a melt rich in magnesium, which depends on the temperature. In these alloys, therefore, it is possible to improve by quenching and internal structural precipitation. However, these heat treatments do not show the full effect here in aluminum-based light alloys and therefore are less generalized. Mg-Al and Mg-Al-Zn alloys can accept heat treatment within the following limits [14].

Mg-Al alloys: 7% <Al <12%
Mg-Al-Zn alloys: 7% <Al + Zn <13% and Al ≥ 5%

If the alloy is cooled in air after being heated for a long time at an elevated temperature sufficient to ensure that the crystals in the particular Mg4Al3 composition are fully solidified, the cooling rate is usually sufficient to maintain a substantially homogeneous saturated solid solution at room temperature that is practically stable. The alloy is called homogenized-stabilized state. The results of the homogenization process are a marked increase in R and A, an increase in fatigue limit, and a slight increase in hardness with elastic limit.

If the pre-homogenized-stabilized alloy is maintained at 150 ºC for a long period of time, the solid solution dissociates and the internal structure of the Mg4Al3 composition region, which is oversaturated, undergoes internal structural precipitation; " Alloy is tempered " It called. This complementary process further enhances the tensile strength, elastic limit and stiffness; the effect is particularly evident for these latter two characteristics; whereas the fatigue limit and the breaking extension fall, and even down to the bottom of the casting, even after casting. Homogenization-stabilization processes are mainly applied to bulk pieces, complementary pans are rarely used; Shaped products (hair, profiles, forged or pressed parts) are usually satisfied with a recrystallization and stress relieving effect [10].

The above mentioned heat treatments are reduced to three basic types. Melt heat treatment, precipitation or aging and annealing. In addition, stabilization-homogenization and stress relieving processes are applied. The first of these is a precipitation type and the latter is associated with tempering. The melt heat treatment consists of heating the alloy material to a temperature at which some components become molten and then dipping them to keep them in solution during cooling.

Mg alloys in many different compositions, like aluminum alloys, can be strengthened with hardening and aging. The ability of alloys to increase their strength depends on the extent to which their components (Al, Zn, Zr, etc.) exhibit heat to melt into magnesium. The heating leads to the melting of excess phases ($MgZn_2$, Al_3Mg_3, $Mg_3Al_2Zn_2$, etc.), after which a supersaturated solid solution is obtained. Then the phases of alloy strengthening are precipitated in aging. A special feature of the Mg

alloys is the slowness of the diffusion process, so that the phase transformations develop slowly. This requires long retention time for hardening (4 to 24 hours) and for artificial aging (16 to 24 hours). For this same reason, alloys can be hardened (submerged) by cooling in air (generally no liquid is used for immersion).

Many alloy castings are hardened in the air after hot working. The alloys can, therefore, be reinforced without pre-hardening them. Ingot and different cast parts are usually subjected to homogenization stabilization at 400-420 ºC for 15 to 30 hours to remove segregation of alloying elements[39]. In the homogenization of Mg alloys, the excess phases precipitated along the grain boundaries melt and the composition is equalized in the whole volume of the grain. This facilitates mechanical work and improves mechanical properties. The hardening that occurs without deformation (uncoiling) is removed by recrystallization annealing at about 350 ºC (the recrystallization temperature of the alloys is 250-280 ºC).

Casting alloys are aged at 200-300 ° C (T1). They are generally heated at 380-420 ºC (T4). Heating is carried out in an air atmosphere of 0.7 to 1.0% SO 2 to avoid oxidation. In order to obtain the maximum strength enhancement effect, the hardening is followed by artificial aging (T6) at 175-200 ºC [10, 39].

As noted above, the qualities of aging Mg alloys change less than they are in Al alloys. For this reason, the heat treatment usually only obtains homogeneous alloys which improve the mechanical properties of alloys by 20% to 35% strength. If the ductility of alloys is reduced by this process is reduced.

Natural aging does not change the internal structure and properties of Mg alloys. The T6 process improves high yield strength and hardness and is therefore recommended for highly loaded castings.

Stabilization is mainly used to prevent the bulk alloys from swelling during operation at high temperatures or to reduce the most. At the same time, it relieves stresses and increases creep strength. Swelling is essentially a volume change that occurs from the coalescence of precipitated components from the solid solution. The stabilization

process results in a negligible amount of swelling in the work, which takes place in large quantities before the casting section is put into service at high temperature [18]. Stabilization can be applied when the cast parts have been treated with F or T4. The process consists of heating to 260 ° C for 4 hours. There is little effect on the mechanical properties of this (hardening) process. However, when the melt is done after the heat treatment, it forms qualities at the T6 hardening level. In the case of casting (F), stabilization T5 hardening occurs in the parts and T7 hardening occurs in the T4 material.

Again as mentioned above, Mg alloys tend to aging very slowly at room temperature. T4 conditional alloys can be aged at room temperature. Thus, after aging AZ63-T4 for 5 years at 22 to 32 ºC, tensile strength increased by about 14%, yield strength increased by 68% and brinell hardness increased by 22%. Within the same time, the ductility decreased by 32% and the impact strength decreased by 57% [10, 39].

After aging AZ63-F at room temperature for five years, the yield limit increased by about 20% and the ductility decreased by 33%; there was no change in their other qualities. AZ92-T4 tends to age more at room temperature than AZ63-T4. All solid solution type cast alloys under F and T4 conditions are capable of aging at room temperature for years. This tendency, however, is not much more important than AZ92 and AZ63 types. All alloys lose their susceptibility to aging at room temperature when converted to T5, T6 or T7 conditions. Dipping may create internal stresses. Aging at moderate temperature to induce the T6 condition promotes dipping stresses. Parts formed from shaped AZ31, AZ61 and other high strength alloys at room temperature or slightly higher temperatures may store internal processing stresses. This, in some cases, may lead to stress corrosion cracking. To prevent this, they must be subjected to a stress relieving heat treatment.

For this purpose, a treatment at 150 ºC for 1 hour is effective. In parts formed at temperatures of 260 ºC and above, this treatment is not necessary, since these stresses are very low [10].

2.8. PREVIOUS STUDIES ABOUT CORROSION, HEAT TREATMENT AND PROPERTIES OF MAGNESIUM ALLOYS

Song et al. [40] observed that whenever Increased zinc concentration in Mg-Zn alloys the corrosion resistance decreased which have a direct relationship with the micro-cathodic effect of the Mg_x-Zn_y secondary phases.

Liu et al. [41] found that zinc element (Zn) enriches along grain boundaries of the alloys to exhibit a network microstructure for both solution treatment (T4) and aging treatment (T6)-treated alloy. For T6 treatment, large MgZn particles are formed on grain boundaries and fine MgZn particles are deposited on the matrix. And the corrosion resistance of Mg-3Zn alloy decreases. T4 treatment could reduce the amounts of MgZn particles and reduce the zinc content of zinc-rich net-segregation and increases the corrosion resistance compared with cast alloy.

Koç et al. [42] indicated that the in vitro corrosion resistance of Mg-Zn alloys was enhanced with the increasing zinc concentration which is caused by their common influence of both the distribution of zinc on the alloy surface resulting in better passive film formation.

Guo [43] interested on the following: (i) the alloys development; (ii) the design criteria materials of biodegradable; (iii) in vitro performances of currently developed Mg-based alloys and (iv) in vivo performances of currently developed Mg-based implants, especially Mg-based alloys under clinical trials.

Kulekci [34] studies have found that the massive use of magnesium and magnesium alloys is due to the improvement in properties and appropriate prices. The use of magnesium and its alloys led to a reduction in weight from 20% to 70% compared to other materials. Resulting in a significant increase in the use of magnesium in automotive components and as well as the knowledge of the forming processes of magnesium alloys increased.

Cai et al. [33] indicated that the microstructure of Mg–Zn alloys are consist of two phases the primary α-Mg matrix phase and Mg-Zn intermetallic phase which mainly distributed along the grain boundaries of the alloys. Where he observed that there was an improvement in the performance of magnesium alloys with increased magnesium content up to 5% of weight, and this corresponds with to fine grain strengthening and second phase strengthening. The polarization test showed that the zinc element had a beneficial effect by forming a positive layer on the surface of the alloys. It was found that an alloyMg-5Zn gave the best anti-corrosion property. further by increasing the content of zinc to 7 of weight gets deteriorate at the rate of corrosion by galvanic couple effect.

Liu, Shan [41] found that the thermal treatment of 380 °C has a simple effect on the corrosion behavior of Mg-3Zn alloys. On the other hand, heat treatment improves corrosion resistance of Mg-6Zn alloys as the decomposition of the Mg-Zn phase decreased micro-galvanic corrosion and the corrosion resistance of Mg-Zn alloys is improved by increasing the heat treatment time.

Zhan, et al. [44] found that the tensile strength of the Mg-Zn-In-Sn alloy higher than the tensile strength of the AZ91 alloy and the corrosion protection is better. This is due to the sedimentation process and its effect on alloys due to small grain sludge and high sedimentation between grain boundaries.

Song and Atrens [21] review the corrosion mechanisms of magnesium and its alloy, So as to give the base design and discovery of new alloys with improved properties and corrosion resistance of these alloys.

Yin et al., [45] the size of extruded magnesium alloy grains can be greatly improved by adding the zinc element. They found that the grain size reduced from 12 μm to 4 μm when zinc content is increased from 0% to 3% and mechanical properties are also improved with this increase in zinc intake. The yield strength (YS) and ultimate tensile strength (UTS) were increased by 54.7 MPa and 69.7 MPa, respectively, when the zinc content reached 3%. The corrosion resistance is variable with zinc content change.

It was found that when zinc content is 1%, the best resistance to corrosion of magnesium-zinc alloys is obtained and degradation of these is achieved when zinc content reaches up to 3%.

CHAPTER 3

EXPERIMENTAL STUDIES

3.1. MATERIAL PREPARATION

3.1.1. Melting and Casting

In the melting and casting of magnesium alloys, an atmospheric controlled electric resistance furnace capable of producing up to 1100 °C, as shown in Figure (3.1) is used. The melting furnace was made of steel material with outer diameter of 340 mm and the inside is covered with refractory brick with a diameter of 19 mm. Filling material is used for heat insulation between steel body and brick. The thermocouple is used to measure the inside temperature.
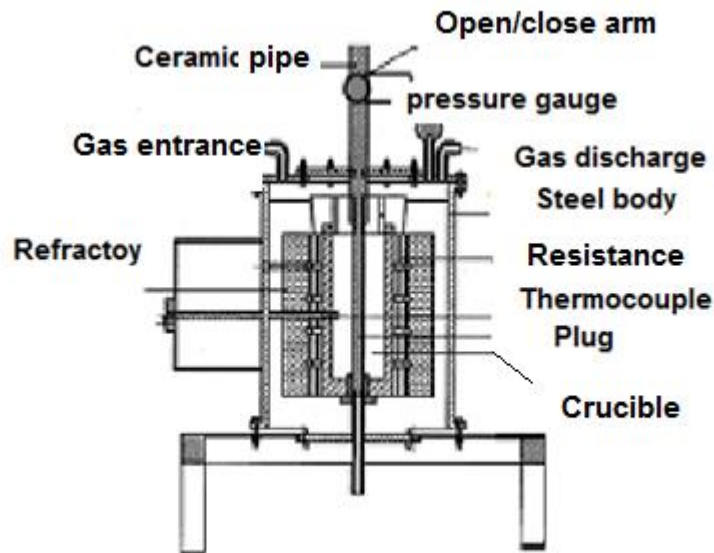

Figure 3.1. Shaped section of the atmospheric controlled melting furnace.

The addition of 99.9% pure Mg and Zinc element for the production of magnesium alloys was carried out with pre-alloy. The test specimens were poured from the pre-alloyed material after being melted a second time. Analyzes of the produced alloys

were made at X-Ray Fluorescence (XRF), Rigaku ZSX Primus II Model, in Karabuk University, Iron Steel Institute.

The melting of the alloys was carried out in a 2 kg capacity graphite crucible of Mg-Mg incorporated into the furnace. For cut off the atmosphere a protective gas Argon (Ar) was added to the furnace during the melting process. The bottom of the graphite crucible is made of a hole system with a diameter of approx. 15 mm, which can be controlled by the opening and closing arm and through which the liquid metal can flow.

The furnace and metal temperature were selected as 750 ºC considering the actual casting conditions. After the furnace reaches the desired temperature, it is allowed to stand for about 10 minutes to reach the casting temperature of the alloy. Zinc is added to the alloy one minute before casting to avoid evaporative zinc loss.

After reaching the casting temperature, the base of the melting crucible is opened by controlling the melting furnace opening and closing arm, and the flow of the molten liquid metal is ensured. Then liquid alloy is poured into a cast-iron mold which was heated 250 ºC having 20 mm diameter and 200 mm length under protective CO_2+ %0.8 SF_6 mixed gas. Schematic view and technical drawing of the metallic mold used is shown in Figure 3.2.
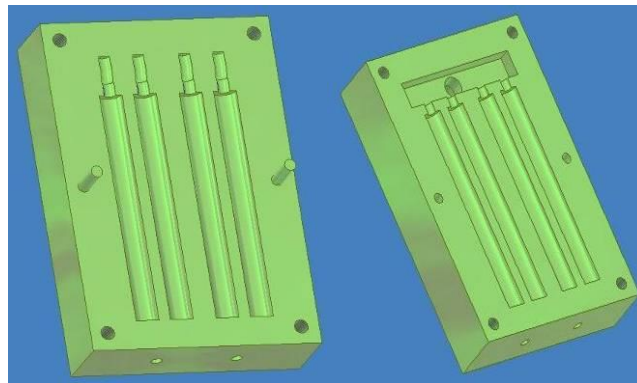

Figure 3.2. Metallic mold used for the experiments.

3.1.2. Samples Preparation

Mg alloys containing 0.5, 1, 2 and 3 wt. % zinc were used in this study. X-Ray Fluorescence (XRF) method were used for chemical analysis of the alloys given in Table 3.1.

Table 3.1. Chemical analyzes of the alloys used in the experiments.

Compound	Al	Zn	Mg
AZ005	0	0.5	Balance
AZ01	0	1.0	Balance
AZ02	0	2.0	Balance
AZ03	0	3.0	Balance

Where (AZ005) : A → Aluminum (0 → 0 Al) , Z → Zinc (0.5→0.5 Zn)

The AZ magnesium alloys were used in the experimental work are 17 mm in diameter and 2.26 cm^2 in surface area.

3.2. MICROSTRUCTURE ANALYSIS

In order to make metallographic investigations by cutting the cylindrical samples of 17mm diameter and 8mm high on the lathe bench, samples of 800, 1000 and 1200 mesh sandpaper are sanded using distilled water and polished with 1μm alumina solution using by polishing equipment, Struers Tegramin-30 model. The polished samples were also etched with 5ml acetic acid, 6gr picric, 10ml distilled water, 100 ml ethanol (Acetic picral). After etching, the samples were examined under optical microscope Nikon MA200 Model, with Clemex camera system, in Karabuk University, Iron Steel Institute.

Microstructure drawings of different alloys before and after heat treatment Images were taken. Zeiss Supra 40 V model SEM is used to examine microstructure, and EDX is used to determine how the secondary phase particles are distributed. Ultra

Plus (FESEM) scanning electron microscope (SEM) was used for microstructural analyzes of the samples as shown in Figure 3.3.

Figure 3.3. SEM device used for microstructure studies.

3.3. HEAT TREATMENT

3.3.1. Heat Treatment Furnace

A cabin type furnace was used for the heat treatment processes. The PLF series has been used for many years in the laboratory as a professional cabin oven reliably. The PLF series, which is produced using brick and fiber insulation elements with many different options, is the ideal choice for general heat treatment. Standard PLF series furnaces are designed to operate up to 1200 ºC. The PLF series furnaces are manufactured using double layer coatings for low external heat protection and high internal heat stabilization and are offered to the user with the front loading option for easy operation. One of the most important advantages of this model is that it is easy and economical to replace the heating elements. The image of the heat treatment furnace used is given in Figure 3.4.

Typical applications of furnaces manufactured for use at temperatures above 1200 °C are high temperature melting, thermal aging, ceramic sintering, metal heat treatment, chemical decomposition and thermal shock testing.

Figure 3.4. Heat treatment furnace.

3.3.2. Heat Treatment Process

For the homogenization heat treatment, the temperature of the furnace was chosen as 400 ºC. At this temperature, the material was left for 24 hours and then cooled in water. For the application of aging heat treatment, 2 different hours were selected at 200 ºC (8, 16 hours). After aging, the material was allowed to cool at room temperature. The experimental material used for this study was Mg-(0.5, 1, 2, 3 wt. % Zn) cast alloy. T4 treatment (solution treatment) was carried out on cast samples at 400 ˚C for 24 hours and then quenched into hot water at around 50-60 ºC. For aging treatment (T6), cast sample was treated at 200 ºC for 8 h and 16 h after T4 treatment and then cooled in room environment. The fluctuation of temperature was controlled within ±2 ºC as shown in Figure 3.5.

Figure 3.5. The samples image in the furnace quenched into hot water.

Samples after the heat treatment was completed, prepared. and subjected to metallographic sample preparation for microstructure, hardness and corrosion tests. Standard metallographic processes were performed for microstructural investigations. The prepared samples were polished with 0.5 μm and 1μm alumina paste. After polishing, the surface of the samples were cleaned with distilled water and ethanol and then dried in air. Metallographic and polished samples are acidic pikral. This is used to reveal the general microstructure of the alloying magnesium alloys. All samples were polished to 2000 grit with SiC paper, fine polished using 0.5 μm and 1μm alumina paste, ultrasonically cleaned in acetone, and dried in air.

Microstructure evolution and variation of Vickers hardness after aging treatment were investigated in this study. To determine the change in the hardness of the samples due to the heat treatment effect. Hardness measurements were performed using a Vickers Hardness tester (Model Shimadzu HMV2) with a steel ball indenter of 2.5 mm in diameter under the load of 5N and maintained for 10s. Hardness values were determined by taking averages of 5 different values. hardness test equipment is shown in Figure 3.6.

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Figure 3.6. Micro hardness tester for hardness measurements.

3.4. THE ELECTROCHEMICAL CORROSION TEST

3.4.1. Sample Preparation and Test Cell

The samples with a diameter of 17 mm, in other words, with a surface area of 2.26 cm^2 was exposed to electrolyte. A reagent grade NaCl (99.5%) and distilled water were used for prepearing. The surface of the samples which were not exposed to electrolyte coated with epoxy. The electrochemical corrosion tests were carried out on 12 samples of magnesium alloy, including 4 samples before the heat treatment process Mg-(0.5, 1, 2, 3wt.% Zn) and 8 samples after the heat treatment process which they have the same analyzes for 8 hours and 16 hours of heat treatment, respectively. Surface of the samples were ground using 600, 800, 1200, 2500 grit SiC paper, respectively and polished using 1μm alumina solution. The samples were also cleaned in distilled water for 5 minutes with ultrasonic cleaner, then rinsed with ethanol and finally dried before the test.

Electrochemical Corrosion test measurements were performed in a standard three-electrode glass cell with a graphite and saturated calomel reference electrode (SCE) in the corrosion laboratory in Karabuk University, Iron Steel Institute. Electrochemical corrosion test cell and sample holder are shown in Figure 3.7
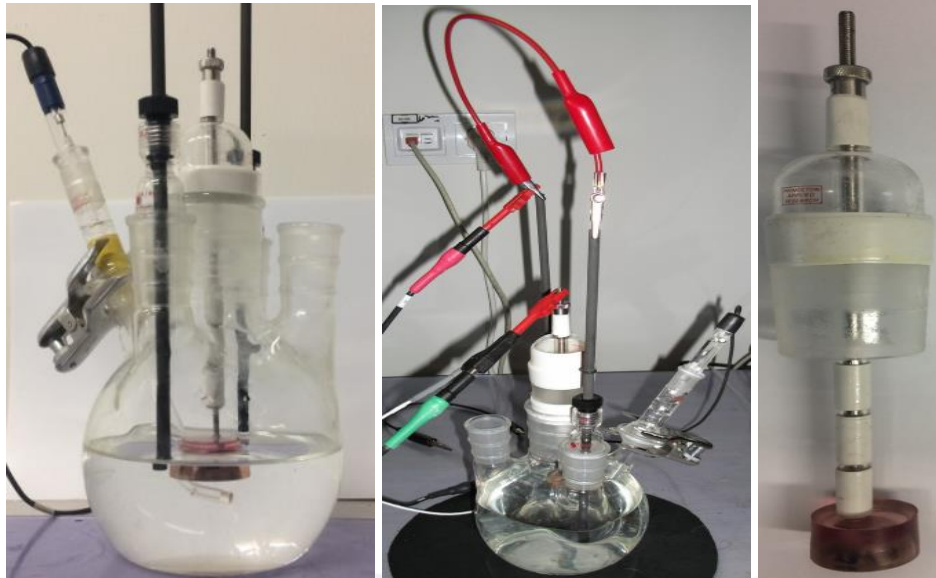
Figure 3.7. Electrochemical corrosion test cell and sample holder.

3.4.2. Experimental Procedure

Electrochemical measurements were performed using a computer-controlled Versa Studio Corrosion Analysis software PARSTAT 4000 model Potentiostat Galvanostat EIS Analyzer instruments in the corrosion laboratory in Karabuk University, Iron Steel Institute. Electrochemical tests were also performed in a standard three-electrode glass cell system consisting of a sample with a fixed surface area of 2.26 cm^2 sample as a working electrode, a saturated calomel as a reference electrode (SCE) and a graphite rod with a diameter of 6 mm as a counter electrode. The working electrode and the graphite electrode surfaces are located at a certain distance from each other, and the reference electrode is located as close as possible to the working electrode. The potentiostat and connection elements used in the tests are shown in Figure 3.8.
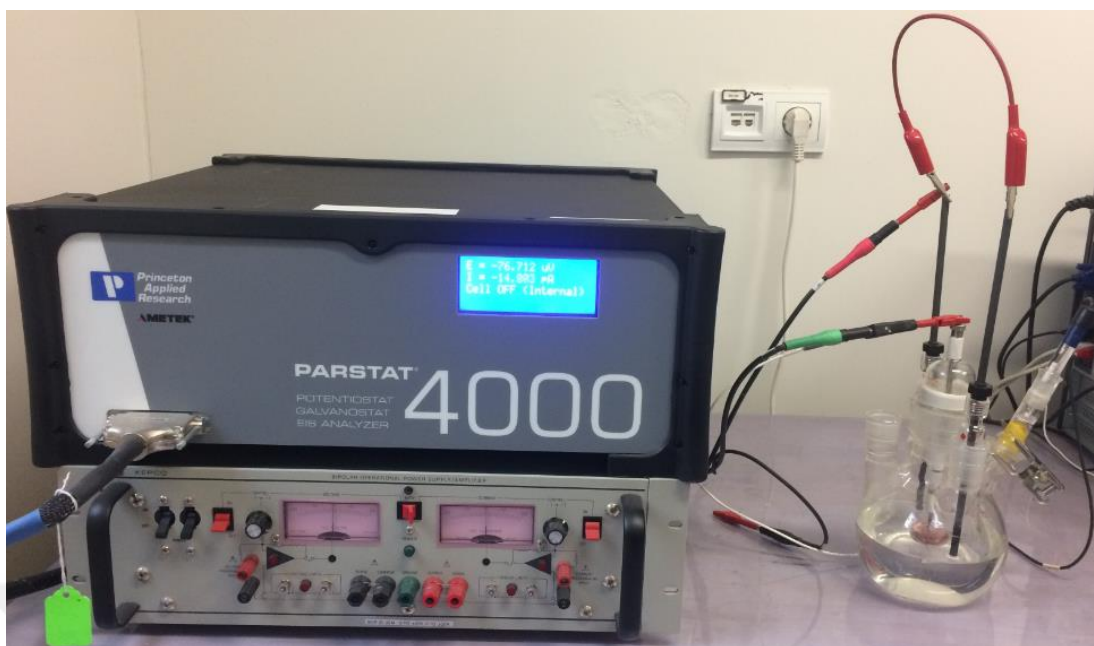
Figure 3.8. Potentiostat with connected test cell.

Experiments were performed at room temperature in a glass cell containing 3.5 wt.% NaCl solution. Each polarisation experiment was carried out holding the electrodes for 45 min at open circuit potential (OCP) to allow steady-state to be achieved. During the experiments the change in corrosion potentials between the working electrode and the reference electrode from the immersion of the reference electrode was measured against time in the first 45 minutes. Potentiodynamic polarization curves were generated by sweeping the potential from cathodic to anodic direction at a scan rate of 1 mV s^{-1}, starting from -0.50 V up to 0.50 V, versus OCP. Each data point for potentiodynamic polarisation tests represents at least average of 3 different measurements.

Corrosion potential (E_{corr}), corrosion current density (I_{corr}) and corrosion rate were calculated by extrapolation from Tafel curves (Figure 3.9) using DC corrosion software [46].

Corrosion rate $\qquad$ CR = 22.85 x I_{corr} $\qquad$ (3.1)

Where CR denotes the corrosion rate (mm / year), I_{corr}, the corrosion current density (mA / cm^2). Figure 3.9 shows E_{corr} extrapolation of the anodic and cathodic Tafel curves for determining the corrosion current density.
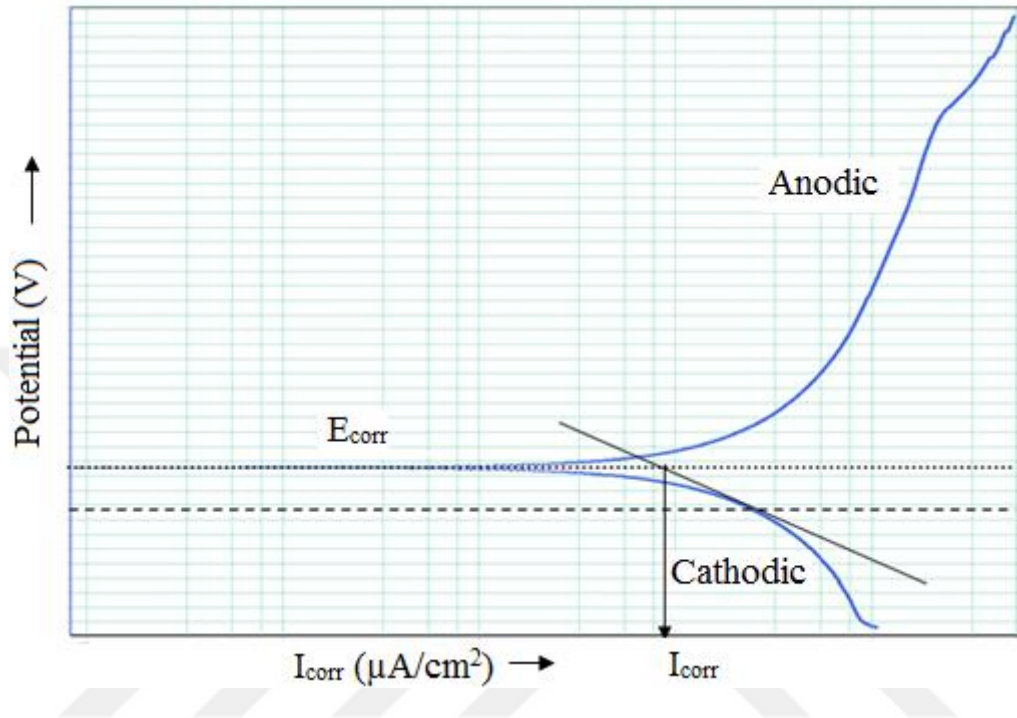

Figure 3.9. Determination of corrosion current density (I_{corr}).

CHAPTER 4

RESULTS AND DISCUSSION

4.1. MICROSTRUCTURES OF THE ALLOYS

The general microstructure of these specimens in this study can be seen in the following optical micrographs. Microstructure studies have shown that the grain boundaries are larger before heat treatment and grain structures are finer after heat treatment. Figure 4.1 (a), (b), (c) and (d) show the microstructure of the Mg-Zn alloys with different Zn concentrations before the heat treatment (as-cast alloys). The grain size of the alloys decreased with the increasing of zinc content, i.e., the grain size of AZ005 ranges from 500 to 700 µm, while zinc content was 3 wt.% (AZ03), the grain size was reduced to 100-200 µm. This refers to an increase in zinc amount determines the grain size of the alloys.
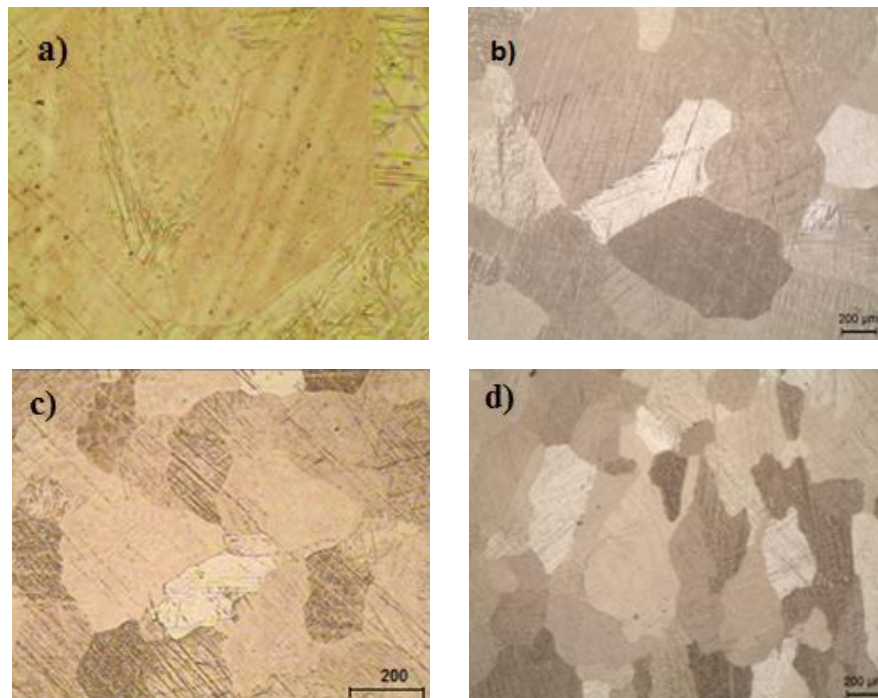

Figure 4.1. Optical microstructures of as-cast magnesium - zinc alloys: (a) AZ005, (b) AZ01, (c) AZ02 and (d) AZ03.

Figure 4.2 shows the SEM micrographs of as-cast AZ03 alloys consisted of the secondary phase particles and other precipitation phase which are rich in magnesium and zinc. MgZn particles looked like bright points. But the SEM micrographs of as-cast Mg-0.5Zn alloy did not appear well because of the small zinc concentration.
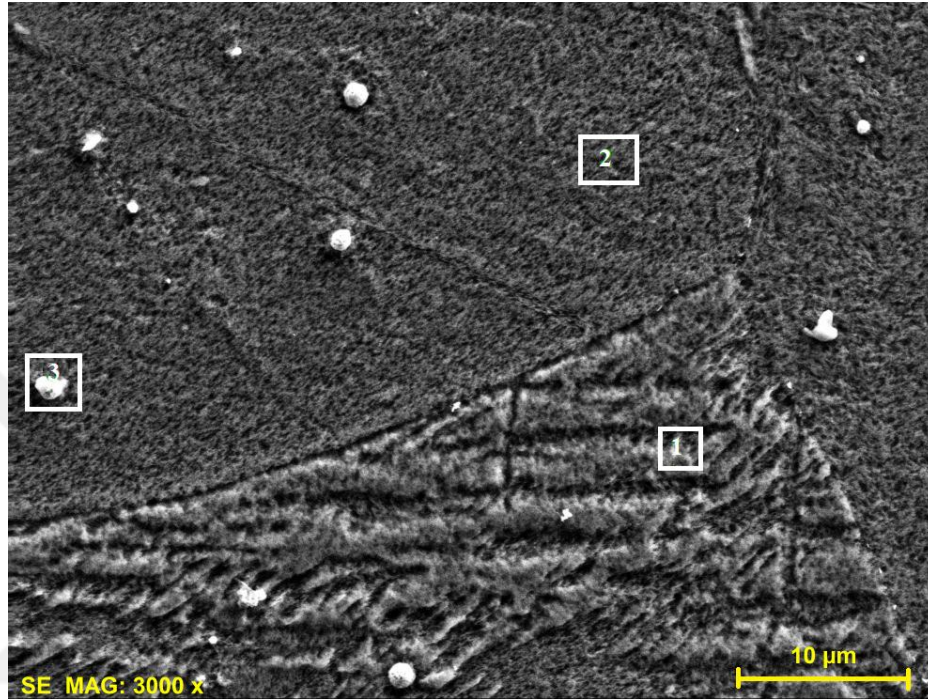
Spectrum	Mass Percent (%)	
	Mg	Zn
1	93.40	6.60
2	94.75	5.25
3	69.29	30.71

Figure 4.2. SEM micrographs and EDX analysis of the as-cast AZ03 alloy.

SEM image and EDS analysis in Fig. 4.2, it was observed that β-phase is formed as well as α-Mg matrix phase in AZ03 alloy containing 3wt.%. In the literature [42], EDS and XRD studies have been reported in which the β phase is the MgZn phase. The EDS analyzes in this study also support this argument.

Figure 4.3 shows the microstructure of the Mg-Zn alloys with different Zn concentrations subjected to heat treatments for 8 hours. The grain size increased and the quantity of Mg-Zn particles reduced after 8 hours treatment. It was found that the

distribution of zinc element in 8hours-treated alloy was more homogeneous than that in cast alloy.

In the literature, experiments show that as the amount of Zn element increases in Mg-Zn alloys, the grain size of Mg matrix decreases [47]. The grain reduction effect of a solid solution element can be determined by calculating the grain growth limiting factor (GRF) [33], the element Zn is 5.31 GRF, Al (4.32) and Y (1.70) have a higher GRF than the elements such as Al (4.32) and Y (1.70), indicating that Zn has a strong grain growth limiting effect, which means that the grain thinning effect is high. According to the Mg-Zn phase diagram (Fig.2.14), up to 2% by weight of the Zn element is completely soluble in the α-Mg matrix.
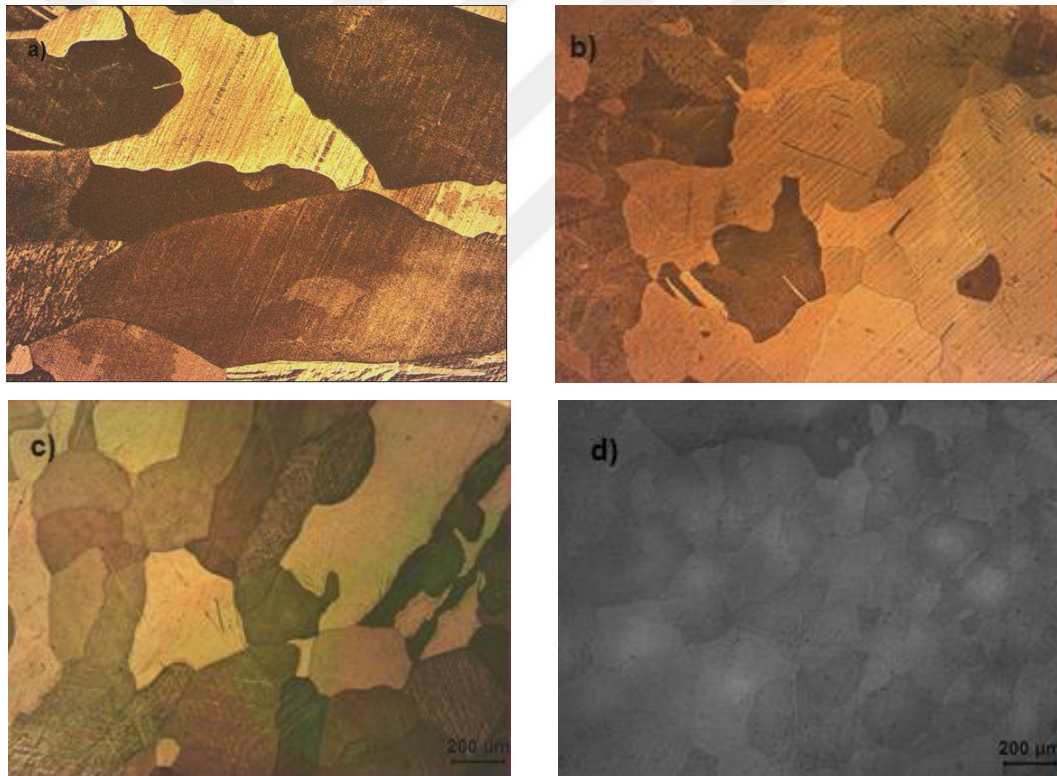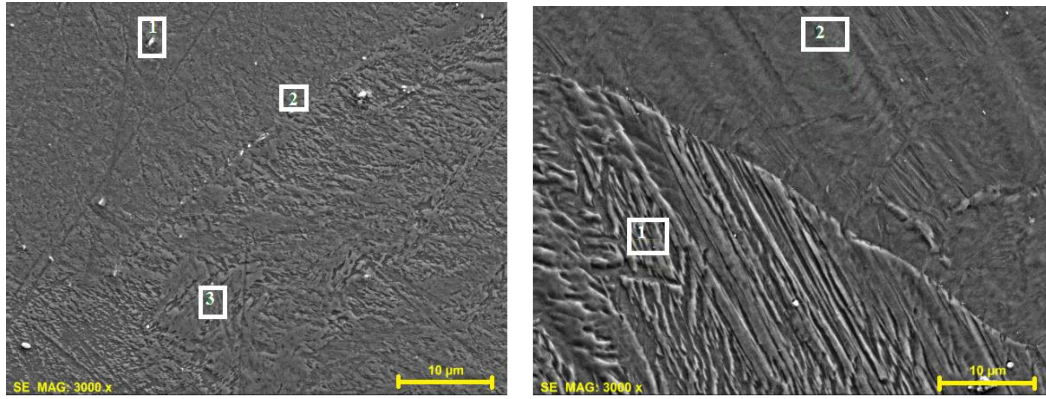

Figure 4.3. Optical microstructures of the 8 hours heat treated alloys a) AZ005, (b) AZ01, (c) AZ02 and (d) AZ03.

Figure 4.4 shows the EDX analysis of the AZ005 and AZ03 alloys after 8 hours heat treatment.

(a)

(b)

Spectrum	Mass Percent (%)	
	Mg	Zn
1	98.15	1.85
2	98.35	1.65
3	98.39	1.61

Spectrum	Mass Percent (%)	
	Mg	Zn
1	94.42	5.58
2	94.26	5.74

Figure 4.4. SEM micrographs and EDX analysis of the alloys after 8 hours heat treatment, a) AZ005, b) AZ03.

Figure 4.5. shows the microstructure of the Mg-Zn alloys with different Zn concentrations subjected to heat treatments for 16 hours.
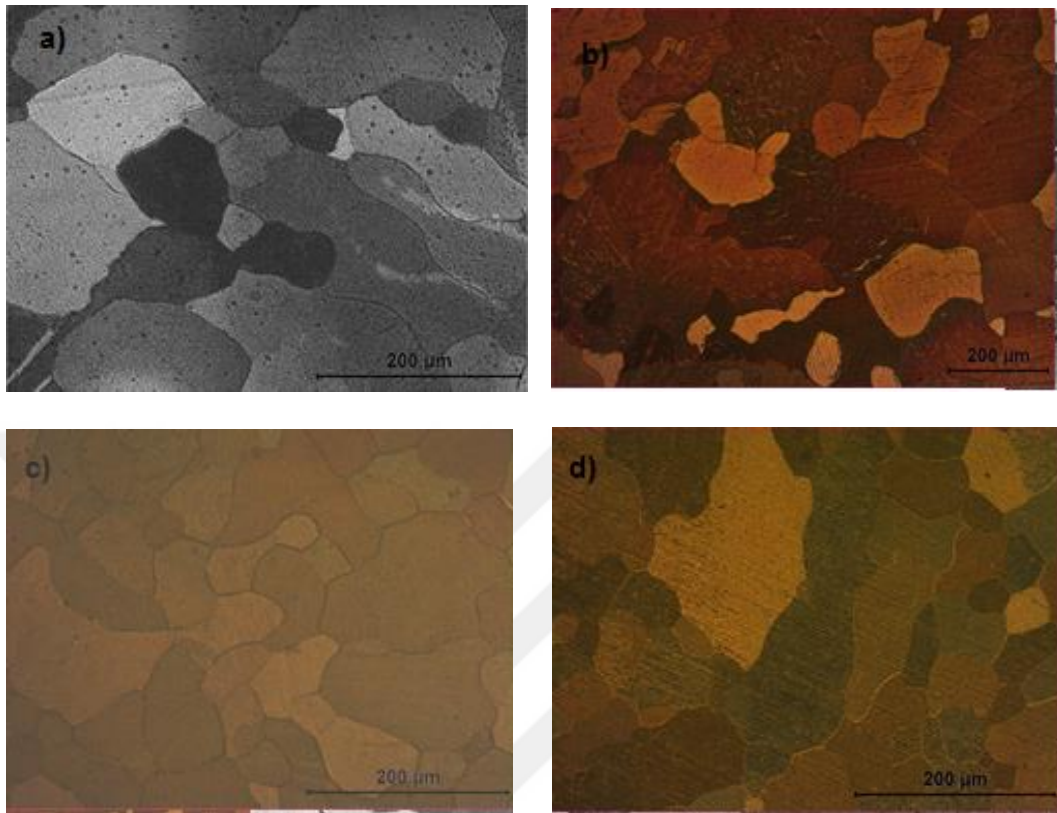

Figure 4.5. Optical microstructures of the 16 hours heat treated alloys (a) AZ005, (b) AZ01, (c) AZ02, and (d) AZ03.

Figure 4.6 shows the EDX analysis of the AZ005 and AZ03 alloys after 16 hours heat treatment. Results showed a considerable zinc enrichment along the grain boundaries to display a network microstructure for both (8h and 16h) T6 alloy processing. For T6 treatment, larger MgZn particles formed mainly on grain boundary and fine MgZn particles precipitated on matrix. Compared with as-cast alloy, T6 treatment could decrease the amounts of MgZn particles, and decrease zinc content of zinc-rich net-segregation.
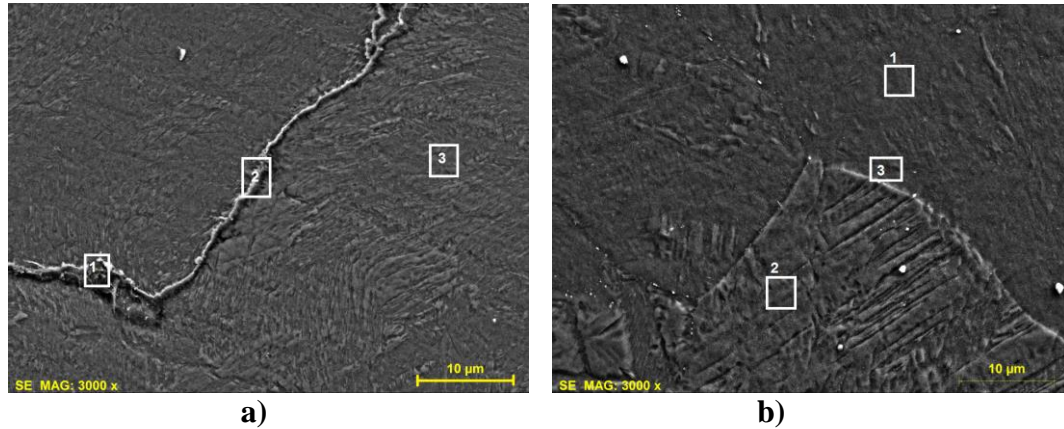
Spectrum	Mass Percent (%)	
	Mg	Zn
1	98.29	1.71
2	98.33	1.67
3	98.06	1.94

Spectrum	Mass Percent (%)	
	Mg	Zn
1	94.56	5.44
2	94.41	5.59
3	91.65	8.35

Figure 4.6. SEM micrographs and EDX analysis of the alloys after 16 hours heat treatment, a) AZ005, B) AZ03.

4.2. HARDNESS TEST RESULTS

The results and values for the hardness test of alloys (Vickers hardness test) resulted in hardness increased significantly with increased zinc concentration and concentration. This improvement and increase in hardness can be due to grain size based on magnesium zinc binary phase diagram [48]. Zinc dissolves into primary magnesium to some extent, and the maximum solubility of zinc element in magnesium is 1.6 wt.% at room temperature, When the addition of zinc content is high e.g., 3 wt.%, magnesium and zinc rich phases will precipitate and contribute positively to the strength and hardness of the alloy [49]. Consequently, zinc effects the solid solution strengthening and precipitation hardening in magnesium-zinc alloys. And also the hardness of the samples decreased before the heat treatment and increased after the heat treatment.

The Vickers hardness results before heat treatment are shown in Table 4.1.

Method: Vickers HV 05

Loading: 500g loading (5N)   Duration: 10 seconds

Table 4.1. Hardness values before heat treatment.

Sample	Hardness (HV5)
AZ005	38.5
AZ01	43
AZ02	45
AZ03	52.5

From the Table 4.1, it can be observed that the hardness of the as-cast alloy increases by increasing zinc content by up to about 36% at AZ03 compared with AZ005.

The hardness of the magnesium zinc alloys before heat treatment is shown in Fig. 4.7
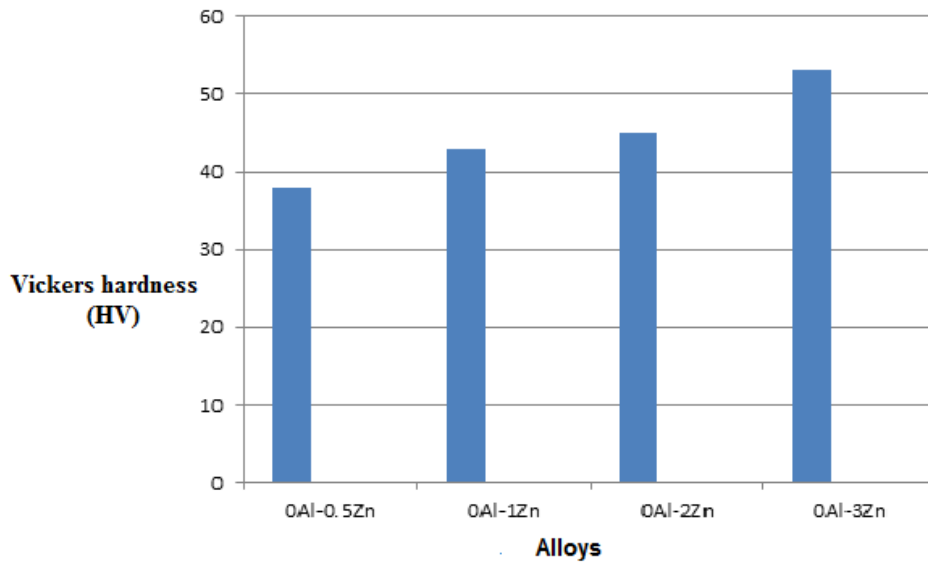

Figure 4.7. The average hardness test before heat treatment.

The Vickers hardness results after heat treatment are shown in Table 4.2.

Method: Vickers HV 05

Loading: 500g loading (5N)

Duration: 10 seconds

Table 4.2. Hardness values after heat treatment.

Alloys	Average (HV) 8 hours	Average (HV) 16 hours
AZ005	35.52	34.04
AZ01	39.82	36.22
AZ02	42.20	41.04
AZ03	49.34	53.82

From Table 4.2 it can be noted that the hardness of Mg-Zn alloys after heat treatments has been reduced slightly in 8 hours and increased in 16 hours, especially when the zinc content is 3 wt.%.

The hardness values of the as cast and heat treated alloys are shown in Figure 4.6.
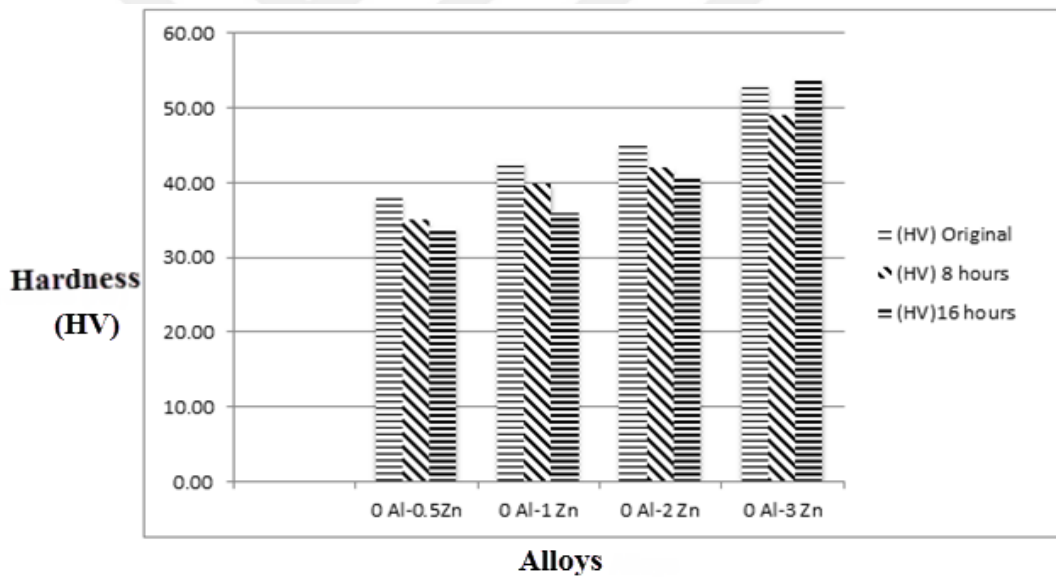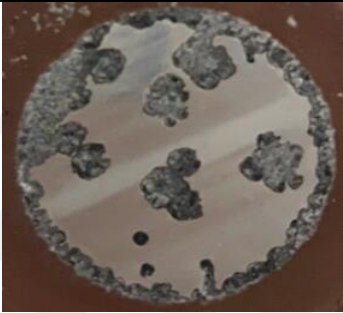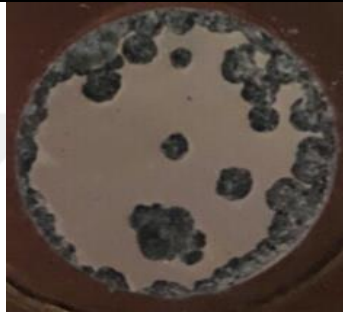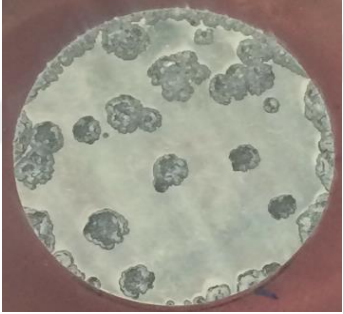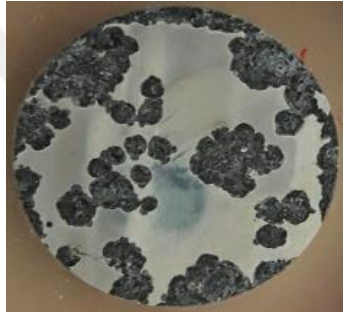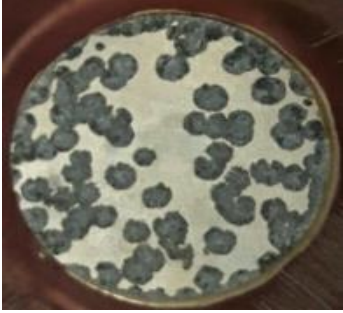

Figure 4.8. The hardness values of the alloys before and after heat treatment.

From Figure 4.8 it is possible to observe that the hardness has been improved by increasing zinc content as in the Mg-3Zn alloy, especially after heat treatment 16 hours. In comparing the zinc content of each alloy separately, it was found that the hardness of the as-cast alloy is greater than after the treatment. But, in the Mg-3Zn alloy is found, the hardness after heat treatment, especially when treated 16 hours, is slightly higher than before heat treatment.

4.3. ELECTROCHEMICAL CORROSION TEST

The macro photographs of the samples after electrochemical corrosion tests are shown in Table 4.3.

Table 4.3. Macrophotos obtained from electrochemical corrosion tests.

Alloys	As-cast	T6 heat treatment	
		8 hours	16 hours
AZ005			
AZ01			
AZ02			
AZ03			

It is clearly seen from Table 4.3 that in the as cast samples as the amount of Zn increases, the pits appearing on the surface increase. As the result of aging heat treatment; it's observed that the pits on the surface of the samples after aging of both 8 hours and 16 hours decreased comparing with the as cast samples and thus it might be concluded that the corrosion resistance improved.

Potentiodynamic polarization curves obtained from as-cast, 8 hours and 16 hours aging heat treatments of AZ005, AZ01, AZ02 and AZ03 alloys in 3.5% NaCl solution are given in figures 4.9 to 4.11 respectively. The corrosion rate (CR), potential (E_{corr}) and current density (I_{corr}) values determined by extrapolation method from Tafel curves are also given in Table 4.4.
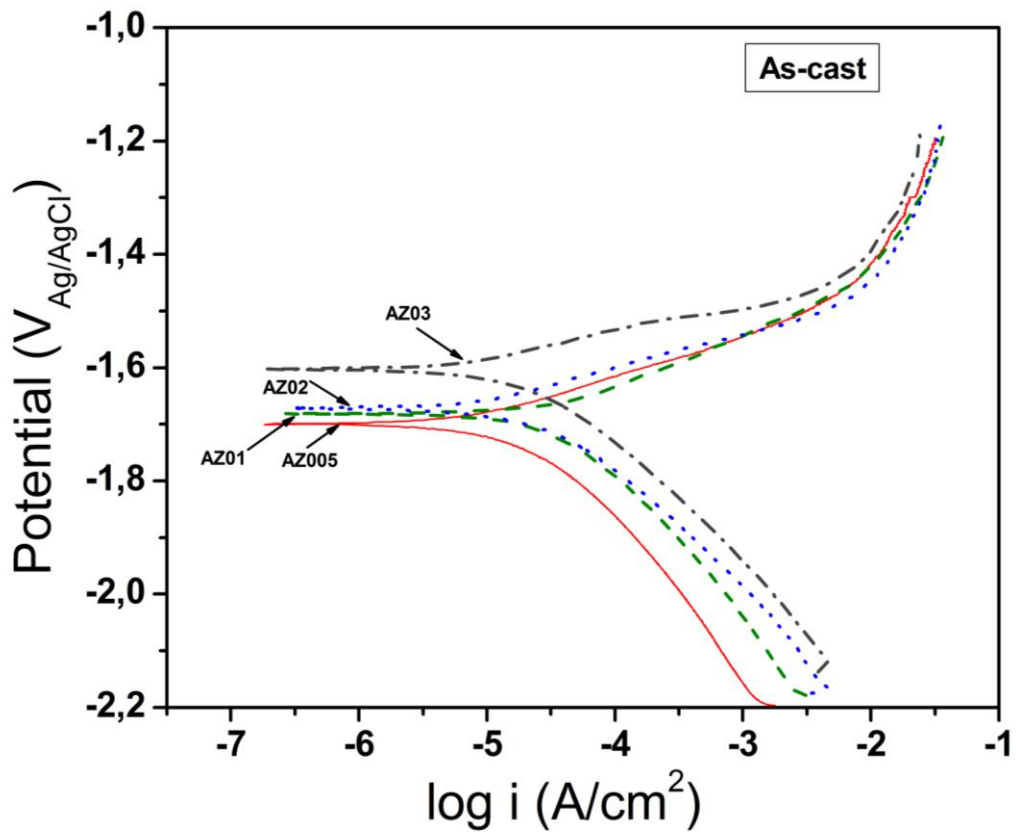
Figure 4.9. Potentiodynamic polarization curves of the as cast magnesium-zinc alloys.
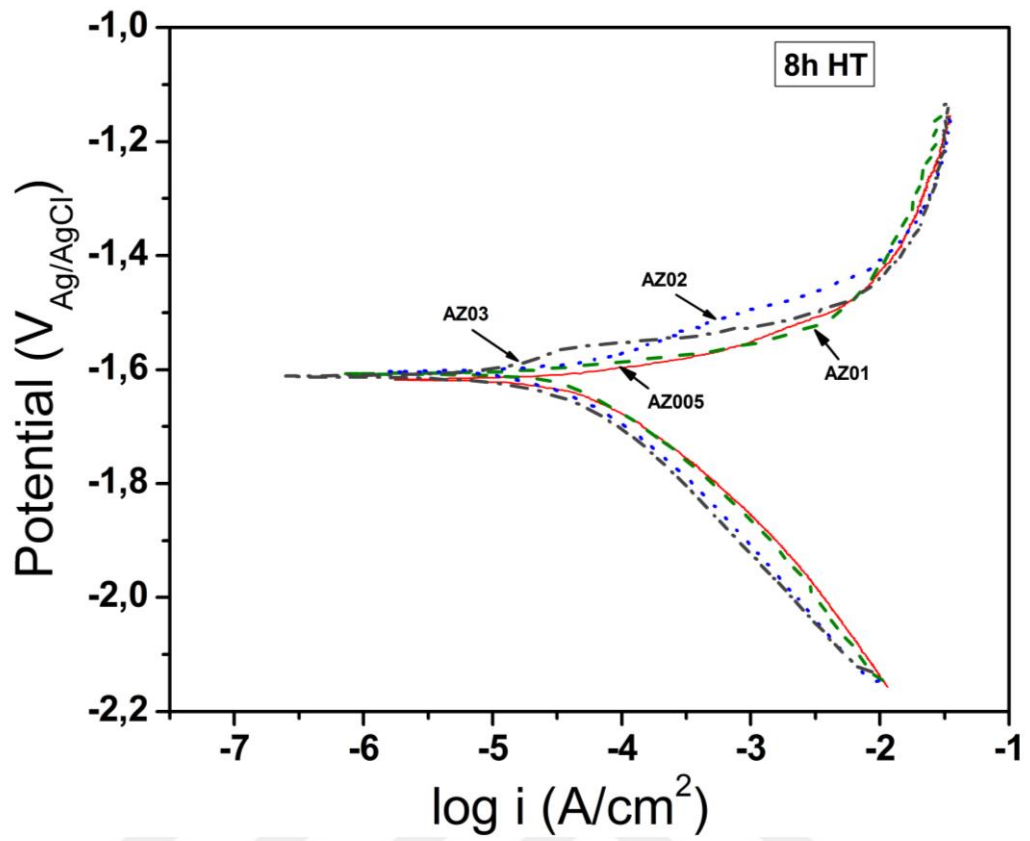
Figure 4.10. Potentiodynamic polarization curves of the magnesium-zinc alloys after 8h heat treatment.
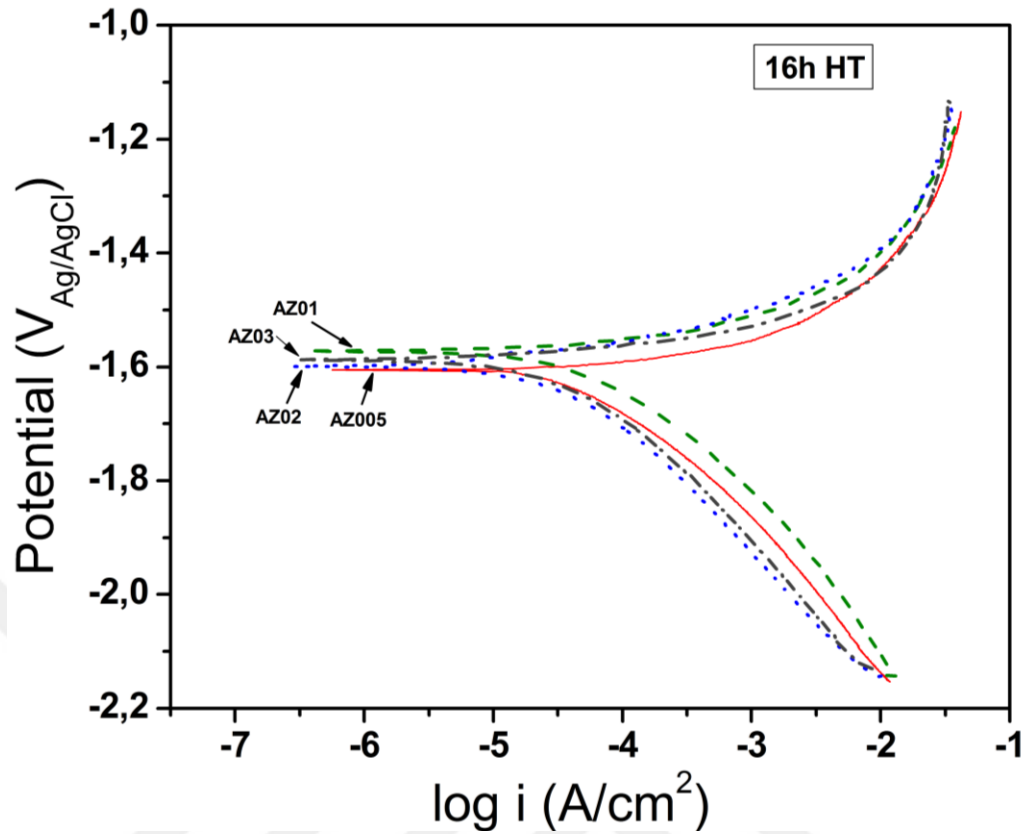
Figure 4.11. Potentiodynamic polarization curves of the magnesium-zinc alloys after 16h heat treatment.

Table 4.4. Corrosion potential (E_{corr}), corrosion current density (I_{corr}) and corrosion rate (CR) values determined from the potentiodynamic curves.

	Alloys	E_{corr} (V)	I_{corr} ($\mu A/cm^2$)	CR (mm/yr)
As-cast	AZ005	- 1.70	18	0.41
	AZ01	- 1.68	33	0.76
	AZ02	- 1.672	40	0.93
	AZ03	- 1.653	45	1.03
8 hours heat treated	AZ005	- 1.617	58	1.33
	AZ01	- 1.607	56	1.29
	AZ02	- 1.602	39	0.91
	AZ03	- 1.612	28	0.64
16 hours heat treated	AZ005	- 1.604	45	1.03
	AZ01	- 1.572	38	0.88
	AZ02	- 1.60	32	0.75
	AZ03	- 1.586	29	0.66

From Table 4.4 when discussing each case of heat treatments alone. The following can be observed:

(i) As- cast alloy

(ii) 8 hours

(iii) 16 hours

From the table 4.4 it can be observed that the corrosion rate of the as-cast alloy increases with increasing zinc content, and when the corrosion potential (E_{corr}) increases the corrosion current density (I_{corr}) increasing with redouble values and the corrosion rate is also increasing especially in AZ03 alloy.

In both heat treatment cases (8 hours and 16 hours) the following can be observed;

1. As zinc content increases, the corrosion rate decreases.

2. As corrosion potential (E_{corr}) increases, the corrosion current density (I_{corr}) and the corrosion rate decreases.

It could be seen the as-cast alloy has the higher corrosion rate in Mg-3Zn than the heat treated alloy.

The potentiodynamic polarization curves of as cast AZ005, AZ01, AZ02, AZ03 alloys are shown in Figure 4.9. Polarization curves showed that as the amount of Zn increases, corrosion potential (E_{corr}) value of AZ005 is more negative (-1.7 V) than E_{corr} value of AZ03 (-1.65 V) while corrosion current density value (I_{corr}) increased from 18 $\mu A/cm^2$ in AZ005 to 45 $\mu A/cm^2$ in AZ03. Corrosion rate (CR) incrased from 0.41 mm/yr in AZ005 to 1.03 mm/yr in AZ03. As the amount of Zn increased, I_{corr} and CR increased at around 2.5 fold, in other words, the corrosion resistant decreases as the Zn ratio increases. It can be suggested that in the galvanic couple of AZ03, MgZn intermetallic phase behaves as an anode and α-Mg matrix phase behaves as a cathode. Therefore, corrosion rate of the as-cast Mg-Zn alloys following: AZ03 > AZ02 > AZ01 > AZ005.

The potentiodynamic polarization curves of AZ005, AZ01, AZ02, AZ03 alloys after 8 hours heat treatment are shown in Figure 4.10 and after 16 hours heat treatment in Figure 4.11. Polarization curves showed that as the amount of Zn increases, I_{corr} values decreased from 58 $\mu A/cm^2$ in AZ005 to 28 $\mu A/cm^2$ in AZ03 after 8 hours heat treatment and decreased from 45 $\mu A/cm^2$ in AZ005 to 29 $\mu A/cm^2$ in AZ03 after 16 hours heat treatment. Corrosion rate decrased from 1.33 mm/yr in AZ005 to 0.64 mm/yr in AZ03 after 8 hours heat treatment and decrased from 1.03 mm/yr in AZ005 to 0.66 mm/yr in AZ03 after 16 hours heat treatment. As the amount of Zn increased, I_{corr} and CR values decreased by 50% and 35% after 8 hours and 16 hours of heat treatment respectively. In other words, the corrosion resistant increases as the Zn ratio increases both after 8 hours heat treated and 16 hours heat treated samples. It can also be suggested that in the galvanic couple of AZ03, α-Mg matrix phase behaves as an anode and MgZn intermetallic phase behaves as a cathode. Therefore, after heat treatment (8 hours and 16 hours) corrosion rate of the as-cast Mg-Zn alloys following: AZ005 > AZ01 > AZ02 > AZ03.

CHAPTER 5

CONCLUSIONS

In this study, effect of zinc (0,5-1-2-3 wt.%) additions and heat treatment parameters on the microstructure, hardness and corrosion properties of magnesium zinc alloys are examined. After the solution heat treatment at 400ºC, the samples subjected to 8 and 16 hour aging heat treatment. Microstructure studies were carried out by optical microscope and scanning electron microscope. Potentiodynamic polarization values were obtained in the electrochemical corrosion test, compared to the as-cast structure.

The results obtained in the studies conducted are summarized below:

1- Microstructure studies showed that the grain size decreased with the increase of Zn content and the MgZn intermetallic phase was formed by the addition of 3 wt. % Zn. The grain boundaries are larger before heat treatment and grain structures are finer after heat treatment.

2- Hardness test results showed that an increase of hardness by 36% was observed with increase of Zn content. The increase in hardness value of the samples subjected to 8 hours of heat treatment was 39%, while the values of 16 hours of heat treated samples increased to 58%.

3- For the as-cast samples, as the amount of Zn increased, I_{corr} and CR increased at around 5.7 fold, in other words, the corrosion resistant decreases as the Zn ratio increases. It can be suggested that in the galvanic couple of AZ03, MgZn intermetallic phase behaves as an anode and α-Mg matrix phase behaves as a cathode.

4- As the amount of Zn increased, I_{corr} and CR values decreased by 50% and 35% after 8 hours and 16 hours of heat treatment respectively. In other words, the corrosion resistant increases as the Zn ratio increases both after 8 hours heat treated and 16 hours heat treated samples. It can also be suggested that in the galvanic couple of AZ03, α-Mg matrix phase behaves as an anode and MgZn intermetallic phase behaves as a cathode.

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RESUME

Fozi Mustafa Salem MAKHLOF was born in Libya in 1967. He completed high school education in Misrata Secondary High School in Libya. After that, he started undergraduate program in Tripoli University, Department of Materials Science and Metallurgical in 1993. Then in 1995, he started to work as a teaching assistant in Mechanical Engineering Department Higher Institute of Comprehensive Occupations Misrata in Libya as well. From 1999 to 2003 he was the head of the Mechanical department in that Institute. He started his Master Science Education in 2015 in Karabuk University. Fozi Mustafa Salem MAKHLOF is married and has 5 children.

CONTACT INFORMATION

Address: Higher Institute of Comprehensive Occupations
            Misrata, LİBYA

E-mail: makfozimak@gmail.com