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Protective coatings on magnesium and its alloys — a critical review

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Abstract

Magnesium and its alloys have excellent physical and mechanical properties for a number of applications. In particular its high strength/weight ratio makes it an ideal metal for automotive and aerospace applications, where weight reduction is of significant concern. Unfortunately, magnesium and its alloys are highly susceptible to corrosion, particularly in salt-spray conditions. This has limited its use in the automotive and aerospace industries, where exposure to harsh service conditions is unavoidable. The simplest way to avoid corrosion is to coat the magnesium based substrate to prevent contact with the environment. This review details the state of the art in coating and surface modification technologies, applied to magnesium based substrates for improved corrosion and wear resistance. The topics covered include electrochemical plating, conversion coatings, anodizing, gas-phase deposition processes, laser surface alloying/cladding and organic coatings.

Keywords

- A. Surfaces and Interfaces
- A. Thin Films
- A. Metals
- D. Electrochemical Reactions
- B. Vapor Deposition

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1. Introduction

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

Unfortunately, magnesium has a number of undesirable properties including poor corrosion and wear resistance, poor creep resistance and high chemical reactivity that have hindered its widespread use in many applications. One of the main challenges in the use of magnesium, particularly for outdoor applications, is its poor corrosion resistance. Magnesium and its alloys are extremely susceptible to galvanic corrosion, which can cause severe pitting in the metal resulting in decreased mechanical stability and an unattractive appearance. Corrosion can be minimized by the use of high purity alloys that maintain heavy metal impurities such as iron, nickel and copper below a threshold value. The elimination of bad design, flux inclusions, surface contamination, galvanic couples and inadequate or incorrectly applied surface protection schemes can also significantly decrease the corrosion rate of magnesium alloys in service (3).

One of the most effective ways to prevent corrosion is to coat the base material. Coatings can protect a substrate by providing a barrier between the metal and its environment and/or through the presence of corrosion inhibiting chemicals in them. In order for a coating to provide adequate corrosion protection, the coating must be uniform, well adhered, pore free and self-healing for applications where physical damage to the coating may occur. One of the problems with magnesium is its chemical reactivity. As soon as it comes in contact with air or water an oxide/hydroxide layer forms on the surface which can have a detrimental effect on coating adhesion and uniformity. Thus, the pre-cleaning process plays a critical role in the development of a good protective coating on magnesium and its alloys.

There are a number of possible coating technologies available for magnesium and its alloys, each with their own advantages and disadvantages. The purpose of this review is to provide a clear picture of the technologies currently available.

2. Coating Technologies – State of the Art

There are a number of technologies available for coating magnesium and its alloys. These include electrochemical plating, conversion coatings, anodizing, hydride coatings, organic coatings and vapor-phase processes. Each of these will be described in detail in the following sections. In this review the term magnesium is used to refer to magnesium and its alloys unless otherwise specified. The chemical composition of some common magnesium alloys is listed in appendix 1.

2.1. Electrochemical Plating

It is often desirable to alter the surface properties of a workpiece in order to improve its corrosion and wear resistance, solderability, electrical conductivity or decorative appearance. This can be accomplished by coating the part with a metal that has the desired properties necessary for the specific application. One of the most cost effective and simple techniques for introducing a metallic coating to a substrate is by electrochemical plating. The plating process can be subdivided into two types: electroplating and electroless plating. In both cases a metal salt in solution is reduced to

its metallic form on the surface of the workpiece. In *electroplating* the electrons for reduction are supplied from an external source. In *electroless or chemical plating* the reducing electrons are supplied by a chemical reducing agent in solution or, in the case of immersion plating, the substrate itself.

Plating of magnesium has been shown to be useful in a number of applications. *Cu-Ni-Cr* plating has been shown to have good corrosion resistance in interior and mild exterior environments (4). However, a plating method has not been developed that can produce coatings to withstand marine or salt splash conditions, thereby limiting the use of magnesium in the automotive, aerospace and marine industries. Electroless nickel coatings have proven useful in the computer and electronics industries for corrosion and wear resistance, improved solderability and creation of stable electronic contacts (5). *Ni-Au* coatings on magnesium have been used in a variety of space applications for improved electrical conductivity and optical reflectance (6). The microencapsulation of Mg_xNi alloy powders by electroless copper, Ni-P, Ni-Pd-P or Ni-B has been shown to increase the thermal conductivity/diffusivity, fatigue strength and lifetime of these alloys which are being developed for use as negative hydride electrodes (7, 8). An immersion process that microencapsulates Mg_2Ni alloy powders in copper using a solution of copper sulfate and nitric acid is extremely promising due to its simplicity, cost effectiveness and elimination of toxic chemicals (9).

2.1.1. Challenges

There are a number of challenges to be met in order to develop a useful plating process for magnesium and its alloys. Magnesium is classified as a difficult to plate metal due to its high reactivity. This means that in the presence of air magnesium very quickly forms a passive oxide layer that must be removed prior to metal plating. The rapid formation of the oxide layer necessitates an appropriate pretreatment of the surface to introduce a surface layer that prevents oxidation but which can easily be removed during the plating process. The extreme reactivity of magnesium metals also means that care must be taken to ensure that the metal reduction pathway is the preferred electroless or electrochemical process, since in many cases loose immersion layers, which inhibit

good adhesion, form readily on the surface by displacement (10). Care must be taken to develop non-traditional plating baths since magnesium reacts violently with most acids and dissolves in acid media.

Magnesium is also prone to galvanic corrosion because most other metals have a more noble electrochemical potential. Electrolytic contact with another metal can cause the formation of local corrosion cells on the surface leading to pitting. Therefore, the metal coating must be pore free otherwise the corrosion rate will increase (11). A minimum coating thickness of 50 microns has been suggested to ensure pore-free coatings of Cu-Ni-Cr for outdoor use (4). Another challenge in the plating of magnesium is that the quality of the metal coating depends on the alloy being plated. This requires the development of different pretreatment processes for different alloys. Alloys are especially difficult to plate because intermetallic species such as Mg_xAl_y are formed at the grain boundaries, resulting in a non-uniform surface potential across the substrate, and therefore further complicating the plating process.

Electroplating poses additional challenges due to an uneven distribution of current density in the plating bath, which results in non-uniform plating of complex shapes, particularly in holes and recessed areas. The technique also uses a lot of electricity, this can significantly increase the cost of the plating process. The electroless plating process does not suffer this disadvantage and coats complex shapes uniformly even inside holes. Another advantage of electroless plating is that second phase particles such as carbides, diamonds or PTFE can be co-deposited during the plating process to improve the hardness, abrasive properties or lubricity of the final composite coating (12). The deposition of alloys with enhanced wear properties and higher hardness values is also readily achieved.

Electroless deposition processes have a limited bath life and the problem is aggravated in the case of magnesium plating due to its high reactivity. An example reported is the process developed by PMD(U. K.) Limited that is capable of six regenerations, each with a 45 minute turn-over time if a strict replenishment schedule is

followed (13). The short lifetime of the baths is a serious limitation both from cost and environmental perspectives. Research on increasing the bath life and eliminating toxic chemicals is necessary in order to create “green” plating processes for coating magnesium.

One criticism of using metal coatings to protect magnesium from corrosion is that the presence of heavy metals reduces the recyclability of the metal. However there are a number of ways that these metals can be stripped from the surface and these are summarized in Table 1. The processes outlined in Table 1 demonstrate that while metal plating may complicate recycling of the metal it is certainly not prohibitive.

Table 1

Table of stripping processes for metal coatings on magnesium

Applicable Metal	Stripping Conditions
Zinc immersion layer*	Soak at room temperature in a solution of 10-15% Hydrofluoric Acid(70%)
Chromium*	Apply reverse current in hot alkaline solution
Copper*	Hot alkaline polysulfide and cyanide solution
Nickel*	15-25% HF + 2% NaNO ₃ at 4-6 V
Copper, Nickel, Tin, Cadmium, Zinc*	1:2:2 mixture of HNO ₃ :HF:H ₂ O
Gold, Silver, Copper, Nickel*	Proprietary alkaline chemical strippers containing cyanide at 20 –60 °C. Addition of NaOH prevents dissolution of magnesium
Copper, Nickel etc.	Plated Magnesium is set as the anode and electrolyzed in an aqueous solution of 180-220 ml/l phosphoric acid + 40-50 g/l Hydrofluoric acid or 150-220 ml/l phosphoric acid + 90-110 g/l ammonium bifluoride. An iron sheet is used as the cathode
Only the plating film is dissolved(15)	
Copper	Immerse in a mixture of ammonia solution and ammonium persulfate.
A protective ammonium magnesium sulfate surface layer protects the base alloy from dissolution (16)	

* Reference (14)

2.1.2. Pretreatment Processes

The most difficult part of plating magnesium is developing an appropriate pretreatment process, once a suitable undercoating is in place many desired metals can be plated. To date zinc and nickel have been directly plated onto magnesium, and are used as undercoatings for subsequent metal deposition. The undercoatings must be non-porous since porosity in underlayers promotes porosity in overlayers. A uniform coverage is especially difficult to achieve on magnesium alloys. The existing processes require many steps and are laborious, time consuming and must be precisely controlled to achieve acceptable adhesion and corrosion resistance. They are also alloy specific and do not work very well on for example AZ91 which is commonly used in the automotive industry for die cast magnesium parts.

The pretreatment requirements vary for different alloys and different plating baths. There are currently two general processes for treating magnesium prior to plating. These are zinc immersion and electroless nickel plating from a fluoride containing bath (17). These two general processes are outlined schematically in Figure 1. Some specific pretreatment processes will be outlined in the next section. Although, there are many variations the current processes predominantly follow one of the two general schemes outlined in Figure 1. The purpose of each of the individual pretreatment steps is outlined in Table 2 (10).

Table 2

Function of individual pretreatment steps in plating processes.

Surface Cleaning	remove soil, debris, oil or grease
Alkaline Cleaning	Mg is passive in alkaline media – wet surface, remove soils, greases etc
Acid Pickle	Remove gross surface scale or oxides and replace with a preferred oxide to be removed later. Etching treatments also provide surface pits to act as sites for mechanical interlocking to improve adhesion.
Acid Activation	Remove residual oxide, minimum etching, minimizes the effect of local corrosion cells by creating an equipotentialized surface
Zinc Immersion	Dissolves oxides, hydroxides-form thin zinc layer to prevent

	reoxidation of Mg
Copper strike	Zn is very reactive therefore most metals can't be plated directly on it. Copper acts as a base for subsequent plating.
Fluoride	Removes oxide and replaces it with a thin layer of MgF_2
Activation	Fluoride treatment is believed to control the rate of zinc or nickel deposition and thus produce more adherent deposits (24) This step has a similar role to acid activation.
Electroless Nickel Plating	A nickel based alloy is deposited on the surface to act as a base for further electroless plating or electroplating

2.1.2.1. Zinc Immersion (18)

The zinc immersion pretreatment process has been criticized for the precise control that is required to ensure adequate adhesion. In many cases non-uniform coverage of the surface is seen with spongy non-adherent zinc deposits on the intermetallic phase of the base alloys (19). The copper cyanide strike that must follow has also been criticized for a number of reasons (19). The first is that it is an electroplating process, which means that it is more difficult to coat complex shapes. Copper deposits slowly in the low current density areas, which allows attack of the zinc by the plating solution. This in turn allows attack on magnesium by the plating solution resulting in non-adherent copper depositing by displacement directly on the magnesium surface. The deposits in these areas are porous and have poor corrosion resistance. The second criticism leveled at the copper cyanide plating process is the high cost treatment of waste generated by the use of a cyanide containing bath. A recent patent (20) attempts to improve this process by eliminating the copper cyanide step from the pretreatment process. The copper cyanide electroplating is replaced by a zinc electroplating step followed by copper deposition from a pyrophosphate bath after the zinc immersion. This patent claims that by creating a uniform zinc film of at least 0.6 micrometers in thickness, adherent plating films can be obtained on any magnesium alloy using the disclosed

process. The zinc electroplating step can occur simultaneously with the zinc immersion process or in a separate step. The process is as follows:

Degrease→Alkaline Clean→Acid Clean→Activation→Zinc Immersion→Zinc Electroplate→Copper Plating

A number of processes based on the zinc immersion pretreatment process have been developed. The three main processes are the Dow Process, the Norsk-Hydro process and the WCM Canning Process (19, 22). One criticism of all of these processes is that they do not produce good deposits on magnesium alloys with an aluminum content greater than 6-7% (21). The general pretreatment sequence for each of these is outlined below for comparison (19, 22).

Dow Process:

Degrease→Cathodic Cleaning→Acid Pickle→Acid Activation→Zincate→Cu Plate

Norsk-Hydro Process:

Degrease→Acid Pickle→Alkaline Treatment→Zincate→Cu Plate

WCM Process:

Degrease→Acid Pickle→Fluoride Activation→Zincate→Cu Plate

The Dow process was the first to be developed but has been shown to give uneven zinc distributions as well as poor adhesion in many cases. A modified version of the Dow process (8) introduces an alkaline activation following the acid activation step. This results in good adhesion of Ni-Au films on AZ31 and AZ91 alloys. The authors have also significantly shortened the pretreatment time, which is important in a manufacturing setting. The Norsk-Hydro process has been shown to improve the quality of the zinc coating on AZ61 alloy in terms of adhesion, corrosion resistance and decorative appearance. Deposits of Cu-Ni-Cr, on samples pretreated with this process, have been shown to exceed the standards for outdoor use (23). Dennis et al (22, 24) show that samples treated with both the Dow and Norsk-Hydro processes give porous zinc coatings and perform poorly in thermal cycling tests. It was found that the WCM process resulted

in the most uniform zinc film and was the most successful in terms of adhesion, corrosion and decorative appearance. However, preferential dissolution of magnesium rich areas on the alloys occurred with all 3 processes, which could limit the effectiveness of any of these pretreatment methods.

A similar process has been used as an undercoating for samples to be plated with a series of metals by electroless and electroplating techniques (25). The authors claim to obtain uniform plating films with good corrosion resistance, solderability and electrical conductivity on intricately shaped and high aspect ratio samples. A slight variation of the pretreatment uses a copper cyanide plating bath that contains a soluble silicate (26). The authors claim to obtain good adhesion on magnesium with this process. Zinc immersion prior to tin plating of magnesium has also been explored (27). A magnesium alloy is treated with a conventional zinc immersion pretreatment and then zinc plated in an aqueous zinc pyrophosphate bath. Tin is subsequently plated to improve the tribological properties of the plated alloy.

2.1.2.2. Direct Electroless Nickel Plating

Difficulties in plating the AZ91 alloy have been cited for the zinc immersion pretreatment processes. In an attempt to address this issue a pretreatment process in which electroless nickel is plated directly onto magnesium alloy AZ91 die castings was developed by Sakata et al.(19). The authors state that uniform, adherent coatings were obtained. In general the pretreatment is as follows:

Pretreat→Degrease→Alkaline Etch→Acid Activation→Alkaline Activation→Alkaline Electroless Nickel Strike→Acid Electroless Nickel Plating

This process has been criticized (11) for using an acid electroless nickel treatment that can result in corrosion of the underlying magnesium if any pores are present in the nickel strike layer.

A simpler process has been developed by PMD (U. K.) Limited (13, 28, 29). The basic sequence of this pretreatment is as follows:

Pretreat→Alkaline Clean→Acid Pickle→Fluoride Activation→Electroless Nickel Plating.

The authors determined that the etching, conditioning and plating conditions had a large effect on the adhesion obtained. An insufficient etch or fluoride conditioning resulted in poor adhesion. It was also determined that using hydrofluoric acid for conditioning led to a wide plating window while ammonium bifluoride resulted in a much narrower (pH 5.8-6.0 and Temperature = 75-77 °C) window for acceptable adhesion. The chromic acid treatment was found to heavily etch the surface and leave behind a layer of reduced chromium. The fluoride conditioning was found to remove chromium and control the deposition rate by passivating the surface. The passivating effect of fluoride was also exploited in the plating of magnesium alloy MA-8 (30). In this case the nickel plating bath contained fluoride to inhibit corrosion of the substrate during plating. The authors report strong adhesion of the nickel film however, the bath life is too short to be industrially applicable. The addition of a complexing agent, glycine, was shown to improve the stability of the plating bath. Another proposed process (31) involves treatment of the sample with a chemical etching solution containing pyrophosphate, nitrate and sulfate, avoiding the use of toxic chromium ions. The process sequence is as follows:

Chemical Etching→Fluoride Treatment→Neutralization→Electroless Nickel Plating

The electroless nickel plating bath does not contain any chloride or sulfate. The plated samples achieved have high adhesion and corrosion resistance. One obstacle to coating magnesium with nickel is that most conventional nickel plating baths are acidic and can attack or corrode the magnesium surface. This problem has been addressed by the development of an aqueous acidulated nickel bifluoride electroplating bath that contains a polybasic acid (32). This bath has been shown to not corrode magnesium.

2.1.3. Noble Metal Plating for Space Applications

Nickel and gold plating on magnesium have both proven useful for space applications. Successful gold plating has been achieved using the following sequence on magnesium-lithium alloys (33):

Degrease→Alkaline Cleaning→Chromic Acid Pickle→Electroplated Nickel→Electroless Nickel→Gold Strike→Electroplated Gold

The initial electrodeposited nickel film is porous but acts as an activator for uniform electroless nickel plating and proved to be a suitable basis for gold plating. Gold plating of magnesium alloy AZ31 has also been achieved using the zinc immersion pretreatment process followed by electroless nickel plating and subsequent gold plating (34). An adherent gold deposit with good mechanical, thermal and optical properties as well as good environmental stability was obtained. It was determined that the immersion zinc produced a fine, adherent coating for subsequent electroless nickel deposition. An acid gold bath was found to give the best gold coating. The surface morphology of the coating was a homogeneous-grain structured zinc layer followed by a hard porous microcracked electroless nickel film with a uniform phosphorous distribution. The final gold layer was crack-free.

Gold plating on magnesium alloy RZ5 has been investigated using a variety of techniques (35). Plating nickel from non-aqueous solutions, as a base for gold plating, was attempted. However, this is expensive and since all the pretreatment steps are aqueous there is a risk of moisture contamination of the bath. The plating bath used was 30 g/l nickel sulfate + 200 ml/l dimethylformamide at a pH=4, 25-30 °C and 10 mA/cm². The zinc immersion and direct electroless nickel plating showed poor results. In the case of zinc immersion, a non-uniform zinc coating was observed. With direct electroless nickel plating non-uniform deposition, excessive corrosion and exfoliation of the deposit occurred. The poor quality of the deposits was attributed to coarse, non-uniform substrate grains with widely varying surface chemical composition. The pretreatment process was altered to create a uniform surface for nickel plating. An AC 5V electrolytic

treatment was added during the fluoride activation stage. The final process is outlined below .

Clean→Acid Pickle→HF dip→AC electrolytic treatment→electroless nickel plating from a fluoride bath→nickel electroplating→gold electroplating.

This strategy was successfully applied to the plating of satellite components, which exceeded their predicted life span of 2 years.

Another possible pretreatment process for plating magnesium alloys with silver or gold (37) involves an anodic treatment of the alloy, followed by coating the surface with an electrically-conductive resin film. Subsequent plating can then be achieved as desired. It is suggested that this plating method can be applied to objects such as satellite embarking devices.

Nickel coatings on magnesium have also been proposed for use in aerospace applications. Direct electroless nickel plating on magnesium alloy ZM21 has been shown to produce coatings with good mechanical, environmental, optical and soldering properties (36). The electroless nickel deposition was carried out after fluoride pretreatment and followed by chromium trioxide passivation. Annealing the samples resulted in precipitation hardening and improved adhesion.

2.1.4. Alternative processes

There are a few plating processes for magnesium that do not use either of the two conventional pretreatment processes. An immersion process whereby magnesium and its alloys can be coated with tin has been described (38). This process produces a tin oxide coating with good corrosion resistance and is comprised of the following treatment procedure:

Degrease→Immerse in chromate solution→Immersion in dibutyl-tin-dilaurate in ethyl cellusolve→anneal at 500 °C.

Another invention (39) involves acid activation of the substrate through contact with an aqueous solution containing HF, which can be derived from NH_4HF_2 , NaF or LiF, and a metal salt of Ni, Fe, Ag, Mn, Pd, or Co. The mineral acids, monocarboxylic acids or oxides of the aforementioned metals are preferred. The metal salt must be soluble in HF, be displaced by the substrate and catalytic to electroless nickel. Current may be applied to increase the deposition rate but is not essential. Electroless nickel plating from an amino borane bath in the presence of an organosulfur compound is then undertaken followed by heat treatment at 150-300 °C to improve the adhesion. The films formed by this treatment are both adherent and continuous. The authors claim that this process works for aluminum, magnesium and zinc however, all cited examples are for aluminum.

A method for plating silver on magnesium has been proposed (40). The process involves electrolytic (pulsed current) cleaning of the substrate in an alkaline solution followed by acid etching and electroplating in a silver containing bath. The authors claim that an adherent and continuous coating can be achieved.

A non-aqueous process for aluminizing magnesium has also been suggested (41). The process involves pretreatment by liquid drop impact erosion with a hydraulic jet spray of finely divided abrasive particles suspended in an inert, anhydrous aprotic media such as oil. A second pretreatment step involves the removal of a thin layer of magnesium by an anodic treatment in an aprotic organo-aluminum electrolyte medium. This occurs via the reaction $\text{Mg} + 2\text{R} \rightarrow \text{MgR}_2$ where R is an ethyl or methyl from the aluminum electrolyte. For magnesium this process must be carried out in an inert atmosphere. The process can be summarized as follows:

aprotic pretreatment→degrease→toluene rinse→anodic treatment→direct immersion in aluminizing bath→cathodic aluminum electroplating (inert atmosphere)

The aluminizing bath consists of an electrolyte with the general formula $MX_nAlR'R''R$ in a suitable solvent. Suitable solvents are aromatic hydrocarbons such as toluene or xylene and ethers such as THF, dipropyl-dibutyl ether or dioxane.

$M = Na^+, K^+, Rb^+, Cs^+$ or a quaternary ions with N, P, As or Sb as the central atom or a tertiary ion with S, Se or Te as the central atom.

$X = F^-, Cl^-, Br^-, I^-, CN^-, N_3^-$ or $\frac{1}{2} SO_4^{2-}$

$n = 2$ or 3

$R =$ organyl radical (ethyl or methyl)

$R' = R$ or H^- or F^- or Cl^- or CN^- or N_3^-

$R'' = R'$ or selected from same class as R'

The deposits are 99.99% pure aluminum and offer a high degree of corrosion protection and a silver-bright decorative appearance. They also have good conductivity, superior ultrasonic weldability and high reflectivity

2.2. Conversion Coatings

Conversion coatings are produced by chemical or electrochemical treatment of a metal surface to produce a superficial layer of substrate metal oxides, chromates, phosphates or other compounds that are chemically bonded to the surface (42, 43). On magnesium, these coatings are typically used to provide corrosion protection and good paint-base properties to the metal (43, 44). Conversion coatings protect the substrate from corrosion by acting as an insulating barrier of low solubility between the metal surface and the environment (45) and/or by containing corrosion inhibiting compounds.

There are a number of different types of conversion coatings including chromate, phosphate/permanaganate and fluorozirconate treatments. As with all surface treatments, cleaning and pretreatment of the sample is crucial to obtaining a good conversion coating.

One of the main disadvantages of conversion coatings is the toxicity of the treatment solutions. The conventional conversion coatings are based on chromium compounds that have been shown to be highly toxic carcinogens (44). The development of an environmentally friendly process is a necessity due to the more stringent

environmental protection laws currently in effect or being proposed. The coating of alloys also represents a significant challenge due to their non-uniform surface composition. The conversion coating must therefore be capable of coating all the elements present in the alloy uniformly (44).

2.2.1. Chromate Conversion Coatings

Chromate conversion coatings can be used as pretreatments prior to a final sealing process or as “post-treatments” after a plating process to improve corrosion resistance, paint or adhesive bonding properties or to provide a decorative finish (46). There are a few general rules that should be followed when applying a conversion coating, these include (45):

1. Substrates with fine grained microstructure respond best to chromating.
2. Co-deposition of other metals is detrimental to the coating process.
3. Proper cleaning and pretreatment of the surface is necessary to ensure optimum coatings.
4. After chromating the substrate should be properly rinsed to remove any residual acid or base which could react with the coating
5. The coating should be air dried at low temperature (70 °C) for a maximum of ten minutes.

The mechanism of formation of chromate conversion coatings (44, 45, 47) is believed to be due to the dissolution of the metal surface, with a corresponding reduction of water or oxygen to form hydroxyl ions, which causes an increase in pH at the liquid/metal interface. This in turn causes precipitation of a thin complex chromium-metal gel on the surface that contains both hexavalent and trivalent chromium compounds (45, 47, 48). Pure chromic acid solutions are not used to form conversion coatings because the deposition rate is too slow (44). Other anions in solution that can act as a catalyst for deposition are required (46), some of these include acetate, formate, sulfate, chloride, fluoride, nitrate, phosphate and sulfamate ions (48). The pH of the solution is the most important factor in controlling the formation of chromate films (48). The as-deposited gel is very soft but hardens upon drying to become hydrophobic, less soluble and more abrasion resistant (48). These coatings provide corrosion protection by

presenting a non-reactive barrier to the environment, through their self-healing properties and by the inhibiting effect of Cr(VI) that is slowly leachable in contact with moisture (45, 47, 48). The hexavalent chromium is reduced during corrosion to form an insoluble trivalent chromium species that terminates the oxidative attack (44). The protection afforded by the coating is proportional to the coating thickness (48). In order to maintain its protective properties the coating cannot be subjected to high temperature ($>66\text{ }^{\circ}\text{C}$) since this would decrease the coating thickness and eradicate the self-healing ability of the coating (45, 47, 48). The coating retains its self-healing characteristics as long as it remains in its hydrated form. The stability of the films at higher temperature can be improved by sealing or painting on top of the conversion layer (45, 47, 48).

Chromate Conversion coatings on magnesium have been shown to have the following structure (49): A dense layer of Mg(II) and Cr(III) hydroxides covers the magnesium surface with a porous overlayer of $\text{Cr}(\text{OH})_3$. This overlayer results from selective dissolution of $\text{Mg}(\text{OH})_2$ from the dense layer. Increasing the thickness of the dense layer has been shown to inhibit the corrosion of magnesium in chloride solutions (49). It has been suggested (50) that the rate of formation of the coating is controlled by the diffusion of chrome (VI) through the deposited coating. The protective properties of the coating can be increased by reducing the porosity of the overlayer through the precipitation of coating components that are insoluble in alkali (50). The authors (50) also suggest that the deposition rate of chromate conversion coatings on pure magnesium can be increased by introducing copper ions into the bath. These metal ions are inert to magnesium but precipitate on the deposited chromium species and act as cathodic sites to enhance deposition.

These coatings have been shown to provide good corrosion protection for magnesium and its alloys in mild service conditions. However due to the significant environmental hazards associated with the use of chromate compounds there is a push to find alternative coating process. The application of chromate conversion coatings for magnesium is discussed below.

Chromate conversion coatings have been shown to significantly reduce corrosion on AZ31C, AZ63A and AZ91C magnesium alloys in salt spray tests (43). However the coatings are thin and are generally not suitable as a final coating for outdoor use.

A study on the composition and protective properties of chromate conversion coatings on magnesium (49) has demonstrated that the protective properties of these coatings are due to the presence of $\text{Cr}(\text{OH})_3$ in their structure. An increase in the amount of $\text{Cr}(\text{OH})_3$ in the dense layer through an increase in chromate concentration in the bath leads to improved protective properties of the coating. The addition of zinc cations to the chromating solution was also shown to improve the properties of the chromate coatings.

The structure of chromate conversion coatings formed using the commercial processes, MX1, MX3 and MX7 on AZ91D has been reported (51). The MX1 process was found to produce a magnesium chromate film while MX7 was shown to produce magnesium phosphate at the surface. The MX3 process produced an amorphous chromium oxide film containing some oxides and fluorides of magnesium and aluminum. Corrosion studies showed that conversion films with a significant amount of oxygen and chrome, such as MX3, gave the best corrosion protection. Another study (52) investigated the structure of surface films formed by the Dow 7 commercial conversion coating process on die cast AZ91D and pure magnesium. On AZ91D the structure of the film is granular while on pure magnesium a porous cell structure was observed which was separated from the substrate by a thin barrier layer at the interface. This structure resembles the structure of films formed by anodizing. The films produced in both cases were composed of MgF_2 , $\text{MgO}_x(\text{OH})_y$, NaMgF_3 , Cr_2O_3 and NH_4^+ . Additional compounds such as $\text{AlO}_x(\text{OH})_y$, $\text{FeO}_x(\text{OH})_y$ and $\text{Mn}(\text{IV})$ were also found in the film formed on AZ91D.

A chromate conversion coating has been developed for magnesium-lithium alloys (47). The coatings were found to be around 8-11 μm in thickness with excellent adhesion even under humidity and thermal cycling tests. The optical and paint-base properties of the coating were also unaffected by humidity and thermal cycling tests.

A number of patents that discuss chromate conversion coatings are also available for review (53-56). These are all based on the technology discussed above with various coating baths. One novel variation involves the deposition of a chromium-silicon coating from a chromite bath that contains a soluble silicate (55). The coating produced is porous which renders it suitable for further processing such as painting. However, the corrosion resistance of the initial conversion coating is poor.

2.2.2. Phosphate/Permanganate Conversion Coatings

Phosphate-permanganate treatments are being explored as an alternative to conventional chromate conversion coatings (57-60). These treatments are more environmentally friendly and have been shown to have corrosion resistance comparable to chromate treatments. A systematic study on phosphate-permanganate treatment of AZ91D and WE43A alloys (57) using a bath containing potassium permanganate and sodium phosphate has shown that homogeneous, non-powdery and uniform coatings can be achieved. The phosphate concentration and pH of the conversion bath were found to have the most effect on the quality of the final coating. The corrosion resistance observed was comparable to chromate coatings. For AZ91 alloys a filiform corrosion morphology with phosphate-permanganate was observed which minimizes the depth of pitting. For WE43 the corrosion behaviour was the same for both chromate and phosphate-permanganate coatings.

Another study investigated the use of phosphate-permanganate treatments for the conversion coating of AM60B die cast magnesium alloys (58). After appropriate pretreatment the samples were treated with a phosphate permanganate process and E-coated (cathodic epoxy electrocoated). It was shown that the treatment provides good paint adhesion. The most important factor in producing best quality conversion coatings was found to be the control of the pH. Another study with the same magnesium alloy (59) demonstrated that with proper sample pretreatment, i.e. sufficient cleaning and acid pickling, magnesium samples with good paint-base performance could be achieved with a phosphate-permanganate bath. The permanganate is said to contribute manganese to the coating and acts as an accelerator without depositing metallic manganese on the

magnesium surface. The coatings were shown to have good corrosion resistance, paint base performance and were composed of an agglomerate of well-formed crystalline phosphate compounds. In a further paper (60) the authors tested this treatment on the AZ91D magnesium alloy. They determined that the phosphate-permanganate treatment can be operated over a wide range of conditions without affecting the corrosion inhibition of the coating produced when pretreatment included either grinding or phosphoric acid pickling. Samples that had been alkaline cleaned showed extremely high corrosion rates perhaps due to non-uniform deoxidation of the magnesium surface. They found that samples pretreated with a phosphoric acid pickle and then phosphate-permanganate gave excellent corrosion resistance and paint-base properties. Another study (51) examined the possibility of producing manganese type conversion coatings on the surface of magnesium alloy AZ91D. After cleaning and surface activation the samples were immersed in a solution containing potassium permanganate and either nitric or hydrofluoric acid. The coating formed in the HF containing bath was very thin and was shown to be amorphous in structure. It contained magnesium fluoride, hydroxides and manganese oxides. The coatings formed in the bath containing nitric acid were substantially thicker and crystalline manganese oxide was observed. The corrosion resistance of these coatings was equivalent to the protection afforded by a standard chromate treatment.

A number of phosphate based conversion coatings can be found in the patent literature. One of these involves treating a magnesium based sample with an aqueous bath containing diammonium hydrogen phosphate (61). The inventors suggest that this results in the formation of magnesium phosphate, its hydrate and magnesium hydrogen phosphate on the surface without any prior pretreatment. This coating was found to have good adhesive properties for subsequent powder coating. Another patent (62) recommends treatment of magnesium with a solution containing sodium ions, condensed phosphate ion and borate ions as a treatment prior to powder coating. Magnesium phosphate conversion coatings have also been shown to protect the internal surface of a magnesium based combustion engine piston (63). A thin layer of magnesium phosphate is formed on the surface of the piston upon dipping in a solution of iron phosphate. This

layer then acts as an adhesive for the combustion products of fuel and lubricants in the engine, which in turn form a protective coating on the piston surface. Conversion coatings composed of zinc phosphate have also been shown to have adhesion and corrosion resistance comparable to coatings formed by conventional anodic oxidation or chromating (64, 65). These films are formed in a solution containing zinc ions, manganese ions, phosphate ions and hydrofluoric acid. Paint-adherent and corrosion resistant coatings composed of magnesium phosphate and magnesium fluoride have also been developed (66). These are formed from phosphate ion and fluoride ion containing solutions at neutral pH. The development of coatings made up of P-Mn, Mn-N and other nitrogen containing species has been described (67, 68). These coatings are formed from a slightly acidic bath containing a phosphorous containing acid, divalent manganese ions and an amine compound. The amine component is believed to prevent excessive etching of the substrate in the acidic media (67). These films were shown to be corrosion-resistant, highly rust inhibiting and strongly paint-adherent (68).

2.2.3. *Fluorozirconate Conversion Coatings*

Fluorozirconate treatments have also shown promise as potential pretreatments for magnesium and magnesium alloy materials. The group IV-A elements such as titanium, hafnium and zirconium are believed to form continuous three-dimensional polymeric metal or metalloid-oxide matrices, from aqueous solutions, in a similar manner as chromium (69). This makes them an attractive alternative for environmentally friendly conversion coatings. These coatings may provide corrosion protection through a galvanic setting or may act as a physical barrier to the environment (69). This has been exploited to produce corrosion resistant coatings, by exposing a metal substrate to an aqueous acidic solution of zirconium ions, stabilized in solution by organic or inorganic oxy-anion compounds (69). Upon drying a continuous polymeric zirconium oxide layer becomes fixed on the surface. In a related patent a conversion coating system composed of mixtures of group IV-A and group III-A elements is proposed (70). The inventors believe that these coatings provide enhanced corrosion resistance over simple zirconium oxide systems due to a redox component in the coating that mimics the chromate redox

model. The preferred embodiment of this patent uses cerium and zirconium in combination.

One difficulty with this type of treatment is its higher sensitivity to contamination with hard water or constituents of the pretreatment baths that necessitates the use of demineralized water rinsing prior to the fluorozirconate treatment (71). In a recent study (72) samples of magnesium alloy AZ91D and AM50A were treated with a commercial fluorozirconate solution followed by powder coating with an epoxy-polyester powder. This treatment was shown to have similar paint adhesion properties as chrome conversion coatings. The samples showed reasonable corrosion resistance in mild corrosive environments but extremely poor resistance to stone chipping, which limits its use in more severe service conditions.

Another study on fluorozirconate treatment of magnesium alloy AZ91 HP (71) has shown that the coating contains predominantly Zr-Mg-Al oxides and hydroxides. Morphological studies concluded that the coating is composed of two layers. The first layer covers the metal surface continuously and is porous and amorphous. The second layer consists of individual crystalline particles rich in MgO/Mg(OH)_2 . Good corrosion resistance was observed and drying temperatures up to 200 °C were shown to have no effect on the quality of the coating.

A recent article concluded that fluorozirconate treatments were not suitable for use in severe corrosive environments (73). The use of fluorotitanate treatments was investigated for this purpose. It was found that the fluorotitanate treatment alone did not provide adequate protection against corrosion in severe corrosive environments. However a combination of fluorotitanate + E-coat + powder paint was shown to be effective in mild corrosive environments.

2.2.4. Stannate Treatments

A process for creating stannate and zincate based conversion coatings on magnesium alloy AZ91B + 0.5% Si has been developed (74). Following pickling and

activation, the samples were treated with one of a variety of immersion tinning solutions or a zincate solution. The coatings showed some corrosion resistance but in both cases only thin layers were formed. Details on the corrosion resistance of these coatings were not given, and further studies are warranted.

A study on stannate treatment of ZC71 and a metal matrix composite of ZC71 + 12% SiC particles has been undertaken (75). After mechanical finishing and pickling the samples were immersed in a stannate bath for selected periods of time. The treatment resulted in the formation of a 2- 3 μm thick, continuous and adherent, crystalline coating of MgSnO_3 on both materials. The nucleation and growth of the coating is completed in about 20 min. The initial nucleation was found to occur at cathodic sites on the surface with crystal growth to a grain size of about 2-5 μm until they coalesced. There was an increase in the corrosion potential of the magnesium surface as the film formation proceeded indicating that the coating does have a passivating effect on the surface. Further corrosion studies are warranted. In a more recent paper (76) the authors examined this process on Magnesium, ZC71 alloy, WE43 alloy and a metal matrix composite with a ZC71 alloy matrix and 12% (vol) silicon carbide particles. They found that crystalline MgSnO_3 was formed on all four substrates by a similar mechanism as discussed above.

2.2.5. Other Processes

A conversion coating on AZ91D that uses a solution containing a food additive and an organic acid has been shown to passivate the metal surface (77). After degreasing, the magnesium alloy is immersed in a solution containing sodium benzoate, sodium glucosate and an organic acid. The films produced were iridescent with netlike cracks and were shown to have slightly better corrosion resistance than a chromate treated sample. The morphology of the conversion coatings provides a good base for painting which can further improve the corrosion resistance of the treated magnesium part.

In an alternative patented process (78), a chemical treatment involving acid pickling in a hydroxy acetic acid solution followed by conversion coating with an organofunctional silane compound has been explored. This process was shown to maintain good paint adhesion and corrosion resistance in salt spray tests for coatings on AZ91D alloy.

The corrosion protection of cerium, lanthanum and praseodymium conversion coatings on magnesium and magnesium alloy WE43 has been investigated (79). The samples were polished, cleaned in water and methanol and dried prior to immersion in a $\text{Ce}(\text{NO}_3)_3$, $\text{La}(\text{NO}_3)_3$ or $\text{Pr}(\text{NO}_3)_3$ solution. A visible, adherent but easily removed coating was produced on the surface. The authors demonstrated that these coatings provide an increase in corrosion resistance for magnesium and its alloys. However, the coatings deteriorate on prolonged immersion in the test buffer solution so their protective effect is short term.

A process for creating cerium- based coatings on various metals has been suggested (80). Optimum coatings are formed in a pH 2.5 solution of cerium chloride and hydrogen peroxide. The inventors demonstrated that the best corrosion resistance on aluminum is obtained with high cerium concentration and 3% hydrogen peroxide. The addition of organic brighteners was observed to further decrease the corrosion rates from $7 \mu\text{g}/\text{m}^2/\text{sec}$ for bare aluminum to $1.5 \mu\text{g}/\text{m}^2/\text{sec}$ for treated aluminum. The inventors suggested that this coating technique may also be applicable to magnesium.

Cobalt conversion coatings have also been proposed (81). However, there has been little work done in this area and all examples cited have been performed on aluminum. The coating, which is composed of Al_2O_3 , CoO , Co_3O_4 and Co_2O_3 (on aluminum), is formed by contacting the substrate with an aqueous solution of a Co(III) hexa-coordinated complex of the form $\text{X}_3[\text{Co}(\text{NO}_2)_6]$ where $\text{X} = \text{Na}, \text{K}$ or Li . The unsealed coating has a porous structure that provides good paint adhesion. In order to achieve improved corrosion resistance it is necessary to seal these coatings. Sealing is discussed in more detail in section 2.4.

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

2.3. *Hydride Coating*

A technique for producing a magnesium hydride coating on magnesium and its alloys by electrochemical means has been developed as an alternative to Cr-based conversion coatings (82, 83). This process involves treating the magnesium substrate, which acts as the cathode, in an alkaline solution prepared by adding alkali metal hydroxide, ammonium salts or similar alkaline materials. A supporting electrolyte may also be added to decrease the solution's resistance. However, the authors caution against the use of chlorides since Cl^- poses the potential of corrosion of the workpiece. Prior to cathodic treatment the samples are mechanically polished, degreased with acetone and acid etched. The preferred treatment conditions and some specific treatment processes are shown in Tables 3 and 4 respectively. The hydride coating thus produced has been found to decrease the corrosion rate of AZ91D alloy by 1/3 which is comparable to the dichromate treatment.

Table 3

Preferred treatment conditions for hydride coating formation

pH	10-14
Temperature	40-80 °C
Cathodic Current Density	20-100 mA/cm ²
Cathodic Current Frequency (biased square wave or intermittent)	0.1-3 Hz

Table 4
Treatment process for hydride coating formation

Stage	Operation	Condition
1	Mechanical Polishing	#600 emery paper
2	Solvent Degrease	Acetone
3	Acid Etch	
	10% HF (w/w)	30 sec., Room Temp.
	or	
	10 % HNO ₃ (w/w)	10 sec., Room Temp.
4	Cathodic Treatment	20-60 °C, intermittent cathodic current (-50 mA/cm ² , 0.1-0.5 Hz), 30 min., pH=12
	NaOH	0.01 M
	Na ₂ SO ₄	0.1-0.2 M

2.4. Anodizing

Anodizing is an electrolytic process for producing a thick, stable oxide film on metals and alloys (45). These films may be used to improve paint adhesion to the metal, as a key for dyeing or as a passivation treatment (45). The stages for processing include (45); 1. mechanical pretreatment, 2. degreasing, cleaning and pickling, 3. electrobrightening or polishing, 4. anodizing using d.c. or a.c. current, 5. dyeing or post-treatment and 6. sealing. The films have a thin barrier layer at the metal/coating interface followed by a layer that has a cellular structure. Each cell contains a pore whose size is determined by the type of electrolyte and its concentration, temperature, current density and applied voltage. Their size and density determine the extent and quality of sealing of the anodized film(45). Coloring of anodized films can be achieved by absorbing organic dyes or inorganic pigments into the film immediately after anodizing, by a second-step electrolytic deposition of inorganic metal oxides and hydroxides into the pores of the film or by a process called integral color anodizing. The latter is achieved by adding organic constituents to the anodizing electrolyte that decompose during the process and form particles which become trapped in the film as it grows. (45, 84) The color may also be controlled by a process called interference coloring. Interference coloring involves

control of the pore structure to produce color by interference of the light reflected from the top and bottom of the pores (84). This process is difficult to control in production.

Sealing of the anodized film is necessary in order to achieve an abrasion and corrosion resistant film. In this step the porous oxide films is sealed off by the precipitation of hydrated base metal species inside the pores. This can be accomplished by boiling in hot water, steam treatment, dichromate sealing and lacquer sealing (45, 84). These films are often inadequate as the only surface treatment but they provide an excellent paint base for a corrosion protection system.

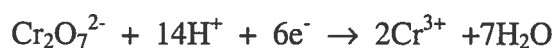
The wear resistance and hardness of anodized films can be improved by operating at a decreased electrolyte temperature and an increased current density. The process is referred to as hard anodizing (84). The properties of the hard anodized coatings can be further improved through the incorporation of solid film lubricants such as PTFE or molybdenum disulfide (84).

One of the main challenges for producing adherent, corrosion resistant, anodic coatings on magnesium results from the electrochemical inhomogeneity due to the phase separation in the alloy. The presence of flaws, porosity and inclusions from mechanical pretreatment can also result in uneven deposition. It can also be difficult to achieve uniform throwing power over all areas of shapes featuring deep recesses, narrow cavities or sharp corners. Enhanced corrosion can occur if the coating contains defects (85). Another disadvantage of this technique is that the fatigue strength of the base metal can be affected by localized heating at the surface during the treatment (86), especially in thicker films. Yet another disadvantage is that the coatings produced are a brittle ceramic material that may not have appropriate mechanical properties for all applications. On the other hand, incorporation of PTFE type particles in hard anodized coatings may have some technically superior functional properties.

In the following sections some specific anodizing treatment processes are outlined.

2.4.1. *Modified Acid Fluoride Anodizing*

Anodizing of magnesium alloy ZM21 has been performed in an anodizing bath containing ammonium bifluoride, sodium dichromate and phosphoric acid (85). The coating is formed by a chemical reaction between the magnesium alloy surface and hexavalent chromium in which magnesium is oxidized by the hexavalent chromium, which is in turn reduced to the trivalent state.



An alternating current is required to ensure replenishment of the reactant concentrations at the metal-electrolyte interface. The coating thus produced is composed of hexavalent and trivalent chromium. It also contains magnesium chromate, magnesium phosphate, magnesium hydroxide and magnesium bifluoride.

The anodic coatings produced by this technique were found to be highly stable when subjected to high humidity, high temperature, thermal cycling tests and thermovacuum tests. They were also deemed suitable for some space applications due to their high solar absorptance, high IR emittance and good optical properties.

2.4.2. *Dow 17 Process (14)*

Chemical treatment no. 17, developed by Dow Chemicals, can be applied to all forms and alloys of magnesium. The anodizing bath employed in this treatment is a strongly alkaline bath consisting of an alkali metal hydroxide and a fluoride or iron salt or a mixture of the two. (87) This process produces a two-phase, two-layer coating. The first layer is deposited at a lower voltage and results in a thin, approximately 5 μm , light green coating. The overlayer is formed at a higher voltage. It is a thick dark green, approximately 30.4 μm , layer that has good abrasion resistance, paint base properties and corrosion resistance. The corrosion resistance of AZ91D alloy treated with this technique

has been subjected to a three-year atmospheric exposure test. Superior corrosion resistance compared to tested conversion coatings was reported (51).

The composition, structure and growth mechanism of anodic films on pure magnesium and magnesium alloy AZ91D produced using the Dow 17 process, have been studied (88). The study confirms that the film has a thin barrier layer at the interface with an overlying, cylindrical pore structure, layer. On pure magnesium, the authors assume that film growth proceeds by the formation of magnesium fluoride and magnesium oxyhydroxide at the metal/film interface and dissolution of the film at the base of the pores. The crystallization of magnesium fluoride and NaMgF_3 proceeds in the overlying porous layer. The films formed on AZ91D alloy were uneven, most likely due to the presence of intermetallic Mg-Al particles located at grain boundaries and the surface porosity. However, the growth mechanism of the coating was similar and a porous cell structure with crystalline particles of MgF_2 and NaMgF_3 was also found in these films.

2.4.3. Anomag Process

The anomag process is a proprietary treatment invented by Magnesium Technology Licensing Ltd. The anodizing bath for this process consists of an aqueous solution of ammonia and sodium ammonium hydrogen phosphate (89). The coating produced is a mixed $\text{MgO}/\text{Mg}(\text{OH})_2$ system with the possibility of additional compounds such as $\text{Mg}_3(\text{PO}_4)_2$ depending on any additives present in the bath. Due to the presence of ammonia in the system, spark formation is repressed, which eliminates the need for cooling equipment. The coatings produced are semi-transparent to pearl colored depending on the presence and concentration of certain additives such as fluoride and aluminate. The properties of these coatings have been investigated by a number of authors and their findings are discussed below.

A study by Guerici (73) found that the thickness and properties of the oxide layer produced using the Anomag process depend on the bath composition, temperature, current density and treatment time. The coating produced has a cellular microstructure similar to that observed for other anodizing processes. The authors found that die-cast magnesium samples treated with the Anomag process, followed by powder coating had

good paint adhesion properties and excellent corrosion protection. Further development in the areas of cost reduction, choice of chemicals used in the process and layer thickness optimization was proposed. Another study on coating AZ91 alloy with this process (90) also showed the formation of a porous film with a pore size of about 6 μm and porosity of 13%. Sealing and painting were shown to reduce the pore size and porosity to 3 μm and 4% respectively. The chemical composition of the film was found to consist mainly of $\text{Mg}_3(\text{PO}_4)_2$. Samples that had been anodized, anodized/painted and anodized/sealed all showed a significant reduction in general corrosion rates. The best results occurred for magnesium treated with the Anomag process followed by painting and sealing. These samples showed a 97% reduction in the general corrosion rate compared to the bare metal. The three step treatment was also shown to reduce galvanic corrosion rates. However anodizing or anodizing/painting without sealing did not reduce the rate of galvanic corrosion.

Fatigue testing of AZ91 samples treated with the Anomag process has shown that there is no change in the fatigue properties compared to the untreated samples (91). The corrosion fatigue properties of these coatings have also been studied (91). The results were not conclusive however it appeared that at low applied stress levels the coating seemed to provide resistance to corrosion fatigue while at higher stress levels no change compared to uncoated samples was observed. An interesting observation was that sealed Anomag coatings performed extremely poorly in these tests. The authors propose that this could be due to an effect of the thermal cure process on the base metal.

2.4.4. *Magoxid-Coat Process (92 93)*

This proprietary process, invented by GmbH Ltd., is an anodic plasma-chemical surface treatment that forms an oxide ceramic layer on magnesium materials. The plasma is discharged by an external power source in a slightly alkaline electrolyte near the surface of the workpiece, which acts as the anode of the system. The oxygen plasma generated causes partial short-term surface melting and ultimately the formation of an oxide-ceramic layer. The anodizing bath for this process is free of chloride and may contain inorganic anions such as phosphate, borate, silicate, aluminate or fluoride (94).

The bath may also contain organic acids such as citrate, oxalate and acetate. A source of cations is also present and may be chosen from alkali ions, alkaline earth ions or aluminum ions. Finally a stabilizer such as urea, hexamethylenediamine, hemethylenetetramine, glycol or glycerin is also added. The coating consists of three layers, a thin (100 nm) barrier layer at the metal surface followed by a low porosity oxide ceramic layer and finally a higher porosity ceramic layer. The final layer acts as a good base for paint adhesion and impregnation treatments. Impregnation of the coating with particles of fluorine polymers has been shown to significantly improve the load bearing properties of the coatings while maintaining good adhesion and corrosion resistance (95). The coating has been shown to consist of mainly MgAl_2O_4 . This process is capable of producing uniform coatings even on edges and cavities. The coatings produced provide wear and corrosion protection although dyeing has been shown to result in a decrease in corrosion resistance.

2.4.5. HAE Process (14)

This treatment is effective on all forms and alloys of magnesium provided no other metals are inserted or attached to the magnesium workpiece. The treatment produces a two phase coating as in the Dow 17 process. At a lower voltage a 5 μm thick, light tan subcoating is produced. At a higher voltage a dark brown, thicker (30 μm) film is produced. Upon sealing the HAE treatment provides excellent corrosion resistance. The dark brown coating is hard with good abrasion resistance but it can adversely affect the fatigue strength of the underlying magnesium, particularly if it is thin. The corrosion resistance of AZ91D treated with this technique has been tested by a three-year atmospheric exposure experiment. Superior corrosion resistance compared to conversion coatings was observed (51).

2.4.6. Galvanic Anodizing (14)

This technique produces a protective black coating with good paint-base characteristics on all forms of magnesium. This process does not require an external source of current. Very thin films are produced with little dimensional change to the workpiece.

2.4.7. Cr-22 Treatment (14)

This process is a high-voltage process that is not currently in use. Green and black coatings can be produced on all alloys by varying the solution composition, temperature and current density. These coatings provide good corrosion resistance for unpainted parts when properly sealed but have been used primarily as a paint base. Hard protective black coatings have also been produced in an aqueous anodizing bath containing chromate, vanadate, phosphate and fluoride compounds (96).

2.4.8. Tagnite Surface Treatment

The Tagnite surface treatment, invented by Technology Application Group Inc., is a chromate-free, anodic electrodeposition surface treatment (97). The surface treatment involves a pretreatment step to create a firmly bonded protective base layer that is compatible to deposition of the anodic coating (98). The pretreatment can consist of, 1.) immersion in an ammonium fluoride bath (98) or 2.) electrolytic treatment in an aqueous bath containing hydroxide and a fluoride compound(99). The anodization bath consists of an aqueous solution containing hydroxide, fluoride and silicate species. This produces a ceramic like coating of SiO_2 at the surface. This process has been shown to successfully coat the internal passages and blind holes of a gearbox (97). The abrasion resistance, wear resistance, paint adhesion and corrosion resistance were all improved compared to the Dow and HAE processes even prior to organic finishing (97-100). Surface sealing of the coating was shown to further improve its corrosion resistance (97).

2.4.9. Miscellaneous processes

A number of patents detailing anodizing procedures with various bath compositions have been granted. Protective coatings with no inherent color can be easily colored and provide a good paint base. These coatings can be produced from an alkali rich aqueous bath containing borate or sulfate anions and phosphate and fluoride, chloride or aluminate ions (101). During the anodizing process a direct current is applied then briefly turned off or polarity is incompletely reversed to allow formation of magnesium phosphate and magnesium fluoride, magnesium chloride or magnesium aluminate(101). The

performance of this bath can be improved by the addition of a buffering agent in the form of an amine compound (102). The wear resistance was determined to be less than 20 mg/10,000 revolutions on a Taber abrasive system, while the good corrosion resistance was demonstrated by the appearance of less than 10 corrosion points/cm², after 240 hrs. salt spray testing (102).

An anodic treatment with an aqueous bath containing silicate, carboxylate, alkali hydroxide, and one or more borate, fluoride or phosphate compound has been reported to have superior decorative appearance, corrosion and abrasion resistance compared to HAE and Dow 17 (103). This process produces a glassy white oxide coating with the chemical composition 2MgO:SiO₂.

Another type of process involves anodizing in an aqueous solution containing a polybasic organic acid such as polyvinylphosphonic acid (104-106). The coating produced is an insoluble metal oxide-organic complex, which, under optimized conditions, shows no porosity at 55,000X magnification and has good corrosion resistance. However, although the inventors suggest that this process should work on magnesium, all examples cited for this work used aluminum as substrate.

An anodizing process for forming a chemically stable and hard spinel compound of MgO-Al₂O₃ on magnesium surfaces has been disclosed in a patent by Gillich et al.(107). The anodizing bath consists of aluminate, alkali hydroxide and at least one boron, phenol, sulfate or iodine compound. The coating is white in color, resistant to corrosion and abrasion and could be easily colored in a conventional dyeing bath.

An anodic treatment that produces a hard, durable, uniform, adherent and corrosion resistant, fluoromagnesium-silicate coating has also been reported (108, 109). There are two variations of this process: in the first case the magnesium substrate is pickled in an aqueous hydrofluoric acid bath prior to anodizing in an aqueous bath containing an alkali metal silicate and an alkali metal hydroxide (108). In the second case the fluoride is part of the anodizing bath (109). In both instances the coating is formed when sparks are

discharged at the surface. This causes the surface to melt with simultaneous deposition of a fluoride containing silicate coating.

2.5. Gas-phase deposition processes

All the processes discussed thus far have been wet chemical surface treatments. Protective coatings can also be produced from the gas phase. These are typically metallic coatings but can include organic coatings such as thermal spray polymer coatings and diamond like coatings. All of these processes have the advantage that they have little negative environmental impact. However, the capital costs associated with these techniques are usually high. In the sections to follow a variety of gas phase surface modification technologies and their application to magnesium protection will be discussed.

2.5.1. Thermal Spray Coatings

In this process the coating material which can be metal, ceramic, cermet or polymeric is fed to a torch or gun where it is heated to above or near its melting point. The resulting droplets are accelerated in a gas stream onto the substrate and the droplets flow into thin lamellar particles and adhere to the surface (110). A number of coating techniques fall under this umbrella including flame spraying, wire spraying, detonation gun deposition, plasma spray and high velocity oxyfuel.

Some of the advantages of this technique include the ability to create a coating of virtually any material that melts without decomposing, minimal substrate heating during deposition and the ability to strip and recoat worn or damaged coatings without changing the properties or dimensions of the part (110).

One major disadvantage is that the process is line of sight and small deep cavities cannot be coated, especially if the surface lies parallel to the spray direction. These coatings also require sealing due to their inherent porosity and mechanical finishing to obtain a smooth finish. One final disadvantage of this technique are the health and safety

issues generated by the production of dust, fumes, noise and light radiation during treatment.

As with most surface treatments, in order to ensure adequate adhesion, the substrate must be properly prepared. The substrate must be both cleaned and roughened prior to the application of the thermal spray coating.

The process has been used to coat a magnesium alloy to be used as part of a satellite (111). Prior to application of a thermal spray coating the substrate was washed and roughened by blasting. An aluminum coating is then applied by thermal spraying followed by sealing with a chromate conversion coating. The coatings were shown to withstand corrosive environments and have good electrical conductivity.

2.5.2. Chemical Vapor Deposition(CVD)

CVD can be defined as the deposition of a solid on a heated surface via a chemical reaction from the gas phase. Advantages of this technique include deposition of refractory materials well below their melting points, achievement of near theoretical density, control over grain size and orientation, processing at atmospheric pressure and good adhesion (112). This process is not restricted to line of sight like most PVD processes so deep recesses, high aspect ratio holes and complex shapes can be coated. Due to the high deposition rate that can be achieved, thick coatings can be produced. However, this process is limited to substrates that are thermally stable at ≥ 600 °C. Efforts are underway to reduce the high temperature requirements and plasma and organometallic CVD processes offset this problem somewhat. A further disadvantage of this process is the toxic nature of the chemical precursors, which necessitates the use of a closed system. Toxic solid byproducts can also be produced which introduces waste disposal costs. The energy cost of this process can also be high due to the need for high deposition temperatures and sometimes low efficiency of the process (112). A variety of CVD processes used to coat magnesium substrates are described below.

Molybdenum coatings from an organometallic chemical vapor deposition precursor have been described (113). It was determined that crack-free, adherent

coatings on magnesium could be obtained at a decomposition temperature of 400 °C with a thickness < 0.5 µm. An increase in corrosion potential from -1.457 V(SCE) to -0.74 V(SCE) was observed in NaCl. The coating underwent partial dissolution but remained homogeneous during polarization. It was concluded that provided the coating is homogeneous, non-porous and crack-free, the resistance of magnesium to general corrosion in neutral chloride solution was improved. CVD has also been used to coat magnesium particles with nickel for use in a magnesium hydride storage device (114).

A plasma-assisted CVD technique has been successfully used to deposit TiCN and ZrCN layers on magnesium alloys AZ91 and AS21 (115). The coatings were deposited at low temperature (below 180 °C) from an organometallic tetrakis(diethyl)-amino metal complex. The topography of the deposited layers was shown to be smooth to domed with a dense to columnar fracture surface. The authors demonstrated that adherent layers with hardnesses of 1400 HK0.01 and 1530 HK0.01 for ZrCN and TiCN respectively could be obtained.

A patented process for producing a protective film on magnesium containing substrates has been disclosed (116). The coating process involves CVD of an intermediate aluminum layer, followed by a metallic oxide layer of titanium oxide, aluminum oxide, zirconium oxide, chromium oxide or silicon oxide. The aluminum precursor and metal oxide precursor must be able to decompose at temperatures less than 430 °C. A final sealing of the surface to reduce porosity can be obtained by immersion in a boiling aqueous bath for 30 minutes. The authors claim that the protective films formed on any magnesium alloy are corrosion resistant and well adhered. Another study claims that SiO₂ films produced on AZ91 alloy by a CVD process show no visible corrosion spots after 240 hours immersion in NaCl (82). This film was also found to be stable in acid solutions and organic solvents.

2.5.3. *Diamond-like carbon films*

Diamond like carbon films can be produced using a number of different processes such as PVD, CVD and Ion Implantation. These coatings are desirable for many

applications due to their high hardness, low friction coefficient, electrical insulation, thermal conductivity and inertness (117). Plasma enhanced CVD has been used to produce amorphous hydrogenated SiC and diamond-like coatings on magnesium (117). Corrosion resistance studies by anodic polarization in the presence of sodium chloride showed both a decrease in the corrosion current density at all potentials and a large positive shift of the potential at which the corrosion current becomes large in chloride containing solutions. The most promising films were obtained with defect free diamond-like coatings, these showed no sign of corrosion upon microscopic examination. Diamond-like carbon films on magnesium alloys with good lubricity, corrosion resistance, adhesion and smoothness have been produced using a CVD process (118). The surface of the alloy is subjected to a CVD treatment using methane and hydrogen to form a diamond-like carbon coating and then treated with a high-frequency plasma CVD process using carbon tetrafluoride. Finally, diamond-like carbon films using methane and a plasma source ion implantation method, to produce adherent films on magnesium, have been reported (119). This process involves creating a graded carbon composition interface between the metal and the diamond-like coating via ion implantation.

2.5.4. Physical Vapor Deposition Processes

Physical vapor deposition involves the deposition of atoms or molecules from the vapor phase onto a substrate. This process includes vacuum deposition, sputter deposition, ion plating, pulsed-laser deposition and diffusion coatings.

2.5.4.1. PVD on Magnesium

The role of PVD processes in magnesium surface finishing can be divided into two sections, the deposition of wear and corrosion protection coatings and the creation of bulk magnesium alloys with unique corrosion resistant properties.

There are a few challenges to overcome in the PVD coating of magnesium substrates. The deposition temperature must be below the temperature stability of magnesium alloys (180 °C) and good adhesion must be obtained despite this low temperature (120). The coating must also have good corrosion resistance. For most PVD

processes the substrate must be in the range of 400-550 °C however, it has been shown that the deposition temperature can be significantly reduced by applying a pulsed bias voltage during deposition (120). TiN coatings produced by this technique on magnesium alloy AZ91 have been shown to be adherent and pore free (120). The load-carrying capacity of these samples was significantly improved by introducing an intermediate layer of electroless Ni-P (120). Corrosion studies have not been reported for this system to date. Another recent article reports the PVD of Cr and CrN multilayer films on magnesium alloy AZ91 (121, 122). These coatings were found to have good adhesion and wear properties but poor corrosion resistance due to the presence of pores in the coating. Upon comparison of monolayered Cr and multilayer CrN coatings a slight increase in corrosion protection was observed for multilayers. Another approach involves coating magnesium alloys with purified magnesium or magnesium alloys (123). The corrosion resistance in this case is thought to come from the decrease in alloying elements that cause galvanic corrosion. A table of weight loss after immersion tests in 1% NaCl for various alloys and AZ31 alloy samples that had been coated with purified magnesium is shown below.

Table 5

Weight loss of magnesium alloys after immersion in 1% NaCl

Sample	Weight Loss (mg/cm ²)
3N-Mg	75
AZ31	3.5
AZ91	0.7
6N-Mg	0.2
Coated AZ31, Evaporation Source: AZ91E	0.3
Coated AZ31, Evaporation Source: 3N-Mg	0.6

The corrosion protection afforded by the purified magnesium coating is comparable to corrosion of the purer, more corrosion resistant magnesium alloys AZ91 and 6N-Mg. In a more recent article (124), these authors investigated the microstructure of PVD deposited magnesium 3N or AZ91 on magnesium AZ31 substrates. They determined by

atomic force microscopy that the deposited coating was composed of faceted magnesium particles which existed as isolated species in the early stages of deposition but grew to cover the surface as deposition continued. Heterogeneous corrosion in 1% NaCl was not observed on these samples although there was a slight swelling of the grains that was attributed to a homogeneous corrosion mechanism through the formation of a $\text{Mg}(\text{OH})_2$ on the surface.

In a patented process (125) PVD/PLD has been used to coat magnesium substrates with titanium or titanium alloy material. A focused laser beam is used to heat and vaporize the titanium or titanium alloy target. The vapor is deposited on the magnesium or magnesium alloy substrate to form a thin film. One drawback of this technique is that it must be done under low pressure conditions ($10^{-6} - 10^{-8}$ torr), and is also a line of sight process.

Another patented process (126), invented by DaimlerChrysler, describes a process for creating an anti-corrosion coating on magnesium materials. The corrosion protection layer described in this patent can be applied as a coating by flame spraying, plasma spraying or sputtering. The layer can also be formed on a surface area of the magnesium material by coating the casting mould prior to pouring the magnesium, by co-extrusion or by plating. The magnesium material to be protected is highly pure magnesium that does not contain iron, nickel or copper. The coating consists of an alloy containing titanium, zirconium or magnesium as the base metal and certain metal additives. The additives are selected from the group consisting of alkali metals, alkaline earth metals, rare earth metals, yttrium, metals from group 12-15 of the fourth or a higher period of the periodic table and manganese. These metals can be divided into two categories. The alkali metals, alkaline metals, rare earth metals and yttrium have a lower quiescent potential than magnesium and therefore act to cathodically protect the underlying metal from corrosion. Metals from group 12-15 of the 4th or higher period and manganese have a high hydrogen evolution overvoltage and protect the magnesium metal by poisoning the cathodic half reaction. The thickness of the corrosion protection layer should be at least 0.2 mm in order to be effective. The patent sites examples of negative contact current

density measurements between the AM50A magnesium alloy and Mg/Mn, Mg/Pb and Mg/In samples.

The use of multilayer materials (127) has also been proposed for anti-wear, anti-erosion and anti-abrasion coatings on lightweight metals. These coatings involve the deposition of an intermediate layer consisting of Cr, Mo, Ni, Ti, Zr, their nitrides and carbides or solid solutions of C and N in these metals. This intermediate layer can consist of a single layer or a stack of several layers with individual thicknesses of 0.5-5 μm . The final layer(s) is a tungsten based deposit such as W, WC, WN and tungsten alloys that is 5-60 μm thick. In scratch tests of anodized aluminum coated with tungsten and anodized aluminum with an intermediate layer of titanium followed by tungsten deposition the critical loads were 5N and 12N respectively. The use of intermediate layers prior to tungsten coating was also shown to improve performance of the aluminum alloys in thermal cycling and erosion testing.

2.5.4.2. Deposition of Surface Alloys

Physical vapor deposition can also be used to create new magnesium alloys in bulk form or as a coating material. The addition of alloying elements to conventionally processed alloys results in the formation of second phase, galvanically active particles that increase corrosion problems (128). Deposition from the vapor phase can be used to provide a high extension of solid solution, even in non-miscible systems (128). Binary alloys such as Mg-Zr, Mg-Ti, Mg-V, Mg-Mn and Mg-Cr have been successfully deposited from the vapor phase(128-136) with thicknesses up to 25 μm . Corrosion studies on these binary alloys have shown that the corrosion rate of vapor deposited magnesium can be reduced by alloying with manganese, zirconium or titanium while chromium and vanadium have a detrimental effect on the corrosion resistance of pure magnesium(129-136). The vapor deposited alloys are columnar in structure and have a high degree of porosity. In-situ mechanical working during deposition has been found to reduce the porosity and eliminate the columnar microstructure around the flail line (130, 131). However the corrosion resistance of the flailed alloys was inferior compared to pure magnesium (131).

2.5.5. *Diffusion Coatings*

Diffusion coatings can be deposited by heating the component to be treated in contact with a powdered coating material in an inert atmosphere. This process produces alloy coatings at high temperatures by the inward diffusion of the coating material into the substrate material (137). Recently this technique has been used to create an aluminum diffusion coating on AZ91D magnesium alloy (138). The diffusion coating was formed by heat treatment of the magnesium alloy in aluminum powder at 450 °C for one hour, under an inert gas atmosphere. An Al-Mg intermetallic compound, 750 μm thick, was formed on the surface. The intermetallic layer formed was shown to have surface cracks but no cracks or pores were observed near the interface of the reacted layer and the magnesium alloy substrate. The surface layer produced was found to consist mainly of δ phase magnesium and γ phase $\text{Al}_{12}\text{Mg}_{17}$.

2.5.6. *Ion Implantation (82)*

Ion implantation involves exposing a surface to a beam of ionized particles. This results in ions being embedded and neutralized at interstitial positions in the substrate to form a solid solution. Bulk properties are not modified. There is very little information available on this process with magnesium. However a study on the corrosion protection of AZ91 implanted with N_2^+ demonstrated that Mg corrosion could be suppressed with an appropriate ion dose.

2.5.7. *Metal Plasma Immersion Ion Implantation and Deposition (MPIID)*

In MPIID the substrate is immersed in a metal plasma and a pulsed negative high voltage is applied to the sample. Ions are extracted from the plasma, accelerated to the substrate and implanted. During the pulse pauses low energy metal ions are deposited on the surface. The metal plasma is usually produced by a cathodic arc discharge (139). MPIID is typically used to enhance film properties through the removal of surface oxide

and creation of an ion implanted intermixed layer prior to metal deposition. A recent article describes this process for depositing chromium on magnesium with a film thickness from 200-300 nm (139). The corrosion behavior of these films was found to be strongly influenced by the formation of an intermixed layer and the particle content of the film. As the particle content decreased the corrosion potential became more noble indicating increased passivation of the sample. This has been attributed to a reduction in the number of film defects.

A primary limitation of this technique is its line-of-sight nature that makes processing of complex shapes difficult.

2.6. Laser Surface Alloying/Cladding (82,140)

Laser surface melting can create metastable solid solutions at metal surfaces where the cooling rate can be as high as 10^{10} K/s. This process is a form of rapid solidification processing but only the surface region is modified. The advantages of this technique include the ability to treat complex geometries, up to millimeters depth of treatment, lower operation cost and greater control of the concentration of the modified layer. This process has been investigated for improved corrosion resistance on Mg-Li and Mg-Zr alloys.

For laser surface alloying a metallic coating and the underlying substrate are melted using a high power laser. The rapid melting, mixing and resolidification cause the coating and substrate to alloy. Cu, Al and Cr coatings have been shown to have more noble pitting potentials and therefore more promising corrosion protection. Improved wear resistance has also been reported for commercial purity magnesium, AZ91 and WE54 alloys that have been surface alloyed with Al + Ni and Al + Si (141). The wear resistance of these substrates was not improved when alloyed with Al + Cu. This process was shown to have improved wear resistance over laser cladding with magnesium containing powders particularly when SiC particles were added to reinforce the surface coating.

In another related process the injection of hard particles of TiC and SiC into a molten pool of magnesium metal, created by a laser beam, has been used to modify magnesium alloy AZ91 to improve resistance to sliding wear (142). The surface was shown to consist of TiC and SiC particles dispersed throughout the cladding layer. These surfaces were shown to have improved wear resistance however opposing materials used for wear testing showed significant wear. The injection of fine particles of Mg_2Si was also studied. These materials showed high wear resistance and little wear of opposing materials.

In another closely related technique, a coating is thermally sprayed onto the substrate and subsequently remelted with a 2kW Nd:YAG laser (143). This technique has been used to coat a 17 vol% SiC particulate reinforced ZK60 magnesium composite with an Al-12.5 wt% Si alloy. The as-sprayed coating was loosely adhered but following laser re-melting complete fusion of the coating to the substrate was observed. Despite this improved adhesion, laser re-melting did not adequately improve the corrosion resistance due to excessive diffusion of magnesium into the laser-melted surface. It was also determined that careful control of the processing parameters is necessary to provide an adequate coating.

Laser cladding of AlSi30 on magnesium alloys AZ91 and WE54 has been shown to decrease volume loss by 38% and 57% respectively in wear tests (141). The authors determined that wear is significantly reduced in vacuum and that the primary wear mechanism in air is loss of adhesion followed by oxidation of wear particles to form hard, abrasive oxide particles.

2.7. Organic/Polymer Coatings

Organic finishing is typically used in the final stages of a coating process. These coatings can be applied to enhance corrosion resistance, abrasion and wear properties or for decorative purposes. An appropriate pretreatment process is required in order to produce coatings with superior adhesion, corrosion resistance and appearance. Magnesium surfaces must be free of surface contamination, smut and loose silicates,

oxides and intermetallic compounds (144). Cleaning processes for magnesium can involve mechanical pretreatment, solvent cleaning or alkaline cleaning. Cleaning is typically followed by a pickling or an etching step coupled with a chemical treatment, such as conversion coating or anodizing. These treatments roughen and chemically modify the surface so that the organic coating will have good adhesion to the surface.

Prior to applying an organic coating to a magnesium casting, all moisture and air must be removed from the pores of the cast part. The presence of moisture or entrapped air results in the formation of holes in the coating due to degassing during the curing process (145). An appropriate primer coating must also be applied to ensure adequate adhesion of the coating

A variety of treatment processes for producing specific decorative effects on magnesium alloys are outlined in Table 6. (14)

Table 6

Organic surface finishing processes for magnesium surfaces

Decorative Effect	Finishing for Interior Use	Finishing for Exterior Use
Bright Metal	Buff + ferric nitrate pickle + clear epoxy or acrylic	Buff + ferric nitrate pickle + clear epoxy or acrylic
Satin Finish	Wire Brush + ferric nitrate pickle + clear epoxy or acrylic	Wire Brush + ferric nitrate pickle + clear epoxy or acrylic
Tinted Clear	ferric nitrate pickle + tinted epoxy or acrylic	not recommended
Dyed Clear	ferric nitrate pickle + clear epoxy or acrylic + dye dip	not recommended
Metallic	Chrome pickle or dilute chromic acid + epoxy, acrylic, polyvinyl butyral or vinyl pigmented with metal powder or paste	Chrome pickle or dilute chromic acid + polyvinyl butyral primer + epoxy or acrylic pigmented with metal powder or paste

Wrinkle	Chrome pickle or dilute chromic acid + standard wrinkle finish	not generally used in outdoor service
High-gloss enameled	Chrome pickle or dilute chromic acid + epoxy, acrylic, polyurethane or alkyd enamel	Chrome pickle or dilute chromic acid + polyvinyl butyral primer + acrylic, alkyd or polyurethane enamel
Smooth Leatherette	Chrome pickle or dilute chromic acid + vinyl cladding	Chrome pickle or dilute chromic acid + vinyl cladding
Textured leatherette	Chrome pickle or dilute chromic acid + vinyl organosol	Chrome pickle or dilute chromic acid + polyvinyl butyral or vinyl primer + vinyl organosol

Another technique for treating magnesium surfaces prior to the application of an organic coating involves exposing the material to an aqueous solution containing an organic compound (146) after appropriate cleaning and pickling procedures. The compound must have a particular structure XYZ, where X and Z are both polar functional groups and Y is a straight chain structure with 2-50 carbon atoms. Some examples of these include 1-phosphonic acid-12-(N-ethylamino)dodecane, 1-phosphonic acid-12-hydroxydodecane, p-xylylene diphosphonic acid and 1,12-dodecane diphosphonic acid. These compounds react with the hydroxide groups on the metal surface through the acid groups to form a chemical bond. There is also a reaction between the remaining functional groups and the subsequent paint coating. These coatings are said to significantly improve paint adhesion and to inhibit corrosion. Another patented process (147) also improves paint adhesion and corrosion resistance for lightweight metals. In this process an ester cross-linked polymer coating is formed by reaction between a polymer rich in carboxylic groups and a polymer rich in hydroxyl groups. This ester cross-linked polymer system is then combined with a group IV element through the addition of one of fluozirconic acid, fluotitanic acid, fluohafnic acid or their

corresponding salts. One main advantage of these two processes is that they are chromate free.

Organic coating systems can include a variety of different processes that make use of organic polymers, such as painting, powder coating, E-coating (cathodic epoxy electrocoating) and the application of lacquers, enamels and varnishes. These systems can be based on a variety of coating resins such as acrylic, alkyd, butyrate, cellulose acetate, cellulose acetate butyrate, chlorinated polyethers, epoxies, fluorocarbons, nitrocellulose, nylon, polyesters, polyethylene, polypropylene, polyurethanes, rubber resins, silicones and vinyls (144). Traditionally organic coatings have been solvent based which poses a significant environmental concern with their use. However alternative processes that eliminate this problem are available. Some of these include powder coatings, the use of compliance solvents and waterborne solvents (144).

The primary function of organic coatings is to act as a barrier between the metal substrate and its environment. It is important that these coatings provide resistance to transport of ions, water, oxygen and charge through the film to the substrate(151). In applications where physical damage is likely to occur it is also important that the coating have self-healing characteristics. This can be accomplished by the presence of corrosion inhibiting pigments or additives in the coating or by the use of a sacrificial anodic compound in the film (151). One patented process (148) demonstrates that the addition of zinc chromate to a phenolic resin primer can significantly improve corrosion resistance. The inventors showed that samples treated with this process have no evidence of corrosion after 1000 hrs salt spray testing while samples coated with a conventional polymer coating were severely corroded after 24 hrs. In another process corrosion inhibition of magnesium is said to be improved by addition of both a corrosion inhibiting leachable pigment (chromate) and an ion reactive pigment in the form of small spherical aluminum particles (149). The metal spheres are believed to react with corrosive ions and help maintain the pH in the alkaline region while the chromate provides self-healing properties by leaching out at defect sites and forming a protective coating.

For an organic coating to act as an effective barrier, it must be uniform and well-adhered to the substrate. Organic coatings that do not meet this criteria often undergo filiform corrosion. In filiform corrosion, filamentous corrosion products appear under a coating (150). There are a number of difficulties in preventing corrosion with organic coatings. Some of these include, difficulty in applying a perfectly uniform film, non-uniform cross-link density in the film, non-uniformity in local pigment volume concentration and swelling or degradation of the polymer upon exposure to various gases or liquids(151). These problems can be minimized by using a multiple layer coating system consisting of a topcoat, that is typically the most hydrophobic and UV resistant coating, and primer and midcoats that have high crosslink density and wet adhesion to the substrate and each other (151). With a multiple layer system it is unlikely that defect areas will overlap, this ensures that the substrate is completely coated with organic material. This has been exploited in a patented system that makes use of a multiple layer coating on a magnesium wheel for improved corrosion and chipping resistance (152). This system consists of sequential layers of a cation electrodeposition coating, liquid coating, powder coating, an additional liquid coating and finally a top coat.

Another process for eliminating pinholes or defects in organic coatings involves the application of an organic sealant to the coating (153). This is accomplished by application of a low viscosity UV curable resin to the sample followed by low temperature curing with UV light.

One application of organic coatings is in the protection of US naval aircrafts from the operational and environmental conditions they are exposed to. In 1989 the standard coating system consisted of an epoxy primer followed by a polyurethane topcoat with a service life of approximately 4-6 years (154). The primer consists of a highly cross-linked epoxy/polyamide system containing titanium oxide as a pigment and strontium chromate as a corrosion inhibitor (154). This layer has excellent adhesion and chemical resistance. The topcoat is a two component polyurethane that is flexible but durable and chemical resistant (154). In some cases a sealant is also applied between the primer and topcoat. Its elastic nature offsets the brittleness of the epoxy and minimizes cracking of

the paint system. There are some challenges associated with this type of system including the use of environmentally unfriendly materials such as VOC's and chromate compounds, inadequate rain-erosion properties and lack of high temperature resistance. A coating with improved rain erosion resistance has been developed with a two component system consisting of a pigmented poly(ether)urethane and a ketimine crosslinker/chain extender(154). These coatings are elastomeric and can absorb and dissipate impact energy however, a topcoat is still required to improve chemical resistance and weathering properties. Some of the environmental concerns have been met by the development of water borne paints and high solids technology such as powder coating. A one coat system has been developed that addresses some of the environmental concerns (154). The Unicoat system is a self-priming two part polyurethane that adheres directly to the substrate. It contains titanium oxide and vesiculated beads that act to whiten and reduce gloss respectively. Zinc molybdate, zinc phosphate and organo-zinc salt pigments are also present as corrosion inhibitors rather than the traditional chromate compounds. A number of silicone based paints that are resistant to temperatures up to 650 °C have also been developed. The use of natural polymers such as polysaccharide graft polymers has also been suggested (155) as an environmentally friendly alternative. These coatings are produced by the hydrolysis-condensation reaction of polysaccharide, such as commercial starches and cellulose, with an antimicrobial agent such as halogen substituted silanes. The examples cited show that on aluminum these coatings have excellent corrosion resistance.

In the following sections, examples of organic coating systems that have been applied to magnesium or magnesium alloy substrates are reviewed.

2.7.1. Painting

One of the most important steps in painting of magnesium is choosing an appropriate primer. Primers for magnesium should be alkali-resistant and based on resins such as polyvinyl butyral, acrylic, polyurethane, vinyl epoxy and baked phenolic (14). The addition of zinc chromate or titanium dioxide pigments is commonly used for corrosion prevention (14).

A study of the corrosion resistance of die cast AZ91D magnesium alloys with paint finishing has been reported (156). Prior to painting, the samples were treated with either a conversion coating or an anodizing process. The surface treatments studied are shown in Table 7. The paint film was applied in two layers. The first layer was a primer containing an epoxy resin applied to a thickness of 25-30 μm and cured at 170 °C for 20 minutes. The final coat was an acrylic paint resin applied to a thickness of 25-30 μm and cured at 150 °C for 20 minutes.

Table 7

Surface treatments applied to magnesium alloy AZ91D prior to painting

Name	Bath Composition
JIS-1	$\text{Na}_2\text{Cr}_2\text{O}_7$, HNO_3
JIS-3	$\text{Na}_2\text{Cr}_2\text{O}_7$, CaF_2
JIS-7	$\text{Mn}(\text{H}_2\text{PO}_4)$, NaF , $\text{Na}_2\text{Cr}_2\text{O}_7$
DOW 22	$\text{Na}_2\text{Cr}_2\text{O}_7$, KMnO_4 , H_2SO_4
DOW 17	NH_4HF_2 , $\text{Na}_2\text{Cr}_2\text{O}_7$, H_3PO_4
HAE-A	KOH , KF , $\text{Al}(\text{OH})_3$, KMnO_4 , Na_3PO_4
HAE-B	KOH , KF , $\text{Al}(\text{OH})_3$, KMnO_4 , Na_3PO_4
U-5	Na_2SiO_3 , carboxylate, fluoride

It was determined (156) that conversion films with a significant amount of oxygen and chrome on the surface (JIS-1 and JIS-3 baths) and anodized films with a thick coating (Dow-17, HAE-B, U-5) gave the best adhesion and appearance of the paint film. The paint coated surfaces were shown to have excellent corrosion resistance since even after 4000 hrs salt spray testing and a 3 year atmospheric exposure test there were no signs of blisters or corrosion.

A recent paper (157) describes the effect of adding conductive polypyrrole(CP) to an acrylic paint, on the corrosion protection afforded by the organic coating. Conductive polypyrroles are believed to react with the metal at defects in the coating under certain

electrochemical conditions. This can act to protect the metal but in some cases corrosion can be accelerated. The protection afforded by polypyrroles is not fully understood; four possible mechanisms have been proposed; 1. the coating may act as a barrier 2. the conductive polypyrrole acts as a sacrificial anode 3. the coating acts as a reservoir for corrosion inhibiting ions that are released as the CP changes redox state 4. CP could act to stabilize a passive oxide layer. Further research is required to precisely determine the mechanism of corrosion inhibition. However, this study did show an improvement in corrosion resistance due to the addition of small amounts of conductive polypyrrole to the paint system.

2.7.2. Powder coating

Powder coating is a process in which a pigmented resinous coating powder is applied to the substrate and then heated to fuse the polymer together in a uniform, pinhole-free film (144). Powder coating is an excellent alternative to traditional painting processes since it is not detrimental to the environment and uniform thick coatings can be obtained in a single operation even on rough surfaces or edges. There is also little loss of coating material during application and even basic resins that are not readily soluble in organic solvents can be applied (144). However, there are a few inherent disadvantages to this technique:

1. The powder must be maintained in a very dry, pulverized form.
2. Thin coatings are difficult to obtain.
3. Color matching and color uniformity can be difficult to maintain.
4. Coating in recessed areas can be difficult.
5. High temperatures required for curing may be unacceptable for some substrates.

As with any coating process, appropriate pretreatment of the surface is critical for obtaining the best surface finish. This challenge was met by Applied Coating Technology Inc. who found that the use of an alternative chromate process in the pretreatment of magnesium alloys was ineffective as a base for powder coating (145, 158). They developed a process that used an organometallic, titanium based conversion coating to achieve the desired results. This process is outlined in table 8.

Table 8

Process for powder coating magnesium alloys

Stage	Operation	Condition
1	Alkaline Clean	3-5 min., 140-160 °C
2	Tap Water Rinse	
3	Etch Primer	1-2 min.
4	Tap Water Rinse	
5	Conversion Coating	2 min., Alodine 5200 (Henkel)
6	Water Rinse	Deionized
7	Blow-off oven	
8	Dry-off oven	250 °F
9	Powder Coating	

Powder coating has also been used to coat magnesium castings of engine valve covers. This company discovered that pretreatment with a process using chromic acid was necessary in order to achieve acceptable adhesion of the coating (159).

Powder coatings can be applied in a number of ways including electrostatic powder spraying, fluidized bed or flame spraying of thermoplastic powders. Flame spraying has been used in the application of ethylene acrylic acid copolymers (EAA) on a variety of substrates (160). In this process the plastic powder is propelled through a flame that heats and melts the polymer and the surface so that the coating particles coalesce and flow into a continuous coating. The EAA polymers have been shown to have excellent adhesion to metals due to the acrylic acid functional groups, which promote adhesion by hydrogen and ionic bonding to the substrate. The surface preparation is critical for obtaining optimum coating adhesion. The more free metal present, the more ionic bonding and consequently the more adhesion. On magnesium this poses a problem due to the very fast oxidation of the surface in air. Any oil or chemical contamination of the surface can also lead to a loss of adhesion or

pinholes formed by degassing of the contaminant during heating. The processing conditions must be carefully controlled in order to achieve the desired adhesion, corrosion resistance, low temperature flexibility and elongation and abrasion resistance. Factors such as particle size and distribution, residence time in the flame, proper blending of additives and degree of cross-linking have a significant effect on the quality of the coating produced.

Satisfactory corrosion resistance in salt spray tests and combined corrosion cycle tests has been demonstrated with the use of an epoxy based powder coating system on magnesium substrates (161). For this process an epoxy based powder containing a curing agent comprised of a polyester resin with carboxyl groups or dibasic acid dihydrazide groups was found to be most effective.

2.7.3. *E-coat*

E-coat or cathodic epoxy electrocoat is a process for painting metal surfaces by charging the metal part negative and submerging it in a tank that contains positively charged paint. The paint is attracted to the metal to form a uniform coating that is subsequently cured by baking (162). These coatings provide some protection against chipping, cracking, abrasion and corrosion. However, the coating is quite thin therefore it should be combined with a thicker top coat. Air pocket formation can also be a problem with this technique therefore parts should be designed to eliminate blind holes.

In a study to improve the protective coatings on magnesium aircraft components (163) it was determined that coatings that had a total thickness of 2 mil performed the best in salt fog corrosion tests. The authors determined that the best corrosion protection of the aerospace magnesium alloys ZE41A-T5 and WE43-T6 was obtained using the following scheme:

Non-chromate conversion coating→ E-coat→Primer→Resin Sealer

This process eliminates the environmental hazard posed by using traditional chromate containing conversion or anodized coatings and was deemed to have excellent

corrosion resistance due to the high impedance values of the coating although atmospheric corrosion studies had yet to be completed at the time of publication.

2.7.4. Sol-gel process

Synthesis of gels by the sol-gel process involves the hydrolysis and condensation polymerization of metal alkoxides. This process can be used to produce polymeric networks of inorganic-organic composite materials. It is possible to form adherent, uniform coatings on metal surfaces by the addition of components, to the reaction mixture, that are reactive with the surface that is to be coated. This process has been shown to produce corrosion-protective coatings on aluminum alloys by a simple wet coating technique through the formation of a stable tailored interface (164). It is also possible to produce coatings with high scratch and abrasion resistance through the in-situ generation of nano-particles in the coating (165). These coatings were tested on magnesium, aluminum and zinc steel. The coatings produced were transparent with excellent adhesion, scratch and abrasion resistance, and corrosion protection. These coatings were shown to be superior to an epoxy coating due to the formation of a very stable tailored metal/nanocomposite interface and the presence of the inorganic backbone in combination with in-situ generated particles. One of the primary advantages of this technique is the excellent adhesion obtained with a minimum of sample pretreatment. The metal surfaces studied in these examples were simply degreased, rinsed and dried prior to dip-coating in the sol-gel mixture. Samples are then cured at relatively low temperature (100 - 220 °C) to give the final product (164, 166). It has also been demonstrated that the coatings can be pigmented to give a colored coating (164, 165).

2.7.5. Polymer Plating

Polymer plating is the electrochemical polymerization of a polymer film on the surface of a substrate that functions as one of the electrodes in the electrochemical cell. This process has been used to deposit triazine disulfide polymers on the surface of magnesium alloy AZ91D (167, 168) by the electrochemical processing of triazine dithiols at the surface of a magnesium anode. Studies on the structure and composition of the films showed that oriented films with a layered structure composed of organic polymer,

Mg(OH)₂ and MgO were produced. It was determined that the highest polymer deposition rate with a minimum of side reactions could be achieved by using 1 M NaOH as the electrolyte and performing the plating operation at a temperature of 20 °C. The polymer films produced were found to suppress corrosion by suppressing the transfer of water, oxygen and electrons to the magnesium surface. Corrosion protection was found to depend on the thickness of the film produced and the type of alkyl substituent on the monomer. The best corrosion protection was observed for the N(C₆H₁₃)₂ substituent and was most likely due to the alkyl chains in the polymer film, which were highly oriented and closely packed. Corrosion protection was also found to increase with increasing film thickness.

A minimum number of pretreatment steps were required prior to polymer plating. In this instance the samples were mechanically polished followed by degreasing in acetone and hot air drying. The corrosion resistance of these coatings was evaluated by electrochemical impedance spectroscopy (EIS) however, the adhesion, salt-spray resistance and scratch and abrasion resistance of the coatings was not evaluated. This process is still in its infancy and will require more study before a marketable process can be developed.

2.7.6. Plasma Polymerization

Polymeric coatings can be applied from the gas phase by exposing a substrate to a reactive gas in the presence of a glow discharge plasma. This has been used to coat magnesium used as actuator arms in disk drives (169). The process outlined in this patent involves exposing the magnesium to a fluorinated alkane, under vacuum, in the presence of a glow-discharge plasma. This results in the formation of a thin uniform fluorocarbon coating on the surface. The low surface energy coating produced is resistant to atmospheric water, chlorine and oxygen. It is also tough, scratch-resistant and smooth. These coatings were not evaluated for their corrosion resistance in salt-spray conditions and while they are most likely adequate for use in a computer system, a more rigorous surface treatment is most likely required for harsher service conditions.

3. Coating Applications in the Automotive Industry

In order to obtain the best surface finish in terms of corrosion and wear protection, decorative appearance and manufacturing ability, it is often necessary to encompass several of the coating techniques discussed. This approach has been successfully applied to the production of a Mg/Al hybrid hatchback for Volkswagen's 3 liter car (170). The inner component of the hatchback is fabricated from die cast magnesium alloy AM50 and covered with an aluminum panel from the outside. In order to prevent galvanic corrosion it was necessary to precoat the magnesium component, which was then bonded and folded with the bare aluminum part. The magnesium part underwent cleaning, acid pickling, chromating, E-coating and finally powder coating prior to bonding and folding to the pickled aluminum part. The whole component was then cleaned, phosphated and E-coated to provide maximum protection. This study demonstrates how magnesium can be adequately protected from corrosion for use as automotive body components.

A multicomponent coating process for finishing magnesium die castings with class A surface quality has also been developed (171). Class A refers to the glossy, smooth appearance that is required for readily visible, outer surfaces of automobiles. Die castings are particularly difficult to finish due to the presence of flow marks, hot tears and contraction cavities. These cavities tend to outgas during thermal curing of coatings creating pinholes in the final film. It is possible to eliminate these by grinding or sanding the surface prior to coating however this poses a serious environmental hazard due to the explosive nature of magnesium dust. The standard coating system currently applied to outer automobile surfaces does not meet class A requirements when used on magnesium alloys. The authors (171) have developed a coating system that shows good paint compatibility, adhesion, corrosion resistance and decorative appearance for die cast magnesium substrates. The process involves applying a conversion coating (chromate, phosphate/permanganate or fluorozirconate) to the surface followed by the application of a filler and finally painting with a basecoat and clearcoat. The filler used is a silicone-modified polyester resin that has improved leveling behaviour and good corrosion inhibition.

4. Conclusions

The examples described in the previous section demonstrate that it is possible to develop appropriate coating schemes for the protection of magnesium for use in automotive components. However, to date, no single coating technology has been developed which functions to adequately protect magnesium from corrosion in harsh service conditions. The current coating schemes are complex, multi-layer systems that incorporate many different technologies and must be conducted very carefully in order to achieve optimum results.

There are a number of patents that claim to have coating processes for magnesium and its alloys. While some of these have direct evidence to support the use of these technologies on magnesium, there are a large number of claims that only provide direct evidence that the coating technology works on aluminum and its alloys. The chemistry of aluminum is quite different from that of magnesium and it is therefore possible that these coatings may not perform as well on magnesium.

There are a number of factors to be considered when developing a coating process for an industrial application. These include capital investment, ease of manufacturing, coating performance and environmental issues.

In the case of electrochemical plating, the capital investment is relatively small. However, there are some serious concerns over waste disposal. The most successful example of electroless plating technology for magnesium has a maximum turnover rate of 6, when a strict replenishment schedule is followed. Further research is required to enhance the longevity of plating baths and to decrease waste generation. The use of toxic chemicals such as chromium compounds, cyanide compounds and fluoride compounds in the pretreatment and plating baths also necessitates further research into the development of “green” plating technologies. Another challenge associated with electroless plating on magnesium is the narrow window for operating conditions in order to obtain optimum coatings. The difference in the surface chemistry of various magnesium alloys also

represents a significant challenge in development of uniform, pore-free coatings. Despite these challenges, this technology does have the potential to produce uniform, corrosion and wear resistant coatings with good electrical conductivity and solderability, at a low cost. Electroplating does not have as much environmental impact due to the relatively long bath life of the plating solutions. However, achieving uniform coatings on complex shapes can be extremely difficult due to uneven throwing power of the current required for metal deposition.

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

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

ceramic, insulating materials and are not appropriate for load bearing applications or applications where electrical conductivity is required.

The use of gas-phase coating processes and laser surface melting/alloying/cladding to modify the surface or create coatings on magnesium is an excellent alternative with respect to its environmental impact. These techniques produce very little and in some cases no hazardous waste. However, the capital cost associated with these techniques is much higher than solution phase coating technologies. These coating processes also tend to be line-of-sight which makes it difficult to uniformly coat complex shapes and inside holes or deep recesses. Finally, the corrosion, adhesion and wear properties, of these coatings, on magnesium, have not been widely documented.

Organic coatings are extremely versatile and can be applied to many metals provided an appropriate pretreatment can be developed for the substrate. The adhesion and corrosion resistance of these coatings are inadequate without pretreatment. Organic coatings are typically the last step(s) in a coating system. They may be applied for a purely decorative effect or to enhance the corrosion resistance of the overall coating system. It is usually necessary to apply multiple layers of these coatings to provide optimum corrosion and wear resistance due to difficulties in obtaining perfectly uniform, pore-free coatings. Some organic coating technologies such as polymer plating, sol-gel coating or plasma polymerization require a minimum of pretreatment steps prior to deposition. However, the adhesion, and corrosion and wear resistance of these coatings have not been widely documented. There are some environmental concerns with the use of solvent borne organic coatings but the development of water-borne and powder coating technologies has led to a decrease in the use of these chemicals.

There are a large number of coating technologies available for protecting magnesium and its alloys. However, the widespread use of magnesium in the automotive industry is still deterred by the lack of appropriate protective coatings that can withstand harsh service conditions. A great deal of research is still required to develop better,

simpler, cheaper coating technologies so we can take advantage of the lower weight and excellent mechanical properties of this material.

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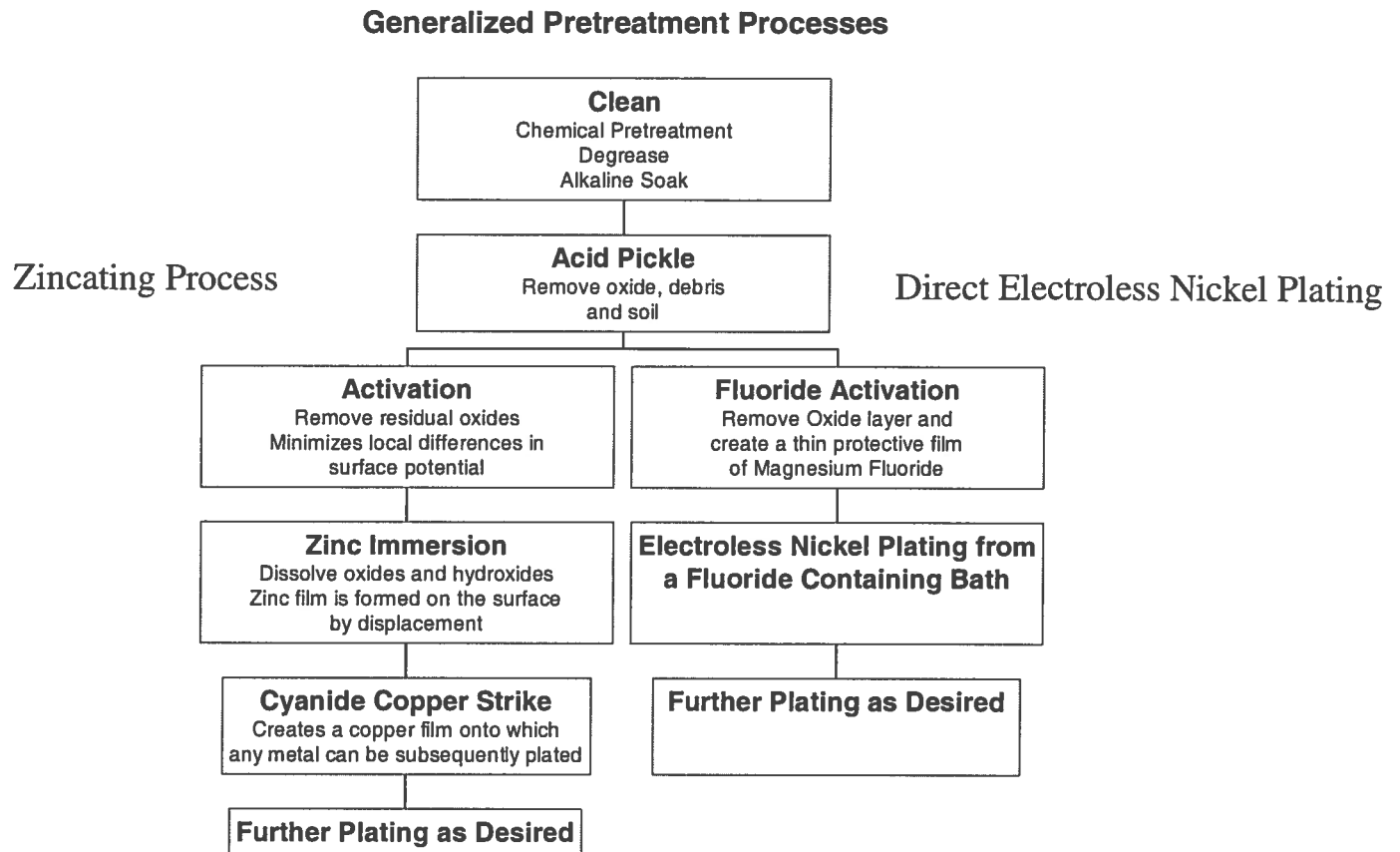


Figure 1. Generalized Pretreatment Processes

Appendix 1

Nominal Composition of Common Magnesium Alloys (weight%)

Alloy	Al %	Mn%	Zn%	Rare Earths%	Zr%	Y%
AM60	6	0.15				
AZ31	3	0.2	1			
AZ61	6.5	0.15	1			
AZ91	9	0.13	0.68			
WE54				3.5	0.5	5.25
ZE63			5.8	2.6	0.7	
ZK21			6		0.8	
ZM21		1.2	2.2			

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