CORROSION PROTECTION OF AEROSPACE GRADE MAGNESIUM ALLOY ELEKTRON 43™ FOR USE IN AIRCRAFT CABIN INTERIORS

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Magnesium alloys exhibit desirable properties for use in transportation technology. In particular, the low density and high specific strength of these alloys is of interest to the aerospace community. However, the concerns of flammability and susceptibility to corrosion have limited the use of magnesium alloys within the aircraft cabin. This work studies a magnesium alloy containing rare earth elements designed to increase resistance to ignition while lowering rate of corrosion. The microstructure of the alloy was documented using scanning electron microscopy. Specimens underwent salt spray testing and the corrosion products were examined using energy dispersive spectroscopy.
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CHAPTER 1
INTRODUCTION

In this work experimental data showing the effect of protective coatings on a magnesium alloy is presented and analyzed. Criteria are established to determine the effectiveness of two aerospace grade coating systems in preventing corrosion. Microstructural evaluation and theoretical data are used to assess the corrosion resistance of the alloy and recommendations for commercial usage are given.

This work focuses on the qualification of one magnesium alloy system for use in commercial aircraft cabin interiors. The necessary requirements for qualification as well as potential issues are discussed. This introduction primarily serves to advise the reader on these requirements and issues. Brief historical information which provides background and reasoning is also given.

1.1. Usage of Magnesium in Commercial Airplanes

The identification and qualification of lightweight materials is a driving factor in transportation technology. Magnesium, as the lightest structural metal, is a strong candidate for applications requiring low weight. With an average density of 1.8 g/cm$^3$, magnesium alloys have only one-quarter the density of stainless and carbon steels and two-thirds the density of aluminum alloys [4, 8, 21]. The alloys of magnesium also exhibit high specific strength, excellent machinability, and capability to absorb vibration and impact [1, 2, 4]. Alloy development in recent years has focused on materials with high strength at elevated temperatures and good creep resistance [6, 11].
Magnesium castings are currently in widespread use within the engine and transmission systems of transport airplanes, primarily in the form of cast structural housings [9]. However, regulations exist which forbid the use of magnesium within the aircraft cabin interior [31]. The Federal Aviation Administration (FAA), as overseer of the regulations pertaining to aircraft safety, has worked with industry groups to analyze the possibility of magnesium alloy usage within the cabin interior and evaluate any potential impact on the established level of safety [29].

1.2. Alloy Selection

There are two traditional systems of magnesium casting alloys: those produced with aluminum and those without. The earliest documented alloying elements were aluminum, zinc, and manganese [46]. In fact, the Mg-Al-Zn system remains one of the most widely used compositions for casting alloys, with a notable example being AZ91. Although the aluminum-based systems exhibit good casting characteristics, they show low response to age hardening and have relatively low strength properties [1].

In magnesium systems for wrought alloys, there are again two major systems: those produced with zirconium and those without. The wrought alloys generally fall into the same categories as casting alloys with the exception that they can be obtained in a number of tempers [54]. In the past, wrought alloys containing thorium were used to produce missile and spacecraft components requiring creep resistance at elevated temperatures. However, due to the radioactive nature of thorium, these alloys are now considered to be obsolete for purposes of future design [55].
Magnesium alloys, in general, exhibit high strength-to-weight ratios, low density, good weldability, and excellent damping characteristics [2]. Properties such as increased creep resistance and superior performance at elevated temperature require alloying elements such as rare earth metals [1, 3]. Corrosion behavior can also be affected positively by the addition of rare earth metals [6]. These factors lead to the selection of magnesium alloyed with rare earths metals. Magnesium Elektron, headquartered in Manchester, UK, has developed a rare earth alloy designated as WE43C. The trade name for this material is Elektron™ 43. This paper will focus on the corrosion characteristics of the wrought Elektron 43 alloy.

1.3. Qualification

In March of 2007, the FAA presented information to the International Aircraft Materials Fire Test Working Groups (IAMFTWG) indicating that there was a revived industry interest in revisiting the use of magnesium alloys in the aircraft cabin interior [29]. In October of the same year, during the Fifth Triennial International Fire and Cabin Safety Research Conference, the FAA presented initial test results of magnesium bars for flammability. Magnesium Elektron provided all samples for testing. Six different alloy systems were evaluated during the initial testing: AZ31, AZ80, ZE41, ZE10, WE43, and Elektron™ 21 [53].
1.3.1. Flammability

In the early stages of qualification, efforts were focused on exploring the flammability properties of magnesium alloys. A study conducted by the FAA in 1964 explored the ignition and burning characteristics of four magnesium casting alloys: AZ61A, AZ31B, AZ80A, and ZK60A [52]. The goal of the testing was to reproduce the conditions of an aircraft power plant fire. To this end, a test apparatus was developed which used a commercial conversion-type oil burner to produce a flame temperature of approximately 2000°F (Figure 1-1).

![Figure 1-1](image)

**Figure 1-1**
Test arrangement for engine casting ignition tests [52]

Initial testing using a small Fisher-type burner and conducted on magnesium bars of varying thickness determined that time to ignition did not vary between specific alloys but was directly related to specimen thickness and airflow over the specimen during the testing. The tests of engine castings weighing between twenty-three and
ninety-one pounds confirmed these observations. Self-heating of the alloys and subsequent combustion was noted to begin at approximately 1000°F. Due to the connection between component thickness and time to ignition, it was noted that small, thin-walled magnesium alloy components had the potential to represent a serious fire hazard.

In re-opening the discussion of magnesium alloy usage, the FAA noted that materials technology has advanced significantly and newer magnesium alloys have differing levels of susceptibility to ignition. The focus of research conducted by the Federal Aviation Administration Technical Center (FAATC) is to ensure that any changes to material, process, or design guidelines will not reduce the level of safety. With this mandate, the FAATC worked with members of industry and raw material producers to develop testing protocols and establish safety parameters for the usage of magnesium alloys in the cabins of commercial aircraft.

As with the 1964 study, the FAATC began testing using an oil-fired burner type laboratory scale test apparatus. The burner was configured according to an existing standard dedicated to the qualification of aircraft seat cushions to flammability requirements, Title 14 Code of Federal Regulations (CFR) Part 25.853(c) Appendix F Part II [33] (Figure 1-2).
Six alloys were selected for analysis, including the newest iterations of AZ80 and AZ31. Testing showed a direct correlation between each alloy’s upper melting range and the time required for the sample to melt. Further, it was shown that alloys including rare earth components, such as WE43, exhibited more resistance to ignition than traditional alloy systems. The FAATC also tested specimens representing machined components of aircraft seating systems, such as legs and spreaders, to further evaluate the importance of consistent part thickness. It was determined that milling and orientation had no impact on the flammability of the samples. However, very thin sections (ranging from 0.0625 to 0.125 inch in thickness) were shown to be very susceptible to ignition and, once ignited, to burn until consumed.

Using the knowledge gained from the initial testing sequences, the FAATC proceeded to full-scale testing. With the input of the industry team, it was determined that primary seat components were a focus for potential usage of magnesium alloys in the aircraft cabin. Primary seat components include large machined parts, such as legs, spreaders, baggage bars, seat back hoops and cross tubes (Figure 1-3). The
most weight could be saved by substituting magnesium alloys in place of the traditional aluminum in these parts due to their comparatively substantial mass in the seat structure.

![Primary structural components of commercial aircraft seats](Image credit: Wichita State University, National Institute for Aviation Research)

The test fuselage for the full-scale testing consisted of a twenty-foot long steel cylinder which was inserted between two halves of a Boeing 707 fuselage. A standard size opening, forty by eighty inches, was used to represent a break in the fuselage. A pan containing fifty-five gallons of JP-8 fuel was placed directly outside of this opening and ignited to produce the fire source. The fuselage mock-up included paneling and carpeting with three rows of triple seats centered around the fire opening (Figure 1-4).
Initial full-scale testing was conducted using seats constructed of traditional materials in order to establish a basis by which to measure the impact of the usage of magnesium alloys (Figure 1-5). Once this baseline was established, additional testing was carried out on seats fabricated with two magnesium alloys: AZ31 and WE43. These alloys were selected based on the results of the laboratory scale testing to represent the worst and best performing material, respectively.
A survivability model using regression equations to determine a fractional effective dose for incapacitation was used to predict the amount of time a human has to escape an aircraft fire. This model takes into account the effects of toxic gases and temperature. The baseline test, using standard materials, showed a time of 250 seconds for incapacitation at the forward location in the cabin. The testing of the seats constructed using WE43 magnesium alloy for the primary components showed that survivable conditions remained for approximately 278. The seats constructed using AZ31 magnesium alloy for the primary components showed survivable conditions up to 265 seconds (see Figure 1-6).

Figure 1-6
Cabin survivability comparison
Image credit: Marker, FAA [74]
The full-scale tests were able to reproduce the effects seen in accidents involving external fuel fires. The rare earth magnesium alloy, WE43, was shown to perform very similarly to aluminum when extinguished. However, the full-scale tests involving AZ31B took slightly longer to extinguish relative to the aluminum-containing baseline test. This indicated that the initial lab scale testing that differentiated between the different alloy systems was valid. The FAATC has proposed that the laboratory scale testing method using an oil-fired burner provides testing conditions which enable discrimination between magnesium alloy grades [29].

Additional studies are in agreement with the theory that rare earths as alloying elements can increase the ignition resistance of magnesium alloys. Gwynne and Lyons [57] have reported that Elektron 43 does not burn when melted and self-extinguishes when the heat source is removed. Testing conducted by the Fire Safety Department, Toulouse Aeronautical Test Centre (CEAT), resulted in the conclusion by researchers there that the use of magnesium alloys inside an aircraft cabin does not increase risk for an in-flight fire [58].
Additional laboratory scale testing, primarily to determine the standard deviation inherently resultant from testing in multiple locations, is currently planned. The industry task group is working actively with the FAATC to establish appropriate critical parameters (pass/fail criteria) for flammability testing of magnesium alloys. Once these parameters are established the FAA will allow the use of the special condition process for the specification of magnesium components in aircraft cabin interiors.

1.3.2. Corrosion

The second concern for industry in considering the use of magnesium alloys is susceptibility to corrosion. Magnesium is one of the most electropositive of metals on the galvanic scale, which ranks metals according to their relative activity in an electrolytic environment. The more active metals, anodes, are the lowest in the series while the least active, cathodes, are the highest (Table 1-1). Because of this property, magnesium serves as a galvanic anode, providing sacrificial protection to other metals when coupled in an electrolyte. When two metals are in contact and an electrolytic coupling is achieved, the magnesium will sacrificially corrode relative to than the other metal. The presence of impurities within the magnesium alloy matrix can also substantially contribute to the rate of corrosion due to the creation of local cathodic cells [20].
Table 1-1: Corrosion potential values for common engineering metals

<table>
<thead>
<tr>
<th>Metal</th>
<th>$E_{\text{corr}}$ (V, SCE)</th>
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<tr>
<td>Magnesium</td>
<td>-1.65</td>
</tr>
<tr>
<td>Zinc</td>
<td>-1.02</td>
</tr>
<tr>
<td>Aluminum 7000 series</td>
<td>-0.88</td>
</tr>
<tr>
<td>Aluminum 1000 series</td>
<td>-0.73</td>
</tr>
<tr>
<td>Iron</td>
<td>-0.5</td>
</tr>
<tr>
<td>Copper</td>
<td>-0.12</td>
</tr>
<tr>
<td>Nickel</td>
<td>+0.01</td>
</tr>
<tr>
<td>Platinum</td>
<td>+0.2</td>
</tr>
</tbody>
</table>

However, corrosion due to the above-mentioned mechanisms requires environmental exposure. Uhlig has noted that under normal environmental conditions, the corrosion resistance of magnesium alloys is comparable to or better than that of mild steels [51]. The application proposed in this work (structural components in aircraft cabin interiors) would be under normal conditions. There is potential that the magnesium components could be exposed to naturally corrosive environments, such as when operating in a highly humid environment or near an ocean. Corrosive environments could also be created within the cabin through the use of cleaners or spillage of liquids such as water, orange juice and soda. Therefore, corrosion and its prevention remain important topics for discussion.

Wear and corrosion are, for the most part, surface related degradations that can be reduced or minimized by manipulation of the surface microstructure and / or composition. It has also been shown that certain coatings are successful at preventing
corrosion in magnesium alloys [4, 10, 13]. This paper focuses on the usage of coatings for corrosion protection.

When exposed to air, pure magnesium develops a gray oxide film, which acts to inhibit further oxidation. In aqueous solutions, a crystalline film of magnesium hydroxide is formed when magnesium dissociates via an electrochemical reaction according to the following mechanism [44]:

\[
\text{Mg(s) + 2H}_2\text{O(l) → Mg(OH)}_2\text{(s) + H}_2\text{(g)} \quad (\text{Equation 1-1})
\]

Anodic Reaction(s)

\[
\begin{align*}
\text{Mg} & \rightarrow \text{Mg}^{2+} + 2\text{e}^- \\
\text{Mg(s) + 2(OH)}^- & \rightarrow \text{Mg(OH)}_2\text{(s) + 2e}^- 
\end{align*} \quad (\text{Equation 1-2, 1-3})
\]

Cathodic Reaction

\[
2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{(g)} \quad (\text{Equation 1-4})
\]

1.3.3. Mechanical Properties

Aircraft seats are required to meet very stringent safety standards, including both dynamically and statically applied loading. For the purposes of testing to these requirements, anthropomorphic test dummies are utilized to provide appropriate ballast and represent passengers. This increases the requirements for material strength in those seat components exposed to the load path.

Dynamic test requirements focus on the ability of the seat to absorb a substantial load while protecting the occupant. There are a number of dynamic tests mandated; depending on the location of the seat in the aircraft, additional factors stressing the structure such as pre-test induced pitch and yaw may be also required. Yaw, in
reference to aircraft, is an oscillation about a vertical axis (Figure 1-8). SAE AS8049 requires that seats placed in repetitive rows must be tested in conditions that simulate aircraft floor deformation. This is accomplished by deforming the test fixture. Various combinations of deformation criteria may be applied [31].

During the 10° yaw test, the sled supporting the seats will be accelerated down a path and must reach an ultimate load of 16G. The purpose of the yaw angle is to evaluate any effect of hard structures within the path of the head excursion of the test dummy. After impact, the data from the test dummies, which are equipped with accelerometers and routed through a data acquisition computer with specialized software, will be analyzed to evaluate blunt trauma [31, 34].

![Illustration of yaw, pitch, and roll](image)

Figure 1-8
Illustration of yaw, pitch, and roll
Figure 1-9
Aircraft seating dynamic test set-up
Image credit: Wichita State University, National Institute for Aviation Research

Other dynamic tests requirements include 14G download structural, 16G longitudinal, and 16G front row head and knee path evaluations. For each test, blunt force trauma, seatback deformation, and sharp edges will be evaluated. The lumbar and femur loads will also be assessed.

These stringent requirements lead to the need for very strong structural components. For an aircraft seat, design, processes, and materials all play a part in the integrity of the structure. Crucial material properties include ultimate and yield strength, percent elongation under load, and impact resistance [31, 34].
CHAPTER 2

HISTORY OF MAGNESIUM

The earliest known usage of magnesium dates back to 1618, when a farmer from the area of Epsom in England noted that his cows refused to drink from a well and that the water had a bitter taste. However, the water was found to have a healing effect on small scratches and rashes. “Epsom salts,” as the compound produced from the water became known, has since been recognized as magnesium sulphate, MgSO4.

In 1755, by experimenting with magnesium carbonate (then known as magnesia alba), Scottish chemist Joseph Black showed that the mineral contained two unique elements. Sir Humphry Davy, an English chemist, is generally credited with the actual isolation of elemental magnesium, in 1808. Davy was using a large battery he had built to pass electricity through various salts. With this method, he was able to discovery or isolate a number of alkali and alkali earth metals. Having used magnesia (magnesium oxide) in his experiment, Davy chose the elemental name accordingly. Magnesia is the district of Thessaly in Greece where magnesia alba was originally found [56].

For several hundred years after its discovery, there were no structural uses found for magnesium metal. In fact, it is only relatively recently, with advanced methods of developing alloys, that magnesium can be considered as a contender with traditional structural metals. Although some European countries did attempt to produce magnesium during the nineteenth century, Germany was the only country to develop steady uses for the metal. In 1868, Germany was the only producer in the world, with the products being mostly used in powder or ribbon form for flashlights and pyrotechnics and as a reducing agent in aluminum [45].
2.1. Elemental Properties

Physically, magnesium is recognized as a silvery, soft metal (Figure 2-1). Having an atomic number of 12, magnesium is located in period 3 and group 2 of the periodic table and is classified as an alkaline earth metal. The melting point of magnesium is 923 K (650°C); this is a very important factor in the ignition behavior of the alloys of magnesium, as it has been observed that the alloys generally ignite around the melting point [30, 58].

![Magnesium metal shavings](image)

**Figure 2-1**
Magnesium metal shavings

Magnesium has a hexagonal close-packed crystal structure under atmospheric pressure. The cell parameter $a$ is equal to 0.3209 nanometers while $c$ is equal to 0.5211 nanometers at 25°C. If alternating close-packed layers of atoms were made up of perfectly hard spheres, the $c/a$ ratio would have the ideal value of 1.633. The actual
measured value is 1.6236, making magnesium very nearly perfectly close-packed (Figure 2-2) [45].

The hexagonal close packed structure of magnesium is directly related to the ductility of the element. At room temperature, the predominate slip system is the basal plan. This limits ductility at low temperatures [22]. However, at higher temperatures the prismoidal and pyramidal slip systems become active and increase formability. This characteristic is very important during the processing of wrought magnesium products [43].

![Hexagonal close-packed crystal structure](image)

**Figure 2-2**
Hexagonal close-packed crystal structure; Image credit: Tosaka

Magnesium is the eighth most common element in the universe and the sixth most abundant metal on earth, comprising about 2.5% of the earth’s surface. However, due to the low standard reduction potential of magnesium, it is never found free in nature [45]. Some common compounds of magnesium include magnesium hydroxide, better known as milk of magnesia, and magnesium carbonate (magnesite), used to treat
wood pulp for the manufacture of paper. Magnesium oxide is a common refractory liner for furnaces used in the production of ferrous and nonferrous metals and cement [50].

2.2. Production

Pure magnesium is very reactive, bonding with other elements easily, and is therefore not found in elemental form. As an alkaline earth metal, magnesium is reactive in water, releasing hydrogen gas when submerged. Powdered magnesium has a very large surface to volume ratio and thus the reaction occurs much more rapidly. However, unlike other alkaline earth metals, magnesium does not tarnish when exposed to air and does not require storage in an oxygen-free environment. This is due to the formation of a protective oxide layer when exposed to air [63].

While magnesium is found in a large number of minerals, only five are generally viewed as commercially viable sources of magnesium ore: dolomite, brucite, carnallite, magnesite, and olivine [50]. Non-mineral sources of magnesium include seawater, wells and lake brines, which all contain magnesium chloride (MgCl₂). Magnesium levels of the Dead Sea, located between Israel and Jordan, have been reported as 4.2% compared with 0.129% for sea water. Although the concentration of magnesium ions varies between different seas, magnesium is the third most common element found in sea water [45].
Table 2-1: Most common minerals used in magnesium production [62]

<table>
<thead>
<tr>
<th>Refer to</th>
<th>Name</th>
<th>Chemical formula and name</th>
<th>Molecular weight (gm)</th>
<th>Occurrence(s)</th>
<th>Total Mg (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 2-3</td>
<td>Dolomite</td>
<td>CaMg(CO$_3$)$_2$ Calcium magnesium carbonate</td>
<td>184.40</td>
<td>Dolostones, limestones, marbles</td>
<td>13.18</td>
</tr>
<tr>
<td>Figure 2-4</td>
<td>Brucite</td>
<td>Mg(OH)$_2$ Magnesium hydroxide</td>
<td>58.32</td>
<td>Mineral alternation of periclase in marble</td>
<td>41.68</td>
</tr>
<tr>
<td>Figure 2-5</td>
<td>Carnallite</td>
<td>KMgCl$_3$·6(H$_2$O) Hydrated potassium magnesium chloride</td>
<td>277.85</td>
<td>Upper layers of saline marine deposits</td>
<td>8.75</td>
</tr>
<tr>
<td>Figure 2-6</td>
<td>Magnesite</td>
<td>MgCO$_3$ Magnesium carbonate</td>
<td>84.31</td>
<td>Igneous and sedimentary rocks</td>
<td>28.83</td>
</tr>
<tr>
<td>Figure 2-7</td>
<td>Olivine</td>
<td>(Mg,Fe$^{2+}$)$_2$SiO$_4$ Magnesium iron silicate</td>
<td>153.31</td>
<td>Mafic to ultramafic igneous rocks</td>
<td>25.37</td>
</tr>
</tbody>
</table>
Figure 2-3
Dolomite

Figure 2-4
Brucite

Figure 2-5
Carnallite

Figure 2-6
Magnesite

Figure 2-7
Olivine

Image credit, Figures 2-3 thru 2-7: Rob Lavinsky, iRocks.com
There are two primary production methods in widespread use: Thermal reduction and electrolysis. Research is ongoing for a third production method, carbothermic reduction. Regardless of the production method, the magnesium ion must be reduced to metallic magnesium. In the electrolytic process, the reduction is carried out with electric current fed into the electrolyte cells. Thermal processes rely on high temperatures to accomplish the reduction [63].

2.2.1. Electrolysis

As early as 1833, Michael Faraday, an English chemist and physicist, obtained magnesium metal from magnesium chloride using electrolysis. In 1852, an electrolytic cell was developed by Robert Bunsen, a German chemist. Using the cell, large quantities of magnesium could be produced. Bunsen’s cell, modified and improved upon by German researchers, was the primary method of production for the next sixty years [56].

In the electrolytic process, salts containing chloride are decomposed. The raw materials may already be in salt form or may go through production steps to be transformed. For example, if sea water is used, the magnesium compounds are precipitated using lime or calcined dolomite. The lime source is mixed with the sea water and allowed to stand in settling ponds or tanks. Magnesium hydroxide, which is insoluble, settles to the bottom and is filtered and concentrated. For example, if calcium hydroxide is used, the following reaction occurs:

\[ \text{MgCl}_2 + \text{Ca(OH)}_2 \rightarrow \text{Mg(OH)}_2 + \text{CaCl}_2 \]  

(Equation 2-1)
Hydrochloric acid can then be added to produce magnesium chloride by the following mechanism:

\[
\text{Mg(OH)}_2 + 2 \text{HCl} \rightarrow \text{MgCl}_2 + 2 \text{H}_2\text{O} \quad \text{(Equation 2-2)}
\]

Once magnesium chloride is obtained, electric current can be applied to decompose the compound into chlorine gas and molten metal. At the cathode, the magnesium ion is reduced by two electrons to magnesium metal:

\[
\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg} \quad \text{(Equation 2-3)}
\]

At the anode, the chlorine ions are oxidized to release chlorine gas and two electrons:

\[
2\text{Cl}^- \rightarrow \text{Cl}_2 (g) + 2\text{e}^- \quad \text{(Equation 2-4)}
\]

The chlorine is collected in gaseous form and recycled. The magnesium metal is cast into primary ingots, which are later re-melted. The electrolytic process results in the recovery of very pure primary metal, ranging between 99.8 and 99.98% magnesium.

2.2.2. Thermal Reduction

The most common raw feedstock for thermal reduction is dolomite. The process involves reducing magnesium oxide using ferrosilicon. The mixture must be shaped into briquettes and heated for several hours at high temperatures (approx. 1150°C) under a vacuum. The low pressure and high temperature results in vaporization of the magnesium metal, which is then condensed to form magnesium crystals known as crowns. The crowns are harvested and re-melted to form pure ingot [61].
2.2.2.1. Pidgeon Process

Developed in Canada by Dr. Lloyd M. Pidgeon during the 1940s, the Pidgeon process is still widely used. In 2001, researchers found that 95% of primary magnesium produced in China was via the Pidgeon process. World production using this method was estimated at 40% [51]. However, the percentage of magnesium being produced in China has risen sharply in the past decade. Current estimates by the US Geological Survey indicate that China now produces 80% of the worldwide magnesium supply [50].

The process consists of three primary steps: conversion of dolomite by calcination to dolime, production of ferrosilicon alloy for the reduction of dolime, and the reduction of magnesium oxide by silicon (in the form of ferrosilicon) [49]. The first step results in the production of carbon dioxide and is highly endothermic:

\[
\text{CaMg(CO}_3\text{)}_2 \rightarrow \text{CaO} + \text{MgO} + 2\text{CO}_2 \quad \text{(Equation 2-5)}
\]

Production of ferrosilicon, step two, is via a carbothermic reaction:

\[
\text{Fe}_2\text{O}_3 + 4\text{SiO}_2 + 11\text{C} \rightarrow 2\text{FeSi}_2 + 11\text{CO} \quad \text{(Equation 2-6)}
\]

The magnesium oxide obtained in step one is then reduced using the ferrosilicon obtained in step two:

\[
2\text{MgO} + 2\text{CaO} + (\text{Fe})\text{Si} \rightarrow 2\text{Mg(g)} + \text{Ca}_2\text{SiO}_4(\text{s}) + \text{Fe} \quad \text{(Equation 2-7)}
\]

The magnesium produced is in the gaseous phase. It is cooled in steel condenser sleeves to produce a magnesium “crown” (Figure 2-8) [45]. Reduced pressure is required for the distillation step and results in high purity magnesium (99.7%). The metal contaminants from the dolomite ore are removed during distillation.
due to the high vapor pressure. Following distillation, the magnesium is re-melted in a protective atmosphere and cast into ingots.

![Magnesium crystals](image)

**Figure 2-8**
Magnesium crystals produced by vapor deposition; Image credit: Warut Roonguthai

The Pidgeon process has several advantages, including the usage of dolomite, which is a relatively plentiful mineral. The process results in a high-purity end product and is relatively simple. China, in particular, has leveraged the availability of excellent raw material as well as the low capital investments required to represent a strong presence in the world market [51].

However, there are serious environmental concerns with the Pidgeon process. The primary source of energy used for the necessary input heat is coal. It is estimated that the heating furnaces and calcination process require 14 – 20 tons of coal per ton of magnesium produced [45]. The global warming impact of the process has been reported as 42 kilograms of carbon dioxide per kilogram of magnesium ingot [49, 60].
2.2.3. Carbothermic Reduction

In recent years, the need for technology promising higher rates of production and lower energy requirements has led to the development of carbothermic reduction. This process begins with magnesium oxide produced by calcined magnesite feedstock. The reaction mechanism is as follows:

\[
\text{MgO}(s) + \text{C}(s) \rightarrow \text{Mg}(g) + \text{CO}(g)
\]  

(Equation 2-8)

The carbon necessary for the reaction could come from a number of sources, including petroleum coke, coal char, charcoal, and graphite.

The carbothermic reduction process has been investigated since World War II with concentration on two primary processing techniques: “quench” and “solvent”. The quench process involves the addition of flux during reduction to promote removal of impurities. Magnesium and carbon dioxide vapors are generated (see \( \text{MgO}(s) + \text{C}(s) \rightarrow \text{Mg}(g) + \text{CO}(g) \) (Equation 2-8) which must be rapidly quenched and collected. A drawback of this approach is avoidance of recombination of the \( \text{Mg}(g) \) and \( \text{CO}(g) \) to form \( \text{MgO} \) (magnesium oxide). Attempting increased rates of quenching resulted in the production a fine powder, further increasing the difficulty of obtaining a pure product.

The second processing technique focuses on separating the steps removing carbon dioxide from the steps of magnesium collection. In this technique, the agglomerated feed enters the reduction stage containing a molten-metal solvent. The molten metal dissolves the reduced magnesium and the carbon dioxide is allowed to naturally escape. The magnesium can then be removed from the solvent under pressure in a vaporization reactor.
Although this appears to be a promising solution, identifying an ideal solvent has proven difficult. Alloys such as lead, tin, and bismuth have been experimented with but all exhibit a tendency to form intermetallic compounds. Research on carbothermic reduction via solvent processing is ongoing, with companies such as CSIRO Minerals investing in process improvement studies [60].

Advantages of the carbothermic reduction process, both the quench and solvent approaches, include lower cost of carbon feedstock as compared to ferrosilicon used in the electrolytic process and reduction in size and cost of capital equipment.

2.3. Recycling

Large magnesium pieces, such as those left when a nesting pattern is cut from a sheet, are easily recycled and require only 5% of the energy needed for the original production process [64]. In 2011, the US Geological Survey reported that 21,000 tons of secondary production was recovered from scrap [50]. In order to make magnesium alloys economically attractive, it will be necessary to recover as much primary alloy as possible.

Swarf, chips, and turnings produced during various secondary operations may have some value as recyclable material, but the value is limited by the added cost of degreasing and drying the chips. Alternatively, chips and swarf can be used for processes allowing for lower purity magnesium, such as the desulphurization of steel.

Contamination is a critical factor in the determination of recyclability. Certain “tramp” elements, especially iron, nickel, and copper cannot be efficiently separated out.
during recycling operations. Tramp elements result in much lower alloy properties, especially corrosion resistance [44, 64].

2.4. Alloy Development

The development of new alloys is driven by the requirements of industry and generally relates to increasing existing properties of magnesium, such as strength at high temperatures. The transportation industry, including aerospace, automotive, and rail, has driven demands for lighter weight materials as emission guidelines become more and more stringent [22, 45]. It has been estimated that each 10% reduction in the weight of a vehicle results in a 5.5% increase in fuel economy. Increases in fuel economy correspond to reduced exhaust gas emissions [46].

High-end automakers have been among the first industries to take advantage of magnesium’s potential for weight-savings. In 1996, the Porsche 911 contained 53 kilograms of cast magnesium alloys. The most commonly targeted components started as non-structural members such as brackets, housings, and instrument panels. However, as technological improvements in alloying have led to higher strength magnesium options, components such as auto body frames, wheels, and seats will be converted [7, 13, 46]. In 2011, wrought and cast magnesium alloys used in structural applications accounted for 40% of the primary metal consumption [50].
2.4.1. Factors Affecting Magnesium Production

The most easily identifiable trends in worldwide magnesium production can be closely related to historical conflicts. During World War II, worldwide production approached 228,000 tons per year. This level would not be reached again for another thirty-five years [22].

Figure 2-9
Worldwide magnesium production trends
Adapted from USGS data [50]

Figure 2-9 illustrates how closely magnesium production has followed conflict and recession. Other factors, such as anti-dumping regulations and tariffs, are also clearly visible in the trend. Magnesium production is currently rising steeply to meet industry demands [20].
2.4.2. Usage

For more than fifty years, Germany was the sole producer of primary magnesium. Early uses for the metal included pyrotechnics and chemical processes such as deoxidation of steel. World War I brought a need for lightweight materials to be used in military aircraft. Production of primary magnesium increased steadily through 1944, but slumped after the war to only 10,000 tons per year.

Germany, Britain, and the United States all produced military aircraft containing large amounts of magnesium alloys both World Wars. In 1937, after only one year of development, German engineers produced a prototype four engine aircraft, the Focke Wulf Condor 200, which contained more than 650 kilograms of magnesium alloys. Other magnesium–containing German models soon followed, including the Messerschmitt 109 and the Heinkel HE-111 [44].

In the United States, the Northrop XP-79 was developed in 1942 with a welded magnesium monococque fuselage to save weight. The US Air Force operated the Convair B-36 bomber from 1949 – 1959. The bomber contained almost 10,000 kilograms of magnesium, earning it the name “Magnesium cloud” (Figure 2-10) [65]. 11% of the airframe weight of the supersonic Northrop T-38 Talon is magnesium. This model is still used by Air Forces of NATO nations, especially for joint training with the US Air Force [48].
In 1934, the British de Havilland Comet flew to Australia in only seventy-one hours. The wheels, wing fairings, and many of the engine components were constructed of magnesium. The Comet is widely recognized as the world’s first commercial jet aircraft [66].

It was the invention of the jet engine that sounded the death knell for the application of magnesium in planes. With significantly greater efficiency and higher thrust relative to propeller drive systems, the jet engine eliminated the need for significant light-weighting efforts by design engineers who were free to apply the heavier aluminum alloys of the day. For the next forty years, the primary usage of magnesium would be as an alloying element in aluminum alloys, with this purpose accounting for more than 44% of applications in 1997 [22, 65, 66].

Figure 2-10
Convair B-36, the “Magnesium Cloud”
2.4.3. Pricing

Due in part to the complex production methods required for magnesium, the metal is more expensive than other primary metals such as aluminum. As China has taken over more of the market share, pricing differences due to production methods have become more evident. China relies almost exclusively on the Pidgeon method, while most Western countries use electrolysis processes.

Table 2-2: China vs. US magnesium pricing
Adapted from USGS data [50]

<table>
<thead>
<tr>
<th>Magnesium Pricing, 2007 - 2011</th>
</tr>
</thead>
<tbody>
<tr>
<td>USD / lb.</td>
</tr>
<tr>
<td>2007</td>
</tr>
<tr>
<td>US Spot Western</td>
</tr>
<tr>
<td>China Free Market</td>
</tr>
</tbody>
</table>

Table 2-2 illustrates the large discrepancy in magnesium pricing between China and the US. This price gap has made it very difficult for Western nations to compete with China. In 2005, the US International Trade Commission (ITC) reviewed duties on magnesium alloy imports from China and Russia and voted to revoke antidumping duties on magnesium imported from Russia. The antidumping duties on magnesium from China were retained. In 2009, a panel was convened by the World Trade Organization (WTO) to investigate allegations by the European Union, Mexico, and the
US regarding export restraints on various metals and minerals in China, including magnesium. The panel found that China failed to justify measures such as export duties and export quotas as legitimate conservation measures, short supply measures, or environmental protection measures. It was further determined that China had enacted requirements such as minimum export price and export licensing which were inconsistent with WTO rules [50].

2.5. Modern Alloys

Cast alloys have always predominated over wrought, particularly in Europe, where traditionally, cast alloys have comprised 85-90% of all magnesium products [44]. Although the Mg-Al-Zn system remains the most widely used, many of the alloys in this series are well over fifty years old. Concerns centering on low mechanical properties and corrosion resistance as well as novel potential applications have driven researchers to develop new chemistry systems and alloy forms. Castings, for example, can be produced in a number of ways, including sand, semi-permanent and permanent mold, and investment casting [22, 26].

The increasing demand for high strength material to be used in structural applications has also led to the development of new alloys for use as wrought materials. In 2005, wrought alloys only accounted for about 1% of magnesium consumption. However, that percentage is anticipated to steadily rise in the next decade [55].

One of the most important advances in new alloy development came early. In 1937, German researchers discovered that zirconium, when used as a magnesium alloying agent, had a strong grain-refining effect. Zirconium and magnesium have very
similar lattice parameters and hexagonal close-packed crystal structures. The saturation of magnesium alloys with zirconium while in the liquid phase leads to a peritectic reaction, which results in the solid α-magnesium phase containing high amounts of zirconium. Alloy systems utilizing zirconium must not contain Al, Si, Fe, Ni, Mn, Sn, Co or Sb. These elements will form zirconium compounds and reduce the solubility of the zirconium. In fact, zirconium has also been successfully used as an iron scavenger, forming iron-zirconium intermetallics in molten magnesium which settle out due to their high density.

Song et al. have demonstrated that a higher concentration of zirconium leads to slower corrosion and lower levels of iron impurities in magnesium alloys. The team tested an alloy with increased levels of zirconium against its standard counterpart in a five day salt spray test per ASTM B117 [70]. The iron content by weight was reduced from 0.013% in the standard alloy, which contained 0.005% by weight zirconium, to 0.004% in the modified alloy, which contained 0.60% by weight zirconium. The corrosion rate, measured in mg/cm²/day, was reduced from 15.65 to 0.31 [28, 45].

Table 2-3 explains the effects of other common alloying elements.
Table 2-3: Effects of alloying elements on magnesium  
Adapted from [25, 45, 67]

<table>
<thead>
<tr>
<th>Alloying element</th>
<th>Weight (%)</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>6 – 10%</td>
<td>Improved strength and hardness</td>
</tr>
<tr>
<td>Beryllium</td>
<td>0.001%</td>
<td>Decreased oxidation of molten magnesium</td>
</tr>
</tbody>
</table>
| Calcium          | 0.3%       | Decreased oxidation of molten magnesium  
                              Increased rollability of sheet products |
| Copper           | 0.05%      | Improved strength at high temperatures; must be used carefully as copper can decrease corrosion resistance if present in excess of 0.05% |
| Iron             | < 0.005%   | Significantly lowers corrosion resistance; 0.005% limit for high-purity alloys |
| Lithium          | 5.5%       | Lowered density, improved formability of wrought products  
                              Increased ductility but lowered strength |
| Manganese        | 0.3 – 1.5% | Iron scavenger; improved salt water resistance |
| Nickel           | < 0.005%   | Significantly lowers corrosion resistance; 0.005% limit for high-purity alloys |
| Rare earth metals| Varies     | Increased strength at elevated temperatures  
                              Reduced weld cracking and porosity in casting alloys |
| Silicon          | Varies     | Increased fluidity in the molten state  
                              Decreased corrosion resistance when iron is present |
| Silver           | Varies     | Improved mechanical properties through increased response to age hardening |
| Thorium          | 2 – 3%     | Increased creep strength at elevated temperatures |
| Tin              | Varies     | Increased ductility when present with aluminum |
| Yttrium          | 4 – 5%     | Increased creep resistance at elevated temperatures |
| Zinc             | Varies     | Increased strength at room temperature when present with aluminum |
| Zirconium        | 0.6%       | Strong grain refinement |
2.5.1. Nomenclature

An international code for designating Mg alloys has yet to be created. There has been a tendency toward adopting the method used by ASTM B275 (Standard Practice for Codification of Certain Nonferrous Metals and Alloys, Cast and Wrought) [41]. In this system, the first two letters indicate the principal alloying elements (refer to Table 2-4). Numbers represent nominal compositions of these elements in weight percent, rounded off to the nearest whole number. Suffix letters A, B, C are chronologically assigned and generally refer to purity improvement. WE43C is an alloy containing approximately four percent yttrium and three percent rare earths.

<table>
<thead>
<tr>
<th>Identifier</th>
<th>Element</th>
<th>Identifier</th>
<th>Element</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Aluminum</td>
<td>N</td>
<td>Nickel</td>
</tr>
<tr>
<td>B</td>
<td>Bismuth</td>
<td>P</td>
<td>Lead</td>
</tr>
<tr>
<td>C</td>
<td>Copper</td>
<td>Q</td>
<td>Silver</td>
</tr>
<tr>
<td>D</td>
<td>Cadmium</td>
<td>R</td>
<td>Chromium</td>
</tr>
<tr>
<td>E</td>
<td>Rare Earths</td>
<td>S</td>
<td>Silicon</td>
</tr>
<tr>
<td>F</td>
<td>Iron</td>
<td>T</td>
<td>Tin</td>
</tr>
<tr>
<td>H</td>
<td>Thorium</td>
<td>V</td>
<td>Gadolinium</td>
</tr>
<tr>
<td>J</td>
<td>Strontium</td>
<td>W</td>
<td>Yttrium</td>
</tr>
<tr>
<td>K</td>
<td>Zirconium</td>
<td>X</td>
<td>Any other</td>
</tr>
<tr>
<td>L</td>
<td>Lithium</td>
<td>Y</td>
<td>Antimony</td>
</tr>
<tr>
<td>M</td>
<td>Manganese</td>
<td>Z</td>
<td>Zinc</td>
</tr>
</tbody>
</table>

Table 2-4: Nomenclature of magnesium alloys [36]
For heat-treated or work-hardened conditions, the designations are specified by ASTM B296, Standard Practice for Temper Designations of Magnesium Alloys, Cast and Wrought [39]. For example, an alloy in the T5 temper has been artificially aged. Table 2-5 explains the treatment for other thermal tempers.

Table 2-5: Temper designations [36, 39]

<table>
<thead>
<tr>
<th>Temper</th>
<th>Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>Cooled and naturally aged to a substantially stable condition</td>
</tr>
<tr>
<td>T2</td>
<td>Annealed (cast products only)</td>
</tr>
<tr>
<td>T3</td>
<td>Solution treated and then cold worked</td>
</tr>
<tr>
<td>T4</td>
<td>Solution heat treated and naturally aged to a substantially stable condition</td>
</tr>
<tr>
<td>T5</td>
<td>Cooled and artificially aged</td>
</tr>
<tr>
<td>T6</td>
<td>Solution heat treated and then artificially aged</td>
</tr>
<tr>
<td>T7</td>
<td>Solution heat treated and then stabilized</td>
</tr>
<tr>
<td>T8</td>
<td>Solution heat treated, cold worked and then artificially aged</td>
</tr>
<tr>
<td>T9</td>
<td>Solution heat treated, artificially aged and then cold worked</td>
</tr>
</tbody>
</table>

2.6. Properties of Magnesium and Its Alloys

Magnesium, in its unalloyed state, has low mechanical properties and is very soft. Table 2-6 contains mechanical data for 99.9 wt% pure magnesium. Varying heat treatments and product forms can have a large impact on mechanical properties.
2.6.1. Alloys Based on the Mg-Al System

One of the earliest identified alloying elements for magnesium was aluminum, providing improved strength and hardness. Zinc, when alloyed in conjunction with aluminum, also increases strength. The alloys in this family are known commonly as “AZ” series. This is still the most widely used alloy family for castings and wrought products.

A crucial development has been the ability to control impurity levels to reduce corrosion rates. Elements such as iron, copper and nickel must be carefully minimized. Another drawback to this system is poor creep resistance at elevated temperatures. The low melting point of the primary phase contributes to grain boundary sliding [46].

2.6.2. Alloys Based on the Mg-Zn System

Mg-Zn alloys are ternary systems with the addition of zirconium for grain refinement and respond well to age-hardening due to finely dispersed precipitates. Examples include ZK30 and ZK60.
It has been found that additions of copper to form the ZC series resulted in increased ductility. Compared to the Mg-Al family, the mechanical properties of Mg-Zn alloys are stable at higher temperatures. Manganese can be added to improve corrosion properties in the ZM series of alloys due to its ability to act as an impurity scavenger and combine with iron [44].

2.6.3. Alloys Based on the Mg-Y System

Mg-Y alloys can be age hardened, have increased corrosion resistance, and high strength at ambient as well as elevated temperatures. In addition, yttrium increases creep resistance at temperatures up to 300°C. A drawback is the higher cost of pure yttrium as an alloying addition compared to aluminum or zinc. However, manufacturers have developed processes to take advantage of mischmetal containing a blend of yttrium and heavy rare earth metals such as gadolinium and erbium to lower expense. The ratio of yttrium to heavy rare earth elements in mischmetal in commercially available alloys is 75 – 80%. [45, 46].

2.7. Corrosion of Magnesium

Magnesium has a natural tendency to form a protective oxide finish when exposed to water, which leads to a dull gray coloration and resists further oxidation. Chlorides, sulfates, and prolonged exposure to moisture can all cause pitting and increased corrosion. Once penetrated, the protective hydroxide film is compromised.

The most common causes of corrosion include poor design, flux inclusions, galvanic couples, and surface contamination. Inadequate surface protection schemes
will also allow corrosion. All of these issues can be overcome with appropriate knowledge and design. The primary purpose of this work is to assess the ability of two coating systems to protect Elektron 43 magnesium alloy [44].

2.7.1. Measuring Corrosion Rate

There are two standard methods for evaluating corrosion rate in magnesium alloys: measurement of weight loss (after salt spray or immersion) and by means of polarization curves to estimate corrosion current density. The weight loss method is generally regarded as more reliable and is used as a standard against which other methods of corrosion rate calculation are measured. The technique is simple and equipment costs are low. However, there is a large chance of experimental error due to the difficulty of retaining all corrosion products when positioning and transporting specimens. Another drawback is that weight loss is simply averaged over the entire specimen and does not provide any insight into the rate of corrosion [28].

The use of polarization curves to measure corrosion current density and extrapolate rate of corrosion is well established with other metals. However, magnesium has been shown by Song et al. to exhibit a non-traditional polarization behavior. The areas of the specimen in which the surface film has been broken could change with applied polarization potential or current density under anodic polarization conditions. Therefore, this method is not recommended for use with magnesium alloys [28].
2.7.2. General Corrosion

In aqueous solutions, an electrochemical reaction results in the dissociation of magnesium with water to produce a crystalline film of magnesium hydroxide and hydrogen gas, as shown in $\text{Mg(s) + 2H}_2\text{O(l)} \rightarrow \text{Mg(OH)}_2 \text{(s) + H}_2\text{(g)}$

(Equation 1-1. The anodic reaction involves the dissolution of magnesium and formation of magnesium hydroxide while the cathodic reaction results in the evolution of hydrogen gas. Hydrogen evolution has been measured at higher rates in areas which are corroding or lack protective film [28].

The anodic reaction is environmentally dependent. Other corrosion products may include sulfite, sulfate compounds, or carbonates. The film formed from this reaction offers considerable surface protection in rural and even some industrial environments (see Figure 2-11). The standard corrosion rate of magnesium lies between that of aluminum and low-carbon steels [55].

![Image of corrosion film formed after salt spray on magnesium alloy](image)

Figure 2-11
Corrosion film formed after salt spray on magnesium alloy
General corrosion can be reduced by utilizing high-purity alloys without introducing flux inclusions. Heavy metal “tramp” elements are especially harmful to corrosion resistance and must be fastidiously avoided during production of high-purity magnesium. Joseph Hanawalt patented a process for supplying a protective atmosphere of carbon dioxide and sulfur hexafluoride to protect magnesium during the molten stage to prevent oxidation [68].

Hanawalt was also part of a team in the early 1940s whose work resulted in the establishment of tolerance limits for heavy metal impurities. Experiments he conducted showed that iron, nickel, and copper are particularly harmful because of their low solid-solubility limits and abilities to serve as active cathodic sites. The corrosion rates of magnesium alloys increased abruptly when the tolerance limits shown in Table 2-7 were exceeded [20, 55, 69].

<table>
<thead>
<tr>
<th>Element</th>
<th>Tolerance (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>5</td>
</tr>
<tr>
<td>Iron</td>
<td>170</td>
</tr>
<tr>
<td>Copper</td>
<td>1300</td>
</tr>
</tbody>
</table>

2.7.3. Galvanic Corrosion

Attack resulting from galvanic corrosion has the potential to be the most detrimental in terms of the impact to satisfactory performance of magnesium components. Two conditions must be satisfied for galvanic corrosion to occur: i) dissimilar metal-to-metal contact and ii) bridging of the bimetal junction by a conductive
solution (electrolyte). Because magnesium has the lowest corrosion potential of all structural metals (see Table 1-1), it will act as the anode. Therefore, magnesium will always corrode preferentially in any galvanic couple.

Poor design and assembly practices which result in unprotected contact between magnesium and another metal can lead to galvanic corrosion. Contact between magnesium and a heavy metal such as iron results in the creation of a completed circuit, with the magnesium corroding preferentially, as illustrated in Figure 2-12 [14, 28].

![Figure 2-12](image)

**Figure 2-12**
Galvanic corrosion of magnesium adjacent to steel fastener

For outdoor use or use in areas where magnesium might come into contact with dissimilar metals and electrolytes, precautions against galvanic attack must be taken. In an aircraft cabin, components are often joined, welded, and butted with dissimilar materials. Cleaning products and spillage of liquids such as juices, alcohols, or sodas can provide the electrolytes. Therefore, it is necessary that magnesium designated for use in aircraft cabins be appropriately protected.
Section 3 will present the results of current research and Section 4 will provide recommendations for standard protective coatings. Design factors must also be considered. When magnesium is joined with another metal, the metal selection should be as near the corrosion potential of magnesium as possible. Coatings such as cadmium or zinc can be used on fasteners to reduce the galvanic corrosion to one tenth the rate. Modified zinc coatings with additional chromate coatings or silicate treatments can further reduce the potential for attack. Aluminum alloys which contain magnesium, in particular the 5000 series, are least severely attacked in chloride media when galvanically coupled.

Assembly techniques can also be leveraged to protect against galvanic corrosion. Faying surface seals are composed of a layer of appropriate sealant sandwiched between two fastened mating surfaces (Figure 2-13). The sealant serves to protect moisture entry. Appropriate sealants for magnesium include polysulfide, epoxy resins, plastic tapes, and non-acidic silicone RTVs.

![Faying surface seal](image)

Figure 2-13
Faying surface seal

Vinyl tapes can be used to separate magnesium from common electrolytes or dissimilar metals. However, the best design practice is to eliminate the electrolytes. This can be accomplished through the addition of drains or shields to prevent liquid entrapment at the dissimilar metal junction. Raised bosses can also be utilized for
screw or bolt installation to keep the metal junction above liquid level. Nylon or materials which are impermeable to moisture should be used for washers, spacers, and gaskets to separate the dissimilar fastener from the metal substrate. The area or dissimilar metal which is exposed can be reduced through the use of studs in place of bolts, where possible.

It is important to note that, especially in the aerospace industry, dissimilar metals are not the only potentially conductive mating component. More airframes and primary interior components are now being constructed using carbon fiber reinforced plastic. The conductivity of carbon also results in anodic corrosion of magnesium. Therefore, both surfaces should be protected [51, 27].

2.7.4. Localized Attack

Localized corrosion is characterized by the breakdown of a passive film which leads to localized attack. The process generally occurs when the relative area ratios of the anode and cathode are small and the electrolyte is weak. This is the corrosion form typically seen on single-phase exposed magnesium alloys without galvanic coupling [20]. Localized corrosion can be split into four distinct categories: Pitting, crevice, intergranular, and filiform corrosion.

2.7.4.1. Pitting

When a smooth machined surface becomes corroded, the surface is roughened by the chemical action. In atmospheric attack, this roughening is a microscopic form of pitting. The two primary wrought magnesium systems exhibit difference in the
appearance of the pits. In Mg-Al systems, the pits in the exposed surface area tend to be narrow and relatively deep. The pits are wider and tend to overlap with a slightly wavy appearance in magnesium alloys containing zirconium.

The corrosion rate can be increased when tramp materials are engrained on the surface of a magnesium alloy. The tramp elements lead to a breakdown in the protective film, lowering passivity. Stable corrosion pits initiate at flaws near the intermetallic particles. An electrolytic cell is then formed wherein the intermetallic particle acts as the cathode and the magnesium matrix as the anode. The α-magnesium matrix will corrode preferentially, leaving the cathodic intermetallics along the grain boundaries [14].

2.7.4.2. Crevice Corrosion

Crevice corrosion is observed when moisture is retained in a crevice. The inability of the moisture to evaporate leads to increased corrosion of the metal in the narrow recess over extended periods. The actual corrosion mechanism is due to the development of an anodic region within the crevice because of the exclusion of oxygen. This results in the acidification of the solution at the tip of the crevice due to the presence of excess H\(^+\) ions that evolve as MgOH is formed, which accelerates the corrosion rate (Figure 2-14) [44].
2.7.4.3. Intergranular Corrosion

Intergranular corrosion occurs at grain boundaries and is due to the precipitation of a secondary phase (see Figure 2-15). Since magnesium is the most anodic structural metal, the grain boundary constituent is invariably cathodic to the grain boundary. Therefore, the corrosion of magnesium alloys is concentrated on the grains. It has been suggested that this form of corrosion in magnesium alloys should be referred to as “granular corrosion” [44].
However, some studies suggest that magnesium can, in fact, experience true intergranular corrosion when cathodic alloying precipitates are exposed to mild corrosive media, such as sodium chloride. In these cases, corrosion attacks along the grain boundaries and forms narrow but deep paths [14].

2.7.4.4. Filiform corrosion

Filiform corrosion is generally associated with metals which have had a protective coating applied. The coating allows water and oxygen to migrate through to the substrate. Dissolved oxygen becomes concentrated near the “tail”, becoming cathodic. The “head” region is depleted of oxygen and becomes anodic. Thus active microgalvanic cells are created across the surface of the metal. This leads to a directionality of the corrosion product in which narrow semicylindrical corrosion filaments radially propagate. The corrosion products form under the surface of the coating, eventually leading to bulges in the coating. Filiform corrosion occurs in tandem
with pitting, though there is disagreement among researchers whether the pits initiate the filiforms or vice versa (Figure 2-16).

Figure 2-16  
Filiform corrosion

Filiform corrosion does not occur on bare pure magnesium. This phenomenon, therefore, illustrates the impact that alloying elements can have on corrosion control and behavior. Other variables, such as temperature, material structure, type and number of coatings, and polarization of the microgalvanic cell also influence the rate of filiform corrosion [14, 44].

2.7.5. Stress Corrosion Cracking

Stress corrosion cracking is the mechanism by which cracks form in a metal due to contact with a corrosive environment. The word ‘corrosive’ can be deceptive, however, as stress corrosion cracking has occurred in moist air and pure water. However, the crack formation is generally noted to have occurred due to exposure with dilute aqueous compounds. Uhlig has identified the following compounds which can impact magnesium, given in order of decreasing severity [44]:
• Sodium bromide, NaBr
• Sodium sulphate, Na$_2$SO$_4$
• Sodium chloride, NaCl
• Sodium nitrate, NaNO$_3$
• Sodium carbonate, Na$_2$CO$_3$
• Sodium acetate, NaC$_2$H$_3$O$_2$
• Sodium fluoride, NaF
• Sodium phosphate dibasic, Na$_2$HPO$_4$

In magnesium alloys, stress corrosion cracking is generally transgranular and includes significant branching (secondary crack formations). This is due to the hexagonal close packed crystal structure, which has less slip systems available and are therefore susceptible to cleavage. Mixed transgranular and intragranular cracking have also been observed. Crack initiation occurs at corrosion pits.
Stress corrosion cracking is directly related to stress sources such as welding, inserts, and structural loading. This makes SCC one of the most significant issues to be overcome for magnesium use in structural applications. It has been shown that SCC can initiate in load conditions equivalent to just 30% of the yield stress of the material, although the relation is not yet completely understood.

There exist a number of recommended design and assembly practices which have the potential to reduce SCC in magnesium alloys. Constant stresses which will be applied over long periods of time should be limited to 30 - 50% of the yield strength in normal atmospheric environments. Tensile residual stresses from welding should be mediated by application of a low-temperature thermal stress relief treatment.

During the design phase of magnesium alloy components, care must be taken to avoid high local stresses due to bolted or riveted joints. When possible pre-formed
parts should be used. Overtorquing of bolts must be avoided and adequate spacing and edge margins should be provided for rivets.

Shot peening and other mechanical processes may be effective in increasing SCC resistance. However, care must be taken to ensure that parts are appropriately cleaned afterwards so that heavy metal contamination does not lead to increased galvanic corrosion. Coatings may extend life but will not totally prevent SCC due to reduced protection resultant from breaks in the coating. Application of multiple coatings is strongly advised.

Alloys in the Mg-Al family have shown to have higher susceptibility to stress corrosion cracking than other magnesium families. Mg-Zn alloys have intermediate susceptibility while alloys that contain neither zinc nor aluminum are the most resistant. Newer alloys such as those containing yttrium and zirconium have not yet been fully studied for susceptibility to stress corrosion cracking. More work is needed in this area before a conclusion can be reached regarding level of susceptibility [14, 20, 44]
2.8. Elektron 43 (WE43C)

The driving factors for magnesium alloys in aerospace – increased creep resistance at elevated temperatures, improved corrosion resistance, and improved mechanical properties - led to the development of WE43. The chemical composition, as shown in Table 2-8, is now in the third iteration. WE43C-T5 has received specification SAE AMS4371 [35]. The alloy has been branded by its developer, Magnesium Elektron, as Elektron™ 43. This report will refer to the alloy as Elektron 43 [36].

Table 2-8: Chemical composition limits (weight percent)

<table>
<thead>
<tr>
<th>Element</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Element</th>
<th>Minimum</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>Balance</td>
<td>Balance</td>
<td>RE</td>
<td>0.3</td>
<td>1.0</td>
</tr>
<tr>
<td>Cu</td>
<td></td>
<td>0.02</td>
<td>Y</td>
<td>3.7</td>
<td>4.3</td>
</tr>
<tr>
<td>Gd + Dy + Er</td>
<td>0.3</td>
<td>1.0</td>
<td>Zn</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>0.005</td>
<td></td>
<td>Zr</td>
<td>0.2</td>
<td>1.0</td>
</tr>
<tr>
<td>Li</td>
<td></td>
<td>0.05</td>
<td>Sm</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td></td>
<td>0.03</td>
<td>Yb</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>Nd</td>
<td>2.0</td>
<td>2.5</td>
<td>Other</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>0.002</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.9. Treatment of Elektron 43

Elektron 43 is well suited for age hardening due to the yttrium and rare earth content. It has been reported that the intermetallics formed through these treatments exhibit little diffusivity and a good coherence to the matrix [3]. The Elektron 43 alloy can be utilized as either cast or wrought material.
The phase diagram of the Mg-Y-Nd system provides some insight into the high strength properties of Elektron 43. Binary compounds of Mg-Nd and Mg-Y are able to form in equilibrium with the magnesium solid solution. Maximum strength is achieved through age-hardening treatments. For the wrought alloy, the T5 temper has been explored in this work.

Yu et al. have reported the impact of the T5 heat treatment on the mechanical properties of this system. Their team found that hot rolled alloy with a T5 temper exhibited an increase in tensile strength. Further, the precipitates in the T5 temper material were smaller than material treated to T6 temper. Overall, the hot rolled alloy samples with a T5 temper were found to have the maximum tensile strength in the same condition as when they have the maximum hardness value [5].
3.1. Sample Preparation

A total of fifteen samples were tested for each alloy: three surface conditions with five samples per group. The samples were numbered for testing, with “M” representing magnesium alloy Elektron 43 and “A” designating aluminum alloy 7075. The numbers 1 – 15 identify the sample number and follow the alloy designation.

Table 3-1: Sample Preparation

<table>
<thead>
<tr>
<th>Group</th>
<th>Pre-treatment</th>
<th>Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1 – M5</td>
<td>Solvent wipe</td>
<td>None; bare</td>
</tr>
<tr>
<td>A1 – A5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M6 – M10</td>
<td>Solvent wipe, hot water or</td>
<td>Trivalent chromate coat</td>
</tr>
<tr>
<td>A6 – A10</td>
<td>chemical clean</td>
<td></td>
</tr>
<tr>
<td>M11 – M15</td>
<td>Solvent wipe, hot water or</td>
<td>Trivalent chromate coat + TGIC Powder coat</td>
</tr>
<tr>
<td>A11 – A15</td>
<td>chemical clean</td>
<td></td>
</tr>
</tbody>
</table>

All samples within each group were treated on the same day and at the same facilities.
3.2. Salt Spray

A 5 +/- 1% by weight sodium chloride solution in a pH range of 6.5 - 7.2 was atomized as a fog into a heated cabinet maintained at 35° C (see Figure 3-1). The samples were placed into the chamber at an angle 15 - 30° from the vertical and tested for a specified amount of time. In this case, all samples were tested for 96 hours per ASTM B117 [70]. Following the test, the samples were rinsed in deionized water not warmer than 38° C and allowed to air dry. The panels were then visually examined for signs of corrosion and assessed according to the criteria specified. The pass / fail criteria for this test were established using MIL-DTL-5541, "Military Specification, Chemical Conversion Coatings on Aluminum and Aluminum Alloys [73]," as a guideline and were as follows:

- No more than five isolated spots or pits per test specimen OR no more than fifteen isolated spots or pits on combined surface of all five specimens
- Spots or pits must not exceed 0.031” in diameter

All samples were tested during the same time period at the same test facility.
3.3. Powder Coat Thickness

To verify that the powder coat treatment was applied according to specification, three samples were chosen for non-destructive thickness testing. An electric probe per ASTM B244 was utilized for the measurements. Eight measurements per panel were taken and the average value was reported. For components used in aircraft cabin interiors, the thickness required for powder coat paint is 0.002 – 0.005 inches.
3.4. Adhesion Testing

Three additional samples of each alloy were processed with the powder coat group of samples. These samples underwent destructive testing to verify adhesion of the coating per Method B of ASTM D3359. In this test, three grid patterns are scribed into the surface of the coating, each with eleven cuts one millimeter apart. 3M 250 tape is applied over the scribe marks and smoothed in place to ensure good contact.

The tape is then removed in one smooth motion at an angle of 180° from the face of the sample. The sample as well as the tape is visually examined for intercoat separation and any adhesion loss was rated per the ASTM standard. The pass / fail criteria for this test was determined to include an allowance for small flakes of the coating to detach at grid intersections; however, less than ten percent of the surface area was allowed to be affected.

3.5. Polishing

Samples of Elektron 43 were received bare, with no surface treatment. The samples were polished using silicon carbide discs on an Allied M-prep with decreasing grit size to 1200 (see Figure 3-2). This treatment was followed by polishing with 3 micron, then 1 micron diamond paste using a low-nap, flocked cloth disc and polishing lubricant. The samples were then dipped in ethanol to remove any residue, cleaned in an ethanol ultrasonic bath, and dried using compressed air.
3.6. Optical Microscopy

Following polishing, samples were examined using a Nikon Eclipse ME600 optical microscope (see Figure 3-3. The grain boundaries were observed at the 100 µm level.
3.7. Environmental Scanning Electron Microscopy

The primary evaluation of microstructure was accomplished on a FEI Quanta environmental scanning electron microscope (ESEM) equipped with energy dispersive X-ray spectroscopy (EDS, see Figure 3-4). Backscattered electron (BSE) detector coupled with the EDS allows for phase identification at high pressures.

Accelerating voltage for analysis was primarily 15 kV, with limited use of higher voltage when necessary to penetrate deeper into the sample. Magnesium is considered a “soft” metal and it was found that 15 kV was generally sufficient to penetrate the surface, even for applications like BSE and EDS.

Figure 3-4
FEI Quanta ESEM with EDS
CHAPTER 4

RESULTS AND DISCUSSION

4.1. Results of Testing: Salt spray

Within the same groups (surface treatments), there was very little difference in performance between the magnesium and aluminum samples. This was an unexpected result, as it was widely believed that the aluminum samples would perform better than the magnesium when coated with trivalent chromate.

In the bare samples, both alloys suffered more than five spots or pits per sample as well as exhibiting at least one spot or pit greater than 0.031” in diameter. The samples which had received trivalent chromate treatment performed the same, except that none of the spots or pits noted in the aluminum group was larger than 0.031” in diameter.

Interestingly, the samples coated with TGIC powder coat also performed in a very similar fashion. There were no pits or spots noted on any of the samples for either alloy. In the figures below, it can be seen that a small amount of general corrosion developed near holes which were drilled in the magnesium samples to allow for the sample to be hung during the powder coat process (refer to Figure 4-12). However, according to MIL-DTL-5541, “holding points during processing or salt spray exposure shall be excluded” from evaluation [73]. The corrosion products were limited to general corrosion and no spots or pits were noted in these areas.
<table>
<thead>
<tr>
<th>Sample ID</th>
<th># of spots / pits</th>
<th>spots / pits &gt; 0.031&quot; diameter (all five samples)</th>
<th>Pass / Fail</th>
<th>Surface Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>&gt;5</td>
<td>Yes, at least one</td>
<td>Fail</td>
<td>None; bare</td>
</tr>
<tr>
<td>M2</td>
<td>&gt;5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M3</td>
<td>&gt;5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M4</td>
<td>&gt;5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M5</td>
<td>&gt;5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M6</td>
<td>&gt;5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M7</td>
<td>&gt;5</td>
<td></td>
<td></td>
<td>Trivalent chromate coat</td>
</tr>
<tr>
<td>M8</td>
<td>&gt;5</td>
<td>Yes, at least one</td>
<td>Fail</td>
<td></td>
</tr>
<tr>
<td>M9</td>
<td>&gt;5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M10</td>
<td>&gt;5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M11</td>
<td>None</td>
<td></td>
<td></td>
<td>Trivalent chromate coat + TGIC powder coat</td>
</tr>
<tr>
<td>M12</td>
<td>None</td>
<td></td>
<td>Pass</td>
<td></td>
</tr>
<tr>
<td>M13</td>
<td>None</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M14</td>
<td>None</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M15</td>
<td>None</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**Table 4-2: Results of salt spray testing – 7075 aluminum**

<table>
<thead>
<tr>
<th>Sample ID</th>
<th># of spots / pits</th>
<th>spots / pits &gt; 0.031” diameter (all five samples)</th>
<th>Pass / Fail</th>
<th>Surface Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>&gt;5</td>
<td>Yes, at least one</td>
<td>Fail</td>
<td>None; bare</td>
</tr>
<tr>
<td>A2</td>
<td>&gt;5</td>
<td></td>
<td></td>
<td>None</td>
</tr>
<tr>
<td>A3</td>
<td>&gt;5</td>
<td></td>
<td></td>
<td>None</td>
</tr>
<tr>
<td>A4</td>
<td>&gt;5</td>
<td></td>
<td></td>
<td>None</td>
</tr>
<tr>
<td>A5</td>
<td>&gt;5</td>
<td></td>
<td></td>
<td>None</td>
</tr>
<tr>
<td>A6</td>
<td>&gt;5</td>
<td></td>
<td></td>
<td>None</td>
</tr>
<tr>
<td>A7</td>
<td>&gt;5</td>
<td></td>
<td></td>
<td>None</td>
</tr>
<tr>
<td>A8</td>
<td>&gt;5</td>
<td>None</td>
<td>Fail</td>
<td>Trivalent chromate coat</td>
</tr>
<tr>
<td>A9</td>
<td>&gt;5</td>
<td></td>
<td></td>
<td>None</td>
</tr>
<tr>
<td>A10</td>
<td>&gt;5</td>
<td></td>
<td></td>
<td>None</td>
</tr>
<tr>
<td>A11</td>
<td>None</td>
<td></td>
<td></td>
<td>Trivalent chromate coat + TGIC powder coat</td>
</tr>
<tr>
<td>A12</td>
<td>None</td>
<td></td>
<td>Pass</td>
<td></td>
</tr>
<tr>
<td>A13</td>
<td>None</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A14</td>
<td>None</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A15</td>
<td>None</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 4-1
M1 – M5, L to R, before

Figure 4-2
M1 – M5, L to R, after

Figure 4-3
M6 – M10, L to R, before

Figure 4-4
M6 – M10, L to R, after

Figure 4-5
M11 – M15, L to R, before

Figure 4-6
M11 – M15, L to R, after
Figure 4-7
M1, Bare; before

Figure 4-8
M1, Bare; after

Figure 4-9
M8, Trivalent chromate coat, before

Figure 4-10
M8, Trivalent chromate coat, after

Figure 4-11
M11, Trivalent chromate coat + TGIC powder coat, before

Figure 4-12
M11, Trivalent chromate coat + TGIC powder coat, after
Figure 4-13
A1 – A5, L to R, before

Figure 4-14
A1 – A5, L to R, after

Figure 4-15
A6 – A10, L to R, before

Figure 4-16
A6 – A10, L to R, after

Figure 4-17
A11 – A18, L to R, before

Figure 4-18
A11 – A18, L to R, after
4.2. Results of Testing: Coating Thickness

The results of the thickness testing are given in Table 4-3. The value given is the average of eight readings per panel. Thickness measurements were taken prior to salt spray testing. All samples measured met the required thickness.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Measured thickness (inches)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesium, M11</td>
<td>0.0023</td>
</tr>
<tr>
<td>Magnesium, M12</td>
<td>0.0027</td>
</tr>
<tr>
<td>Magnesium, M13</td>
<td>0.0022</td>
</tr>
<tr>
<td>Aluminum, A11</td>
<td>0.0020</td>
</tr>
<tr>
<td>Aluminum, A12</td>
<td>0.0022</td>
</tr>
<tr>
<td>Aluminum, A13</td>
<td>0.0026</td>
</tr>
</tbody>
</table>

Table 4-3: Powder coat thickness
One magnesium sample, M12, was chosen at random for verification and the thickness of the powder coat was measured using the FEI Quanta environmental scanning electron microscope. The coating was measured at ~68 µm, which equates to ~0.0027 inches. The average of the original readings, before salt spray, was 0.0027 inches. The verification reading was taken after salt spray and shows that there was virtually no change in the thickness of the coating.

Figure 4-25
M12, powder coat thickness verification
4.3. Results of Testing: Coating Adhesion

The results are given in Table 4-4. In the ASTM standard, adhesion loss is rated on a scale of 1B to 5B, with 1B representing complete separation and 5B representing no separation. All tested samples were scored with a 5B.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Result</th>
<th>Score</th>
<th>Pass / Fail</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesium, M16</td>
<td>Edges are completely smooth</td>
<td>5B</td>
<td>Pass</td>
</tr>
<tr>
<td></td>
<td>No squares detached</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Magnesium, M17</td>
<td>Edges are completely smooth</td>
<td>5B</td>
<td>Pass</td>
</tr>
<tr>
<td></td>
<td>No squares detached</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Magnesium, M18</td>
<td>Edges are completely smooth</td>
<td>5B</td>
<td>Pass</td>
</tr>
<tr>
<td></td>
<td>No squares detached</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aluminum, A16</td>
<td>Edges are completely smooth</td>
<td>5B</td>
<td>Pass</td>
</tr>
<tr>
<td></td>
<td>No squares detached</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aluminum, A17</td>
<td>Edges are completely smooth</td>
<td>5B</td>
<td>Pass</td>
</tr>
<tr>
<td></td>
<td>No squares detached</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aluminum, A18</td>
<td>Edges are completely smooth</td>
<td>5B</td>
<td>Pass</td>
</tr>
<tr>
<td></td>
<td>No squares detached</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 4-26
M16, before

Figure 4-27
M16, after

Figure 4-28
M17, before

Figure 4-29
M17, after

Figure 4-30
M18, before

Figure 4-31
M18, after
4.4. Results of Optical Microscopy

Figure 4-38 shows the distribution of precipitates throughout the single –phase α-magnesium matrix. The grain boundaries are regular and clearly defined. The scale bar is set at 100 μm.

Figure 4-38
Precipitate distribution
4.5. Results of Environmental Scanning Electron Microscopy

Analysis began with the goal of verifying the reported chemistry of the Elektron 43 alloy. Unique microstructures were located using ESEM, then the surface was mapped using EDS. Figure 4-39 depicts an arrangement of three cubic precipitates, some of which are located on grain boundaries.

![Cubic precipitates](image)

**Figure 4-39**
Cubic precipitates

Scanning the structure against known elemental composition resulted in positive identification of the cubic particles enriched in yttrium and zirconium.

![Magnesium matrix](image)
![Yttrium precipitates](image)
![Zirconium precipitates](image)

**Figure 4-40**
Magnesium matrix

**Figure 4-41**
Yttrium precipitates

**Figure 4-42**
Zirconium precipitates
In other images, precipitates with spherical morphology could be seen (Figure 4-43). Analysis of these areas revealed these structures to be composed primarily of neodymium and yttrium.

![Spheroidal precipitates](image)

**Figure 4-43**
Spheroidal precipitates

**Table 4-5: Elemental composition of spheroidal precipitate**

<table>
<thead>
<tr>
<th>Element</th>
<th>% weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>84.63</td>
</tr>
<tr>
<td>Y</td>
<td>11.44</td>
</tr>
<tr>
<td>Zr</td>
<td>0.68</td>
</tr>
<tr>
<td>Nd</td>
<td>3.25</td>
</tr>
</tbody>
</table>
The cubic precipitates in Figure 4-43 were also analyzed and determined to have the composition shown in Table 4-6. The cubic precipitates appear to be almost entirely composed of yttrium.

Table 4-6: Elemental composition of cubic precipitate

<table>
<thead>
<tr>
<th>Element</th>
<th>% weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>38.79</td>
</tr>
<tr>
<td>Y</td>
<td>55.34</td>
</tr>
<tr>
<td>Zr</td>
<td>0.80</td>
</tr>
<tr>
<td>Nd</td>
<td>5.07</td>
</tr>
</tbody>
</table>

Figure 4-44 shows the tendency of the precipitates to emerge at grain boundaries.

Figure 4-44
BSE image illustrating dynamic recrystallization
Figure 4-45 illustrates the uniformity of precipitates.

Figure 4-45
Parallel precipitates
In general, the grains can be seen to be very uniform throughout the single phase $\alpha$-magnesium matrix.

Figure 4-46
Uniform structure of matrix
4.5.1. Analysis following Salt Spray Testing, Bare Samples

Following salt spray testing, the samples with the most evidence of corrosion products were selected for additional analysis. Squares were cut from the corners of samples from each surface coating condition: bare, trivalent chromate treatment, and trivalent chromate treatment plus powder coat.

Figure 4-47
M2, bare: Corrosion products
As shown in Figure 4-48, the overall scan of the M2 sample revealed magnesium oxide as the primary corrosion product. At the microscopic level, magnesium oxide has a needle-like appearance. Magnesium hydroxide is also present, in the form of plates. Sodium and chlorine from the sodium chloride solution were also detected.

Figure 4-48
Chemical analysis of corrosion products – sample M2
The crevice shown in the bottom left of Figure 4-47 was selected for further analysis. Within the crevice, the percentages of sodium and chlorine were found to be very slightly higher than on the overall sample. The amount of magnesium within the crevice was slightly less than the average. Other elements remained proportionally equivalent.

This finding indicates that the sodium chloride solution was able to penetrate the magnesium matrix, initially via a pitting mechanism.

![Figure 4-49](image)

**Figure 4-49**
Crevice in sample M2

![Figure 4-50](image)

**Figure 4-50**
Chemical analysis of corrosion products in crevice – sample M2
An interesting phenomena was observed in a different area of the M2 sample. A precipitate rich in zirconium and yttrium appeared to impede the formation of corrosion products. This behavior has been documented in zirconium-enriched MEZ alloys by Song [28].

Although the impedance of the corrosion products would initially appear to be a positive reaction, it must also be noted that the protective film afforded by those products is lost. Figure 4-51 clearly shows an area in the upper left hand corner which has begun to exhibit the characteristic waviness and overlapping of pitting seen in Mg-Zr alloys.
4.5.2. Analysis following Salt Spray Testing, Trivalent Chromate Samples

The samples from the second group, which had received a trivalent chromium coating, displayed a thicker layer of corrosion products. The characteristic needle-like structure of magnesium oxide and plates of magnesium hydroxide are still clearly visible in Figure 4-52.

Figure 4-52
Corrosion products, sample M9, trivalent chromium coating
The chemical analysis of the overall area of the sample verifies these observations (Figure 4-53). A greater concentration of corrosion products was observed. Interestingly, traces of yttrium and zirconium, which were not seen in the analysis of the bare samples, are also observed.

Figure 4-53
Chemical analysis of sample M9
The sample treated with trivalent chromate exhibited the characteristic cracking of the film with the corrosion products on the surface (Figure 4-54).

Figure 4-54
Cracking of trivalent chromate film
Figure 4-55
Trivalent chromate coating on magnesium, no salt spray testing
Image credit: Dr. Bruce Davis, MEL

Figure 4-56
Trivalent chromate coating on magnesium, after salt spray testing

Figure 4-55 and Figure 4-56 illustrate the appearance of the trivalent chromate film without salt spray testing and following salt spray testing, respectively. EDS measurements of the surface reveal the chromium and fluorine components of the chemical film (ref. Table 4-7). The presence of these elements verifies that the film is still present on the sample following salt spray testing.

Table 4-7: Chemical analysis of cracks in sample M9

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Element</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>10.86</td>
<td>Y</td>
<td>6.46</td>
</tr>
<tr>
<td>O</td>
<td>41.65</td>
<td>Zr</td>
<td>4.97</td>
</tr>
<tr>
<td>F</td>
<td>1.71</td>
<td>Cl</td>
<td>2.92</td>
</tr>
<tr>
<td>Na</td>
<td>0.89</td>
<td>Cr</td>
<td>2.57</td>
</tr>
<tr>
<td>Mg</td>
<td>27.97</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4.5.3. Analysis following Salt Spray Testing, Powder Coated Samples

Analyzing the powder coated samples proved to be a challenge as standard voltage accelerations destroyed the coating. Lowering the voltage acceleration did not allow a clear image capture. Therefore, the primary information available is EDS data. Figure 4-57 was captured using only 2.4 kV; therefore the figure lacks detail. It was also difficult to assess the sample at high levels of magnification due to the deleterious effect on the coating surface.

![Figure 4-57](image)

**Figure 4-57**
Sample M12, powder coated
Even with the challenges faced in analyzing the powder coated sample, valuable data was captured. Figure 4-58 illustrates the very low rate of magnesium detected. Carbon, oxygen, nitrogen, aluminum, and silicon are all components of the TGIC powder coat chemistry. At 0.60 weight percentage, the magnesium value detected is negligible.

Figure 4-58  
Chemical analysis of powder coated sample M9
CHAPTER 5
CONCLUSION

5.1. Summary

It was shown that the magnesium alloy Elektron 43 performed at the same level of corrosion resistance of aluminum alloy 7075-T651 for all three surface conditions: bare, trivalent chromate coated, and trivalent chromate coated plus powder coated. Both alloys exhibited similar corrosion patterns of pitting in the bare and trivalent chromate treated conditions. In the samples which were treated with trivalent chromate plus powder coat, the corrosion products were negligible for both alloys.

Adhesion testing showed that the trivalent chromate coating formed an excellent substrate for the powder coat. All samples were rated at the highest level; no loss of protective coating was observed.

Analysis of the Elektron 43 alloy prior to testing was accomplished using a FEI Quanta ESEM equipped with EDS. The alloy composition was verified to meet the manufacturer’s specifications overall. It was determined that the artificial aging process resulted in a multi-phase material containing α-magnesium matrix, yttrium/zirconium cuboids and yttrium/neodymium precipitates. The grains were recrystallized and evenly distributed. Cubic particles mostly located along grain boundaries were determined to be primarily composed of yttrium. A smaller number of spheroid precipitates were observed and determined to be composed of yttrium and neodymium.

The Elektron 43 samples were also examined following salt spray testing. On the bare samples, the corrosion products were composed of magnesium oxide and magnesium hydroxide. The lack of the protective films resulted in pitting.
The samples which received a trivalent chromate coating exhibited the same corrosion products, but in thicker sections. EDS revealed the presence of fluorine and chromium from the damaged coating.

The samples which received a trivalent chromate coating as well as powder coat performed very well. No pitting, cracks, or other corrosion was evident. Corrosion products were limited to areas that had not been protected, such as tooling holes. The surface of the powder coated sample exhibited no build-up of corrosion products. EDS analysis verified this observation, with the amount of detected magnesium substrate being negligible.

5.2. Recommendations

The results of the analysis on both the bare and trivalent chromate coated samples indicates that it is absolutely necessary for magnesium alloys to have a more robust and protective coating than trivalent chromate alone. The trivalent chromate coating did not prevent the build-up of corrosion products such as magnesium oxide; however, it did serve as an excellent substrate for adhesion of the powder coating.

The results for the samples which were treated with chromate conversion coating plus powder coating were excellent. The adhesion of the coating was found to be outstanding. No corrosion products were detected on the protected surface of the samples. There was no evidence of any cracking or pitting. Further, the surface maintained aesthetic appearance following testing; an important consideration for aircraft interior components.
These results suggest that, in terms of corrosion, Elektron 43 can easily be treated with industry standard coatings (trivalent chromate and TGIC powder coating) and likely will meet the requirements for usage in aircraft cabin interiors. It is cautioned that, even with excellent protective coatings, dissimilar metal contact and liquid entrapment should be eliminated during the design phase.
APPENDIX

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