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NSWC TR 85-88

# CORROSION RESISTANT MAGNESIUM-BASED MATERIALS FOR NAVAL APPLICATIONS

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and still experimental anticorrosion surface modification techniques are assessed for magnesium.

Special emphasis is given to the magnesium-graphite fiber composite system, identified as unique for certain space satellite applications by virtue of its very high stiffness, near zero coefficient of thermal expansion (CTE), and high electrical conductivity. Some evidence of potential corrosion problems with this composite material in the prelaunch environment and a mechanism possibly responsible for this are presented. Relatively brief discussion is devoted to achieving the desirable properties of Gr/Mg composites using alternative materials.

Finally some recommendations are made for corrosion protection of magnesium-based materials for naval systems in light of recent research efforts. Additional consideration again is given to the potentially important Gr/Mg composite system.

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FOREWORD

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This report reviews the corrosion related properties of magnesium, magnesium alloys, and magnesium based composites. It attempts to place in perspective the corrosion behavior/limitations of these materials in environments likely to be experienced by naval systems. Too often, past uses of magnesium based materials have been made with little appreciation of the role of impurities, fabrication methods, proper installation procedures, or physical limitations. This has led to some unwarranted past corrosion failures in marine related structural uses. Therefore, a current reluctance exists to consider new developments for expanded applications of these materials. The prospects of magnesium based composites reinforced with graphite and other fibers are discussed.

This report is essentially a fresh, though quite cursory, look at magnesium/magnesium based materials for naval systems in light of modern developments in fabrication and corrosion protection methods.

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## CHAPTER 1

### INTRODUCTION

Modern materials requirements for diverse naval marine and aerospace systems will require new classes of special structural materials. In some cases, conventional superalloys, stainless steels, or titanium alloys can meet the requirements. However, shortages and political considerations regarding critical elements may make their eventual replacement necessary. In other cases, particularly in air and space borne systems, new lightweight, high strength materials must be developed.

The primary purpose of this report is to review the more recent literature on corrosion protection of magnesium based alloys and composites. Particular goals will include: (1) the deduction of reasonable impurity limits for the starting magnesium base metal subsequently to be used in alloy or composite, (2) review of important traditional protection methods, and (3) potential application of new or novel techniques. In addition to the more common situation of marine environments, special consideration is given to the application of magnesium based materials to space structures.

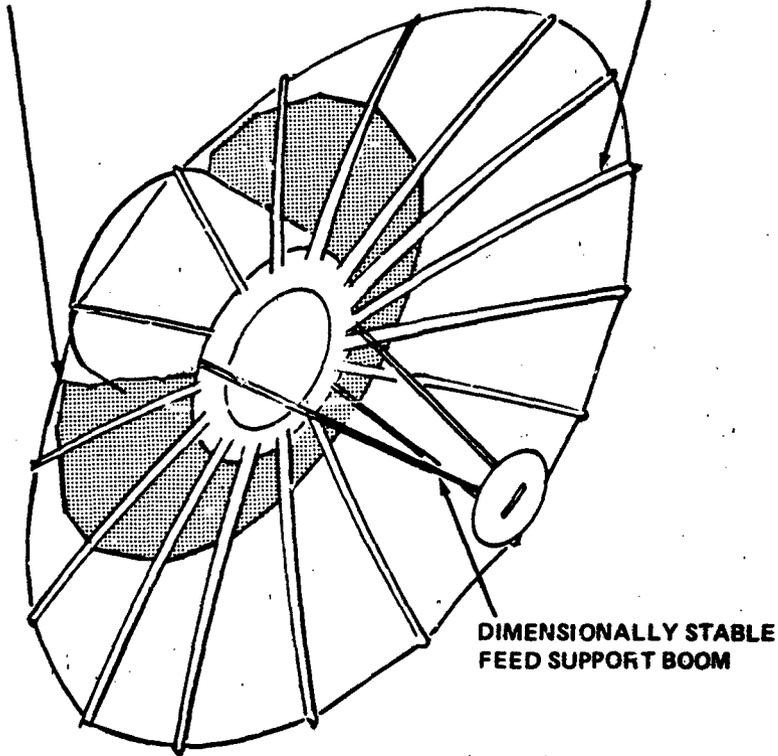
### MOTIVATION

Prior to the discussion of magnesium corrosion properties and protection methods, it is appropriate to develop a motivation for the effort. The example of magnesium based composites for space systems should serve this purpose. Figure 1 illustrates some critical satellite components which are candidates for the new structural materials. Up to this time, the workhorse materials for such components have been aluminum alloys and epoxy based fiber composites. Lightweight materials with stiffness and strength higher than those currently available would be desirable for some applications but essential for others. Weight reduction is only part of the story.

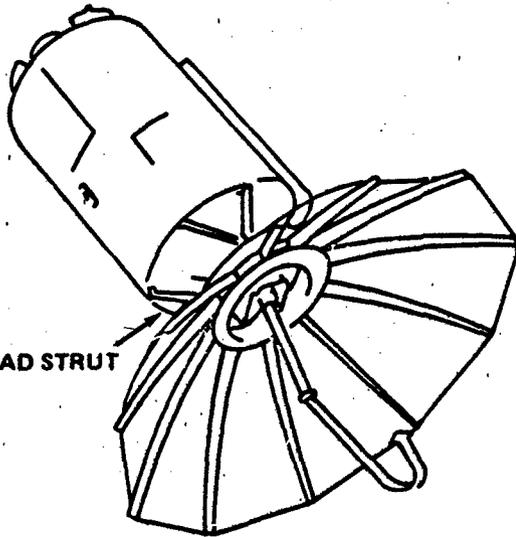
Replacements for aluminum components ( $\rho = 2.7$  g/cc) must possess measurably better physical properties and comparable workability. Beryllium ( $\rho = 1.85$  g/cc) was determined to be the only pure element with specific stiffness and light weight sufficient for these advanced satellite components. However, complete dedicated special fabrication facilities are required for working with Beryllium because of its extreme toxicity in handling and machining. The next feasible candidate is magnesium ( $\rho = 1.74$  g/cc). Since

ADVANCED SOLAR ARRAY PANEL

DIMENSIONALLY STABLE ANTENNA RIB



PAYLOAD STRUT



(FROM REFERENCE 1)

FIGURE 1. SOME METAL-MATRIX COMPOSITE APPLICATIONS IN EARTH-LOOKING SATELLITES

there exists a reasonable body of previous research and experience with this metal, it emerges as a logical choice. In fact, magnesium has been identified by the GAO as the only truly domestic light structural metal.

A magnesium based material suitable for the satellite system components shown in Figure 1 will require reinforcement. Figure 2 compares the properties of specific stiffness and resistance to thermal deformation of various fiber/magnesium reinforced composites with other candidate materials. Due to their low density, high strength, and stability, graphite fibers are the reinforcements of choice for these composites. The outstanding combination of specific stiffness and thermal deformation resistance of these composites is unequalled. Quick damping of relative motion of satellite members after a maneuver requires high specific stiffness. Resistance to dimensional distortions in orbit due to thermal cycling requires a very low coefficient of thermal expansion (CTE). Certain Gr/Mg composites have a near zero CTE. Other advantages include: excellent thermal conductivity, good electrical conductivity (EMI shielding), minimal space charging, no moisture absorption, no outgas by-products, and high temperature capability.<sup>1</sup> This combination of advantages leaves little doubt why considerable efforts have been devoted to improving fabrication and overcoming the remaining shortcomings of this material.

Having cited this potential use of a high tech magnesium based material, it should be noted that Navy requirements for lightweight, strong substitute metals do not end here. It will be one goal of this report to investigate the applicability of magnesium based alloys (and composites) to the spectrum of Navy needs. In point of fact, the use of magnesium has been largely avoided in marine systems. We want to investigate the basis for this and whether recent developments might warrant a change in this policy. We begin by examining the corrosion properties of the magnesium surface.

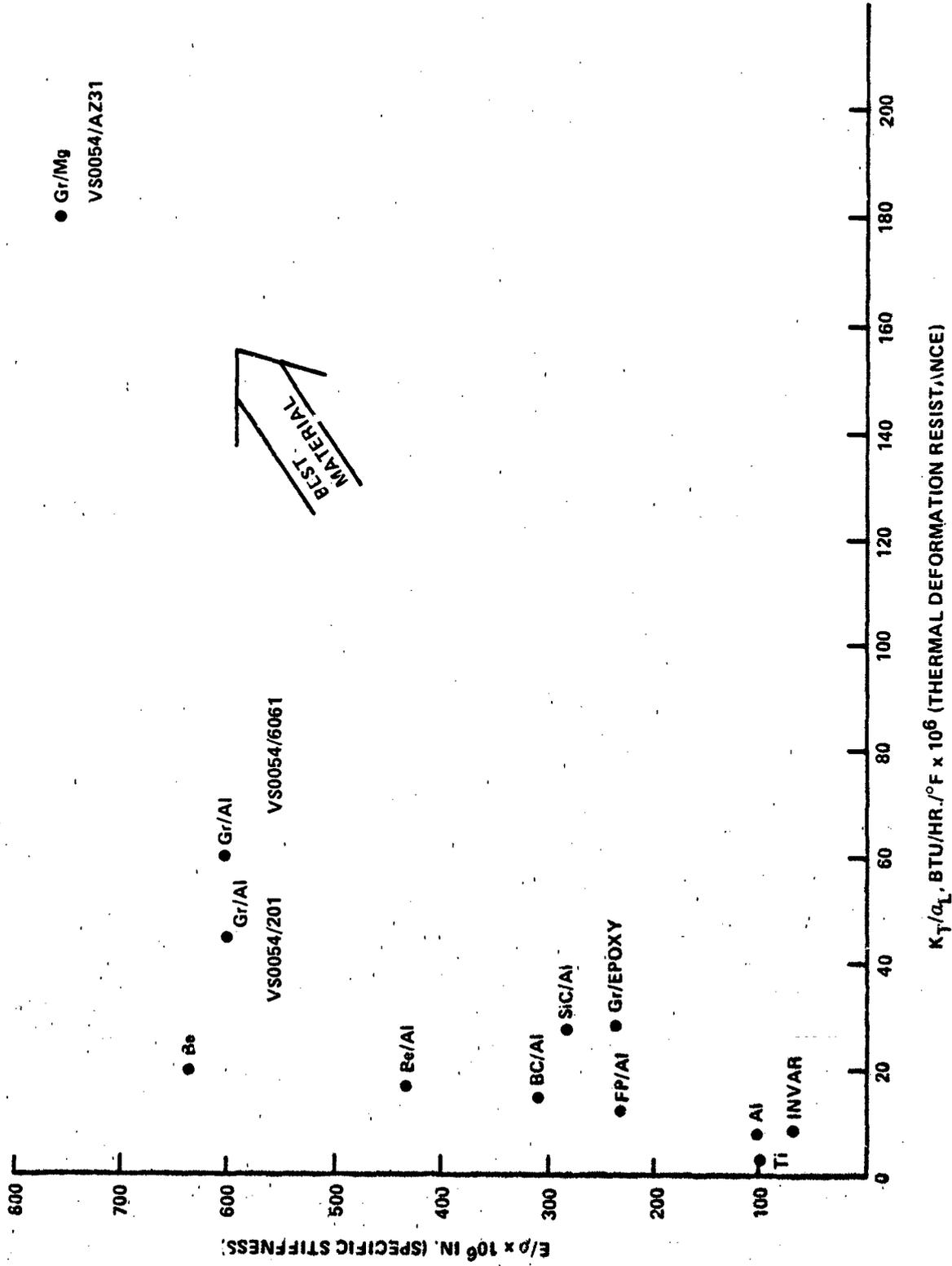


FIGURE 2. FIGURE OF MERIT, SPECIFIC STIFFNESS VERSUS THERMAL DEFORMATION RESISTANCE

## CHAPTER 2

## CORROSION PROPERTIES OF MAGNESIUM SURFACES

## SOME PHYSICAL PROPERTIES OF MAGNESIUM

Important physical constants of the element magnesium in the present context are given in Table 1. With few exceptions, there is no appreciable corrosion of magnesium near room temperature unless water is present. The reaction in this case is often described by the equation:  $Mg + 2H_2O = Mg(OH)_2 + H_2$ . In neutral and alkaline environments, the magnesium hydroxide deposits as a film which, although not as effective as the oxide layer formed on aluminum, can offer considerable protection to the metal.

## THE PROTECTIVE FILM

Electron diffraction studies have confirmed that magnesium and conventional magnesium alloys, exposed to humid air, exhibit excellent stability with oxidation rates of less than 100 Å per year (<.0004 mils per year (mpy)), provided no condensation occurs. If condensation is present, the  $Mg(OH)_2$  film is rapidly destroyed. For example, a 400 Å thick magnesium layer is dissolved in less than a day. The normally amorphous film then contains crystalline  $Mg(OH)_2$  (Brucite). Likewise, tests show that pure magnesium (99.5+% purity < 10 ppm Fe + Ni + Cu) immersed in distilled water, from which acid atmospheric gases have been excluded, is also highly protected. However, this good resistance to corrosion in water at room temperature decreases with increasing temperature, corrosion becoming particularly severe above 100°C. For example, a particular alloy (A231B) has a corrosion rate of 17 mpy at 100°C but 1200 mpy at 150°C. The  $Mg(OH)_2$  crystalline (Brucite) film has a layer lattice which undergoes easy basal cleavage which is probably responsible for the observed cracking and curling of the film of pure magnesium in distilled water. The relatively high pH (10.4) of the  $Mg(OH)_2$  film causes magnesium to resist strong bases well. High purity magnesium is reported<sup>2</sup> to have a corrosion rate of  $10^{-2} - 10^{-3}$  mpy when exposed to 2N KOH solution at 25°C.

As would be anticipated from the high pH of magnesium hydroxide, magnesium is subject to dissolution by most acids. Indeed, even in dilute solutions of strong and moderately weak acids, magnesium dissolves as rapidly as the acid can diffuse to its surface. There are a few exceptions, such as hydrofluoric acid, where an insoluble surface film of  $MgF_2$  is formed which protects against further attack. Also of significance in the corrosion of magnesium is the effect of acid gases in the atmosphere. The atmosphere contains a substantially constant 300 ppm  $CO_2$  and normally 1 ppm of  $SO_2$ , unless augmented to several ppm by the

TABLE 1. SOME PHYSICAL CONSTANTS OF MAGNESIUM

Melting Point	650°C
Boiling Point	1107°C
Density	1.74 g/cc
Oxidation State	2+
Atomic Radius	1.60 A
Ionic Radius	0.65 A
Ionization Energy	176 Kcal/g-mole
Specific Heat	0.25 cal/g/°C
Thermal Conductance	0.38 cal/cm <sup>2</sup> /cm/°C/sec
Electrical Conductance	0.224 microhms <sup>-1</sup>
Heat of Fusion	2.14 K-cal/g-atom
Heat of Vaporization	32.517 K-cal/g-atom
Crystal Structure	Hexagonal Close Packed

presence of combustion products. The dominant film anion after weathering is  $\text{CO}_3^{2-}$  found in the form  $3 \text{Mg CO}_3 \cdot \text{Mg (OH)}_2 \cdot 3 \text{H}_2\text{O}$  (hydromagnesite) or similar compound. In urban industrial locations  $\text{Mg SO}_4 \cdot 6 \text{H}_2\text{O}$  and  $\text{Mg SO}_3 \cdot 6 \text{H}_2\text{O}$  can predominate. The latter are highly soluble and are easily washed away, reexposing the surface. The hydroxide and carbonate mixed films noted above lose their protective capability by conversion to the soluble crystalline forms. Corrosion rates for pure magnesium samples varied from 1.2 to 12 mpy when immersed in distilled water in contact with the atmospheric gases. The rate was only 0.6 mpy when atmospheric gases were restricted. The above discussion indicates the rather complex interaction of atmospheric gases, contact with water containing dissolved ions, and temperature on the corrosion rate of pure magnesium.

#### ELECTROCHEMICAL BASIS FOR MAGNESIUM CORROSION

Most corrosion is generally accepted as electrochemical in origin and magnesium is a relatively simple metal to describe from this perspective. In accord with regular practice the two half cell reactions can be written:



In actual situations the magnesium electrode potential is much more positive (passive) than its thermodynamic potential would indicate because of the insulating effect of the generated surface film. The most positive potentials are observed in pure water and alkaline solutions containing subcritical amounts of certain anions. These potentials are usually near the hydrogen electrode reversible potential or readily ennobled thereto by application of a very small anodic current. Only in environments of this type, and then only under good aeration, does oxygen reduction play a significant role in magnesium corrosion. As the potential is lowered due to the presence of anions, oxygen reduction becomes negligible relative to hydrogen evolution. The ability of an anion to reduce the magnesium potential appears to depend on the solubility of its magnesium salt. It has been suggested<sup>3</sup> that anions are carried by electrochemical transport to anodic sites on the metal surface, where they form the magnesium salt which is acidic to the hydroxide film and therefore damaging. For example a low electrode potential and rapid uniform corrosion rate is observed with pure magnesium in 3M  $\text{Mg Cl}_2$ , supporting this model.

Examples of these activating anions are:  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{SO}_2^{-2}$ , and  $\text{Cl O}_4^-$ . In the presence of salt solutions of these anions, magnesium (and its alloys) becomes several tenths of a volt active to the hydrogen electrode potential. Further, in such environments, magnesium shows great resistance to polarization (anodic protection), even when large anodic current is applied. Therefore, all that is necessary for rapid corrosion are sites for the easy discharge of hydrogen. However, it should be pointed out that the hydroxide film itself is not an effective site for hydrogen discharge, probably because of its poor electronic conduction. Effective sites are elements of low hydrogen overvoltage

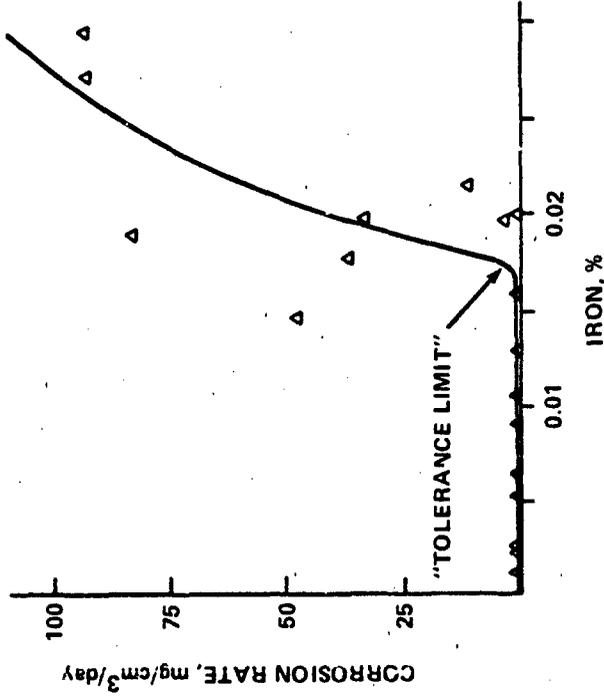
such as iron, copper, or nickel which may be present as alloy impurities, surface contaminants from processing or from reduction of salts in the environment. The elimination or control of these low overvoltage surfaces is an important aspect of magnesium production and use. This subject is treated further below.

#### EFFECT OF ALLOYING ADDITIVES AND IMPURITIES ON CORROSION RESISTANCE OF MAGNESIUM

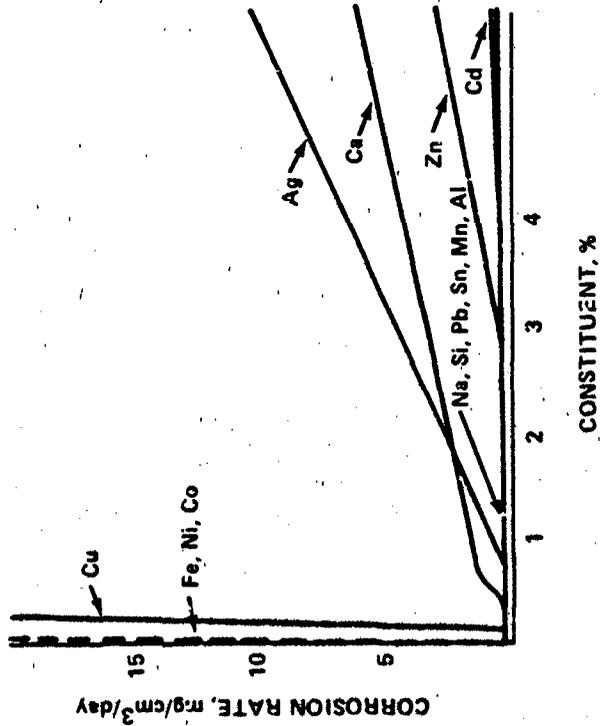
Efforts to improve seawater (and sea mist atmosphere) corrosion resistance of pure magnesium have shown that its performance in this regard is not significantly exceeded by any of its alloys. Rather extensive work has been done in measuring the effects of various metal additions.<sup>4,5</sup> The principal results of such alloying and impurities are summarized below.

Carefully distilled pure magnesium (> 99.99 percent), containing <10 ppm iron plus nickel plus copper, was subjected to alternate immersion tests in 3 percent sodium chloride solution at 20°C. A corrosion rate of about 12 mpy was noted. Similar corrosion rates were found subsequently with even higher purity fractionally sublimed magnesium (99.999 percent) containing less than 5 ppm iron plus nickel plus copper.<sup>6</sup> Results of this research also showed that up to 5 percent Pb, Sn, or Al has little or no effect on the corrosion rate of pure Mg. Na, Si, and Mn, likewise, showed no adverse effect even when present in excess of their solid solubility limits. Subsequent measurements indicated that Th, Zr, Be, Ce, Pr, and Nd each showed no adverse effects.

The corrosion rate, however, was increased when Mg was alloyed with the following elements in excess of the (tolerance) amounts shown: Zn (2 percent), Ca (0.3 percent), Ag (0.5 percent), Cu (0.1 percent), Fe (0.015 percent), and Ni (0.0005 percent). The increase in corrosion rate when the tolerance limit was exceeded was gradual with Zn; more rapid with Ca and Ag; and precipitous with Cu, Fe, and Ni. Data on tolerance limits and corrosion rate dependency are shown in Figure 3. The addition of 1 percent Mn increased the tolerance limit for nickel to about 0.01 percent but had little effect on other tolerances. The addition of 1 percent Zn did not appreciably affect the tolerances for Fe, Cu, and Ni, but made the corrosion rate dependency less severe when this was exceeded. Probably the most important alloy of Mg is that with Al. Al additions in the 2 to 10 percent (wt) range form useful alloys and have no direct adverse effect on corrosion properties, except for lowering somewhat the tolerance limit of Fe. Addition of 0.2 percent Mn, however, stabilizes this limit in the presence of 2 to 10 percent Al. Finally, the addition of 1 to 3 percent Zn to the Mg-Al-Mn alloys increases the tolerance limits for Fe, Ni, and Cu. For these reasons, both Mn and Zn are added to most commercial Mg-Al alloys. Some alloys have been designed with all of the above considerations in mind, subject to the conditions of satisfactory castability and mechanical properties.



B. EFFECT OF IRON ON THE CORROSION OF PURE MAGNESIUM - CORROSION RATES DETERMINED BY ALTERNATE IMMERSION IN 3% NaCl



A. CORROSION OF MAGNESIUM BINARY ALLOYS - CORROSION RATES DETERMINED BY ALTERNATE IMMERSION IN 3% NaCl

(FROM REFERENCE 6)

FIGURE 3. CORROSION RATE DEPENDENCE ON IMPURITY CONTENT OF MAGNESIUM IN 3 PERCENT NaCl SOLUTION

## CHAPTER 3

## CORROSION OF MAGNESIUM-BASED MATERIALS IN ION BEARING ENVIRONMENTS

The corrosion of magnesium (alloys) depends upon several factors each of which includes interaction with moisture. There are two main processes: (1) conversion of the protective surface film to soluble bicarbonates, sulfites, and sulfates which are washed away by rain; and (2) stimulation of local cell action by chloride ions (Chapter 2). Both types of atmospheric corrosion may be expected to be operative to some degree at aerospace component surfaces if they reside in a coastal atmosphere prior to launch.

## ATMOSPHERIC CORROSION IN THE ABSENCE OF CHLORIDE ANION

In areas far from the ocean, processes described by (1) above predominate. In this case, atmospheric  $\text{CO}_2$  and  $\text{SO}_2$  chemically react with the protective surface film rendering it soluble. The film subsequently washes away, exposing fresh surface to the gases. The corrosion resulting from this activity is generally uniform and not too severe except under extreme atmospheric conditions. Coatings and surface treatments (Chapter 4) have been developed which afford reasonable protection from this type of uniform corrosion.

## GALVANIC CORROSION IN THE PRESENCE OF THE CHLORIDE (ELECTROLYTE) ANION

Corrosion by mechanism (2) above will be important in ocean proximity storage areas. Basic galvanic corrosion occurs when two dissimilar metals (alloys) are brought into contact in the presence of an electrolyte. For our purposes, this electrolyte is the seawater or  $\text{Cl}^-$  bearing ocean atmosphere. An electrolytic cell is formed. The more anodic metal of the couple suffers the loss of some valence electrons. It then forms a soluble chloride compound on its surface in the region of contact.

Galvanic couples are often set up when two "incompatible" metals are fayed or bonded together in an assembly used in contact with an electrolyte solution. Magnesium and its alloys are particularly vulnerable in this regard as Table 2 indicates. This shows the galvanic series of important metals and alloys in seawater environment. Magnesium and its alloys head the list as the most anodic. If, for example, magnesium is immersed in seawater (or sea mist atmosphere) in contact with iron or nickel, it will corrode rapidly at surfaces

TABLE 2. GALVANIC SERIES IN SEAWATER

Cathodic (Most Noble)	Platinum
	Gold
	Graphite
	Titanium
	Silver
	Zirconium
	Type 316, 317 Stainless Steel (passive)
	Type 304 Stainless Steel (passive)
	Type 410 Stainless Steel (passive)
	Nickel (passive)
	Silver Solder
	Cupro Nickels (70-30)
	Bronzes
	Copper
	Brasses
	Nickel (active)
	Naval Brass
	Tin
	Lead
	Type 316, 317 Stainless Steels (active)
	Type 304 Stainless Steel (active)
	Cast Iron
	Steel or Iron
	Aluminum 2024
	Cadmium
	Aluminum (commerically pure)
	Zinc
Anodic (Active)	Magnesium and Magnesium Alloys

(From "Zircadyne™ Corrosion Data" published by Teledyne Wah Chang, Albany, OR, 97321)

adjacent to points of contact. Factors which moderate the impact of such corrosion are its ease of prediction, location, and means of avoidance. Some of these will be discussed in Chapter 4.

#### ROLE OF IMPURITIES IN MAGNESIUM

The presence of certain impurities (discussed in Chapter 2) in magnesium really constitutes a special case of galvanic corrosion by the mechanism of "local action." Here, the role of incompatible metal in contact is played by an impurity site on the metal surface. Atoms of magnesium surrounding the site lose electrons and form a salt compound. A region of enhanced corrosion surrounding the impurity results. One such site will produce a pit shaped corrosion region. The action of many impurity sites is to produce a corrosion condition uniform in appearance but very severe.

#### COMPOSITES: GRAPHITE-MAGNESIUM

Magnesium metal-matrix composites (MMC's) and, in particular, graphite fiber-magnesium composites constitute a case for special consideration. This is due primarily to their inherently large interfacial area of dissimilar materials. Discontinuous composites contain short fiber reinforcement of random orientation in the matrix. Continuous composites contain oriented long fiber reinforcement extending over component dimensions. Continuous MMC's have undergone greater development and are most important at present.

Continuous Gr/Mg composites generally consist of multi-filamented tows of a graphite yarn, having excellent tensile strength and other properties, immersed in parallel bundles into the magnesium metal matrix. In practice, the yarn is often chemically pretreated with special coatings intended to minimize fiber thermal degradation in fabrication, promote wetting, and impart beneficial characteristics to the magnesium/fiber interface. Usually the pretreated yarn is coated in a magnesium melt to produce a composite wire. The wires are laid out and hot pressed in a process called "consolidation." The volume percentage of fiber reinforcement may be varied over a considerable range. To the extent determined by the fiber and metal host, standard metallurgical methods of extrusion, rolling, etc., can be applied in forming the composite. Such composites can be fabricated having the desirable properties for aerospace use noted in the introduction. The nature of the fiber-metal interfacial bond plays an important role, as does the transverse fiber strength, in determining the transverse properties of the composite. This strength, as determined by a rather small transverse modulus  $E_t$ , is generally somewhat deficient. This is a matter of some concern as MMC's are considered for space applications; it will require additional research and novel approaches to solution.

Figure 1 shows a graphite fiber/aluminum composite plate after a 6 month atmospheric corrosion test. The plate was thoroughly painted and exposed about 1 meter from calm seawater. Sea spray contact, therefore, could be considered partial or occasional. The extent of corrosion is evident. The exposure appears to have caused delamination of the plate along the fiber axes.

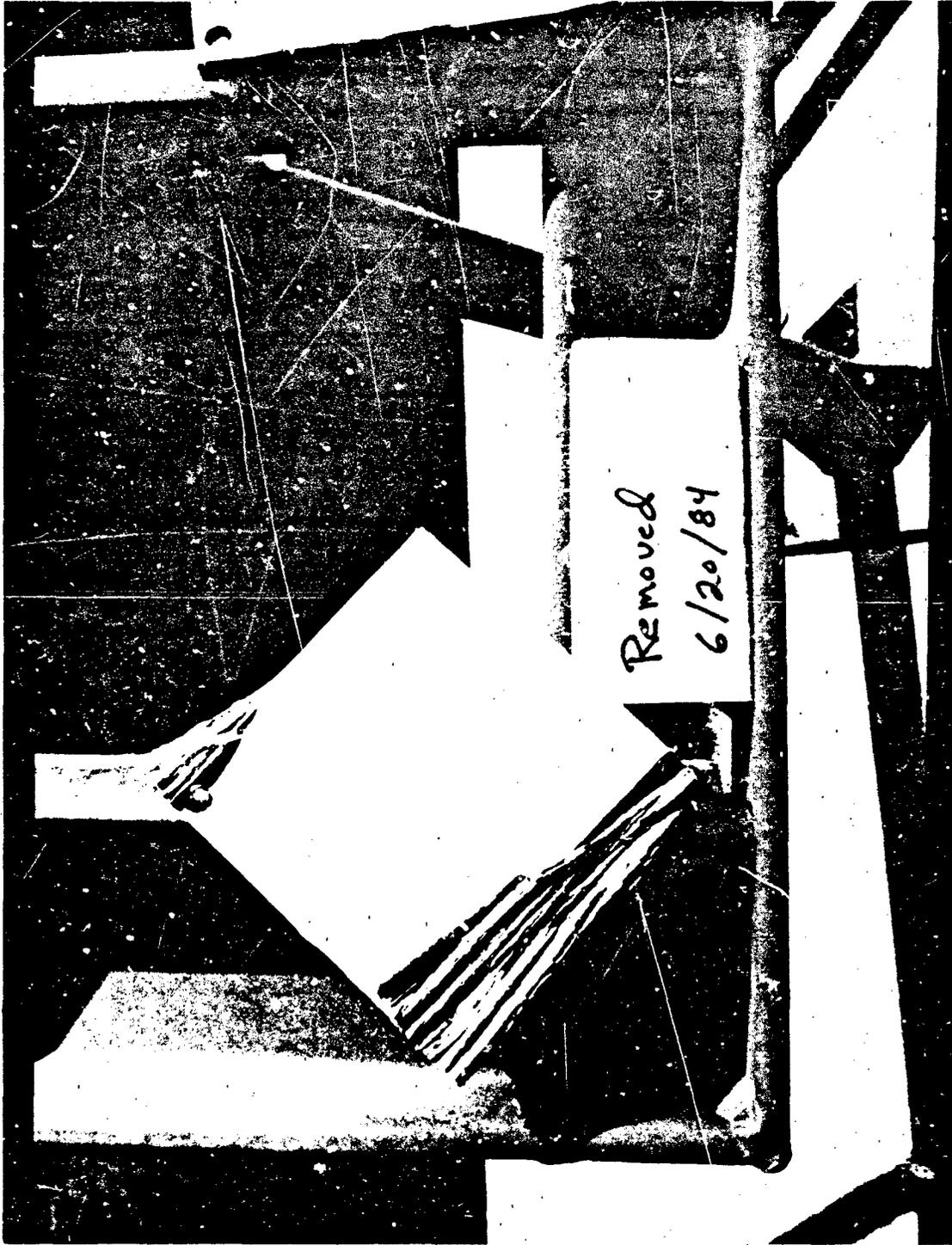


FIGURE 4. GRAPHITE FIBER/ALUMINUM COMPOSITE TEST PLATE, EXPOSED TO CALM MARINE ATMOSPHERE AT NSWC FT. LAUDERDALE, FLORIDA, CORROSION TEST FACILITY (COURTESY CORROSION GROUP, NSWC)

Crowe states in a recent report<sup>7</sup> on localized corrosion effects in graphite/aluminum composites:

"The general observations are that corrosion proceeds preferentially at wire-foil, foil-foil, and wire-wire interfaces causing separation and yielding  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  corrosion product. The degradation process, once initiated, proceeds rapidly by exfoliation causing disintegration of the composite. Disintegration may be accelerated by corrosion product wedging at the flaw. The normal corrosion reaction in an open configuration yields, through a series of steps,  $\text{Al}(\text{OH})_3$  corrosion product. The  $\text{Al}(\text{OH})_3$  when freshly formed, is gelatinous but becomes a white gritty hydrated Bayerite  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  on aging. This corrosion product is observed in copious quantities on exfoliated sheets.  $\text{Al}_4\text{C}_3$  formed during consolidation at the graphite/aluminum interface may also be important since the  $\text{Al}_4\text{C}_3\text{-H}_2\text{O}$  reaction also produces  $\text{Al}(\text{OH})_3$ . The process is exacerbated by the low transverse strengths (typically 20 MPa) in these materials."

Godard, et al.<sup>8</sup> conclude:

"Although it is not a metal, graphite (a form of carbon) is electrically conducting, and tends to promote strong galvanic corrosion of aluminum when placed in contact with it in the presence of moisture. In aggressive marine atmospheres, it has a stronger influence on aluminum than either copper or steel. Graphite smears on an aluminum surface promote pitting of the aluminum in the presence of water."

Analogous test results on magnesium/graphite samples are not readily available. Corrosion by the mechanism will be more severe since magnesium based materials are relatively more anodic than aluminum (alloys) in the seawater environment.

The corrosion scenario in Gr/Mg composites may be as follows: Impinging salt bearing moisture corrodes the composite surface by mechanisms discussed above. When the moisture (electrolyte) reaches a fiber-matrix interface, it promotes the formation of  $\text{Mg CO}_3$  or  $\text{MgO}$  and  $\text{Mg Cl}_2$ . The reactions proceed rapidly along the interface, swelling the composite and allowing the electrolyte to penetrate still deeper. The corrosion becomes catastrophic and the composite completely breaks down. Protection against this type of corrosion will present a serious challenge. Most common surface coatings do not have the intimate adherence and mechanical durability required to completely prevent penetration of the reactive moisture. Effective corrosion inhibition might require development of a new fiber surface treatment, to be applied before consolidation.

There is probably no insurmountable barrier, however, to adequate corrosion protection of Gr/Mg composites. A tailored fiber end/or well chosen surface treatment from the modern techniques available should provide satisfactory corrosion resistance under anticipated exposure conditions.

## CHAPTER 4

## CORROSION PROTECTION TECHNIQUES

## DISSIMILAR METALS

The problem of galvanic corrosion is reduced by generally avoiding co-fabrication with an incompatible metal such as Fe, Cu, or Ni or to thoroughly insulate points of contact. As this clearly is not always possible, other measures must be taken. Drain holes should be provided so that chloride solution does not accumulate at the couple. The dissimilar metal junction should be well sealed so that solution does not enter between the faying surfaces. If this is done, the current in the electrolyte leg of the galvanic circuit is forced to flow along a thin and thus highly resistive film. In practice this limits the galvanic activity to small zones along the line of junction between the two metals.

Various paint and surface treatments are effective in reducing galvanic attack,<sup>9</sup> after the above steps have been taken. Generally paint systems which perform well on zinc or aluminum are satisfactory for magnesium, particularly when applied over a chemical or electrochemical prepaint surface treatment. Since alkali ( $Mg(OH)_2$ , etc.) forms on any point of damage to the painted surface, a good organic coating must have high resistance to alkali. For this reason, paints with vinyl or ether linkages (vinyl or epoxy paints) are generally recommended in preference to those with ester groups (alkyds, nitrocellulose). Prepaint chemical and electrochemical treatments retard this alkaline surface condition, allowing most types of metal paints to be used. In severe environments, where maximum corrosion resistance and freedom from peeling is required, the paint should be an alkali resistant type. Inhibitive pigmentation with slightly soluble chromate base can be used in the primer for optimum corrosion resistance.

A primer or one coat finish can be applied by a process of electropainting (electrophoretic deposition) from a water dispersed resin base paint. The paint film is applied by making the component the anode in a tank containing diluted water solubilized paint under dc potential. Electropainting provides the best one coat protection since the process combines the surface anodization/paint application operations.

Another process used on magnesium (alloy) parts intended for dissimilar metal assemblies is immersion in a stannate solution. This treatment provides good protection and paint base and does not require electrical equipment. It retards galvanic corrosion in much the same manner as the galvanizing of steel.

Aluminum is the important compatible metal with magnesium. Aluminum and magnesium are often combined in structures in which strength and stiffness per unit weight are important. Aluminum rivets are used in magnesium structures, since magnesium itself is not well suited to this purpose due to its lack of cold plasticity. While some aluminum alloys can cause significant galvanic corrosion to magnesium alloys, the main principles governing the galvanic compatibility of aluminum and magnesium alloys under exposure to chloride solutions have been quite well established.<sup>10</sup> This compatibility also might allow fabrication of a magnesium rich Mg-Al alloy with strength, stiffness, and corrosion characteristics adequate for use in aerospace components. This possibility is discussed among the recommendations in Chapter 4.

#### PROTECTION OF COMMERCIAL MAGNESIUM ALLOYS FROM UNIFORM CORROSION

There are other effective protective coatings for magnesium alloys besides those noted above. Magnesium can be electroplated by processes employing the conventional plating sequence of copper-nickel-chromium. This provides good appearance, corrosion protection, and abrasion resistance. Various chromating solutions have been developed for corrosion protection. The individual preparation used depends largely upon requirements for appearance of finish, abrasion protection, and shipment and storage. Each provides a good combination of protective properties.<sup>9</sup> Special types of chromating treatments have been developed. Perhaps the best of these films for superior scratch hardness, resistance to abrasion, and good resistance to corrosion is a chrome manganese chromate film. Magnesium alloy castings have been successfully protected by a chrome manganese bath operating at room temperature.<sup>11</sup>

Alternative modern methods of applying protective metallic coatings have become available. One such method, magnetron sputtering from metal targets, has been used to improve tribological and wear characteristics of light non-ferrous metal alloys.<sup>12</sup> Various atmospheres are used to produce the desired metallic compound films. A wide range of materials can be deposited without the limitations inherent in conversion coatings and anodization. Deposition of thin coatings at room temperature (or below) preserve strength and fracture properties and provide good friction and wear characteristics. Some of the compounds which are able to be produced as very adherent films by sputtering include: TiN, TiC, WC, HfN, ZnC, etc. Although the major thrust in the application of such films has been in providing wear protection, various tests also have indicated their potential for corrosion inhibition.

In concluding this discussion of surface treatments, we note the comment of Hillis:<sup>5</sup>

"Magnesium's true salt water durability has not been realized . . . the effects of heavy metal contamination, when present, are not easily overcome. That is, chemical treatments, even chromate based, have little if any effect on samples with sufficient contamination to produce corrosion rates in excess of 200-300 mpy in salt spray. On the other hand, chromated and cathodic epoxy coated test panels with low contaminant levels . . . when scribed and placed in salt spray, have passed 1000 hours of salt spray with only very minor corrosion along the scribe. Therefore, whether untreated or treated and painted, metal purity is of prime importance for good salt water durability."

#### GRAPHITE-MAGNESIUM COMPOSITES

Favorable physical parameters single out Gr/Mg as a material of choice for satellite applications despite some deficiencies. However, the presence of large area (treated) fiber/metal interfaces can promote greatly accelerated corrosion (Figure 4) compared with an ordinary magnesium sample of equal metal purity.

The use of specially developed low impurity magnesium alloys<sup>13</sup> as matrix metal in the composites could be recommended. Such a base metal should provide fewer corrosion sites along interfacial regions with which impinging ions from a salt bearing environment can interact. This improved purity base metal coupled with an effective fiber surface treatment could significantly enhance its corrosion resistance.

Some caution is necessary concerning the compatibility of coatings with space satellite components, however. Except for the special high quality metallic films used on some surfaces for thermal control, coatings have potential disadvantages. They add weight to the system, especially over large area thin sections, and can affect dimensional tolerances. The coating must be stable over skin temperature changes encountered during operation. Coatings must not be subject to outgassing. Should flaking or outgassing occur in satellite operations, debris might accumulate on instrument windows and control surfaces. This could affect sensitive calibrations, jeopardizing the long term accuracy of sensor performance. The above comments are especially pertinent to coatings applied on graphite-magnesium composite structures. Any failure by undercutting, flaking, etc., of same in the prelaunch environment will increase the potential for later problems. In any case, reliance solely on surface coatings for protection may be inappropriate for satellite components.

## CHAPTER 5

## CONCLUSIONS AND RECOMMENDATIONS

In light of the foregoing discussion, the requirements for new magnesium based materials in satellite structural applications are quite demanding. On the one hand, the magnesium based material must have markedly superior performance characteristics to those materials currently in use, as indicated in part by the comparisons of Figure 2. On the other hand, whatever combination of alloying, reinforcing, coating, etc., is performed on the material, both its physical properties and corrosion resistance in saline atmosphere must be acceptable. The following recommendations can be made based upon the considerations above.

## PURE MAGNESIUM

Based upon the results of corrosion tests cited above, very pure magnesium should be used as the base metal for alloying or reinforcing. This will ensure the highest possible degree of uniform corrosion resistance of the starting material. Special corrosion resistant magnesium alloys such as that reported in Reference 13 should be tested in this capacity.

## ALLOYING

Alloy stiffening or precipitation hardening might be attempted using pure magnesium as starting material. The idea here would be to alloy this with relatively small percentages of another lightweight, soluble metal with appropriate heat treatment to improve strength and stiffness while maintaining satisfactory corrosion resistance. An example of this process is provided by entries of Figure 2. In the figure, aluminum has an E/p (specific stiffness) value of about  $100 \times 10^{+6}$  and Beryllium of about  $600 \times 10^{+6}$ . The optimum alloy combination of the two has a value of about  $400 \times 10^{+6}$ . It follows the "rule of mixtures" prediction of a linear combination of constituent properties in the product alloy. Unfortunately, many metallurgical requirements must be satisfied for success with a stiffened magnesium alloy. Good corrosion resistance requires the proper microstructure in a precipitate hardened alloy. Also, the alloy phase diagram must have a region of terminal solid solution configured such that a significant precipitate of the alloying metal results at room temperature. It might be possible to find an alloy of magnesium which is solid solution hardened, but this generally requires avoiding intermetallic compositions or mixed phases which are usually brittle. One would be restricted to the metals of low density, good tensile strength, and acceptable corrosion

properties, which have favorable phase diagram with magnesium. Obviously, prodigious effort already has been expended in this pursuit. Three possible alloys are Mg-Li, Mg-Be, and Mg-Si.

The magnesium-lithium system will definitely experience corrosion problems although alloys of low percentage Li may prove more stable than graphite-magnesium in saline atmosphere. Mg-Li alloys must be fabricated under oxygen free conditions. Fabrication of Mg-Be involves exposure to Be toxicity. However, the phase diagrams of both Mg-Be and Mg-Si given in Figure 5 each show the formation of a single intermetallic phase. This condition might lend itself to a strengthening along the axis of directionally solidified magnesium rich alloys by formation of elongated fiber like grains of the intermetallic phase.

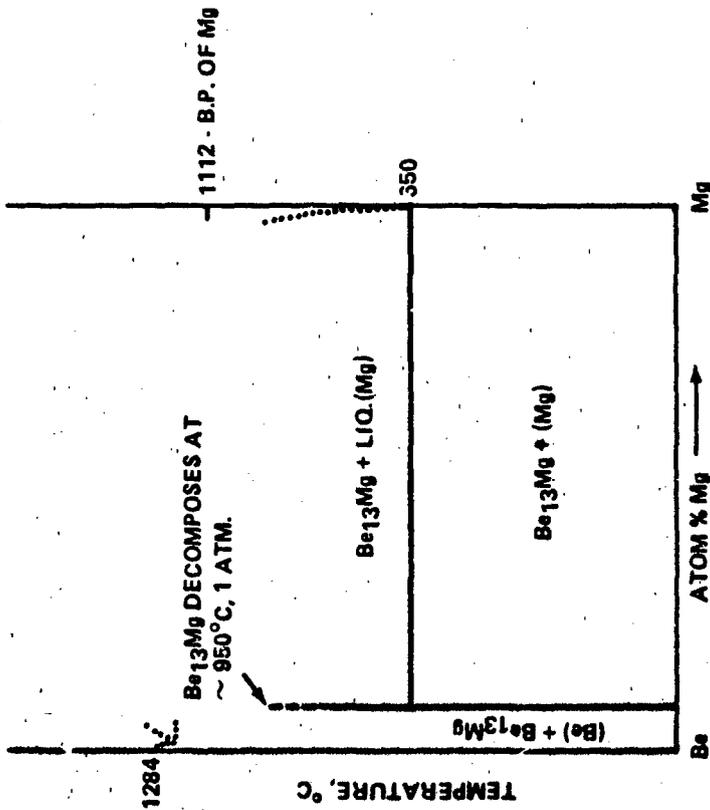
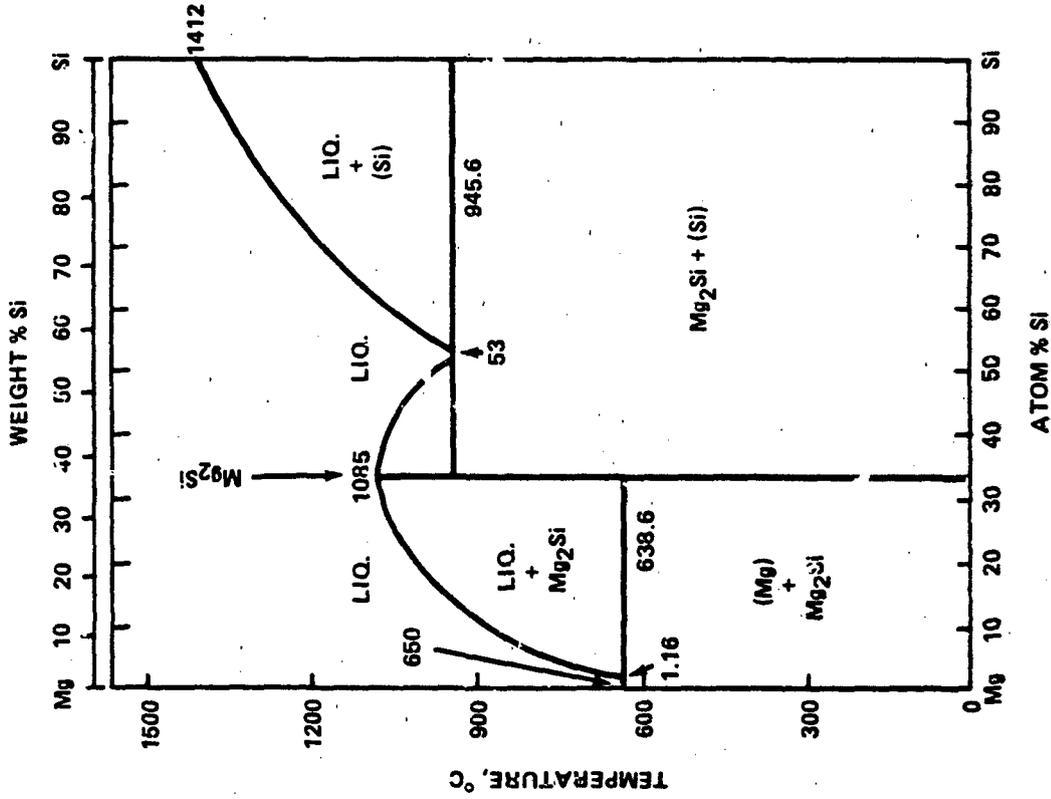
A final possibility here is the alloying of magnesium with aluminum. Figure 6 shows the phase diagram of this system. The shape of the region of terminal solid solution at the magnesium rich end admits the possibility of precipitation hardening since much of the 10 to 12 percent aluminum soluble at 425°C will be driven out as the alloy is brought down to room temperature. Magnesium alloys containing a few percent aluminum have been in successful use for years. They show increased corrosion resistance due to accumulation of aluminum atoms in the weathered protective film. Ternary alloys containing both lithium and aluminum could provide the increased stiffness desired and sufficient corrosion resistance.

Any attempt to strengthen magnesium by alloying must take into account, in addition to metallurgical considerations, the atomic weight and mole fraction of the alloying element. Even if stiffening occurs, too great an increase in density of the alloy will cause no improvement in the value of  $E/\rho$ . All this being said, the chances of producing a high performance, magnesium based alloy from the perspective of Figure 2 are probably not very good. However, this recommendation has been made on the premise that achievement of significant property improvements by simpler alloying techniques might obviate the need to employ graphite fiber reinforcement in magnesium for some applications.

#### COATINGS

Coatings in general are quite effective when properly selected and applied for the particular anticipated conditions on magnesium and its alloys. These have been discussed briefly above with information in Reference 9 and related articles. Certainly the most effective of these should be tested on magnesium-graphite composites. However, the nature of the corrosion failure of this system indicates that applied external coatings probably will be only moderately successful in seawater environments.

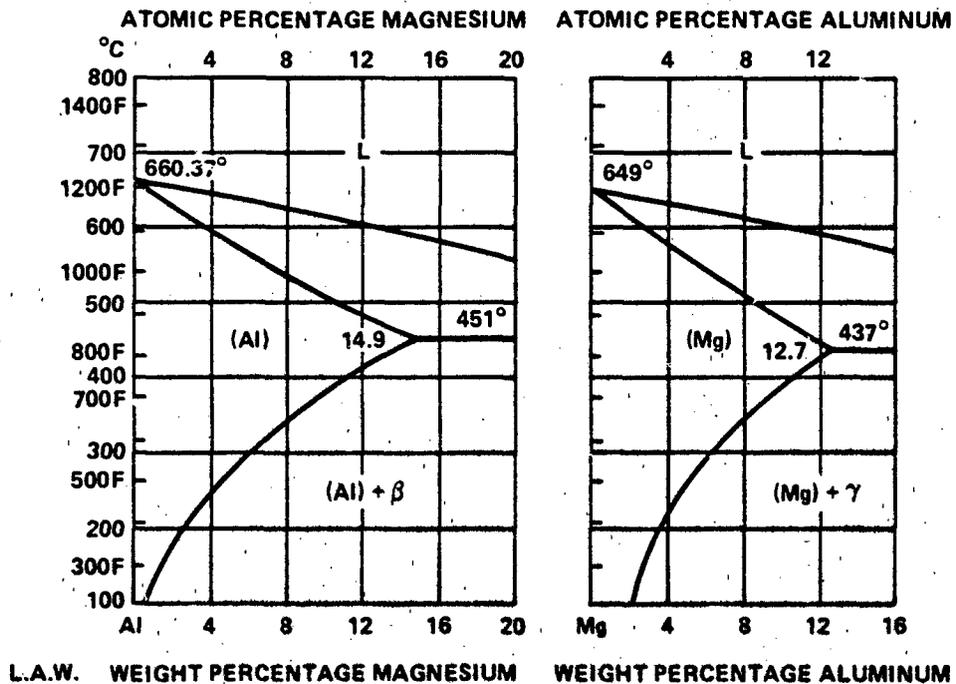
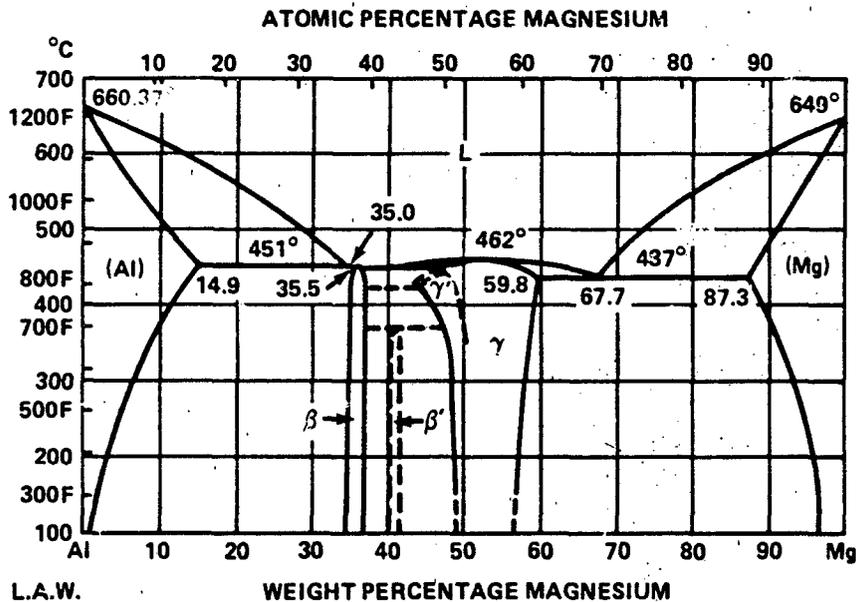
Sputtered coatings may be the exception. Some tests have shown the effectiveness of sputtered coatings in corrosion protection of MMC's. This technique was discussed briefly in Chapter 4. The excellent bonding is produced by a combination of electron beam surface cleaning followed by coating with the



(FROM "CONSTITUTION OF BINARY ALLOYS" BY M. HANSEN, MCGRAW (1958))

FIGURE 5. PHASE DIAGRAMS OF MAGNESIUM-BERYLLIUM AND MAGNESIUM-SILICON

Al-Mg ALUMINUM-MAGNESIUM



(FROM ASM METALS HANDBOOK VOL. 8 (EIGHTH EDITION))

FIGURE 6. ALUMINUM-MAGNESIUM PHASE DIAGRAM

sputtered metallic film. If the chamber atmosphere contains a gas such as nitrogen, "reactive" sputtering can take place and metallic nitride films can be applied. In the few tests of sputtered films on MMC's, the coatings were not sufficiently resistant to abrasion, but harder coatings could be developed using this approach.

Another protection method is cladding by explosive bonding techniques with a durable metal such as Titanium. While it will be feasible to protect and stiffen some members by cladding, this is not a basic solution to the problem. Cladding obviously has the disadvantages of adding weight and introducing complications and expense into fabrication. Metal foil bonding to the edges of Gr/Mg MMC's, however, might help prevent the rapid infiltration along fiber axes observed in Figure 4.

#### SPECIAL METHODS

One technique involves formation of the silicide  $Mg_2Si$  in the surface layer and Mg-C interfaces. This can be accomplished under the proper conditions by diffusing silane  $SiH_4$  into the composite surface at elevated temperature.<sup>14</sup> Catalytic surface treatment may be required prior to exposure to the silane. The technique is apparently quite general and other group IIIA and IVA materials such as germanium, boron, and aluminum can be deposited. When the metal silicides are exposed to oxygen under the proper conditions, a thin layer of silicon dioxide is formed on the surface. This layer of  $SiO_2$  is continuous and tightly bound to the metal, which it protects from oxidation. An alternative method of applying silicon based coatings is proposed in Reference 15. However, the method may be subject to the limitations discussed above on coatings.

Still another method produces the dielectric layer on the fiber surfaces prior to fabrication of the composite.<sup>16</sup> The fibers are passed through various organometallic solutions (alkoxides) and pyrolyzed or hydrolyzed to yield the desired coating. Graphite fibers, coated by this process with silicon dioxide ( $SiO_2$ ), are found to have quite uniform adherent coatings. These treated fibers are readily wet by liquid magnesium. Examination of the interfacial layer indicate the presence of magnesium silicate. The metal oxide coatings form strong chemical bonds with both the graphite fibers and the metal matrices. These form composites with relatively higher transverse strength, better corrosion resistance, and improved high temperature stability compared with previously produced composites. The corrosion resistance attained using this method should be compared with that of previous composites. The dielectric oxide (silicate) coating on the graphite fibers may deny an electrical pathway along the interfaces to microscopic corrosion currents responsible for the observed corrosion.

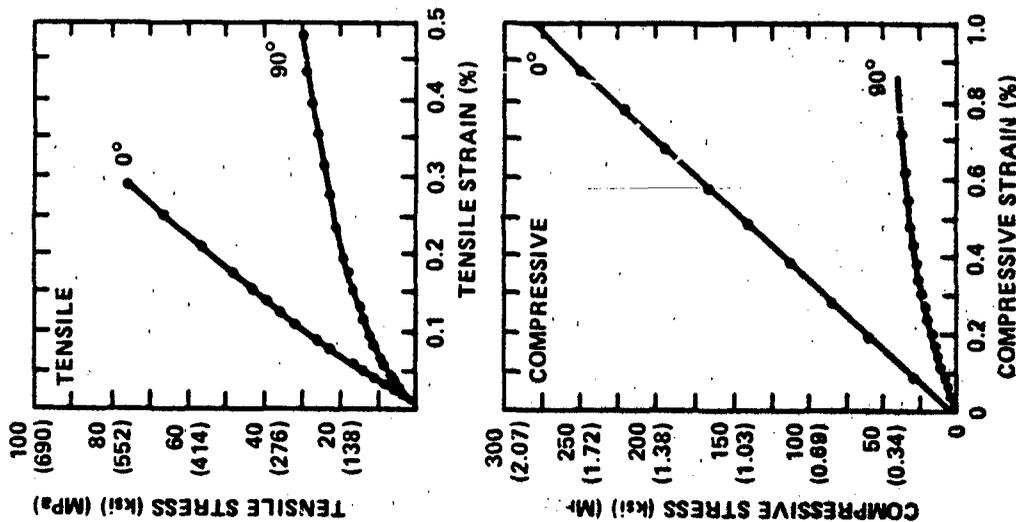
The second technique involves ion implantation into the surface of the fabricated composite. In this process, atoms of the element to be implanted are produced from a source, ionized, and accelerated by a machine such as a Van de Graaff generator. The ions impinge on the surface and embed themselves to distances up to 10,000 Å or so, depending upon their energy. The implanted ions subsequently form chemical compounds with metal (and perhaps fiber) atoms in the surface region. In principle, almost any element can be ionized and implanted. If, for example, nitrogen is implanted into a magnesium based material, magnesium nitride ( $Mg_3 N_2$ ) will be formed in the surface layer. If silicon is used, magnesium silicide ( $Mg_2 Si$ ) will be formed with silicon carbide (SiC). These ions occupy bonding sites and form surface layer compounds sufficient to retard or block subsequent oxidation. The extent of protection will need to be verified experimentally. There have been recent extensions to this technique to include acceleration of ionized monomer gases and collisional implantation.<sup>17</sup>

These special methods have the advantage of not adding an external coating to the component. Problems of added weight and potential coating debris are avoided.

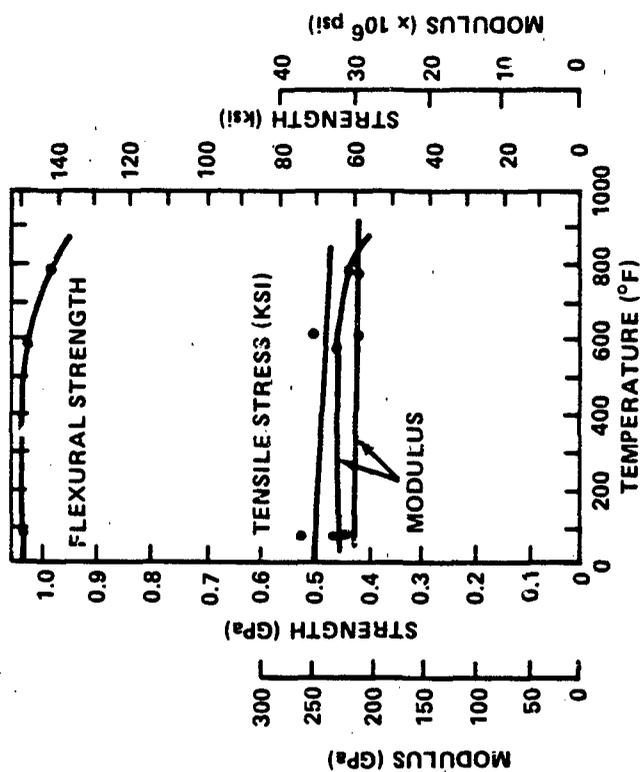
#### COMPOSITE SUBSTITUTES

Fiber electrical conductivity is an important link in the mechanism of severe corrosion observed in graphite fiber MMC's. Attempts should be made, therefore, to find a nonconducting substitute for graphite reinforcement. There is sound evidence that use of nonconducting reinforcements improves composite corrosion resistance.<sup>18</sup> Comparison corrosion tests on magnesium based composites using nonmetallic reinforcements should be carried out to establish a baseline in this area. Two possible materials fitting this description are fiber (FP) alumina ( $Al_2 O_3$ ) and silicon carbide (SiC). In fact, a reexamination of Figure 2 shows that both fiber FP and silicon carbide do improve the specific stiffness of pure aluminum. However, gaining significant improvements in specific stiffness of magnesium composites using these fibers will be more difficult. Alumina fiber (3.9 g/cc) and silicon carbide whiskers (3.22 g/cc) are probably too heavy for reinforcement of magnesium based satellite components. Likewise, their moduli and tensile strengths are lower than those of high grade graphite fibers. Of equal importance,  $Al_2 O_3$  or SiC reinforcements do not yield the substantial reduction in CTE required in these applications.

In other applications, however, the picture is brighter for alternative fiber reinforcement. Encouraging results are reported (Reference 17) on a critical helicopter transmission component cast of an alumina (FP)/Mg composite. Suggestions are made regarding other stiffness-critical applications in aircraft engines, missile components, power transmission housings, and rotating shafts. This technology appears to be fairly mature. Figure 7 indicates some important tensile properties of an alumina (FP)/Mg composite.



A. STRESS/STRAIN BEHAVIOR OF 50% FP/Mg COMPOSITES



B. EFFECT OF TEMPERATURE ON TENSILE AND FLEXURAL PROPERTIES OF FP/Mg CASTINGS (50 VOL % FIBER LOADING)

(FROM REFERENCE 17)

FIGURE 7. SOME PROPERTIES OF ALUMINA FIBER (FP)/MAGNESIUM COMPOSITES

Substantial efforts are underway to produce economical high strength ceramic fibers. Pyrolysis of fibers made from a melt drawing process converts them to high strength silicon carbide/silicon nitride.<sup>19</sup> The resulting fibers have potential as reinforcements in MMC's as well as in ceramic matrix composites. Graphite tends to form the undesirable product magnesium carbide during fabrication unless protected. The new ceramic fibers have the double advantage of thermal stability and an electrical conductivity  $10^{-6}$  that of graphite. These ceramic fiber properties should be favorable for successful composites with magnesium.

SiC/SiN fibers have reasonably good mechanical properties. Their tensile modulus of  $29 \times 10^6$  psi is somewhat below the  $34-30 \times 10^6$  psi of general purpose graphite fibers. Their tensile strength was reported at 105,000 psi for early fibers made by simple techniques. Process refinements are underway. Higher strength levels may be anticipated, though probably not the 200,000 psi of the latest graphite fibers. Vapor deposited SiC filaments of larger diameter (5 mils) measure  $60 \times 10^6$  psi flex modulus with tensile strengths up to 450,000 psi. All this research activity demonstrates how rapidly fiber technology is advancing. It may be possible in the near future to produce corrosion resistant Mg based composites employing high performance ceramic fibers. Such composites could find early application in space structures where stiffness, not necessarily strength, may be of prime importance.

#### INERT ATMOSPHERE STORAGE

Failing other protective methods, the possibility of inert atmosphere storage remains for Gr/Mg composite satellite components. Such protective systems are often used on electrical systems, rare documents, etc., to forestall oxidation. A protective atmosphere of dry nitrogen would be maintained on the composite subsystems and ultimately the entire space structure until shortly before launch. Obviously, access to the structure(s) would need to be maintained for the installation and testing of instruments.

In practice, the protection could be accomplished by enclosing the entire assembly in a polymer bag made of material such as hypalon. This polymer, for example, is tough, impermeable, and is stable in the environment over many years. Resealable openings for accessing instruments could be provided. Dry nitrogen gas would be allowed to fill the bag, displacing the air and moisture. A slight nitrogen overpressure would maintain an essentially oxygen free condition within the bag. Water vapor sensors attached at various points could be set to warn of system malfunction. The bag assembly would be removed prior to launch. This protective system would be effective, conceptually simple, and probably not prohibitively costly. It would eliminate worries about flaws or instability of a coating or added weight to the structure. Obviously, this approach is feasible only for space bound components.

## SUMMARY

In summary, designing magnesium based components for corrosion resistance requires a rather detailed knowledge of the intended service conditions. Failure to take these fully into account in a corrosion protection program has prompted comments such as follows:

"Magnesium, like other metals, is subject to corrosion under certain conditions. However, despite magnesium's good corrosion resistance, the metal suffers from a reputation as an easily corroded material."<sup>20</sup>

Thus maximum corrosion resistance of magnesium based structures will be obtained by:

1. limiting corrosion producing impurities (i.e., principally Fe, Ni, and Cu) to low levels,
2. eliminating contamination by traces of salt based fluxes in casting operations,
3. using appropriate combination of mechanical, chemical, electrochemical, and film coating techniques,
4. taking proper precautions against entrained salt bearing fluids and galvanic coupling with incompatible metals such as Fe or Ni, and
5. application of modern surface modification techniques.

Gr/Mg composites have unique properties for certain satellite applications, despite some shortcomings. Methods in category 5 or isolation storage likely will be necessary for prelaunch corrosion protection. Successful magnesium based MMC's for many applications almost certainly will be fabricated using other fiber reinforcements. These might include fiber alumina, newly developed high strength SiC fibers, improved Sialon fibers,<sup>21</sup> or compound SiC/SiN fibers. Although the proper combination of materials and chemistry has not yet been found for a widely useful, moderately priced magnesium based MMC, prospects for its near term development appear good. Indeed, expanded overall usage of magnesium based materials in marine, airborne, and space bound systems seems inevitable.

## REFERENCES

1. Armstrong, H. W., "Satellite Applications of Metal-Matrix Composites," DARPA Contract, ARPA Order 3411, Air Force Materials Laboratory WPAFB, M.L. Duhl, Project Engineer.
2. Barelko, E. V., and Kabanov, B. N., DOKLADY SSSR 90, 1059-62, 1953.
3. Robinson, J. L., and King, P. F., Journal of the Electrochemical Society, 108, 1961, p. 36-41.
4. Dundas, H. J., Corrosion Resistance of Die Cast Magnesium Alloys, AMAX Specialty Metals Corp., Magnesium Division, Utah Report ISJ-1324, Jun 1982, P.O. Box 1568, Ann Arbor, MI 48106
5. Hillis, J. E., The Effects of Heavy Metal Contamination on Magnesium Corrosion Performance, SAE Publication #830523, 1983.
6. Hanawalt, J. D., Nelson, C. E., and Peloubet, J., Trans. American Institute of Mining & Met. Eng., 147, 1942, pp. 273-99.
7. Crowe, C. R., "Localized Corrosion Currents From Graphite/Aluminum and Welded Sic/Al Metal Matrix Composites," NRL Memorandum Report 5415, p. 9, 1984.
8. Godard, H. P., et al., The Corrosion of Light Metals, (New York: John Wiley and Sons, 1967), p. 41.
9. DeLong, H. K., "Practical Finishes for Magnesium," Metal Progress, Jun 1970, p. 105-1-8.
10. Bothwell, M. R., J. Electrochem. Soc., 106, 1959, pp. 1014-1018.
11. Krishnadas Nair, C. G., Ramaswamy, T. L., and Narayana, A., "Studies on Chromating of Magnesium Alloys," J. Electrochem. Soc. India, 30, 2, 1981, pp. 115-121.
12. Ramalingam, S., Shimazaki, Y., and Winer, W. O., "Magnetron Sputtering of Non-Ferrous Aerospace Alloys for Wear Protection," Thin Solid Films, 80, 1981, pp. 297-303.
13. Magers, D. M., and Morales, H. J., "High Purity Magnesium Die Casting Alloy," Die Cast Engineering, 1984.

REFERENCES (Cont.)

14. Maugh II, T. H., "A New Route to Intermetallics," Science, Vol 225, #4660, 27 Jul 1984.
15. McKaveney, J. P., and Simpson, V. P., "Composition for Corrosion Protection Using Metal Silicides or Alloys of Silicon and Metals," U.S. Patent #4,360,384, 23 Nov 1982.
16. Katzman, I. A., "Carbon-Reinforced Metal-Matrix Composites," U.S. Patent #4,376,803, 15 Mar 1983.
17. Taylor, S. R., et al., Implantation of Ionized Monomer into Aluminum Alloy 6061 for Marine Corrosion Protection, David Taylor Naval Ship R & D Center, DTNSRDC-84/046, Jul 1984.
18. Dhingra, A. K., "What are Fibers Doing in Metal Castings?" Chemtech, Oct 1981, pp. 600-607.
19. Process Makes Ceramic Fiber Precursor, report in Advanced Materials P.O. Box 6249, Hilton Head, SC 29938, 23 Jul 1984.
20. Clark, G., "Magnesium Corrosion Prevention," Light Metal Age, Vol. 40, 9-10 Oct 1982, p. 14.
21. SiC and Sialon developments reported in New Materials/Japan Vol. 1, No. 5, Summer 1984, Elsevier Science Publishers B.V., Amsterdam.

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