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16. Abstracts Magnesium resources within the United States are substantial; therefore, world conditions will not affect supply directly. Because magnesium production is energy intensive, the cost and availability of energy could affect production.

The U.S. magnesium industry is strong, accounting for the production of about one-half of total world consumption. U.S. magnesium technology is equally strong, with individuals, companies, and institutions recognized as world leaders in magnesium science, research, and technology.

While magnesium may be substituted for a wide range of materials, its substitution for aluminum, the yardstick used in this study, appears to offer the greatest potential. However, current U.S. magnesium consumption is only about 2 percent of that of aluminum and no ready substitution of magnesium for aluminum is possible until the magnesium industry expands considerably. Significant expansion will occur only if the cost of producing an object in magnesium is relatively lower than the cost of producing the same object in aluminum. While lowering the relative cost of producing magnesium itself is possible, most opportunity lies in lowering the relative costs of fabricating parts. Opportunity exists for large expansion in the consumption of magnesium for structural purposes but will not occur without intensive attention to the fabrication costs and development of new applications.

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REPORT OF
THE PANEL ON TRENDS IN USAGE OF MAGNESIUM
of the
COMMITTEE ON TECHNICAL ASPECTS OF
CRITICAL AND STRATEGIC MATERIALS

NATIONAL MATERIALS ADVISORY BOARD
Commission on Sociotechnical Systems
National Research Council

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This report has been reviewed by a group other than the authors according to procedures approved by a Report Review Committee consisting of members of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine.

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I. SUMMARY CONCLUSIONS AND RECOMMENDATIONS

A. Conclusions

1. While magnesium is a suitable substitute for a wide range of metallic and nonmetallic materials, its substitution for aluminum offers the greatest potential.

2. The quantity of magnesium "ore" (minerals, brine, and seawater) present in the United States is essentially limitless but the reduction of that ore to metal is energy intensive and increased metal production would depend upon the availability of energy.

3. The production of magnesium theoretically requires approximately the same amount of energy as the production of aluminum; however, with current technology, more energy actually is used to produce magnesium than to produce aluminum (whether they are compared on a weight or a volume basis). Considerable potential exists to reduce the amount of energy needed for magnesium production and to obtain economic credit from the energy-intensive magnesium by-product chlorine.

4. Relief from magnesium shortages (such as those experienced in 1974) would require the building of additional reduction facilities that could not be brought to capacity in less than three years.

5. Expansion of the U.S. magnesium industry depends upon reduced costs relative to competing materials and improved application technology. While primary production costs are not likely to be reduced relative to the principal competitor, aluminum, substantial cost reductions can be made in converting the raw metal to useful articles. If bauxite prices rise to the point at which domestic aluminum ores are economical, the relative costs for magnesium will decline moderately.

6. Die casting, extrusion, hot forging, and machining are the most competitive methods for converting magnesium alloys into useful articles while sand or permanent mold casting, rolling, or any type of cold deformation are the least competitive.

7. The three major applications of magnesium currently are:

   a. Metallurgical (e.g., alloying in aluminum which is expected to grow at 8 percent per year through 1980, making ductile iron, and desulfurizing blast-furnace hot metal which has the potential of 100 million pounds per year if a low-cost commodity is developed for the steel in industry).

   b. Chemical and electrochemical (e.g., reducing $TiCl_4$ to Ti, making organic chemicals via the Grignard reaction, and cathodically protecting steel from corroding by being the anode in a corrosion circuit).

c. Structural* (e.g., lawn mower housings, chain-saw parts, automotive die castings, and materials handling equipment).

8. The use of magnesium for military and aerospace applications has decreased markedly over the past 10 to 15 years. However, in times of severe shortages of aluminum, magnesium could be utilized in some corrosion-sensitive structures, such as aircraft, but additional costs for design, manufacture, and maintenance would be involved.

9. Magnesium could make its greatest impact as a substitute for aluminum in structural applications in times of shortages, if in sufficient supply. Magnesium is suited technically as an aluminum substitute in many structures at somewhat higher costs, but technological and cost improvements must be made if large-scale expansion is to occur in this category in normal times.

10. The principal advantages of magnesium in structural applications are its low density, good modulus, and excellent machineability; the principal disadvantages are its high reactivity with oxygen and nitrogen when molten, low corrosion resistance in slightly acidic environments, and relatively low strength in the tensile mode.

11. About 13 percent of the magnesium that reaches the market-place as magnesium-rich material is recycled; about 4 percent of the magnesium alloyed in aluminum is recycled. This recycling results in an overall recovery of about 6 percent of the magnesium that reaches the marketplace in recoverable form.

B. Recommendations

Because of the increasing problems encountered in obtaining foreign commodities, many individuals argue that the U.S. should strive to increase its use of minerals with which it is well endowed. Should such a policy be considered desirable for magnesium, the following items are recommended as promising avenues for stimulating the production and use of magnesium:

1. Methods for reducing the unit energy required to produce magnesium and for recovering by-product chlorine should be sought.

2. Efforts should be continued to improve the economic base of raw materials for magnesium through search for new evaporite and brine deposits and systematic study of geologic formations containing chemically pure dolomite.

3. Beneficiation of natural $MgCl_2$ sources is necessary to take full advantage of by-product chlorine.

4. Methods should be developed to lower the cost of converting magnesium into useful articles. Efforts should be concentrated on molten magnesium handling to reduce melt loss, on casting techniques or alloy changes to realize greater casting efficiency, and on forming techniques

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* This term, applied to magnesium, differs from the connotation in metals, such as steel and aluminum, where structural refers only to design/critical strength members.

or alloy changes to use less costly forming procedures. Some exploration of rolling techniques that are more applicable to the hexagonal crystal structure than current practice should be made.

5. Some fundamental studies of the corrosion behavior of magnesium in slightly acidic water should be undertaken. While considerable work has been done in this area, continuance of good programs is required.

6. Methods for improving the strength of magnesium alloys for structural applications should be sought.

7. A program should be established to develop reliable corrosion-protective systems for magnesium involved in dissimilar metal couples or water traps to bolster magnesium usage in structural applications.

8. A strong effort (technical and economic) should be made to retain magnesium contents in aluminum during recycling of aluminum.

9. A stronger secondary market for magnesium should be established. An immediate problem is the mechanical separation of magnesium-base alloys from structures (e.g., automobiles) containing a wide variety of materials.

II. INTRODUCTION

This study was undertaken by the Panel on Trends in Usage of Magnesium of the NMAB Committee on Technical Aspects of Critical and Strategic Materials at the request of its sponsors, the General Services Administration and the U.S. Bureau of Mines. The Panel was charged with assessing the potential for wider use of magnesium in order to reduce U.S. military and civilian dependence on materials based on imported ores or metals. The Panel addressed three major questions: (1) How available is magnesium if wide-scale substitution is required? (2) How well can magnesium be converted to useful articles as a substitute? (3) How well will an article made of magnesium perform when compared with the same article made of another material?

It quickly became apparent to the Panel that while magnesium conceivably could substitute for a wide range of metallic and nonmetallic materials, its substitution for aluminum offered the greatest potential. Magnesium is a relatively new member of the metals community and its low density orients it toward aluminum substitution. Aluminum's growth in its early years is similar to that of magnesium at present and aluminum may be considered as a "pacing parameter" of magnesium's future; accordingly, in the Panel's study, concentration was on comparisons of magnesium with aluminum.

Because reliance on magnesium depends upon the existence of a healthy industry, the Panel examined the present magnesium industry, its past history, and its probable future. The future was divided arbitrarily into "short range" (up to five years) and "long range" (up to fifteen years). An important part of this examination was an assessment of magnesium's ability to compete on the open market with aluminum.

Production costs for aluminum and magnesium were reviewed to determine whether the costs of producing either could be altered substantially. Particular attention was given to (1) new or improved technology that could lower the production costs of either metal by reducing the amount of energy needed to produce it, and (2) the effect on the costs of aluminum production if domestic, non-bauxitic raw materials were used instead of imported bauxite. Also, the economics of various fabrication processes for magnesium were examined to determine whether possible changes in fabricating techniques would change the relationship of the costs, and therefore prices, of finished parts made of magnesium vis-a-vis competitive materials.

In considering future consumption of magnesium, particular attention was given to end-uses for magnesium and its alloys that appeared cost-effective (i.e., applications in which magnesium products would be no more expensive than products of competitive materials and in which magnesium's properties could create a measurable economic advantage).

Each subsequent chapter of this report, based on data collected between June 1974 and May 1975, is devoted to one phase of the industry and each shows both the technical and economic relationship of magnesium to principal competitive materials. No attempt was made to compile a list of suppliers and fabricators currently working in the magnesium industry. Such information can be obtained from the International Magnesium Association, 1406 Third National Building, Dayton, Ohio 45402.

III. SUPPLY AND DEMAND

A. Supply

Magnesium-bearing raw materials are abundant, geographically widespread, and strongly competitive in world markets. The principal raw materials are seawater, magnesite, brucite, olivine, dolomite, brines, and evaporites. Uses of these materials are shown in Figure 1.

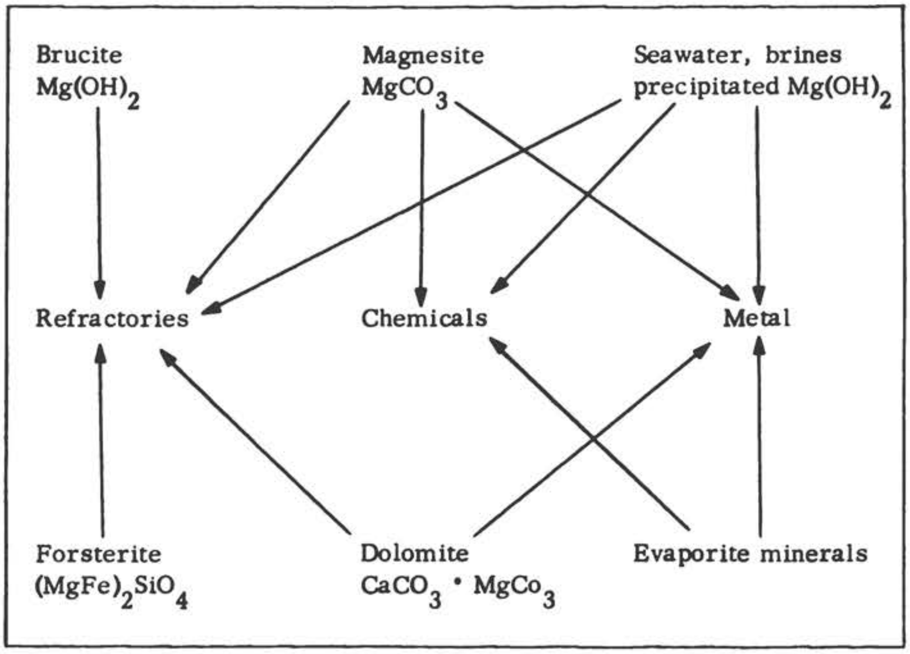

FIGURE 1. Use of the Principal Raw Materials of Magnesium
SOURCE: Bodenlos and Thayer, 1973.

Magnesium metal was extracted from dolomite and magnesite on a large scale during World War II, but its domestic recovery from these sources ceased in the years following the war. Seawater recovery of magnesium oxide for metal production was initiated in 1940 and, in subsequent years, seawater magnesia supplanted magnesite as the primary source of refractory raw material. Magnesium compounds have been recovered from deep-well brines in Michigan and other states while deep-well oil field brines in Texas and brines from the Great Salt Lake also have yielded magnesium compounds and metal. Since World War II, dolomite has provided the largest single source of magnesium-bearing compounds although previously fosterite, the magnesium-rich variety of olivine, was mined in North Carolina and in Washington. The primary magnesium capacity of the various plants in the world is presented in Table 1 (for a detailed discussion of U.S. and world magnesium-bearing raw materials and recommendations concerning further geological study, see Appendix A).

TABLE 1. Plants, Locations, Processes, and World Primary Magnesium Capacity as of January 1, 1975

Country, Producing Company and Plant Location	Process	Annual Capacity (million pounds)	Projected Additional Capacity or New Capacity (million pounds)
Canada			
Chromasco Corporation Limited (Haley, Ontario)	Silicothermic	24.0	No announced expansion
China, People's Republic of			
State owned: Antung Plant (Antung, Manchuria)	Silicothermic	Not available	Plant status unknown
Yingkow Plant (Liaoning, Manchuria)	Silicothermic	Not available	Plant status unknown
Yungki Plant (Kirin, Manchuria)	Silicothermic	Not available	Plant status unknown
France			
Société Générale du Magnesium (Marignac, Haute-Garonne)	Magnetherm	22.0	11.0 additional, 1980
Italy			
Società Italiana per il Magnesio e Leghe di Magnesio (Bolzano, Venezia, Tridentina)	Silicothermic	24.0	No announced expansion
Japan			
Furukawa Magnesium Company (Koyama, Tochigi)	Silicothermic	14.0	No announced expansion
Ube Industries, Ltd. (Yamaguchi, Yamaguchi)	Silicothermic	11.0	No announced expansion
Showa Denko K.K. (Chichibu, Saitama)	Thermal	0.44	Pilot plant -- startup 6/9/75
Norway			
Norsk Hydro Elektrisk A/S (Heroya, Telemark)	I.G. Farben-industrie	88.0	33.0 additional, 1977
Norsk Hydro Elektrisk A/S (Mongstad, Hordaland)	Electrolytic	- 0 -	120.0 new capacity, 1980-82
Union of Soviet Socialist Republic			
State owned: Berezniki Plant (Berezniki, Molotov)	Electrolytic	Not available	Plant status unknown
Dneprovsk Plant (Zaporozhye, Ukraine)	Electrolytic	Not available	Plant status unknown
Solikamsk Plant (Solikamsk, Ural)	Electrolytic	Not available	Plant status unknown
Uralsk Plant (Uralsk, Kazakh)	Electrolytic	Not available	Plant status unknown
United States of America			
American Magnesium Company (Snyder, Texas)	Electrolytic	20.0	40.0 additional, 1979
NL Industries, Inc. (Rowley, Utah)	I.G. Farben-industrie	90.0	No announced expansion
Northwest Alloys, Inc. (ALCOA) (Addy, Washington)	Magnetherm	- 0 -	48.0 new capacity, 1975-76; 32.0 additional, 1980
The Dow Chemical Company (Freeport, Texas)	Dow cells	240.0	30.0 additional, 1978
The Dow Chemical Company (new plant, site may be located outside United States)	Based on current Dow technology	- 0 -	100.0 new capacity, 1978

NOTE: Data from U.S. Bureau of Mines.

Table 2 summarizes U.S. Bureau of Mines and U.S. Bureau of the Census data on United States magnesium supplies and exports. Announced magnesium production capacity in the United States is 53.5 percent that of the world; however, in 1973 the United States accounted for only 46.9 percent of all magnesium produced worldwide with secondary recovery contributing 12.6 percent to the total of about 280 million pounds.

B. Demand

Table 3 presents the history of U.S. magnesium consumption (by end use) since 1963. Comparing these data with the production information provided in Table 4 indicates that there is obviously a shortage. The shortfall has been eliminated principally by drawing from the U.S. Strategic Stockpile but this resource now is exhausted. A continuation of the shortage into 1974 has resulted in an increase of about $0.40 per pound (to about $0.82 per pound) in the world price of magnesium.

TABLE 2. Total Magnesium Ingot Supply in the United States (in millions of pounds)

Year	Primary Production	Secondary Production	Imports*	Stockpile Sales	Exports	Total
1963	152	18	5	3	33	145
1964	159	24	5	9	34	163
1965	163	27	6	7	37	166
1966	160	30	8	21	31	188
1967	195	27	19	29	26	244
1968	197	31	9	0	39	198
1969	200	27	8	44	55	224
1970	224	24	6	39	71	222
1971	247	29	7	10	49	244
1972	242	31	9	8	35	255
1973	245	35	7	40	79	248

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* Includes imports of waste and scrap; unwrought, unalloyed and alloyed; and wrought products.

NOTE: Data from Department of the Interior, Bureau of Mines; Department of Commerce, Bureau of the Census; and General Services Administration.

TABLE 3. Consumption of Primary Magnesium Metal in the United States by End Uses (in millions of pounds)

	Year										
Use	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972	1973
Structural Products											
Castings:											
Die	11	10	11	10	17	15	15	18	15	19	21
Permanent Mold	3	1	2	1	1	1	1	1	1	1	2
Sand	7	4	6	8	8	7	5	3	2	1	3
Wrought Products:											
Extrusions and Forgings	7	9	12	14	21	23	26	25	16	18	19
Sheet and Plate	11	10	10	12	a/	a/	a/	a/	6	8	8
Subtotal	39	34	41	45	47	46	47	47	40	47	53
Distributive and Sacrificial Uses											
Alloys	46	47	57	66	67	69	75	73	75	87	103
Cathodic Protection (anodes)	6	10	9	9	10	11	12	12	15	13	16
Chemical	1	5	8	9	10	b/	b/	17	18	19	23
Nodular Iron	b/	b/	b/	b/	b/	5	5	9	13	15	17
Powder	2	b/	b/	b/	b/	b/	b/	11	b/	b/	b/
Reducing Agent for Ti, Zr, etc.	6	8c/	17	17	13	12	15	13	18	12	14
Other	1	4	7	18	34	29	37	6	7	12	5
Subtotal	62	74	98	119	134	126	144	141	146	158	178
TOTAL	101	108	139	164	181	172	191	188	186	205	231

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a/ Included with extrusions.

b/ Included with "other" under distributive uses.

c/ Excludes uranium production.

NOTE: Data from U.S. Department of the Interior, U.S. Bureau of Mines.

C. Analysis of Demand

1. Civilian and Nonaerospace

a. Nonstructural

Magnesium is used nonstructurally largely in chemical and metallurgical reactions (these uses also have been termed "distributive" or "sacrificial"). U.S. Bureau of Mines data indicate that, in 1973, approximately 73 percent of primary magnesium was used for nonstructural purposes.

and about 97 percent of this amount was used as shown in Table 4 in which the Panel also presents its estimate of consumption in 1980. Each of these uses is discussed separately below in terms of current demand, factors affecting demand, and future demand. Because of the many uncertainties in the world economic picture, both pessimistic and optimistic demand forecasts are presented whenever it was considered important.

TABLE 4. Nonstructural Uses of Magnesium

Use	Magnesium Consumption (millions of pounds) 1973	1980 (estimate)	Panel Comment
Aluminum Alloying	101	170	Constrained by aluminum supply. Could expand greatly after 1980.
Nodular Iron	17	28	Mature market.
Desulfurization of Blast Furnace Metal	Not Available	20	Could increase by factor of 5, if economics were proper.
Reducing Agent Ti, Zr, Hf, U, Be	14	28	
Chemical Reaction Processes	23	20	Use of lead-free gasoline might cause decrease
Cathodic Protection			Impressed cathodic protection could reduce market.
Primary	16	20	
Secondary	6*	8*	
Others	7	8	
TOTAL	178	294	

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* Not included in total.

NOTE: Data from U.S. Bureau of Mines plus Panel estimate.

(1) Aluminum Alloying

The largest market for magnesium is as an alloying agent in aluminum, and it is sold to the aluminum industry as primary remelt ingot. Table 5 shows the amount of consumed magnesium for aluminum alloys since 1969.

TABLE 5. Total Use of Magnesium in Aluminum (millions of pounds)

Year	Amount
1969	74.8
1970	73.1
1971	74.9
1972	86.9
1973	101.7
1980 (estimate)	170.0

NOTE: U.S. Bureau of Mines data plus Panel forecast.

Most of this magnesium is used to make several major aluminum alloys, principally those used in containers and tank plate (beverage can bodies usually are made from a 1 percent magnesium alloy while the "tear off" lids are from a 4.5 percent magnesium alloy; tank plate most often is an alloy containing 4.5 percent magnesium.) Beginning in 1971, the beverage can market (and later the tank plate market) became a large user of aluminum and, consequently, magnesium. Although this level of demand is expected to remain high, the rate of growth should decline and the Panel's 1980 estimate represents considerably less than a straight line extrapolation. Thus, the Panel estimated an 8 percent per year increase in use between 1973 and 1980 assuming (a) a stable lid market increasing approximately with Gross National Product (GNP), (b) an increasing can body market tripling with GNP, and (c) a slightly decreasing tank plate market.

Factors influencing the container markets include: technological advancement in the steel industry that will permit it to recapture some of the can lid business; lack of metal avail-availability; and wider recycling of aluminum cans that reduce the need for primary metal. Tank plate demand has grown as the energy situation stimulated worldwide construction of large tankers for carrying liquid natural gas (LNG) to the industrial countries. While this market is less than 10 percent of the can market, its impact on magnesium usage is measurable because the alloy used contains 4.5 percent magnesium and the recycling of the tanks is in the distant future. Demand should increase about 3 percent from 1974 levels through 1980.

Recent efforts by the automobile manufacturers to reduce weight potentially could open a large tonnage market for aluminum auto body sheet. Alloys most likely to be used for body sheet contain 2.5 or 3.5 percent magnesium, and if aluminum sheet is selected for only a few applications, this market could consume 10 to 20 million pounds of magnesium per year by 1980 and essentially double that amount by 1985.

Historically, the price of magnesium has had only a minor influence on its use as an alloying element in aluminum; however, it conceivably could become a major factor in the container and auto body markets. Product price is so sensitive that considerable effort is expected from the aluminum industry to hold down cost. Development of new alloys containing less magnesium, reduction in magnesium loss by better melting techniques, and more effective use of recycling will receive increasing attention as magnesium price becomes constraining.

(2) Nodular Iron

Nodular iron, invented by the International Nickel Company in the late 1940s, offers physical properties that approach those of steel and the castability and ease of processing of cast iron. Magnesium-treated gray cast iron, this new material, has been exploited rapidly by the automotive and other industries (e.g., in the automotive industry its substitution for forged steel in crankshafts lowered manufacturing costs and improved quality while in the cast iron pipe industry it essentially has replaced cast iron and tremendously improved strength and impact resistance).

While nodular iron has not achieved use in all its potential applications, the major tonnage markets are being served now and the rapid growth rate experienced in the past should not continue. Its use in some markets (currently served by malleable iron, steel, and cast iron) should be realized, however, and an increase in its use of 5 to 10 percent per year for the next 15 years seems reasonable. The magnesium consumption estimate for 1980, shown in Table 4 is 28 million pounds and, beyond that, the growth rate is expected to be more gradual and tied to the total cast iron market. No dramatic increase or decrease is foreseen.

No viable substitute either from an economic or technical standpoint appears to threaten magnesium as the preferred nodularizer in the nodular iron industry, if the cost of magnesium does not balloon out of economic proportion.

(3) Desulfurization of Blast Furnace Metal

External desulfurization of blast furnace metal prior to its conversion to steel has been practiced to a limited extent for many years using reagents such as soda ash, calcium cyanamide, and calcium carbide. During the past several years, interest in external desulfurization has increased tremendously for the following reasons:

- Improving Steel Properties. The relationship of sulfur content to notch toughness, formability, and surface finish is well known in the steel industry. Recently, the more enlightened consumers (auto, pipe, etc.) requested the basic steel producers to lower the sulfur content of certain steels to meet specific property requirements. In most cases, the only reliable method for accomplishing this is to desulfurize the blast furnace metal while carefully controlling the sulfur input in the scrap and alloy portion in the steel heat.

- Salvage. Blast furnaces are charged to produce iron to a given sulfur target level. Swings on each side of the target are normal but, occasionally, the swing is very high, resulting in casts with higher sulfur than the basic oxygen steelmaking process can handle. When this happens, the steelmaker scraps the cast or externally desulfurizes it to a workable level.

- Blast Furnace Productivity. The principal parameters that affect the output of any blast furnace are coke rate, coke quality, ore type and quality, alkali content of coke and ore, and stone rate (basicity). Increasing coke costs, coupled with lower overall quality of the burden materials, have stimulated several companies to permit (either partially or full time) the sulfur in their blast furnace operations to run at higher levels than their previous practice. In these operations, the cost of external desulfurization is more than offset by the coke savings and the increased furnace productivity.

The use of external desulfurization is increasing rapidly all over the world. External desulfurization to improve properties and salvage is expected to increase and plateau at a point equivalent to 10 percent of the total blast furnace production. Desulfurization, however, offers the greatest potential for increasing furnace productivity and its use could result in a market equivalent to 1 pound of magnesium per ton of blast furnace metal produced in the world.

In today's desulfurization market, the two favored reagents are calcium carbide and magnesium. The two favored application methods are gaseous injection and plunging. Calcium carbide, magnesium powder, magnesium-lime powder, and magnesium-aluminum powder have been injected successfully. Mag-coke, magnesium-iron shaving briquettes, and other magnesium containing briquettes have been plunged successfully.

Today's abnormal market conditions make it impossible to predict accurately at what rate the basic steel industry will incorporate external desulfurization. The estimate of 20 million pounds for 1980 (Table 4) is an extrapolation based upon gradual growth. Its actual growth rate will be influenced strongly by economic considerations. The recent escalation in magnesium price may influence the market toward calcium carbide; however, technological improvement in the method of adding magnesium could overcome some base price inequity. If the use of magnesium can be made economically attractive, the market for desulfurization could reach 100 million pounds per year by 1980.

(4) Reducing Agents

Magnesium is used as a reducing agent in the production of several metals. Most important of these, from a magnesium standpoint, are titanium and zirconium.

Titanium sponge is produced by reacting $TiCl_4$ with sodium or magnesium. Of the three major titanium producers in the United States, the RMI Company uses sodium while Titanium Metals Corporation of America, Inc. (Timet) and Oregon Metallurgical Company, Inc.

use magnesium. Timet recovers the magnesium after the titanium reduction reaction by electrolyzing $MgCl_2$ back to magnesium and chlorine, and primary magnesium is needed only to make up recovery losses. Because of these factors, the new magnesium required for producing titanium is only about 20 percent of the total titanium market. Titanium market growth predictions are reasonably good. While the aerospace program has recovered somewhat and appears to have increased its need for titanium, commercial applications of titanium are beginning to grow faster than aerospace applications. Thus, estimates of the 1980 titanium market indicate a 25 to 30 million pound increase over 1973. If 20 percent of this increase requires primary magnesium, the increase in magnesium will be 5 to 6 million pounds.

Almost 100 percent of the zirconium produced is reactor grade and is used to clad nuclear fuel rods. Zirconium provides the least resistance to neutrons passing through it while hafnium has the opposite property and is used for control rods to absorb or restrict neutrons, slowing down the nuclear reaction. Nuclear fuel rods must be replaced at about three-year intervals; therefore, the demand for zirconium should grow because of the new nuclear plants being built and the replacement rods required for an increasing number of existing plants. The two producers are Wah Chang and AMAX.

The outlook for the zirconium industry is exceptionally good, and a 10 to 15 percent growth rate should be attainable easily for the balance of the 1970s. A growth rate exceeding 15 percent could materialize if the roadblocks for the nuclear power industry were reduced or removed.

Table 4 shows a prediction of a 1980 magnesium consumption for reducing agent double the 1973 usage. At 28 million pounds per year, this category would equal the magnesium used for nodular iron.

(5) Chemical Reaction

All of the magnesium consumed by the chemical industry is used as a Grignard reagent producing different end products. Most of the magnesium is used for the production of tetramethyl lead (TML). This compound, as well as tetraethyl lead (TEL) is used in gasoline motor mixes to increase the gasoline octane rating and reduce engine knocking. To meet government regulations for reducing the lead content in gasoline, the refiners added aromatic hydrocarbons to increase the gasoline octane rating. A given amount of TML increases the octane level more than TEL when there is a higher level of aromatic hydrocarbons in the gasoline; therefore, the demand and use of TML should be stronger and longer lasting than that for TEL. The balance of the magnesium consumed by the chemical industry is used to produce magnesium sulfonates for lubricating oil additives and other chemicals using magnesium as a Grignard reagent.

Overall, the chemical industry demand for magnesium should be relatively constant at 20 million pounds per year for the balance of the 1970s. In some areas the expected growth will be offset by losses due to the increasing consumption of "lead free" gasoline.

TABLE 6. Current and Potential Industrial Structural Uses of Magnesium

End Use	Current Products	Potential Products
Transportation Equipment	Fuel Pumps (D)	Engine Blocks and Heads (D)
	Oil Seals (D)	Car, Truck Body Parts (D)
	Steering Column Shrouds (D)	Rapid Transit Components
	Transmission Parts (D)	Fender Extensions (W)
	Wheels (D)	V-Belt Pulleys (W)
	Motorcycles (D)	Windshield Wiper Parts (D)
	Snowmobiles (D)	
	Tractor Grilles (D)	
	Engine Fan Spacers (W)	
Consumer Products	Lawn Mowers (D)	Playground Equipment (W)
	Toys (D)	Lawn Furniture (W)
	Luggage (W)	Office Furniture (W)
	Ladders (W)	Golf Clubs (W)
	Vacuum Cleaners (D, W)	Skis (W)
	Film Cameras (D)	Bicycles (D, W)
	TV Cameras (D)	Cooking Utensils (W)
	Hand Tools (D, W)	Griddles (W)
	Business Machines (D, W)	Pianos and Organs (G)
	Typewriters (D, W)	Camping Equipment (D, W)
	Carpenter Levels (W)	
	Tennis Raquets (W)	
	Baseball Bats and Masks (D)	
	Back Packs (W)	
	Computer Tape Drives (W)	
	Movie and Slide Projectors (W)	
Machinery and Tools	Reciprocating Machine Parts (D, W)	Plumbing Products (D)
	Textile Machinery (D, W)	Tape-Controlled Machines
	Tooling Plates (W)	All Portable Tools
	Precision Inspection Equipment (W)	
	Chain Saws (D)	
	Masonry Tools (W)	
	Small Engine Parts (D)	
	Drilling Machines (W)	
Electrical and Electronic Products	Electric Motor Housings (W)	Fuel Cells (W)
	Connectors and Switch Housings (D)	Telephone Parts (W)
	Radio and TV Transmitters (D)	Antennas (D)
		Electron-Optics Parts
Construction and Materials Handling	Scaffolding (W)	Conveyors (W)
	Lifting Cages (W)	Air Carrier Vans (D)
	Loading Ramps (W)	Bridge Railings
	Concrete Handling Equipment (W)	Metal Buildings
	Bulk Shipping Containers (W)	Laminated Decking
	Hand Trucks (W)	

D - Die castings. W - Wrought products. G - Gravity castings.

(6) Cathodic Protection

The amounts of magnesium used in cathodic protection, shown in Table 6, include secondary as well as primary magnesium. Anodes represent an important outlet for magnesium scrap and constitute about 27 percent of the total cathodic protection market. This percentage should remain essentially constant through 1980 unless the price ratio between primary and secondary magnesium varies drastically. Anodes of secondary magnesium have been competitive because of their lower cost, but any appreciable change in primary price or metal availability that influences price could shift the balance of secondary to primary.

The cathodic protection industry is expected to grow 20 percent per year for the next four to five years and then level off. Its rapid growth is due primarily to the Pipeline Safety Act that requires all gas and hazardous pipelines to be cathodically protected by 1976. Since many of the gas utilities have not instituted adequate cathodic protection programs, the cathodic protection service companies think that the compliance date must be extended at least two years. Therefore, the high level of growth should continue to 1977-78. Since the average anode life is about 10 to 15 years, a continuous replacement market and new pipelines should enable this industry to operate at a reduced level thereafter.

Significant progress has been made in recent years towards the use of impressed current anodes. This improvement, coupled with the increased cost of magnesium, is expected to reduce the percentage of the anode market committed to magnesium. The small amount of growth indicated in Table 4 actually could become a decrease if impressed current anodes become appreciably less expensive than magnesium anodes.

(7) Others

There are some important but low-tonnage items that use magnesium for nonstructural purposes. Among these are graphic arts supplies (photoengraving sheet) and batteries. Since these uses represent less than 3 percent of the total, they will not be discussed in detail. Major new market developments are not expected to demand an appreciable percentage of the magnesium consumed.

b. Structural (Industrial)

The choice of a material for a given structural application is based on (in order of importance): (1) the ability of the material to perform the required function, (2) the cost of producing the article in the chosen material relative to its production in other materials that also will perform the function, and (3) the cost of keeping the article in service over a long period of time. While selling effort in terms of advertising, direct selling, and applications development play an important role in materials choice, even a very large selling effort will not help unless the material is competitive in terms of the three criteria cited above.

Magnesium, in various forms, has proven serviceable in a large number of applications, some of which are listed in Table 6. Those applications identified as "Potential

Products" have been proven in engineering tests but have not been put into production; therefore, opportunity exists for magnesium to be made into useful articles that could result in significant expansion of the market.

For further analysis, it is convenient to categorize structural products in terms of the method used to make a part -- i.e., gravity casting, die casting, and working. Each of these methods has its own significance with respect to magnesium and understanding their merits is important.

Magnesium gravity castings offer lower tensile properties than those of aluminum and fabrication costs are high. Therefore, they are used only when performance is overwhelmingly important (e.g., in military and aerospace applications for bulky parts when weight is more important than tensile strength). Once magnesium gravity castings are selected for use in a specific application, continued usage is insensitive to material cost since this cost is a small fraction of total cost.

Magnesium die castings offer mechanical properties equal to those of aluminum and fabrication costs are lower. Thus, the performance criterion is met and, in a large number of applications, the service costs are equivalent for magnesium and aluminum (e.g., automotive engine parts). Cost of the part is therefore most important in materials choice. Since, for die castings, material cost is a large fraction of total cost, the final cost of an article is quite sensitive to material price.

Magnesium wrought products offer tensile properties considerably lower than those of aluminum and fabrication costs are about equal to those for aluminum. The costs of two basic raw materials, sheet and extrusions, used in wrought products also varies for magnesium and aluminum; magnesium sheet is more expensive than aluminum sheet while the cost of magnesium extrusions is about the same as that of aluminum extrusions (see Section VI, Fabrication, for details). Articles are therefore more likely to be made of magnesium extrusions than of magnesium sheet but even then the low tensile properties of magnesium limit its use. Article cost is sensitive to material cost since the latter is usually a significant fraction of total cost, and service costs can be more of a problem with wrought products than with die castings since appearance is more often an important consideration.

Thus, it is clear that the use of magnesium in the form of gravity castings or wrought products will not expand greatly without major technical breakthroughs. A major expansion of magnesium use in the form of die castings, however, is feasible without change in the properties of magnesium provided the cost is competitive with aluminum.

It is instructive now to examine the consumption of magnesium in structural markets as given in Table 7. Gravity casting volume depends upon military demand, die-castings have become asymptotic to about 20 million pounds per year, and wrought products are asymptotic to about 25 million pounds per year. The latter two production methods are not likely to change further (except for general GNP growth) unless the controlling factors are changed.

TABLE 7. Consumption of Magnesium for Structural Products (millions of pounds per year)

	Gravity Casting		Die Casting		Wrought		Total
Year	Pounds (million)	Percent of Total	Pounds (million)	Percent of Total	Pounds (million)	Percent of Total	Consumption (million lbs)
1963	9.36	24	11.16	29	18.48	47	39.00
1964	5.92	17	9.51	27	19.22	56	34.65
1965	7.55	19	11.20	28	21.86	53	40.61
1966	9.18	20	9.96	22	26.35	58	45.49
1967	8.81	19	16.73	36	21.03	45	46.57
1968	8.69	19	14.67	32	22.56	49	45.92
1969	5.93	13	14.97	32	26.22	55	47.12
1970	3.99	9	18.00	39	24.50	52	46.49
1971	1.81	5	14.94	39	21.43	56	38.18
1972	2.87	6	18.65	39	25.89	55	47.41
1973	4.61	9	20.83	39	27.69	52	53.13

NOTE: Data from Bauer, 1969.

Since the major limitations on wrought products are the mechanical properties for extrusions and the inherent high cost of sheet, a lower material cost would shift the usage of magnesium upward; however, it is not likely to increase beyond 30 to 40 million pounds per year. If a genuine breakthrough were made in properties and relative material cost were reduced, substantial growth, of course, would occur, but this is not believed to be likely within the next 15 years.

If the above statements regarding the demand for magnesium die castings depending almost exclusively upon relative cost are true, then demand depends directly upon the ratio of the price of magnesium die-casting ingot to that of aluminum die-casting ingot. Between the late 1950s and early 1970s the price of magnesium die casting ingot was about $0.30 per pound and that of aluminum was about $0.22 per pound, yielding a ratio of 1.36; it establishes one point for the demand/ratio relation (ratio of 1.36; demand of 20 million pounds per year). Since the demand is relatively low at this ratio, there is reason to believe that magnesium is used only for those applications in which it performs better than a competitive material. Examination of the specific current applications confirms this.

It is extremely difficult to estimate the potential volume of demand for magnesium die castings as a function of the ratio of price (magnesium/aluminum); the data provided in Table 8 is a good attempt (Campbell and Fisher, 1975). While qualitative, the magnesium:aluminum price premise in Table 8 probably is correct. It is to be noted that the ratio of 1.36 in Table 8 is at about a stagnation point.

TABLE 8. Effect of Metal Price Ratio on Automotive Markets

Magnesium:Aluminum Price Ratio	Effect on Magnesium Usage
1.1 to 1	Major penetration of automotive market possible.
1.25 to 1	Slow penetration of structural markets typical of past 20 years.
1.5 to 1	Little acquisition of new markets. Existing applications would decline by product obsolescence, and hence total market would probably decline slowly.
2.0 to 1	Loss of existing applications to be feared, with the extent depending on the length of time that this ratio was expected to persist.

NOTE: Data from Campbell and Fisher, 1975.

The most significant secondary factors that can influence demand are listed in Table 9, which has been compiled from surveys of current and potential suppliers and users of magnesium die castings. These factors are reasons most often given by respondents for decisions not to operate an in-house die casting facility or for not using magnesium die castings at all. Some of these, such as the concern for fire and safety hazards, undoubtedly are exaggerated and are minimal with modern manufacturing technology. Others, such as the single supplier market, high melt losses, excessive flux usage, scrap handling problems and the low productivity of cold chamber die casting machines, represent a very real economic penalty and will continue to do so unless ameliorated by research and development.

The concern for fire and safety hazards associated with magnesium casting undoubtedly stems from awareness of the uses of magnesium in incendiary weapons and strong actinic light sources. Compared to other metals, the differences are in degree, not in kind. Many metals, other than magnesium, are pyrophoric when in a finely divided state and these usually need surface protection when melted in air. With modern technology, good housekeeping in the plant, and accepted chip handling procedures, fires and safety hazards should not be a restraining factor to the expansion of magnesium usage.

TABLE 9. Reasons Often Cited for Not Using Magnesium Products

Use	Economic and Environmental (including plant environment)	Technological
Mill Products	Cost Uncertain availability Only one source of sheet and plate Lack of information on processing costs No established secondary magnesium market Chip handling problems	Corrosion problems Lack of stiffness Low hardness Poor wear resistance Low fatigue strength High thermal expansion Sensitive to stress risers Creep rate higher than aluminum Hot cracking (in alloys with a low solidus and pronounced segregation) Poor surface finish compared to zinc alloys More porosity problems than with zinc die castings Painting problems
Casting In-House	Cost Only one supplier of ingot Fire and safety hazards Need to isolate operation from rest of plant Meticulous housekeeping required compared to zinc and aluminum Scrap handling problems Corrosion from traditional flux usage	Capital investment in aluminum die casting machines and associated equipment not readily convertible to magnesium Larger die casting machines needed for equivalent weight castings than for aluminum and zinc Alloy segregation at the casting surfaces Metal losses in melting and in metal transfer higher than for zinc and aluminum Costly flux required compared to zinc and aluminum Precision part support and thin flash required to prevent casting breakout on trimming Higher injection pressure needed for sound castings compared to zinc Must be sealed or impregnated for oil tightness under pressure (true also for aluminum)

Some specific areas requiring concerted (and successful) research to make magnesium more viable are:

(1) Increasing casting yields in production

(2) Decreasing melting and remelting losses

(3) Improved molten metal protection

(4) Better flux and fluxing techniques

(5) Improved scrap reclamation methods

(6) More effective and lower cost finishes and coatings

(7) Greater resistance to corrosion

(8) Better high temperature properties

(9) Improved deep drawability at room or slightly elevated temperatures

(10) Reduced alloy segregation in the lower cost alloys

(11) Improved metal transfer technology, particularly for large castings

(12) Reduced sensitivity of castings to hot cracking

(13) Stronger sheet and extrusion alloys not subject to stress corrosion cracking when welded without stress relief

(14) Improved and less expensive wear-resisting coatings

(15) More rational procedures for maximizing weight substitution ratios in product design

Solid progress in these areas undoubtedly would increase demand without changing the price ratio. Of course, prospects for success would be much better for some investigations than for others. Two currently promising developments are worthy of note. These are the use of sulfur hexafluoride with air as a protective atmosphere in place of flux and the substitution of hot chamber for cold chamber die casting machines. If these two developments reach their full potential, together with good progress on other problems, the result could be the equivalent of reducing the price ratio by 0.20 to 0.25. Thus, major penetration of the automotive markets might be possible at a ratio of 1.30 to 1.35.

2. Aerospace (Structural)

a. Past and Current Demand

The only available data on uses of magnesium in aerospace systems were accumulated through 1963 and are presented in Table 10. The data show the percentage of magnesium structural products used in aerospace systems through 1963 with estimated values from 1964 through 1973.

During World War II, it became essential to reduce the time delay in furnishing munitions, supplies, and troops to remote theaters of operation. Accordingly, development was initiated to increase cargo capacity, speed, and range for military aircraft that were limited by the power available from reciprocating engines, early jet engines, and the engines used in missiles.

To increase payloads and range, it was necessary to reduce the overall weight of the systems by using lighter weight materials, such as magnesium alloys, wherever possible.

In many instances, the early production models contained the most magnesium. Subsequent versions of the same system that resulted from continued refinement in air frame design, new equipment, and more powerful engines generally contained fewer magnesium components in critical areas. In the earlier aircraft, sheet, plate, forgings, extrusions, tubular products, and castings were used. Typical applications were in external fuselage and wing skins, structural members, engine compressor casings, gear box housings, and landing gear wheels. The missiles and space vehicles, introduced after 1950, also employed significant amounts of magnesium in terms of their total weight although the overall quantity used was small.

TABLE 10. Magnesium Structural Product Usage in Aerospace Systems

Year	Aerospace Systems (millions of pounds)	% of Total Consumption
1954	20.1	57
1955	25.0	59
1956	25.4	59
1957	19.1	52
1958	15.6	50
1959	18.6	50
1960	12.4	48
1961	13.0	32
1962	13.5	32
1963	11.7	30
1964-73	< 11 (estimated)	< 30 (estimated)

NOTE: Unpublished data from Dow Chemical Company.

The early commercial aircraft that were produced after the introduction of jet propulsion also used appreciable quantities of magnesium. As new modifications and new designs were introduced, the magnesium specified was reduced steadily and, in some cases, eliminated entirely. In private and business aircraft, magnesium currently competes with aluminum for internal cast components such as bell cranks, fittings, and control wheels.

After 1960, the government aerospace effort was concentrated largely in space vehicles and missiles. The combination of well-documented case histories of service difficulties and the ability to achieve mission objectives through advanced materials, structures, and propulsion technology minimized reliance on magnesium. Since 1960, there has been renewed activity in the development of numerous types of military aircraft. The use of magnesium in these systems is minimal and confined to subsystems that can be protected adequately to avoid corrosion and associated maintenance problems.

While magnesium has been used in National Aeronautics and Space Administration (NASA) launch vehicles and on manned and unmanned spacecraft, the total usage has been very small and is declining. Because of their high specific strength, favorable stiffness at minimum weight, and high damping capacity, magnesium alloys were used successfully in Ranger space probes, Nimbus weather satellites, and the scientific mission Explorer and Mariner vehicles. The principal problem with magnesium alloys in these applications has been corrosion protection during fabrication and pre-launch. Anodic coatings, such as Dow 17®, have provided effective protection but have introduced other problems with reduced electrical and thermal conductivity because of the dielectric nature of the coating. NASA currently has no research in progress involving magnesium and its alloys. On the other hand, there has been much less usage in the current vehicles such as the Viking (unmanned Mars explorer) and the space shuttle.

b. Reasons for Reduced Use of Magnesium in Aerospace Systems

Because aerospace systems constructed after 1950 were placed in service during peacetime, their operational activity was distributed over a much longer time period than under wartime conditions. Aircraft were exposed to a wide variety of environments including humidity and temperature cycling during each flight with landings in arctic, desert, marine, and tropical locations. Under these conditions, moisture from the air, sometimes laden with salt, would collect in crevices and contribute to serious corrosion.

Since magnesium is chemically active, both general and dissimilar metal corrosion were encountered. Although the magnesium components were protected by coatings, normal operations (such as cargo handling and servicing) caused wear and mechanical damange leading to general corrosion. Attachment of magnesium components by mechanical fasteners created crevices or pockets that were natural sites for moisture collection leading to serious dissimilar metal corrosion. The seriousness of the corrosion could not be detected readily in inaccessible areas and complete disassembly was required for examination.

As the corrosion problem became more acute, designers tended to replace magnesium components in critical areas with aluminum rather than rework or use new magnesium components. One example was the replacement in all Air Force aircraft of magnesium wheels by aluminum because fatigue cracking was initiated by pitting corrosion. Nevertheless, a number of magnesium components on both Air Force and Navy aircraft are operating in corrosive environments with reasonably low incidence of corrosion. Corrosion cannot be eliminated completely but it can be minimized by proper joint design, dissimilar metal insulation, manufacturing quality control, and maintenance. In space vehicles of the nonreusable variety, the operational environment of outer space minimizes the corrosion problem but these systems represent an insignificant usage of magnesium.

c. Factors Affecting Selection of Magnesium for Aerospace

In the past, aerospace procurement depended solely on performance specifications that left materials selection up to the contractor. Unsatisfactory service experience has persuaded the procuring agencies to take a more active role in accepting or rejecting contractor-proposed procedures and practices. Contractors must now give careful attention to materials selection, fabrication processes, corrosion prevention, and all design innovations.

While there has been no attempt to specifically exclude the use of magnesium alloys as a result of reported maintenance problems and service failures, the various government agencies have issued documents severely restricting the application of magnesium in aerospace vehicles. Typical of the statements in these documents is the following paragraph from NASA Document SE-R-0006 on "General Specification for Materials and Processes" (National Aeronautics and Space Administration, 1973).

> Magnesium: Magnesium alloys shall not be used in the primary flight control system, for landing wheels, for primary structure, or in other areas subject to wear, abuse, foreign object damage, abrasion, erosion or at any location where fluid or moisture entrapment is possible.

Similar Air Force and Navy documents are cited in Section VIII, References and Bibliography.

d. Prognosis of Future Demand

During the past two decades, there has been a dramatic reduction in the amount of magnesium alloys used in any given aerospace system. In many instances, the total weight employed on a particular system is low but may include a number of different small components. The main deterrent to wider application is poor corrosion resistance. Since all customers, both government and commercial, are concerned increasingly with extending the operational and storage life and with reducing maintenance costs, each proposed use of magnesium is scrutinized closely.

Although inadequate corrosion resistance is the major limitation on the use of magnesium in current and future aerospace systems, other properties also restrict wider application. Among these are low strength, limited elevated temperature capability, low fracture toughness, and low stress corrosion resistance compared with competing materials. These factors, together with cost, are analyzed in the process of selecting the optimum materials of construction for efficient load-bearing structures. Therefore, research concentrated solely on improving corrosion resistance will not lead to necessarily greater use of magnesium alloys.

Present research does not indicate any dramatic improvements in the mechanical properties listed above. Accordingly, magnesium usage in aerospace is predicted to remain at less than 20 million pounds per year as far ahead as 1990.

IV. PRIMARY METAL PRODUCTION PROCESSES

Elsewhere in this report,it is shown that in certain applications magnesium offers chemical and metallurgical properties not easily provided by other materials. In mechanical applications using casting and wrought products, magnesium's serviceability closely parallels that of aluminum if aluminum's superior electrical or corrosion properties are not essential. In these applications, magnesium could replace aluminum, depending on the economic factors involved.

Future consumption of magnesium therefore depends, in part, on the supply prices of magnesium relative to other materials, especially aluminum. If, in the future, aluminum prices rise substantially above magnesium prices, future trends in consumption may be quite different than if magnesium prices rise substantially above aluminum prices.

This section describes the current and prospective production technologies and relative production costs of magnesium and aluminum ingot. In the foreseeable future, magnesium ingot is projected to be 25 to 40 percent more expensive than aluminum ingot per pound but approximately equivalent in price per unit volume.

A. Recent Trends in Costs and Prices of Aluminum and Magnesium Ingot

To provide a historical representation of the relative production costs of magnesium and aluminum, their recorded list prices are examined over the period 1953 through 1974. The list prices of the two metals are presumed to be proportional to their costs of production. List prices are probably more representative of long-run average production costs than spot transactions prices that tend to fluctuate substantially in response to demand and supply conditions over the business cycle.

Table 11 and Figure 2 show the history of magnesium and aluminum prices over the period 1953 through 1974. The trends in both prices are quite similar. The prices of both magnesium and aluminum increased steadily during the post-Korean boom years of 1953 through 1957 and levelled off for the succeeding decade. The U.S. price of magnesium metal remained constant at $0.36 per pound from 1957 through 1970. The average annual price of aluminum ingot actually declined from its peak in 1957 to a low of $0.226 in 1963, and then increased gradually to $0.29 in 1971. The magnesium price increased slightly between 1970 and 1973, while the aluminum price declined slightly from its peak in 1971 to $0.25 in 1973. Both prices increased substantially in 1974 and, by May 1975, the price of magnesium had reached $0.82 per pound plus freight, while the price of aluminum had reached $0.39 per pound delivered.

As Figure 3 shows, a very slight upward trend is apparent in the relative prices of magnesium and aluminum, but the trend is not pronounced sufficiently to enable any conclusions to be drawn from it (particularly if the unusual events of 1974 are ignored). The ratio of the two prices over the

TABLE 11. Average List Prices of Magnesium and Aluminum, 1953-73 (in cents per pound)

Year	Magnesium	Aluminum	Magnesium/Aluminum (ratio of prices)
1953	26.5	20.93	1.27
1954	27.7	21.78	1.27
1955	31.1	23.67	1.31
1956	34.7	26.01	1.33
1957	36.0	27.52	1.31
1958	36.0	26.89	1.34
1959	36.0	26.85	1.34
1960	36.0	27.23	1.32
1961	36.0	25.46	1.41
1962	36.0	23.88	1.51
1963	36.0	22.62	1.59
1964	36.0	23.72	1.51
1965	36.0	24.50	1.47
1966	36.0	24.50	1.47
1967	36.0	24.98	1.44
1968	36.0	25.57	1.41
1969	36.0	27.18	1.32
1970	36.0	28.72	1.25
1971	37.0	29.00	1.28
1972	38.0	26.45	1.44
1973	38.3	25.33	1.51
1974	61.7	31.55	1.81

NOTE: 1953-70 magnesium prices are from American Metal Market, 1972.
1971-73 magnesium prices were obtained from a phone call to the American Metal Market, Somerset, New Jersey.
1953-74 aluminum prices are from American Metal Market, 1974.

years 1953-73 ranged between 1.25 and 1.59, averaging about 1.39. In 1974, the ratio rose to 1.81, although this is probably a short-term aberration. If these figures bracket the relative costs of production of the two metals, the primary metal cost for magnesium has been between 25 and 50 percent greater than that for aluminum on a weight basis and has been roughly equal to aluminum on a volume basis. This is especially true since aluminum was governed by federal price-control regulations for all of 1974 while all other nonferrous metals were decontrolled in late 1973.

B. Present Day Processes for Aluminum and Magnesium Production

Magnesium has been produced commercially using three types of process: (1) electrolysis of $MgCl_2$, (2) ferro-silicon reduction of calcined dolomite (CaOMgO), and (3) carbon reduction of MgO. Because the U.S. government operated several variations of these processes in the early

FIGURE 2. List Price of Magnesium and Aluminum, 1953-74
(cents per pound)

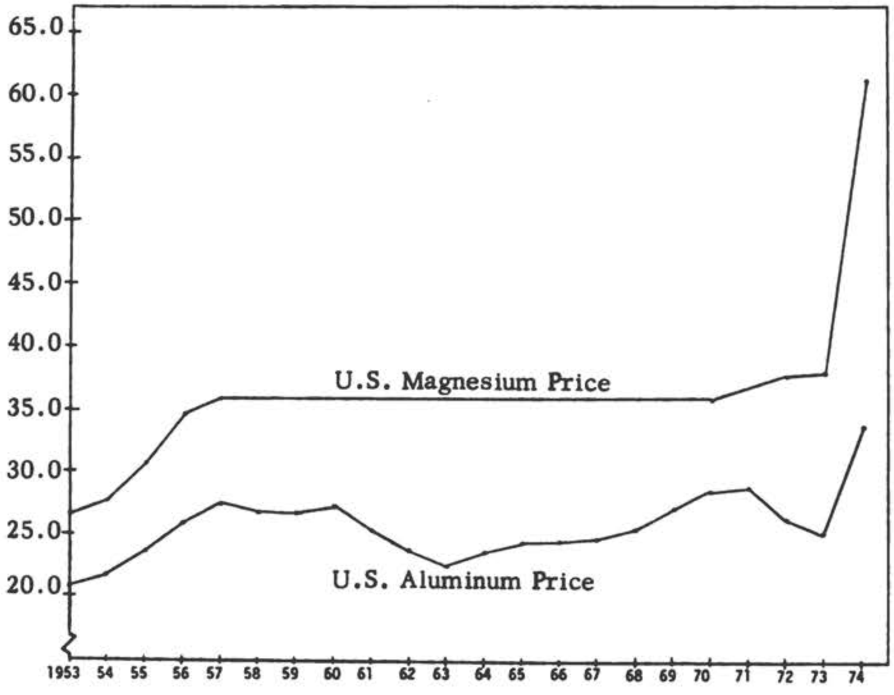
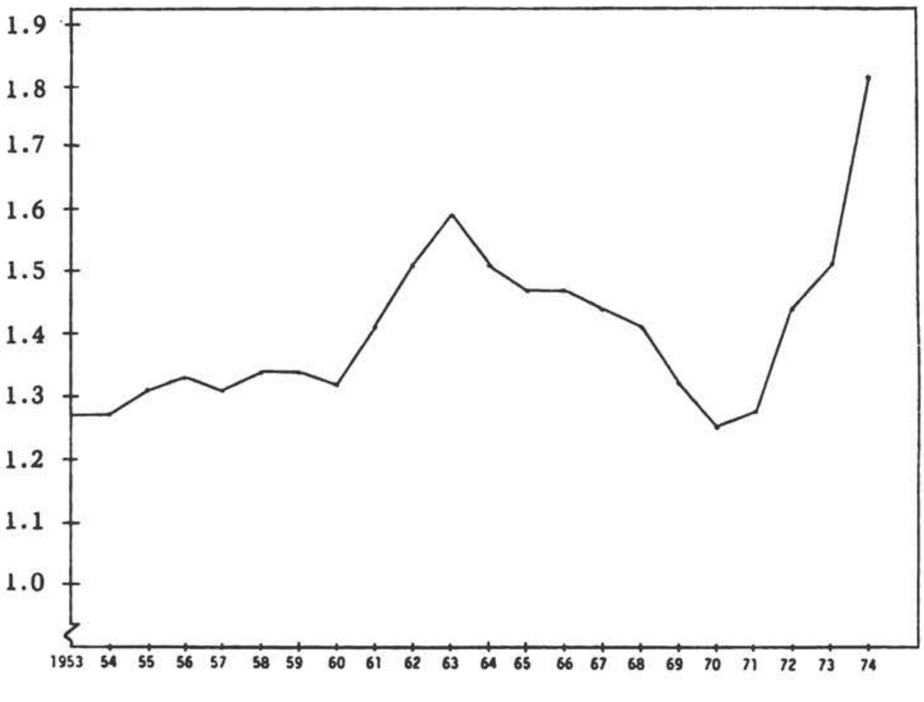


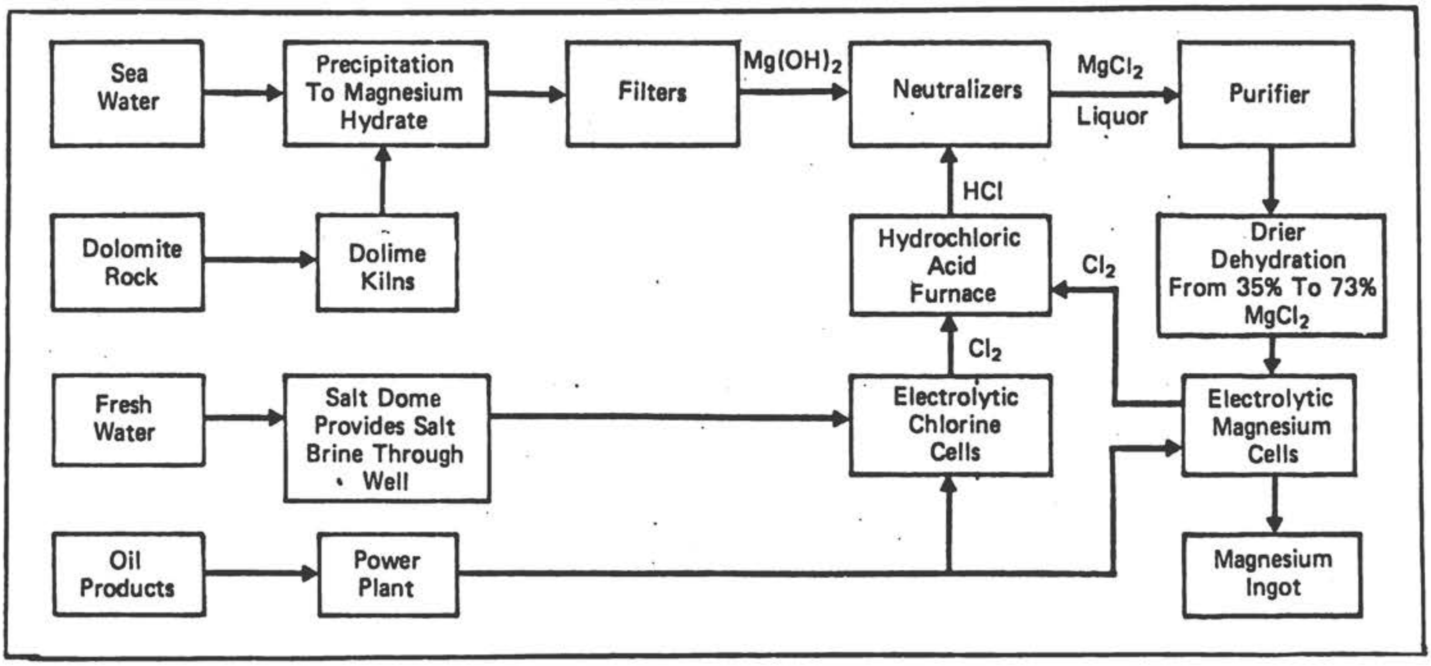
FIGURE 3. Ratio of $\frac{\text{List Price of Magnesium}}{\text{List Price of Aluminum}}$, 1953-74



1940s, detailed information on efficiencies and costs during that period are available. During the past 30 years, some processes succumbed to the pressures of competition. Of the electrolysis processes the Dow process (electrolysis of a bath fed with $MgCl_2 \cdot 1.5\ H_2O$) produces more than 95 percent of the U.S. magnesium supply (Figure 4). A second variety (electrolysis of a bath fed with anhydrous $MgCl_2$, the original German I.G. process) operates at many places in the world and produces more than 95 percent of the balance of the world supply of magnesium. Of the ferro-silicon reduction processes, the Pidgeon variety plants (small externally heated vacuum retort) have all been discontinued in the United States although a few very small plants continue to operate in several foreign countries. Two varieties of the ferro-silicon process survive: the Italian plant at Bolzano (internally heated retort, batch operation), and the French (Figure 5) Magnetherm process (continuous reactor with fluid slag-batch magnesium condenser). A plant also is being constructed by Alcoa at Addy, Washington, with an annual capacity of 24,000 tons. There is currently no appreciable production of carbothermic magnesium anywhere in the world.

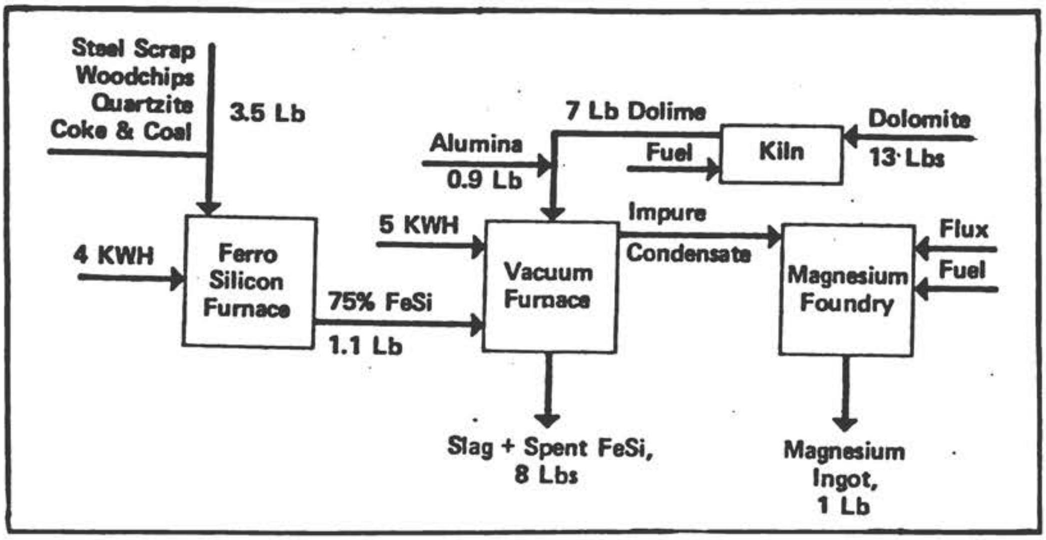
Virtually all aluminum is produced by the Bayer-Hall-Heroult technology in which alumina is produced from bauxite by a chemical process and aluminum then is produced from alumina by electrolysis.

FIGURE 4. Dow Magnesium Process Flow Diagram



SOURCE: Dow Chemical Company.

FIGURE 5. Pechiney Magnetherm FeSi Process



SOURCE: Faure and Marchal, 1964.

C. Factor Inputs for Aluminum and Magnesium Production

Table 12 shows approximate ranges of the major factor inputs for the principle technologies for producing magnesium and aluminum in the United States. The data are for hypothetical plants and do not represent actual factor inputs used in existing plants today. Data are given for the Bayer-Hall process for producing aluminum, the electrolytic process for producing magnesium using a bath-feed of $MgCl_2 \cdot 1.5H_2O$, and the magnethermic process for producing magnesium. The Bayer-Hall data are for an integrated aluminum-alumina plant. It should be emphasized that these data are illustrative only and the factor inputs listed for the different processes may not be fully comparable.

The factor inputs shown in Table 12 are for new greenfield integrated plants. The electric power and other raw material inputs, except for the feed ores, are presumed to be purchased or produced internally at costs comparable to market prices. Resource inputs needed for environmental controls are included in the capital cost figures. The factor inputs shown do not include resources needed for transportation of finished product, miscellaneous and operating supplies, supervision and managerial overhead, research and development, normal profit margin, and selling expenses. However, the annualized capital costs do allow for 10 percent interest cost, 5 percent depreciation, and 5 percent maintenance costs. Also it should be noted that the figures do not include credits for by-product production. The data for the magnethermic process include the costs of ferro-silicon needed for magnesium production but not the costs of silicon production for commercial sale.

As the data show, the electrolytic magnesium process uses slightly more electricity, nearly 7 times the thermal energy, and nearly twice as much labor as the Bayer-Hall aluminum process. The electrolytic magnesium process also requires a moderately higher capital investment than the Bayer-Hall aluminum process. On the other hand, the magnesium process is based on essentially free seawater while the aluminum process generally requires 4 to 5 tons of bauxite per ton of aluminum. The cost of bauxite from some sources has risen substantially during the past year as a result of sharply higher producer country levies.

TABLE 12. Important Factor Inputs for Aluminum and Magnesium Production

Factor Inputs	Magnesium Electrolysis of $MgCl_2 \cdot 1.5H_2O$	Magnesium Magnethermic	Aluminum Electrolytic, Bayer-Hall
Electric Power (kwh)	17,750*	17,600	17,000
Thermal Energy (thousand BTU)	140,000**	60,000	21,450∓
Labor (man hours)	28-30	18-20	15
Fixed Capital (dollars/ton)	$1,800-2,400	$1,700-2,200	$1,800-2,200
Hydrochloric acid (tons)	0.5		
Caustic (pounds)			200-600
Fluoride (dollars)			$10-14
Carbon (tons)		0.5-1.0	0.5
Graphite Electrodes (tons)	0.1	0.1	
Oyster Shells (tons)	8.2		
Alumina (tons)		0.8-1.0	
Bauxite (tons)			4-7
Dolomite (tons)		11-13	
Quartzite (tons)		2.0-2.2	

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* Does not include electricity used for chlorine production.

** 142 mcf of natural gas per ton converted to thousand BTU per ton and rounded downward to reflect recent economies. Does not include natural gas used for chlorine production.

∓ 19,500 thousand BTU of thermal energy per ton of aluminum is used at the alumina stage, on the assumption that 1.95 tons of alumina are used per ton of aluminum. About 1,950 thousand BTU of thermal energy is used at the aluminum stage per ton of aluminum. The sum of these two numbers equals 21,450 thousand BTU of thermal energy.

NOTE: Data on the magnesium-electrolysis process are from the U.S. Bureau of Mines. Data on the other two processes are from industry sources. Data shown do not include costs of transportation, selling costs, corporate overhead, and miscellaneous and operating supplies. For electrolytic Mg production, these latter supplies include: cell pot (0.0005646 per ton of Mg), KCl (0.003 tons), CaF (0.0014 tons), S (0.09 tons), flux (0.016 tons), materials for plant maintenance ($32 per ton in 1973), and operating supplies ($14 per ton in 1973). The total costs of these inputs in 1974 dollars would be about $80.

The magnethermic process uses less electric power, thermal energy, labor and capital per ton of magnesium than the electrolytic magnesium process but requires substantial tonnages of dolomite, quartzite, and alumina. In comparison to the Bayer-Hall aluminum process, the magnethermic process uses slightly more electric energy, thermal power, and labor, about the same fixed capital, and substantially higher tonnages of feed materials.

D. Relative Costs of Producing Aluminum and Magnesium

Table 13 shows approximate ranges of long-run average costs of important factor inputs for production, including capital charges for producing aluminum and magnesium from new plants. This table is based on the data in Table 12, current market prices, and costs of the input materials. The costs in this table do not represent the costs of any existing aluminum or magnesium plant and are intended only for the purposes of comparison. In addition, no allowance is made for the value of by-products. Because all costs are not included, the data for the different technologies are not fully comparable.

TABLE 13. Costs of Important Factors of Producing Aluminum and Magnesium with No Credit for By-products (in dollars per ton)

		Magnesium		Aluminum
Future Inputs	Price or Cost	Electrolysis of $MgCl_2 \cdot 1.5H_2O$	Magnethermic	Bayer-Hall-Heroult
Electric Power	1¢-1.6¢-2.0¢/kwh	$178-284-355*	$176-282-352	$170-272-340
Thermal Energy	$1-$2-$3/million/BTU	140-280-420	60-120-180	50-100-150
Labor	$6.24/hour	175-187	112-125	94
Fixed Capital	@ 20% per year**	360-480	340-440	360-440
Hydrochloric Acid	$25-27/solution ton (36% content)	36		
Caustic	$4.155/100 pound			8-25
Fluoride				10-14
Carbon	$50-100/ton		25-100	25-50
Electrodes	$1440-1465/ton	145	145	
Oyster Shells	$3.70/ton	30		
Alumina	$120/ton		90-120	
Bauxite	$13/ton (without export tax)			52-91 (100-175)
Dolomite	$5-10/ton		55-130	
Quartzite	$8-15/ton		16-33	

			Bauxite Cost	
Energy Scenarios			Low	High
Current Energy Prices	1297-1427	1191-1495	921-1086	969-1170
Low Energy Prices	1064-1196	1025-1329	769-934	817-1018
High Energy Prices	1521-1653	1321-1625	1039-1204	1087-1288

* The three figures indicate low, middle, and high prices calculated for the three energy cost scenarios shown at the bottom of the table.

** Assumes long-run interest cost of 10%, depreciation of 5%, and maintenance of 5% per year. Does not include allowance for profit margin.

NOTE: Backup data available from James C. Burrows, Charles River Associates, 1050 Massachusetts Avenue, Cambridge, Massachusetts 02138. Prices are late 1974 and early 1975 prices.

In all cases, costs were calculated for three energy cost scenarios. The middle scenario assumes a cost per BTU of thermal energy of about $2.00 per million BTU, which is currently the approximate energy equivalent cost of No. 1 and No. 2 distillate fuel in the United States. The prices of distillate fuel used for this calculation correspond to market prices for crude oil per barrel in the $10 to $12 range. The low scenario assumes that the price per BTU of energy is $1.00 per million BTU and the high scenario assumes that the price is about $3.00 per million BTU. For aluminum production, costs also were calculated using both low and high bauxite costs. The higher bauxite costs reflect the higher bauxite levies of several major producing countries.*

As these data show, the electrolytic and magnethermic processes for magnesium have roughly comparable costs. Both processes are more costly per ton of ingot than the electrolytic aluminum process.

Table 14 shows that, at current prices, the cost of the important factors of production of electrolytic magnesium is approximately one-third higher than the cost of aluminum with low bauxite costs and about one-fourth higher than the cost of aluminum with high bauxite costs. The cost disadvantage of magnesium increases as energy prices rise. As energy prices increase, the relative costs of the magnethermic process decline with respect to electrolytic magnesium and to aluminum.

TABLE 14. Ratios of Costs for Producing Magnesium and Aluminum (in terms of weight)

	Ratio of Electrolytic Magnesium to Bayer-Hall Aluminum		Ratio of Magnethermic Magnesium to Bayer-Hall Aluminum	
Energy Prices	Low Bauxite Cost	High Bauxite Cost	Low Bauxite Cost	High Bauxite Cost
Current	1.36	1.28	1.34	1.26
Low	1.33	1.23	1.38	1.28
High	1.42	1.34	1.31	1.24

NOTE: Ratios calculated by averaging low and high end of cost ranges shown in Table 13, and dividing.

Thus, with currently prevailing technologies, the cost per ton of magnesium ingot apparently will be 25 to 40 percent higher than the cost per ton of aluminum ingot, depending on trends in energy and bauxite costs. This differential is consistent with the historical trend in the relative prices of the two materials.

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* Recently, a number of bauxite-producing countries sharply increased their levies on bauxite production. If bauxite costs increase much more, U.S. aluminum producers may turn to domestic nonbauxitic ores requiring different technologies for conversion to alumina. Apparently, these technologies will not result in substantially higher alumina costs than those already prevailing as a result of the higher bauxite costs. The cost of processing nonbauxitic ores into Al_2O_3 may be reduced appreciably by the production of valuable by-products, such as potash and superphosphates.

E. Future Trends in Production Technology and Costs of Aluminum and Magnesium

One of the most significant differences between the electrolytic production of aluminum and magnesium is that the feed for the aluminum cell is Al_2O_3. The Al_2O_3 electrolyzes to aluminum at the cathode and to oxygen at a carbon anode that is consumed at the rate of about 0.5 pounds of carbon per pound of aluminum without producing a commercial by-product. In the magnesium cell, the feed is $MgCl_2$ that is electrolyzed to produce magnesium at the cathode and chlorine at the graphite anode. Thus, for about the same electrical energy input, the magnesium cell produces a second product, chlorine, a major commodity. Most future magnesium plants probably will be built to use this advantage. A total energy of 115,000 BTU per pound has been cited for the NL Industries process for producing magnesium with Cl_2 as a by-product from the brine of the Great Salt Lake (Aqua, 1974). In addition to the reduction in the net cost of magnesium production due to the credit for the by-product chlorine of the NL process, the total purchased energy requirement for this process is reduced greatly by using solar evaporation to concentrate the Great Salt Lake brine.

A new process for aluminum has been announced by Alcoa. The first unit at Palestine, Texas, will have a capacity of 15,000 tons per year. Compared with the Bayer-Hall process for aluminum, the new process is estimated to have lower capital costs but higher direct operating costs. The electrical energy requirement for electrolysis will be about 30 percent lower. Aluminum and chlorine will be produced in a bi-polar cell. The chlorine will be recycled to react with Al_2O_3 to produce the $AlCl_3$ for electrolysis. Pollution problems will be reduced because of the absence of fluoride fumes. The process also eliminates the need for cryolite but may require makeup chlorine and power for the chlorination step.

The Dow Chemical Company also has announced progress in a new magnesium technology that may reduce electrical energy up to 50 percent by use of a new process design. In addition, the existing seawater process is being improved to reduce its power consumption.

While it is difficult to generalize about the effects of technological changes on future costs of production, the costs of both magnesium and aluminum (in real terms) may decline somewhat in the future and energy consumption for the production of both metals may decline significantly. The potential for commercial sales of by-product chlorine and the potential utilization of lower grade ores or higher cost bauxite for aluminum suggest that magnesium ingot may improve its future competitive position moderately relative to aluminum. However, it seems unlikely that magnesium costs will decline significantly below the historical range of 25 to 40 percent more than aluminum costs (in terms of weight.)

V. PROPERTIES OF MAGNESIUM AND MAGNESIUM ALLOYS

A. Pure Magnesium

Magnesium, a silvery-white metal of the divalent alkaline earth group, is number 12 in the periodic table of elements. Liquid magnesium solidifies at 650° C (1,202° F) to a hexagonal close-packed crystal. This hexagonal structure leads to significant anistropy in some physical and mechanical properties, particularly linear coefficient of expansion, modulus of elasticity, and electrical conductivity.

Magnesium is high in the electromotive series with a standard electrode potential of -2.40 volts against hydrogen. Most pure magnesium is extracted by electrolysis of $MgCl_2$ in a fused salt electrolyte and sold with a minimum purity of 99.8 percent. For structural applications, magnesium is alloyed with a number of different alloying constituents since pure magnesium has relatively low strength (see Appendix D for more details).

B. Magnesium Alloy Systems

Since pure magnesium, like all pure metals, exhibits relatively low strength properties, it must be alloyed with other metals to develop structurally useful properties and characteristics. The alloying elements used with magnesium enhance the strength properties by one or more of the following mechanisms: (1) solid solution hardening, (2) precipitation hardening, (3) dispersion hardening, and (4) grain size control. In wrought magnesium alloys, significant strength also is attained by cold or warm working. Cold work, solid solution hardening, and grain size control are the important factors contributing to the strengthening of wrought alloys while solid solution hardening and precipitation hardening together with grain size control are the important factors contributing to the strengthening of cast alloys. The alloying elements commonly used today with magnesium are: aluminum, zinc, manganese, zirconium, rare earth metals, thorium, and silicon. Extensive research work has been done on alloys containing lithium and yttrium; however, no commercial alloy containing either of these elements is available commercially today. (The principal effects of each important alloying element can be found in Appendix D.)

1. Chemical and Electrochemical Properties

The chemical and electrochemical applications for magnesium take the largest percentage of the total magnesium used and are based on the superiority of magnesium's basic electrochemical properties over those of its two closest competitors, zinc and aluminum, as shown in Table 15. This superiority is especially true when the comparison of the electrode potentials is made.

Many attempts have been made to increase magnesium electrode potential without lowering its electrochemical capacity. Alloying with small amounts of mercury, thallium, and lead has increased its electrode potential; however, these elements also can lower the anode efficiency. With magnesium's theoretical electrode potential at -2.34 volts, further research in this area is indicated; however, chances for success would be less than 25 percent for substantial improvement and magnesium already has a higher potential than its competitors. When magnesium is compared with zinc and aluminum as to capacity (ampere hours per pound of metal used), magnesium is second best, as indicated in Table 15.

TABLE 15. Basic Electrochemical Properties of Magnesium, Zinc, and Aluminum

Metal	Electrode Potential Ref $CuSo_4$ 1/2 Cell	Anode Capacity (amp hrs/lb)
Magnesium	-1.55 to 1.75 volts	500
Zinc	-0.90 to 1.10 volts	335
Aluminum	-1.00 to 1.10 volts	1,200

The rewards would be great if the theoretical electrochemical equivalent (1,000 amp hrs/lb) from a magnesium alloy could be realized. With the combination of high potential and anode capacity, use of magnesium for cathode protection and perhaps primary batteries would expand rapidly. Much research effort has been expended on this study and, probably, the chances of success are below 10 percent.

Studies of the characteristics of the protective films on magnesium alloys have been very fruitful in the past and, undoubtedly, many more improvements will be forthcoming during the next 15 years. These improvements may come from altering the natural film on magnesium by new and improved chemical treatments and from improving the film by alloying. The elements aluminum and manganese have a strong influence on the protective quality of the film on their magnesium alloys. Improving the film characteristics by these two methods has nearly a 100 percent chance of success. Making the alloys "stainless" or inert has little or no chance of success.

Adjusting the film characteristics of magnesium to control a reaction when the metal is used as a chemical has great possibilities. This would be important in the following applications:

a. Grignard reaction
b. Pyrotechnics
c. Reducing agents
d. Metallurgical additions (such as nodular cast iron)

The ideal activity will vary with the application, and applied research along these lines must be specific to each application. Possibilities of success in this area of research should be high (80 percent). (See Appendix D for further details.)

2. Mechanical Properties

Magnesium alloys have good mechanical properties (described in detail in Appendix D). Since aluminum is the logical target for magnesium expansion, the mechanical properties of magnesium will be compared with those of aluminum.

a. Tensile Properties

The tensile properties of magnesium castings compare very favorably with those of aluminum. According to statistics (Metals Handbook 1961), at least 73 percent of aluminum sand castings and 44 percent of permanent mold castings are made with alloys 108, 113, 319, and 43 that are no stronger than AZ92A. The other aluminum alloys commonly used (356 and D132) have only a slightly higher tensile yield strength and lower tensile strength. Higher yield strengths of 40 ksi can be achieved by special processing of aluminum-copper alloys, a small part of the casting market. In the laboratory, magnesium alloy castings competitive on a strength/weight ratio have been produced using costly alloying elements (e.g., yttrium), but cost would prohibit their use in most applications. The properties of aluminum (380) and magnesium (AZ91B) die castings are essentially the same. The slightly higher strength of 380 aluminum in test bars usually is not maintained in actual die castings. Higher strength can be obtained by using special aluminum alloys (e.g., aluminum 32) but is not required normally. Recent unpublished laboratory work on magnesium alloys containing unusually high zinc has shown that stronger magnesium die castings also may be produced.

The mechanical properties of wrought aluminum vary widely. Tensile yield strength varies from 5 ksi for a 1100-0 to over 70 ksi for 7075-T6 while ductility (tensile elongation) drops from about 40 to 10 percent. AZ31B, the workhorse wrought magnesium alloy, fits within the lower half of this range. Its tensile yield strength varies from 22 to 32 ksi while elongation varies from about 10 to 25 percent. Compressive yield strength is lower (14 to 26 ksi). ZK60A extrusions offer higher strength (35 to 45 ksi yield); thus, the tensile properties of wrought magnesium alloys are competitive with those of the soft and intermediate strength aluminum alloys. The competitive picture is less favorable at high strength levels. High strength can be obtained with wrought magnesium, but expensive alloy elements (e.g., yttrium) or processes (e.g., pellet extrusion) are required. On the other hand, high strength in aluminum can be achieved by simply heat treating alloys containing common elements such as copper, magnesium, and zinc. Since high-strength wrought magnesium alloys are relatively expensive, their use is quite limited.

b. Creep

The creep resistance of the conventional magnesium alloys (e.g., cast AZ92A and wrought AZ31B) is adequate for temperatures up to about 149° C (300° F). Better creep resistance at higher temperatures can be obtained with magnesium alloys containing rare earths and thorium but cost is increased. Aluminum alloys, on the other hand, have adequate creep resistance at temperatures up to about 232° C (450° F), placing magnesium at a competitive disadvantage at intermediate temperatures of 149 to 232° C (300 to 450° F). This problem has been largely overcome in die castings through the introduction of silicon-containing magnesium alloys (e.g., AS41A and AS21X1) that provide good creep resistance up to about 191° C (375° F) at little increase in cost over AZ91B, the standard magnesium die casting alloy. These silicon-containing magnesium alloys are used currently in automotive applications at Volkswagen. Similar improvement in the creep resistance of wrought products can be achieved at a modest increase in cost by using magnesium alloys containing small amounts of rare earth elements.

c. Fatigue

The fatigue strength of magnesium alloys falls as the number of cycles is increased to about 10^5. Beyond this point, however, the rate of descent for many alloys shows a sharp decrease and the S-N curve may become almost flat beyond 10^6 cycles. On the other hand, the fatigue strength of wrought aluminum alloys continues to decrease significantly with increasing cycles. Therefore, magnesium alloys compare favorably with high strength aluminum alloys after a large number of cycles (e.g., 5×10^8). For example, the fatigue strength of 6062-T6 aluminum extrusions was 16 to 18 ksi after 10^7 cycles compared to 18 to 20 ksi for AZ31B. The fatigue strength of most magnesium and aluminum cast alloys is 10 to 13 ksi (5×10^8 cycles). Aluminum appears to offer an advantage in die castings in which its fatigue strength of 380 alloy (at 5×10^8 cycles) is higher than that of AZ91B (21 vs. 14 ksi).

The fatigue strengths of many magnesium alloys are lowered by the presence of notches for magnesium-aluminum alloys, both cast and wrought. A notch with a stress concentration factor (SCF) of 2.0 lowers the fatigue strength by ~40 percent and a notch with SCF of 5.0 lowers the fatigue strength by ~70 percent.

d. Damping Capacity

The damping properties of the common magnesium alloys generally have little practical significance although they are better than those of their aluminum counterparts. The excellent damping characteristics of magnesium, coupled with its low density, are the primary factors in material selection where damping is a prerequisite (e.g., instrument mounting plate in a missile). However, the damping capacity of magnesium is impaired seriously by strengthening through alloying, heat treatment, or strain hardening, and may be sacrificed for improved castability. Special binary magnesium alloys containing zirconium, silicon, or manganese, that have significant damping capacity, can be produced in wrought and cast form but their limited mechanical properties and generally poorer produceability (higher cost) severely limit their use to date (Erickson, 1975).

e. Modulus of Elasticity

The modulus of elasticity of magnesium is 6.4×10^6 psi at room temperature. This means that the specific modulus (E/ρ) of magnesium is about the same as that of aluminum. However, since the stiffness of a structural member is proportional to the modulus (E) times the cube of its thickness (t^3), magnesium is much stiffer than aluminum of the same weight (e.g., magnesium can provide the same stiffness at 77 percent the thickness of aluminum). This characteristic is very important in applications where weight is a primary factor.

f. Dent Resistance

The dent resistance of magnesium alloys compares very favorably to that of aluminum alloys and mild steel in spite of its lower strength. Tests conducted in the 1950s by Dow and Samsonite Corporation showed that, on the basis of equal weight, the dent resistance of AZ31B-H24 sheet is better than all aluminum alloys except 7075-T6 (Dow Chemical Company, 1960). On the basis of equal thickness, AZ31-H24 was superior to 6061-T6 and mild steel. Accordingly, magnesium alloys are particularly attractive for applications where denting impairs the utility or appearance of the part. A current example of the importance of dent resistance in the selection of magnesium for a new product is the die cast baseball bat.

g. Effect of Temperature

Increasing test temperature adversely affects the properties of both magnesium and aluminum but the decline in strength is more rapid for the common magnesium alloys. As noted above, the strength of magnesium at elevated temperatures can be enhanced by the addition of metals (e.g., rare earths or thorium), but the cost of the magnesium alloy is increased. In fact, magnesium-thorium alloys are superior to the best aluminum alloys at relatively high temperatures (e.g., 500 to 600° F [260 to 316° C]) and are used in special applications that can afford the cost premium. Magnesium alloys generally are affected to a lesser degree than aluminum alloys by simple exposure to elevated temperatures because precipitation hardening is much more important to the aluminum alloys. Accordingly, the properties of magnesium alloys in the soft or -F temper compare favorably with those of aluminum alloys.

Decreasing test temperature below 32° F (0° C) gradually increases the strength of cast and wrought magnesium alloys at the expense of ductility. At -100° C (-148° F) the properties of most magnesium alloys are similar to their properties at room temperature. At very low temperatures (e.g., ~ -200° C [-328° F]); however, the ductility and impact properties of magnesium become quite limited (~ 1 percent elongation and ~ 1 ft-lb). Aluminum alloys, on the other hand, are much more ductile at such low temperatures. In fact, the tensile elongation of many aluminum alloys is higher at -200° C (-328° F) than at room temperature. Therefore, magnesium does not compete successfully with aluminum for cryogenic applications.

h. Effect of Environment

The environment can influence significantly the properties of magnesium alloys. Most magnesium alloys subjected to a continuous high stress (e.g., 20 ksi) undergo stress corrosion when exposed to the weather, even in a rural environment. Wrought magnesium alloys containing substantial amounts of aluminum (e.g., AZ31B) are particularly prone to stress corrosion and fail within about 100 days at 20 ksi (AZ31B must be stress relieved when it is welded). This problem may be largely avoided by using wrought magnesium-zinc alloys (e.g., ZE10A sheet) that have better resistance to stress corrosion. The fatigue strength of magnesium continues to drop with increasing number of cycles in humid air when condensation is present instead of almost leveling off (as it does in dry air). High-strength aluminum alloys also are prone to stress corrosion and to corrosion fatigue but do not appear as sensitive as magnesium alloys. Some work on corrosion fatigue of magnesium strongly indicates that tough paint coatings almost completely eliminate the negative effects of high humidity and condensation.

VI. SEMI-FABRICATION AND FINISHING*

A. Economic Comparisons in the Fabrication of Light Metals

Potential growth in the magnesium industry is closely related to its competitive position with respect to aluminum. Growth in the magnesium industry generally will result from either overall growth in the light metals industry, of which magnesium will get some fraction, or its ability to replace aluminum in some uses. To estimate the possitilities within a free market, the relative economic positions of magnesium and aluminum as they are likely to evolve over the next several years should be determined. A critical evaluation is the final comparison of product performance and total cost but this evaluation can be broken into comparisons of prime metal production costs, fabrication costs, and operational costs of the final product. This section summarizes the fabrication cost comparisons. Other sections of the report indicate how changing technology or changing energy costs might influence the ultimate cost structure.

The general comparisons of magnesium with aluminum fabrication costs are indicated in Table 16.

TABLE 16. Comparative Fabricating Costs of Magnesium and Aluminum

Method	Costs
Direct-Chill Casting	Costs about equal on a volume basis
Rolling	Relatively more difficult to roll Mg into thin sheets than Al
Extrusion	Costs about equal on a volume basis
Forging	Al forges somewhat faster than Mg forging; energy costs about equal
Powder Metallurgy	No market for Mg powder in structural use
Sand, Permanent Mold, and Investment Casting	Mg at a disadvantage; high metal risers needed leading to relatively low yields and multiplying the higher melting costs of Mg
Die Casting	Costs about equal on a weight basis; energy only a minor part of total cost
Machining	Mg has about a factor of 2 advantage over Al in labor and capital costs; energy only a small part of the total machining cost
Forming and Drawing	Mg at a significant disadvantage; elevated temperature required for Mg and only room temperature for Al
Joining	Welding properties similar; Mg at a disadvantage when joints are subject to corrosion
Surface Finishing	Mg requires surface finishing in more applications than Al to protect against corrosion

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* See Appendix D for discussion of fabricating and finishing.

In summary, the fabrication processes in which magnesium is most competitive are die casting, extrusion, and machining. Fabrication is least competitive by sand or permanent mold casting, rolling, or any type of forming.

The energy requirements for die castings are approximately 8,500 BTU per pound for aluminum and 9,000 BTU per pound for magnesium; therefore, on a volume basis, die casting magnesium is less costly with respect to energy consumption. The energy requirements for die casting either metal is about 10 percent of that required to produce the prime metal.

B. Production of Magnesium Ingot for Wrought Products

1. Fabrication

Fabrication of magnesium wrought products starts with the production of extrusion ingot, forging ingot, and rolling slabs that generally are made by the direct-chill (D.C.) continuous casting process. The method is similar to that used for casting aluminum ingot but some modifications are made to accommodate the unique characteristics of magnesium.

2. Energy Requirements and Other Costs

In the current crucible method for melting and processing magnesium alloys for D.C. casting, the energy requirement ranges from 8,000 to 10,000 BTU per pound in contrast to 6,000 BTU per pound required to process aluminum-base alloys in reverberatory furnaces. An additional 0.06 to 0.07 kwh per pound are required for the electrical equipment used in the casting operation and in the pollution control equipment. Productivity is significantly lower for magnesium (i.e., about 350 pounds per man-hour are produced in contrast to 750 pounds per man-hour for aluminum alloys.)

3. Future Needs

In the United States today, there are three continuous round billet casting machines, one continuous slab casting machine, and at least four intermittent casting machines. These machines provide adequate casting capacity and should continue to do so for many more years at the currently anticipated level of wrought product applications.

The D.C. casting process is developed fully. Improvements in this method of processing, such as introduction of SF_6 for molten metal protection, will yield only small incremental changes in the overall economics of the processes for producing magnesium wrought products. However, an important need in magnesium fabrication technology is a reliable process for casting re-roll stock directly for the production of thin gauge sheet without the use of expensive 4-high breakdown and finishing mills. This is discussed in more detail below. (See Appendix C for details.)

C. Rolling

Even though hot rolling magnesium has reached an excellence approaching the breakdown of aluminum alloys, the high cost of the large 4-high mills for the limited amount of magnesium produced by passing through these mills drastically increases the cost of magnesium sheet rolling operations. Continuously cast re-roll strips should be the answer to this problem. Considerable research could be done to develop methods to replace the costly hot rolling of magnesium into re-roll stock.

In the re-rolling plate (from 0.180 inch down to any customary sheet gauges), metal yield of 50 percent and less for the usual range of commercial gauges (together with the low productivity associated with the large number of steps required) make magnesium rolled sheet and coil production almost uneconomical for commercial applications. For these gauges, magnesium rolling technology should explore the steel industry's processing of such metals as stainless steel and other high-strength steel alloys. New equipment, such as cluster mills of various designs and planetary mills, was designed to increase the amount of reduction and, therefore, to decrease the time required to roll these products. These methods and mills, entirely different from the conventional sheet and strip rolling mills of the mass-producing steel-rolling industry, made stainless sheet and strip a viable commercial product.

If rolled magnesium sheet is to become more competitive with aluminum, metal yield and economics must improve considerably. To stimulate this improvement, two things should be done:

1. Rolling metal from a form other than the present cast rolling-mill ingot should be started (e.g., a cast product made on Hunter-Douglas machines or a re-roll coil made from pellets, powder, or relatively small particles).

2. Rolling mills and auxiliary equipment that are considerably less capital-intensive than the conventional 4-high rolling mills and their supporting equipment should be devised and used; this equipment would reduce drastically the large number of passes required to produce thin gauged sheet.

In the past decade or two, a number of new and revolutionary rolling methods and mills have come into being. Some are used extensively for the mass rolling of hard-to-roll metals, and they fall practically into the category of low-investment, high-reduction mills for special metals and alloys. Essentially, they are high-reduction-per-pass mills based on the principle of very small working rolls. The small working rolls reduce the horsepower requirements markedly and consequently the rolling mill frame is much lighter and smaller. These factors result in reduced investment for the building, the foundation, and the mill itself.

The use of small working rolls permits greatly increased reduction per pass and reduces the total number of passes required. Some of these mills are commercially available (e.g., the so-called "cluster mills" or the more refined "planetary mills"). A very simplified version of the small working roll and high-reduction mill is the ingeniously designed pendulum mill. In an experimental program using a pendulum mill, some magnesium alloy was reduced 85 percent in one pass while on a conventional modern 4-high mill, this reduction would have required six passes and six interspersed annealing and reheating cycles. Planetary mills have even greater potential.

The combination of high-reduction, low-entry speed mills and direct-cast re-roll coils could be an excellent solution and efforts should be intensified to perfect a re-roll coil-casting process for magnesium.

D. Extrusion

Extrusion is a process that converts solid cast billets into a variety of shapes (e.g., round rods, squares, rectangles, angles, tubing, U-channels, T-shapes, or any nonstandard configuration either hollow or solid) by forcing the billet through a die with an orifice representing the desired shape. Any extrusion press capable of extruding aluminum alloys--after minor modifications of tooling, speed control, cooling bed, run-out tables, and temperatures--is readily usable for the extrusion of magnesium or its alloys.

1. Costs for Extruding Magnesium

The costs, including energy, for extruding magnesium and aluminum on comparable equipment to comparable shapes are about the same on a volume basis. However, the cost of casting, scalping, and finishing the billets is higher for magnesium, resulting in the overall cost for converting primary magnesium to an extruded section being higher than that for primary aluminum. The ratio of cost per pound of magnesium to cost per pound of aluminum depends greatly on the specific extruded section but varies from about 1.6 to 4.

2. Future Needs for New and Improved Methods

The processes and equipment for extruding magnesium have about the same degree of perfection as those used for aluminum extrusions. However, the costly process of casting, scalping, or pre-extrusion of billets for smaller presses are serious handicaps. Extruding of pellets, powder, or any form other than the cast or pre-extruded billets could considerably improve production economics and reduce energy requirements. Casting and pre-extrusion require as much energy per pound as the final extrusion of the pre-extruded billet into the finished shape required.

E. Forging

Of all magnesium products, forgings have the best combination of mechanical properties and are specified in lieu of castings when a higher-strength lightweight part is required. Forgings sometimes are used because of their pressure tightness and machineability (rather than their high strength) and when they are more economical than castings in a production run.

Magnesium forgings can be produced in the same variety of shapes and sizes as forgings of other metals. The maximum size is limited primarily by the available equipment. Tolerances, while varying somewhat with size and design, can be held to the same limits as in normal forging practice for other metals.

Magnesium forged shapes can be produced as hand, conventional die, close-tolerance, or rolled-ring forgings. For extremely long production runs, the cost per forging is less for magnesium (excluding the cost of the metal) than for steel and many other metals because of the low forging temperatures and the resultant increase in die life and lower die maintenance costs. When an analysis is made of the costs of magnesium forgings versus other lightweight forged materials in applications such as aircraft, the analysis must include the projected maintenance costs to prevent corrosion of the magnesium during the lifetime of the aircraft.

The majority of magnesium forged products are used on missiles, spacecraft, airplanes, and helicopters. The largest are ring-rolled forgings that are produced in diameters up to 100 inches for use as internal stiffeners on certain spacecraft and missiles. Such aerospace systems contain a variety of small components fabricated from the various forged products. With the exception of transmission cases in helicopters, magnesium forgings in airplanes and helicopters have been limited mainly to small nonstructural components.

F. Powder Metallurgy

Application of conventional powder metallurgy techniques to magnesium and magnesium alloys is extremely difficult and only partially successful. The rather tenacious and stable hydroxide film on the surface of magnesium presents a formidable barrier to the process of consolidation by compaction and diffusion. Only limited success has been attained in achieving a sound, useful product even when extremely high compaction pressures and prolonged sintering have been used.

In the late 1940s, extensive research and development work, partly with the support of the U.S. Air Force, was initiated on the direct extrusion of magnesium alloy powders. This program, which continued through the late 1950s, investigated many alloys systems and combinations of alloys. The work was performed almost exclusively with powder atomized by the impingement of a high-velocity gas stream on the liquid metal or by a rapidly rotating disc in contact with a rod.

By careful control of oxidizing gases in the atomizing medium, it was possible to achieve almost perfectly spherical powder particles (called pellets) that had good, free-flowing characteristics and facilitated handling and transport at the extrusion press. Further, the rapid rate of solidification in the atomizing process produced an extremely fine grain size, a characteristic that is highly beneficial to the properties of wrought magnesium alloys. The small particle size of pellets and the fine grain structure also produced a more uniform dispersion of alloying constituents. The use of powders as the starting material in the extrusion process also permitted introducing magnesium alloy constituents that normally cannot coexist in the alloy because of interferences occurring in the molten state. Such alloying is accomplished by adding the interfering constituents into separate alloys and then co-extruding a mixture of the two alloys. An excellent example of this phenomenon is the strong interference between aluminum and zirconium, two elements that cannot coexist in molten magnesium. Investigation of extrusion of mixtures of various magnesium-aluminum and magnesium-zirconium alloy pellets and mixtures of elemental aluminum powder and magnesium-zirconium alloy pellets revealed excellent strength and ductility values. However, none of the novel alloys developed by this extensive work achieved commercial usage. Only for a brief period and only in one Air Force application was alloy ZK60B produced on a semi-commercial basis. ZK60B carried essentially the same chemical specifications as ZK60A, its sister alloy produced by extruding cast ingots. About a 20 to 25 percent increase in yield strengths was achieved, the most significant improvement being in compressive yield strength. Pellet-extruded alloy ZK60B never achieved full commercial status and has not been available for over 15 years since the realized improvement in strength was not sufficient to justify the extra cost.

Today, the possibility of producing extrusion billets by powder compaction is being studied again. Although still experimental, enough work has been done to show that an alternative to D.C. casting to obtain extrusion billets is isostatic compression of magnesium alloy powder. Green billets of sufficient strength to permit shipping and handling at the extrusion plant can be prepared with a density of 95 percent of theoretical. When the billets are extruded in a normal manner, good products are obtained. Because less material is lost via the powder route and because the entire process from powdering to extrusion can be automated more easily, the cost of extrusions could be lowered by this technique.

G. Sand, Permanent Mold and Investment Casting

1. Basic Casting Technology

The simplest way to make a shape is by casting and magnesium followed that route in the early years of its development. The basic technique of magnesium sand and permanent mold casting has not changed substantially from the early days. The greater complexity of present castings and the higher quality standards, particularly when referring to aerospace castings, result more from the technological improvements of molding, core making, and other foundry processes rather than from developments in processing the metal itself, a technique that has remained comparatively static.

a. Casting Alloys

The common alloys used for sand and permanent mold castings are included in Table C-4, Appendix C. Alloys containing aluminum and zinc as the principal alloying elements (AZ alloys) are the mainstay of the industry in North America. Magnesium-zirconium alloys, to which other strengthening alloying elements must be added, have replaced the use of AZ alloys in Europe to a large extent but are being accepted only now in North America. Additions of rare earth metals and thorium to magnesium-zirconium alloys are used for applications requiring good strength characteristics at moderately elevated temperatures.

b. Melting and Alloying

The melting of relatively small batches of alloy consisting of pre-alloyed ingot plus clean process scrap in steel crucibles is practiced widely. The furnaces or settings are principally of the fuel-fired tilting crucible or lift-out crucible type. Normally, the same crucible is used for melting and for pouring the molds. In the larger foundries, molten metal is transferred from a tilting melting crucible to a smaller pouring crucible and, in some cases, the bailing-out method (using a small steel hand ladle) is used.

Pre-alloyed ingot is used most commonly. When it is not, aluminum, zinc, thorium, and rare earth metals are added in the elemental form. Manganese and zirconium can be added either as hardeners or as reducible salts. Even where pre-alloyed ingot is used for making magnesium-zirconium alloys, it is necessary to add additional amounts of zirconium, in excess of the theoretical amount and with vigorous stirring, to achieve full alloying and to attain the optimum degree of grain refinement. Magnesium-aluminum-zinc alloys are degassed with chlorine and are grain refined by superheating or by a carbon inoculation process. Copious quantities of flux are sprinkled on the surface of the melt to prevent oxidation and burning. Fluxes also are used for refining the melt to promote the settling of oxides and other undesirable insoluble impurities. The flux cover is maintained throughout the molten metal operations and removed only at the last minute before pouring into the mold. Burning during the pouring operation is suppressed by dusting the surface with sulfur or other oxidation inhibiting agents. A few foundries are using SF_6 to protect the metal surface during pouring.

c. Sand Casting Process

Both the older green-sand and more modern dry-sand techniques are employed in molding. The CO_2-silicate and the shell molding process are used to produce molds and cores. In each of these molding and core making processes, quantities of inhibiting materials must be used to prevent reaction between the molten magnesium being poured into the mold and any moisture present in the mold. In addition, it is common practice to flush the mold with SO_2 gas just prior to pouring to prevent reaction of the metal with air.

Metal is poured from a crucible directly into the mold through a sprue. At the bottom of the sprue, a screen is used to prevent oxides and skins from entering the casting. Pouring temperatures range from 732 to 788° C (1350 to 1450° F); the higher end of the range is used for zirconium-containing alloys to retain the maximum amount of zirconium solution. Approximately 85 percent of the metal in the crucible is poured and the remainder is reprocesses in subsequent melts.

d. Permanent Mold Process

The permanent and semipermanent mold processes are used effectively to produce relatively simple castings and when the production run justifies the initial cost of the mold. Molds generally are made of gray iron or "Meehanite" and either steel or sand cores are used. The mold usually is coated with a sodium silicate/kaolin coating to control solidification and to prevent sticking. The mold is maintained at 260 to 371° C (500 to 700° F) during casting and flushed with SO_2 gas each time to minimize oxidation. Generally, fewer alloys are adaptable to this process than to sand casting because a greater resistance to hot-shortness is needed for satisfactory operation. All other procedures of melt preparation and casting are the same as for sand casting.

e. Investment Casting

Extremely thin cast sections and accurate dimensions are obtainable using the investment casting process. The advantages of using this method are sufficient in some applications to justify the very high mold costs.

f. Low-Pressure Die Casting

Low-pressure die casting, which is more similar to the permanent (or semi-permanent) mold process than to die casting, is believed to have considerable future potential. The die employed is similar to the permanent mold. The molten alloy is forced into the mold from below by gas pressure (between 200 and 100 psi) on the surface of the molten metal. The complexity of casting shape is comparable to the normal permanent mold process.

The advantages of this method are that very small risers are used (producing very high casting yield); the castings have very good surface finish; and the soundness of the casting permits heat treatment. The full exploitation of this process applied to magnesium has not occurred yet.

2. Costs and Energy Requirements

Costs of producing magnesium alloy sand and permanent mold castings are extremely high. Two major factors contribute to this unfavorable competitive situation: (1) the need for exceptionally large risers to create the required head for feeding the castings; and (2) large metal losses during melting, alloying, and casting. Other factors that contribute significantly to cost are: extensive use of expensive fluxes and sand inhibitors, prolonged heat treatments, and energy requirements. Energy requirements per pound of metal melted are the same as in pressure-die casting (i.e., 8,000 to 10,000 BTU per pound).

Generally, risers represent 75 to 80 percent of the metal poured into the mold. This means, that each pound of magnesium is remelted four or five times before it leaves the foundry as a finished casting. Under present fluxing techniques in the foundry, magnesium incurs a loss of approximately 5 percent with each melting in contrast to a 1 to 2 percent loss realized in melting aluminum-base alloys. This combination of high melt loss and large recycle ratio has a compounding effect on costs. Further, other costs, such as energy, fluxes, and inhibitors, are multiplied by the same factor of 4 or 5. Aluminum alloys not only have lower melt loss but also require much smaller risers; accordingly, 50 to 75 percent of the metal poured actually is in the finished casting. Thus, under present market conditions, the same casting is estimated to cost 5 to 10 times more in magnesium than in aluminum.

3. Environmental Impact

Sand and permanent mold foundries are faced with environmental problems similar to, but more serious than, those confronting D.C. billet casting plants. Airborn emissions from the melting operations consist of MgO, flux dust, and HCl fumes. Sulfur dioxide is used in so many places in the foundry that it is a prevalent source of airborn contamination. In addition to its use on the melt floor, it is also a common protective atmosphere in heat treatment. The application of chromate and fluoride surface treatments for protection of castings during shipment presents waste water problems with highly acidic effluents containing chromium and fluoride ions. The foundry also must dispose of a large amount of solid wastes, such as sludge from the melting operations and large quantities of spent sand (containing inhibitors) that cannot be reclaimed or recycled. In recent years, these pollution problems have required the installation of additional scrubbers, electrostatic precipitators, and other sophisticated control equipment that added to the operational costs.

4. Future Needs and Trends

Sand and permanent mold casting are inherently high cost processes and will remain limited to the production of high-integrity aerospace parts. However, certain trends in the overall industry will benefit the foundry operations.

The development of fluxless melting techniques, based on the use of an air/SF_6 mixture to protect molten magnesium from burning, reduce substantially the high melting costs that result from the high recycle ratio. Further, elimination of, or reduction in, the use of flux will reduce the environmental problem and, hence, the costs associated with pollution control.

It is anticipated that zirconium-containing magnesium alloys will replace the conventional AZ alloys in North America at an accelerating rate even though they are costlier to melt and contain costlier alloying ingredients (particularly zirconium). These alloys will benefit even more from the use of fluxless melting than AZ alloys.

One way of overcoming the high recycle ratio is by using the low-pressure die casting process more extensively. Dies for this process can be designed to have good feeding characteristics without using excessive risers. Substantial economic advantages may be realized by using an automated low-pressure die casting process that couples the greatly reduced recycle ratio with reduced melting costs. Use of this process for magnesium should be encouraged.

All in all, opportunities exist for improving the economic picture in making sand and permanent mold castings but not to the degree necessary to make them fully competitive with aluminum castings; however, they always will be used for premium applications. The low-pressure permanent mold, on the other hand, presents an opportunity second only to pressure die casting for expanding the usage of magnesium.

H. Pressure Die Casting of Magnesium

Magnesium is the world's lightest die castable metal and has excellent castability. Only 1 pound of magnesium is required for a 15 cubic inch die casting while 1.5 pounds of aluminum or 3.6 pounds of zinc are required for the same casting (section for section). In many ways, magnesium alloys have better die casting characteristics than aluminum.

Its overall good response to the pressure die-casting process is attributed to the following properties of magnesium:

1. Low density--contributes directly to a comparatively low price per unit volume

2. Low volume heat capacity--requires faster filling of dies; therefore less heat must be extracted by the mold for each shot as compared with rival metals and greater productivity (faster casting cycle) is possible

3. Low sticking tendency--castings are less likely to stick in the dies since iron does not alloy readily with magnesium; die lubrication, although often desirable, is sometimes almost completely eliminated and higher metal pressures are possible

4. Longer life--dies tend to have 30 to 40 percent longer life because of the lower heat requirement and relative non-sticking of magnesium

5. Faster metal velocity--for given ram pressure, velocity is faster with magnesium than with aluminum (1.9:1.6) or zinc (1.9:1.0)

6. High stiffness-to-weight ratio--magnesium encourages the design of large, thin-walled castings

As a result, magnesium die castings can be produced with less draft and closer tolerances, in more intricate shapes, at faster rates, and in larger volume from a properly designed die than aluminum die castings.

1. Alloys

The alloy composition that has been adopted most widely in the United States for pressure die casting of magnesium is AZ91B. The composition and properties of alloy AZ91B are given in Table 17. This alloy has a much wider freezing range than the common aluminum- and zinc-base pressure die casting alloys. Heat treatment normally is not applied. Other alloys have been used for die casting magnesium; none of them are used in the United States but they do find extensive use in Europe for automotive crank cases, power trains, and wheels.

2. Die Casting Systems

Magnesium currently is cast by the hot- and cold-chamber processes. In the hot-chamber system, the pressure chamber through which molten metal is injected into the die is immersed in the holding pot. It has the same temperature as the molten metal in the crucible. In the cold-chamber system, the pressure chamber is not immersed in the molten metal. Liquid metal is transferred from the holding pot to the pressure chamber by a hand ladle or mechanical metering device.

Both systems offer advantages and have limitations. There is no time delay for ladling in the hot-chamber process since the pressure chamber is ready for the next shot as soon as the die is closed. Consequently, one obtains a faster cycle time, an advantage for small parts.

Since metal is injected at the holding pot temperature, a greater uniformity of quality can be maintained. The major problems with the hot-chamber system are related to materials of construction, seals, oxidation and the high metal temperature.

TABLE 17. Mechanical and Physical Properties of AZ91B Alloy

Property	Measurement
Tensile Strength	34,000 psi
Tensile Yield Strength	23,000 psi
Proportional Limit	12,000 psi
Elongation in 2 inches	3%
Shear Strength	20,000 psi
Compressive Yield Strength	22,000 psi
Ultimate Compressive Strength	58,000 psi
Hardness--Brinell	67
Hardness--Rockwell E	75
Modulus of Elasticity	6,500,000 psi
Modulus of Rigidity	2,400,000 psi
Poisson's Ratio	0.35
Specific Gravity	1.81
Density	0.066 lb/in^3
Thermal Conductivity at 100 to 300° F (38 to 149° C)	0.12 to 0.16 cal/cm^3/cm/°C/sec
Coefficient of Thermal Expansion at 65 to 212° F	0.000015 in/in/ °F
Electrical Resistivity at 68° F	14.3 microhm-cm

NOTE: Data from Dow Chemical Company, "Magnesium in Design," 1967.

Cold-chamber machines, which account for about 95 percent of all magnesium die castings produced, have lower maintenance costs than hot-chamber machines because moving parts are not immersed continuously in molten metal and the metal temperature is lower. Scrap and metal losses are generally higher than in the hot-chamber process.

It should be noted that zinc is die cast exclusively on hot-chamber machines while aluminum is universally die cast on cold-chamber machines. Only magnesium is cast using both systems, thereby taking advantage of the best qualities in each method.

3. Protective Atmospheres

A major difference between die casting magnesium and other metals is the need for a protective atmosphere over molten magnesium to prevent burning. The common approaches to this problem are use of a SO_2 atmosphere or a thin layer of metal chloride flux. Both methods have their limitations. The recent development of air + SF_6 atmosphere is most beneficial in protecting molten magnesium and is being used in production at an increasing rate.

4. Die Materials

The die material, H-13 tool steel, is used almost exclusively in magnesium pressure die casting and is heat treated conventionally to Rockwell C (Rc) 45-47. H-13 also is used in die casting aluminum. However, in magnesium usage, a 30 to 50 percent increase in die life (up to 250,000 shots) is usual.

5. Applications

Magnesium die castings are used in a wide variety of applications such as business machines, instruments, portable hand tools, household goods, photo and optical goods, appliances, sporting goods, luggage, electrical equipment, aerospace systems, military items, engines, automobiles, and toys. In Europe, a substantial number of magnesium die castings are used in the automobiles--Volkswagen, Porsche, and Fiat. Many engine parts, axle and transmission housings, support brackets, gear covers, and wheels (Fiat) are magnesium die castings. At least 50 pounds of magnesium are used in each of these various compact cars. Over the years, several die-cast magnesium parts have shown satisfactory service in the U.S. automobile market (e.g., the fuel pump air body and cover).

The advantage of magnesium's light weight in lawn mower parts and chain saws is apparent. Its lightness has resulted in the development of portable chain saws weighing less than 10 pounds.

6. Future Developments

The following areas appear to offer significant potential for growth during the next five to seven years:

a. Hot-chamber die casting machines for relatively small magnesium parts, particularly those requiring quality surface finishes

b. Molten metal metering for cold-chamber machines (more efficient, trouble-free units should be appearing on the market)

c. Air + SF_6 protective atmospheres (already a reality and future growth seems assured)

d. Automation of the cold-chamber machine (should be gradual and start probably with die temperature control followed by shot-end control and molten-metal metering)

e. Magnesium die castings for structural parts (should occur because of demand for less weight resulting from energy-saving requirements)

In the long run (15 years), higher-strength die-casting alloys (heat treatable) as well as creep-resisting alloys are expected to be developed. Also, in the long run, the coupling of the hot-chamber process with a new magnesium chrome-plating process is expected to yield decorative magnesium parts (particularly for the automotive industry) with significant weight and cost savings.

I. Machining

The standard measure of machinability of the cutting-tool industry is magnesium since magnesium and magnesium alloys offer: (1) four to five times longer tool life than any other commercial metal, (2) shorter machining time, (3) superior surface finishes with one cut where more cuts are required for other metals, (4) minimum chip handling costs due to well broken chips, and (5) low tool build-up.

Magnesium's superior machinability permits machining at extremely high speeds. Cuts of heavier depths and higher feed rates and speed than are used on other metals are normal in machining magnesium. The life of high-speed steel cutting tools used in machining magnesium equals the life of carbide-tip tools used in machining other metals. The excellent surface finish on machined magnesium is the result of its minimal tearing or dragging tendency.

The free-cutting characteristics of magnesium produce well-broken chips and lessen tool loading. Accordingly, the power requirements to remove a given amount of magnesium metal are lower than for any other commonly machined metal. Tables 18 and 19 quantitatively compare the machinability of various metals on the basis of machining speed for different operations and relative power requirements for removing a given amount of metal.

When machining magnesium, a major departure from practice with most other metals is that dry machining is possible. Dry machining usually is preferred in machine lathes, mills, and drill presses while machines of a more complicated nature often depend on a coolant to wash chips out of the machining area to a collection sump. Whenever magnesium is machined on the latter type of equipment, a mineral seal oil should be used in sufficient volume to flood cutting operations and wash accumulations of chips to the collection area. No water-based coolants, such as water-soluble oils or oil-water emulsions, of any kind can be used on magnesium because they intensify a magnesium fire if one should start.

TABLE 18. Comparative Machining Speeds (ft/min)

Metal	Turning, Rough	Turning, Finish	Drilling (5-10 mm drill)	Milling (100 mm miller, (1 mm cut)
Steel	130-650	200-10,000	50-100	60-70
Cr-Ni Steel	60-300	100-400	20-65	30-45
Cast Iron	100-300	200-400	40-130	45-60
Aluminum	250-2,500	400-4,000	200-1,300	650-1,000
Magnesium	Up to 4,000	6,000-8,000	500-1,700	650-1,700

NOTE: Data from Emley, 1966.

Precautions also must be taken when grinding magnesium, the only operation that must be done wet (with water). Usually grinding a surface on magnesium is unnecessary since extremely fine finishes can be obtained by the machine cut; however, in some instances flat surfaces must be ground rather than machined and a wide variety of equipment is available. The problem involves the quick disposal of the fine magnesium dust that builds up in the water because the magnesium fines react slowly in the water to release hydrogen gas. Accordingly, this fine grinding dust must never be allowed to build up wherever it may become partially dry, and the grinding sludge must be disposed of immediately according to a prescribed procedure.

TABLE 19. Relative Power Required to Machine Metals

Metal	Relative Power Required (1 = lowest)
Magnesium Alloys	1.0
Aluminum Alloys	1.8
Brass	2.3
Cast Iron	3.5
Mild Steel	6.3
Nickel Alloys	10.0

NOTE: Data from Dow Chemical Company, "Magnesium in Design," 1967.

Regarding future developments, it is anticipated that as magnesium penetrates deeper into the automotive field, magnesium transfer machines may be built for transmission cases, crank cases, and other important components. In addition, as primary production of magnesium increases, machine turnings and other scrap from machining operations should increase. Techniques for efficient reclamation of this material and a strong secondary market should develop.

J. Forming and Drawing

Magnesium may be brake formed, stretch formed, spun, drawn, or impact extruded in operations similar to those used with aluminum alloys. Due to the high springback and inherently low flow ductility of magnesium at room temperature, however, these forming operations are done best in the temperature range of from 204 to 371°C. Integrally heated tooling and preheated blanks generally are used in forming magnesium. Deep draws and severely spun parts may require full anneals during the stages of completion. Little change in these operations is expected unless alloy characteristics change.

K. Joining

1. Welding

Magnesium may be welded by the same processes (fusion, spot, seam, flash, inertia, and electron beam) generally used to weld aluminum. Fusion welding is done by the gas tungsten arc, gas metal arc, oxy-hydrogen, oxy-acetylene and electron beam. The gas tungsten arc process, using high-frequency alternating current and argon shielding, is used most commonly for the fusion process.

Wrought alloys generally welded are AZ10, AZ31, M1A, ZE10, HK31, and HM21, with AZ31 being the most common. Cast alloys commonly welded are AM100, AZ63, AZ81, AZ91C, AZ92A, EK41, EZ33, K1A, EZ41, Qe22, and sometimes ZK61, with AZ91C and AZ92A. To avoid cracking problems, castings invariably require preheating, and most cast and wrought alloys require post-weld stress relief.

The wrought magnesium alloys may be spot or seam welded. Either a mechanical brush or chemical cleaning procedure is required to produce uniformly low surface resistance. Welding machines of the type and power applicable to aluminum are also suitable for welding magnesium. Wrought magnesium alloys may be flashwelded also. The machines must have fast upset and high current capabilities similar to those required for aluminum alloys. Arc and percussion stud welding are used to attach fasteners to the wrought alloys and some of the more fusion-weldable cast alloys.

In five to seven years, the development of weldbonding and spot weld sealing techniques should allow usage of these processes in more severe environments.

2. Brazing and Soldering

Most magnesium alloys may be brazed by the torch, furnace or dip braze processes. The preparation and fixturing of assemblies is done in a similar manner to that used for aluminum alloys. Flux is used in all cases and must be removed completely after brazing to avoid future corrosion. Magnesium may be soldered directly by heat and use of reactive fluxes. Solder alloys are generally combinations of zinc, tin, and cadmium. Special precautions must be used in removal of the flux residue. The solder joints in some environments may corrode rapidly. The base metal also may be plated with zinc, tin, or copper as an aid in solder wetting. In some applications, ultrasonic soldering has been used and does not require a flux.

3. Adhesive Bonding

Success or reliability of adhesive bonding applied to magnesium depends greatly on the environment to which the parts will be exposed. Surface treatments used prior to bonding are:

a. Light Dow 17® treatment

b. Sulfuric-nitric etch followed by $NaOH+Na_2CO_3$ rinse

c. Alkaline (NaOH) etch followed by $Ca(NO_3)_2+CrO_3$ rinse

Noncritical or low-shear applications (including furniture, interior furnishings, luggage, and electronic, commercial, and light military items) have used treatment (a) and cyanoacrylate, anaerobic, phenolics, and hot-melt adhesives. Some of these adhesives, however, are not compatible with long-term high-humidity exposure.

High-shear applications require the use of surface treatments (b) or (c) and epoxies or modified epoxies. Adhesives with curing agents corrosive to magnesium must be avoided. After bonding with surface preparations (b) or (c), suitable surface treatment must be applied to the parts. When the parts may be exposed to severe environments, such as salt and moisture, sealant may be applied to the exposed bonded interfaces to prevent entry of moisture. Entry of moisture in time will result in corrosion at the interface of the adhesive and magnesium resulting in delamination. It must be noted, however, that treatment baths for adhesive bonding generally contain chromates that require special disposal.

In 5 to 7 years, improved surface treatments and low modulus adhesives may allow use of magnesium in more severe environments. In 15 years, the advantages of laminated construction for toughness and prevention of catastrophic failure may catalyze further adhesive bonding developments that are lightweight and durable in a corrosive environment.

4. Mechanical

In using mechanical fasteners for magnesium alloys, consideration must be given to the environment in which the assembly will be used. Bare aluminum rivets or tin- and cadmium-plated screws in drilled or punch holes in bare magnesium have given good service in products not exposed to weather or moist environments. Such joints, however, may be subject to severe corrosion in high-humidity or seacoast locations. Large fasteners in magnesium that require frequent removal or high torque must use a helical coiled stainless insert in tapped holes to increase holding power and eliminate thread damage. Nonmetallic fasteners are good in magnesium parts as the galvanic corrosion potential is eliminated.

In five to seven years, high-strength fasteners, galvanically dissimilar from magnesium, may be used in conjunction with fastener countersink protective measures developed for aluminum structures.

5. Assembly Practice

Faying surfaces of magnesium to dissimilar metals (including fasteners) may require application of sealing or insulating materials to a degree that will depend on the severity of the anticipated environment. Magnesium parts used exclusively inside buildings under normal conditions may require only a hot chromic acid or an anodized surface treatment of the magnesium. For parts occasionally exposed to weather, the minimum requirement might be priming or painting the faying surfaces and holes prior to installation of fasteners.

When parts are exposed to high humidity or salt moisture that might otherwise penetrate the joints, sealers must be used during the assembly sequence. Sealers as film tapes or other forms may be applied to the faying surfaces. Under these conditions, dissimilar metals in contact with the magnesium must be isolated electrically from the magnesium by using nonmetallic washers under boltheads or nuts and applying sealant or primer to the fastener shanks. After assembly of the joints, sealant should be applied to any exposed crevices that might allow the entry of moisture.

In five to seven years, fastener countersink protective systems demonstrated for aluminum structure may be utilized effectively on magnesium.

L. Surface Finishing

Although alloys of magnesium provide acceptable service in mild environments, their propensity to corrode under more aggressive conditions precludes their use without protective treatments or coatings. The relatively high resistance to corrosion of uncoated alloys in humid environments and in fluoride solutions is well recognized.

Magnesium and its alloys can be protected by applying suitable chemical or electrochemical pretreatments to the surfaces over which resin or paint systems may be applied. Four categories of surface treatments for corrosion protection, resistance to abrasion and wear, and protection from environments while imparting electrical continuity or high-frequency shielding are:

- Chemical conversion coatings (e.g., chromate)
- Electrochemical coatings (e.g., anodic oxide)
- Metallic coatings (e.g., nickel, tin)
- Organic coatings (i.e., paint, polymeric resin)

1. Cleaning

Prior to the application of chemical conversion or metallic coatings that in turn may be coated with paint or resin, thorough cleaning of the magnesium alloy surface is necessary to assure a uniform and adherent coating system.

The removal of soil is accomplished by immersing the work into a hot alkaline cleaning solution. Excessive oil or grease should be removed by solvent or vapor degreasing methods prior to alkaline cleaning. Since magnesium alloys are not attacked by caustic solutions, heavy-duty industrial alkaline cleaners may be used for oil film removal from the alloy surfaces.

Alkaline cleaning processes may be made more efficient by the use of electrolysis. Magnesium parts to be cleaned are made cathodes and the steel container the anode. Typical electrochemical cleaning conditions involve direct current, current density of about 2 amperes per square meter at 6 volts per 10 minutes.

The final step of any cleaning process should be the pickling of the metal parts in acid solution, followed by thorough rinsing with water immediately prior to application of surface treatments (such as chromates or anodic coating) and finishes. Anodic coating should be applied as soon after cleaning as possible. The removal of oxides prior to pretreating is essential. Also, adherent metallic or silicious particulate contaminations (from machining or grinding operations, steel ball or glass bead peening) must be removed. To accomplish this, rough castings of magnesium alloys generally are grit or shot blasted.

For oxide or metallic contaminant removal, sulfuric or nitric-sulfuric acid solutions generally are employed, if dimensions of the metal parts are not critical. When dimensions must be maintained, chromic acid pickling will serve. For die castings, chromic-nitric-hydrofluoric acid or phosphoric acid solutions are suitable. Hydrofluoric acid or fluoride anodic cleaning (MIL-M-46080) are particularly efficient for the removal of silicious contamination following sand or glass-bead peening of the magnesium alloy surface. Fluoride anodizing is especially helpful in removing silicious constituents from the surfaces of high silicon alloys prior to subsequent coating applications. Practical methods and details concerning chemical cleaning, electrochemical cleaning, and pickling are offered by various publications (Dow Chemical Company, "Magnesium Finishing," 1967 and 1970; Metal Finishing Guidebook and Directory, 1975; ASM Handbook, Vol. II, 1964; and MIL-M-3171, 1966.

2. Resin Sealing

The sealing of small pores or voids in magnesium castings is recommended to enhance the performance of protective coating systems. Resin sealing operations should be performed after machining or grinding, prior to application of any surface treatment or full coating system (MIL-I-6869D, 1971).

3. Peening

Peening information for magnesium alloys is not well developed. The technology lags behind that of steel or aluminum (i.e., the application of conventional peening procedures to magnesium alloys will not produce peening intensities achievable in the other metals). Conventional ball or bead blasting produces a shallow stressed thickness that may be compromised or negated during processing and applying protective coatings (Found, 1951). More work is needed, particularly in assessing the value of peening of magnesium alloys relative to fatigue endurance.

4. Chemical Treatments

Chromate conversion coatings, which are produced chemically by simple immersion in the appropriate solution, are used to produce decorative and protective surfaces and as a pretreatment to improve adhesion of paint films. Of a variety of treatments fitting in this class, two coatings--i.e., Dow 1® and Dow 7®--will be discussed.

The Dow 1® treatment, also referred to as chrome pickle, results from a simple acid-chromate immersion process and is employed extensively as an interim protective coating for cast or wrought magnesium alloy materials and for fabricated items (Dow Chemical Company, "Magnesium Finishing," 1970). Generally, it is not specified as a paint base but is serviceable for such performance. When so used and an effective chromate inhibitive primer is included in the paint system, the Dow 1® treatment, even in a marine environment, can perform as well as the Dow 7®, that normally is selected for use with paint systems. The Dow 7® treatment also results from simple immersion of magnesium materials in a hot acidic-dichromate solution. It offers good performance as a corrosion preventive (when used without paint) and improves the general performance of paint or resin systems applied over it. Chrome-pickle and other chromate conversion coatings are used extensively as the sole protective measure for automobile die castings, ladders and scaffold, dock boards, portable conveyors, and other commercial products. The energy requirement for applying the Dow 7® process to magnesium alloys is considerably higher than the energy needed for the chromate conversion coatings (MIL-C-5541B, 1970) on aluminum alloys. The effluent control problems are practically identical whether using solutions for aluminum or magnesium.

5. Anodic Treatments

Anodic coatings on magnesium are much softer and less protective than they are on aluminum. They are produced by the electrochemical oxidation of magnesium surfaces in specific aqueous electrolyte mixtures (MIL-M-45202, 1968). On the whole, this class of coating provides maximum corrosion resistance to the base metal. Anodic coatings may be used with or without subsequent organic coating systems.

Several processes exist for applying such coatings but two are more widely preferred--i.e. the Dow 17® and the HAE® processes. Each of these, with slight modifications, will produce either thick or thin compact oxide coatings. The thin coatings primarily serve as a base for paint or resin barrier coatings. The thick coatings provide a high degree of corrosion resistance without paint coatings and give excellent performance when painted. The thin coatings are materially softer than the thick coatings which are exceptionally hard and resistant to erosion and wear. Thick HAE® coatings are hardest and are deemed best for erosion resistance in a variety of applications of magnesium alloys.

All the anodic coatings harbor small voids or pores where perforating corrosion may initiate. Consequently, to forestall such limited-area corrosion in unpainted anodically coated magnesium, the surface is sealed with a resin or wax. Further, sealing permits easy burnishing of the surface and effectively reduces the coefficient of friction.

6. Metallic Coatings

Performance needs for magnesium alloys may require their surfaces to have metallic coatings. Such requirements are established with full knowledge that metallic coatings are incompatible to varying degrees with the underlying magnesium metal and that a high potential for acceleration of corrosion exists if the metallic coatings contain voids, are damaged, or the necessary supplemental coating protection is omitted.

Some metallic coating systems are employed on magnesium parts. They involve predepositions of certain metals, over which desired deposits of tin, nickel, silver, gold, or alloys may be made. Generally, these coatings are for electronic applications where solderability, electrical continuity or grounding, or corrosion resistance are needed. In structural components requiring radio frequency bonding, the coating is likely to be tin or nickel.

Electrodeposited metals on magnesium alloys usually involve a zinc immersion deposit or a special etching treatment as a basic preparation for subsequent plating. A step-wise schedule would involve pickling the part to activate the surface, immersion in a zincate solution or chemical etching, copper strike, and standard plating practices for depositing the principal metallic coating (tin, nickel, silver or gold).

In order to realize consistent good quality electroplated coatings, the plating baths and operating procedures must be controlled closely. Procedure controls for plating on magnesium alloys are more critical than those for plating on aluminum, and the costs usually are greater than for plating on other metals. Further, the reworking and reclamation costs for stripping of plated magnesium purposes are higher.

A procedure for electroless deposition of nickel on magnesium is available. This is an autocatalytic reduction process that occurs at all the metal-solution interfaces and uniquely results in uniform deposits and dimensional integrity on all metal surface points of the part contacting the solution, regardless of the complexity of the shape or intricacy of contour of the part. The usual electrodes, power sources, and pumping and filtering equipment needed for electrolytic plating are unnecessary.

Vapor deposition techniques are practical for applying metallic coatings on magnesium alloys. Because of the relatively thin coatings produced by this means, vapor-deposited coatings cannot be used on structural magnesium alloy parts without further protection (e.g., organic coatings).

7. Organic and Ceramic Coatings

Paint coatings are applied on magnesium alloy parts for protective and decorative purposes. In military applications, the metals usually are painted to provide protection in marine environment service. Because of the strong alkalinity of magnesium, a hydroxide corrosion product develops on the metal in neutral environments if it is exposed bare. Accordingly, an organic coating system, possessing high resistance to alkali, is mandatory. Before applying paints or resin coatings, the magnesium surface must be prepared using chemical or electrochemical conversion coating treatments (i.e., chromate or anodic processing) that will enhance overall protection and promote adhesion of the organic topcoating system.

For severe service environments, alkali-resisting primers, based on polyvinyl, acrylic, polyurethane, or epoxy resin vehicles must be used. Superior corrosion resistance is achievable with primer formulations containing corrosion inhibiting pigments, usually chromates of zinc or strontium. In some commercial applications, painting primarily serves decorative purposes.

For this, a wide variety of pigmented matte, semi-gloss, and glossy lacquers or enamels are available for interior or exterior service. Some paint systems improve markedly in hardness, flexibility, and density and achieve better adhesion to the substrate if they are are baked following air drying.

Epoxy or modified epoxy resin solution formulations are dip-applied and may be baked and successively redipped to seal and envelop the part. Sometimes, they are applied to cast magnesium alloy parts. These resins are generally more costly to apply because of the repetitive process (two redippings are normally specified). Their cost-quality advantage is not always realized.

Porcelain enamel can be applied on magnesium alloys having an adequately high melting point. Alloys AZ61, AZ80, and ZK60 would not be amenable for such coating. Porcelain enameling results in long-lasting, attractive coatings, offering excellent abrasion and corrosion resistance.

VII. SECONDARY RECOVERY

Magnesium can be recycled from scrap magnesium-base or aluminum-base alloys into new useful material. In recycling aluminum-base alloys, the magnesium content of the alloy is retained in the preparation of new forms of aluminum-containing magnesium. Due to the difference in the melting practice between magnesium and aluminum, recycling from magnesium-base alloys can be accomplished with about a 5 percent loss of the starting magnesium, while recycling aluminum alloys containing magnesium can be done with about a 10 percent loss of the magnesium.

There are a number of uses of magnesium, such as cathodic protection, chemical reactions, nodular iron production, from which no magnesium is recoverable. Therefore, in assessing the proportion of recycled processed magnesium, the amount going to these uses must be eliminated. During processing, such as rolling, extrusion and casting, the scrap material produced generally is recycled directly by the processor himself (and is termed "revert" or "run-around" scrap); therefore, this amount also must be eliminated in assessments of the efficiency of magnesium recycling.

Table 20 indicates how much magnesium was recovered from scrap in the United States during the 1969-73 period. Additional scrap is imported and processed for U.S. consumption, but a clearer picture is obtained by limiting consideration to the domestic markets. Overall, about 6 percent of the primary magnesium that reaches the marketplace in a recoverable form is recycled. Based on the scrap recovery of materials such as iron and copper, a reasonable goal is 25 percent; therefore, today's recovery level is very low and improvement could significantly affect magnesium supply. In 1973, for example, an additional 10,800 tons would have been available from the 60,000 tons per year produced in the previous five-year period.

Reprocessable material from magnesium-base alloys can be divided into five categories: cast, sheet and plate, fabrications and extrusions, turnings, and foundry scrap (gates, risers, dross). Based upon 1974 experience, these categories contributed to secondary recovery as shown in Table 21.

Review of Table 20 indicates that the area offering greatest potential for increased recovery is preservation of the magnesium values in aluminum-base alloys. Since about 80 percent of the magnesium consumed as an alloying element in aluminum is in beverage-can lids and containers for transporting liquid natural gas, the recycling of the magnesium in these end products into the same markets should be maximized where technically and economically feasible. Today, a large fraction of the total magnesium in aluminum collected for reprocessing is lost permanently by deliberate removal with chlorine.

TABLE 20. Secondary Recovery of Magnesium (in millions of pounds)

Magnesium Recovery	1969	1970	1971	1972	1973
Total Magnesium					
Total Primary Consumption	95,132	93,495	92,166	103,691	115,558
Potentially Recoverable	60,935	59,790	56,543	67,167	77,430
Run-Around Recovery	10,479	9,262	11,560	12,639	13,535
Total Recoverable from Market	50,456	50,528	44,983	54,528	63,895
Actually Recovered	2,991	2,780	3,143	2,989	4,101
Percent Recovered	6%	5.5%	7%	5.5%	6.5%
Magnesium-Base Alloys					
Total Recoverable Primary Consumption	23,560	23,247	19,093	23,709	26,570
Run-Around Recovery	4,767	4,564	6,722	6,993	7,417
Total Recoverable from Market	18,793	18,683	12,371	16,716	19,153
Actually Recovered	1,700	1,518	1,719	1,445	2,529
Percent Recovered	9%	8%	14%	9%	13%
Aluminum-Base Alloys					
Total Recoverable Primary Consumption	37,375	36,543	37,450	43,458	50,860
Run-Around Recovery	5,712	4,698	4,838	5,646	6,118
Total Recoverable from Market	31,663	31,845	32,612	37,812	44,742
Actually Recovered	1,291	1,262	1,424	1,544	1,572
Percent Recovered	4%	4%	4%	4%	3.5%

NOTE: Based on data from U.S. Bureau of Mines

In addition to the potential for more complete collection and reprocessing of domestic scrap, several thousand tons of magnesium enter the country every year as Volkswagen engine blocks and transmission housings. This source has not been tapped to any significant degree because of the expense of separating the magnesium values from other materials such as inserts and because of the lack of an adequate collection system.

TABLE 21. Secondary Recovery of Magnesium from Magnesium-Base Alloys

Reprocessible Material	% of Secondary Mg Recovery
Cast Material	34
Sheet and Plate	19
Fabrications and Extrusions	14
Turnings	13
Foundry Scrap	20

In summary, while no large technical obstacles exist to the recycling of magnesium, too small a portion is reprocessed due to the relatively low poundage of such obsolescent scrap. A concerted effort should be made to recycle any aluminum that contains high percentages of magnesium into the same applications so that the magnesium is retained. Efficient recycling of the magnesium values in junked Volkswagens also should be explored.

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APPENDIX A

U.S. AND WORLD MAGNESIUM-BEARING RAW MATERIALS

1. Minerals

a. Magnesite

Magnesite occurs mainly in four types of deposit: as crystalline masses replacing dolomite, as impure crystalline masses replacing ultramafic rocks, as cryptocrystalline masses in ultramafic rocks, and as sedimentary beds and lenses.

Crystalline magnesite deposits range in size from pockets containing 20,000 to 30,000 tons to bodies containing more than 100 million tons. Grade is as critical as size, particularly for magnesite used in the manufacture of high-purity refractories.

Only two districts in the United States contain large deposits of crystalline magnesite--one at Gabbs, Nevada, and the other in Stevens Country, Washington; small deposits occur in New Mexico and Texas. Magnesite mixed with talc and with or without quartz occurs in lenses replacing dunite or serpentinized dunite; these types occur in several areas. The only crystalline magnesite deposits in ultramafic rocks in the United States are found in northcentral Vermont.

Cryptocrystalline magnesite deposits, also known as bone magnesite, tend to be much smaller than crystalline deposits. They occur throughout the coast range and on the west slope of the Sierras in California. The largest group of veins is at Red Mountains, California. Several smaller deposits are known in Oregon and Pennsylvania.

Sedimentary magnesite is present in the southwest United States. Magnesite is interbedded with dolomite, elastic rock, and strata of volcanic origin. Individual beds may cover less than 100 acres and range in thickness from inches to several feet. The grade of some sedimentary magnesite deposits is high but the thin beds cannot be mined economically.

b. Brucite

Brucite in mineable concentrations is rarely found; however, two such deposits are associated with magnesite at Gabbs, Nevada. Other than at Gabbs, brucite has been found within the United States in small amounts only in New Mexico.

c. Olivine

The magnesium-rich variety of olivine, forsterite, forms a rock called dunite. Within the United States, fresh dunite makes up most of the Twin Sisters Mountains east of Bellingham, Washington, and it occurs as smaller masses in North Carolina.

d. Dolomite

Dolomite used to recover magnesium metal formerly was quarried in Alabama, Connecticut, New York, Ohio, Michigan, Mississippi, and Washington. A new plant under construction at Addy, Washington, is designed to use dolomite as raw material to produce magnesium. The largest resources of high-purity dolomite in the United States are in the central and eastern parts of the country, but the details of distribution are incompletely known and some potentially valuable deposits may be endangered by urban spread and by zoning regulations that restrict or prevent quarrying in populous areas. In other areas such as Indiana, pure dolomite is mined for crushed stone and lime.

Exploitable dolomite formations occur extensively in Kentucky, Tennessee, Missouri, and states adjacent to the Great Lakes and in more restricted areas in the Appalachian and Rocky Mountain regions. Only a few places ultimately will be principal sources of high-calcium limestone and high-purity dolomite. The chief source of high-purity dolomite in the United States is the Niagara Group in western Ohio.

e. Brines and Evaporites

Commodities derived from brine and evaporite deposits include magnesium compounds. The known quantities of brines and evaporites provide theoretical resources that are much larger than the amount expected to be used.

Some commodities can be derived from both brines and evaporites. Future resources of these commodities thus are found in diverse forms of "ore" that may vary in grade by one or two orders of magnitude. Brines, in essence, are a very low grade material and are exploited only because they are large and can be processed inexpensively. However, in some areas, the brine now extracted is controlled by petroleum production. Most productive brines allow production of other commodities (co-products), such as potassium salts, so that shared processing costs contribute to their commercial feasibility as raw materials. Evaporites, in contrast, generally are mined from high-grade ore bodies. Proximity to market and efficiency in mining, extraction, and transportation remain important factors in the economic potential of most deposits.

2. U.S. Position

In the United States, the bulk of magnesium-bearing compounds and the metal are recovered from seawater, brines, and dolomite (elsewhere in the world, they are obtained from magnesite). Presently, the more costly sources, such as evaporite minerals, are little used.

The apparent U.S. reserve of magnesite in 1970 was placed at 65 million tons. Data are not available to determine the fractions in recoverable and subeconomic resources, but probably less than half of the identified resources are commercially recoverable under present prices and required grades. Hypothetical resources are limited to unexplored magnesite at depths below known deposits. Perhaps 20 million tons of subeconomic resources seems a reasonable estimate. At least an additional 50 to 100 million tons of magnesite constitutes a subeconomic resource within the magnesite-talc deposits in Vermont.

Resources of fresh dunite in Washington total billions of tons and those in North Carolina total more than 200 million tons. Recoverable resources of brucite remaining in the Nevada deposits are said to be small, probably not more than 1 to 2 million tons. Resources of high-purity dolomite are adequate for thousands of years. Transportation costs will continue to be a major factor in future sources of supply of high-purity dolomite. Recoverable resources of magnesium chloride in the Great Salt Lake are said to exceed 600 million tons.

Many brines that are exploited contain abnormally large amounts of bromine, iodine, calcium chloride, and magnesium. Some of the brines are pore waters in the oil fields, some are deep-well brines from marine salines in rocks peripheral to them, some are from thermal springs or wells, and some are surface or subsurface brines that are associated with Quaternary salt lakes or seas. Although deep subsurface brines contain large quantities of dissolved solids, few basins outside of the known or potential petroleum and gas fields have been explored. The geologic factors controlling the distribution of valuable brines are not well understood and the number of unexplored basins containing valuable brines cannot be estimated reliably.

Evaporites and brines are the main source of several industrial and agricultural minerals important to the U.S. economy. Some evaporites contain an appreciable quantity of magnesium that is recovered as magnesium chloride in a by-product solution from potash operations.

Marine evaporites are thought to have been formed by evaporation of seawater in barred basins or on broad shelf areas where circulation was restricted. Non-marine evaporite deposits include near-surface saline and associated minerals formed by evaporation of lakes in closed basins; the deposited minerals depend upon the composition and temperature of the brine at the time of crystallization.

Analysis of cuttings, cores, gamma-ray data, and other logs of exploratory boreholes drilled primarily for petroleum has been responsible for most evaporite discoveries in recent years. The recognized association of petroleum and marine evaporites means that a high percentage of the basins favorable for evaporites in the United States has been explored by oil companies. Analyses of near-surface brines from relict lakes have been used with some success to locate exploitable non-marine evaporite deposits in arid regions but such analyses have not been successful elsewhere.

3. World Position

Magnesium-bearing compounds are processed into high-temperature refractories, chemicals, and magnesium metal. They are derived from minerals, brines, and seawater. Resources from which magnesium-bearing compounds may be recovered range in size from large to practically unlimited, and are globally widespread. Identified resources of magnesite throughout the world are in excess of 12 billion tons and those of brucite equal several million tons. Resources of dolomite, forsterite, and the magnesium-bearing brines constitute a resource of billions of tons; the resource contained in seawater is practically unlimited.

Two billion tons of talc-rich magnesite have been reported at Savinsk, in Eastern Siberia (Wicken, 1960). Total identified resources consist largely of crystalline magnesite associated with dolomite; but at least 1 billion tons consists of crystalline magnesite replacing dunite.

Identified resources of bone magnesite are not well known but older compilations indicated many tons. Bone magnesite is being mined at present at a rate of more than 1 million tons per year, indicating that past resource estimates of bone magnesite were conservative.

The tachyhydrite deposits of Sergipe, Brazil, must be cited as a large new resource. The upper zone alone is reported to contain about 4 billion metric tons of the mineral, equivalent to 380 million tons of magnesium metal. Similar deposits also have been found in Gabon and Zaire, Africa. Tachyhydrite ($CaMg_2Cl_6 \cdot H_2O$) is so soluble, even in drilling brines, that its occurrence may have been overlooked in other evaporite sequences.

4. Problems for Research

Methods to recover magnesium-bearing compounds and the metal from a wide variety of natural resources have been developed successfully. Efforts are continuing to produce stronger refractories, to increase the efficiency of recovery processes, and to develop new magnesium-bearing alloys.

The geology of magnesium-bearing mineral deposits is reasonably well known. Not enough is known, however, about the genesis of deep-seated magnesium-rich brines. The world's resources of bone magnesite should be reappraised in view of the current demand for it as a dead burned refractory.

Although much general information about the potential resources and distribution of chemically pure dolomite in the United States is available, detailed information about the chemistry and distribution of these rocks is relatively sparse. Systematic study of these formations should be undertaken to identify favorable areas that can be protected from urban spread, and, thus, provide an adequate supply of suitable material in future.

The abundance of evaporites and brine resources indicates that no shortage is imminent. However, efforts to find new and more economic deposits should be continued. Because such deposits would supply large quantities of the basic materials required by industry, cost would be an important factor in the price that the consumer pays for the product and it is imperative to have resources that would permit the end products to be produced and transported to the consumer at low cost.

The magnesium contained in seawater is practically unlimited. However, locations for seawater magnesium plants are not as plentiful as would be at first assumed from consideration of the extent of the coastline. Factors such as seawater quality, coastal topography, sources of lime or dolomite, and market locations as well as energy and transportation costs must be considered in selection of plant sites.

5. Recommendations

a. Study the genesis of deep-seated magnesium-rich brines as a guide to search for, and locations of, unexplored basins containing valuable brines.

b. Reappraise world resources of bone magnesite.

c. Continue effort towards finding new and more economic evaporite and brine deposits.

d. Systematically study geologic formations containing chemically pure dolomite.

APPENDIX B

ALUMINUM

Imports of bauxite and alumina, mainly from Jamaica, Surinam, and Australia, supply approximately 87 percent of the U.S. requirements for manufacture of aluminum metal and certain refractories, abrasives, and chemicals. Bauxite mined in Arkansas, Georgia, and Alabama supplies the remaining 13 percent. Barring unforeseen developments, the growing requirements of the aluminum industry in the United States will be met by imports of increasing amounts of aluminum metal and alumina rather than bauxite ore.

Domestic resources of bauxite--approximately 40 million tons reserves and 250 to 300 million tons potential resources--are inadequate to fulfill the long-term demand; however, the United States has virtually inexhaustible potential resources of aluminous materials other than bauxite.

For a long time, high-alumina clays have been considered to be the most favorable potential source of aluminum from nonbauxitic rocks in the United States. The total resource of clays containing as much as 25 percent alumina is very large but the deposits that may be major economic potential sources of aluminum are more limited and may be in the order of nearly 10 billion tons.

Alunite, used as an ore of aluminum in the Soviet Union, reportedly has been found in large quantities in Utah. Recovery of alumina from alunite has been demonstrated successfully in pilot plants. Interest in use of nepheline, also used in the Soviet Union as a source of alumina, has been noted elsewhere; large deposits of this raw material reportedly exist near Laramie, Wyoming.

Large quantities of dawsonite and nahcolite are present in strata associated with the rich oil-shale deposits in the Piceance Creek basin, northwestern Colorado. Alumina for production of aluminum metal and sodium aluminate for use in water-pollution control are potential products of dawsonite in the Colorado oil-shale deposits. Other less promising potential resources include aluminous shale and slate, aluminum phosphate rock, igneous rocks, saprolite, coal ash, and copper-leach solutions.

Geologic research is needed on the nonbauxite sources of aluminum in the United States inasmuch as the detailed geologic information available on the potential resources is inadequate.

APPENDIX C

PROPERTIES OF MAGNESIUM AND MAGNESIUM ALLOYS

1. Properties of Pure Magnesium

a. Physical Properties

Magnesium is a silvery-white metal of the divalent alkaline earth group and is number 12 in the periodic table of elements. The isotopes 24, 25, and 26 occur naturally in the approximate ratio of 7:1:1, respectively, giving magnesium an atomic weight of 24.32. The absorption cross section of the magnesium atom for thermal neutrons is among the lowest of all metals. Physical properties for the pure metal are given in Table C-1.

Liquid magnesium solidifies at 650° C (1202° F) to a hexagonal close-packed crystal with a density increase of 4.2 percent. The lattice constants of the crystal are included in Table C-1 and show that the c/a ratio deviates from the ideal value for close-packed spheres (1.633) by only 0.55 percent. Magnesium undergoes no allotropic modifications in the solid state. The density of magnesium at room temperature is 1.74 grams per cubic centimeter or 0.0628 pounds per cubic inch, making it the lightest metal having properties and characteristics useful in commercial structural applications.

The hexagonal close-packed structure leads to significant anisotropy in some physical and mechanical properties. The properties most affected by crystal orientation are linear coefficient of expansion, modulus of elasticity and electrical conductivity; only the values of these properties for polycrystalline material are included in the accompanying table. The linear coefficient of expansion of magnesium is not too different from that of aluminum but both are significantly higher than that for either steel or copper. The electrical conductivity of magnesium is 38.6 percent of the International Annealed Copper Standard (IACS) as compared to 64.94 percent IACS for aluminum. Electrical conductivity is markedly dependent on orientation, temperature and alloy content. Thermal conductivity is relatively independent of orientation and temperature but markedly dependent on alloy content. The remaining physical properties listed in Table C-1 are self-explanatory. For a more complete discussion of the temperature, orientation, and alloying effects on the physical properties of magnesium the reader is referred to Section VIII, References and Bibliography. A very complete tabulation of the physical, as well as chemical and mechanical properties of pure magnesium, is given in the Metals Handbook (American Society for Metals).

b. Chemical and Electrochemical Properties

Magnesium is high in the electromotive series with a standard electrode potential of -2.40 volts against hydrogen. This is only 0.3 volts more noble than sodium. However, in

TABLE C-1. Physical Properties of Pure Magnesium

Property	Magnesium Measurement
Some Atomic Properties	
Atomic Number	12
Atomic Weight	24.32
Neutron Absorption Cross Section	
Atomic	0.59 Barns/atom
Macroscopic	0.00254 cm^{-1}
Volume and Elastic Properties	
Crystal Structure	Close-packed hexagonal
Lattice Parameters	
c	5.199 kx
a	3.202 kx
c/a	1.624
Density at 20° C (68° F)	1.74 grams/cu.cm. or 0.0628 lb/cu. in.
Linear Coefficient of thermal expansion at 20 to 100° C (68 to 212° F)	26×10^{-6}/°C or 14.5×10^{-6}/°F
Young's Elastic Modulus	6.4×10^{6} psi
Rigidity Modulus	2.5×10^{6} psi
Poisson's Ratio	0.35
Phase Changes	
Melting Point	650° C or 1202° F
Boiling Point	1105° C or 2030° F
Vapor Pressure at Melting Point	2.75 mm
Density of Solid at Melting Point	1.65 gr/cu. cm. or 0.0596 lb/cu. in.
Density of Liquid at Melting Point	1.58 gm/cu. cm. or 0.0570 lb/cu. in.
Latent Heat of Fusion	88 cal/gram or 158 Btu/lb
Latent Heat of Vaporization	1260 cal/gram or 2260 Btu/lb
Volume Contraction on Solidification	4.2%
Thermal and Electrical Properties	
Specific Heat at 0 to 100° C (32 to 212° F)	0.25 cal/gr/°C
Entropy	0.288 cal/°C/gram
Thermal Conductivity at 20° C (68° F)	0.37 cal/cm^2/sec/°C/cm
Electrical Conductivity at 20° C (68° F)	2.24×10^{5} mho/cm^3
Electrical Resistivity at 20° C (68° F)	4.45 microhm-cm

NOTE: Data from Emley, 1966.

most aqueous environments magnesium exhibits a much more noble behavior resulting either from polarization or from the formation of a protective film, consisting principally of $Mg(OH)_2$, that attains equilibrium at a pH of 10.4. Since $Mg(OH)_2$ is not amphoteric, the protection is maintained throughout the alkaline region. In addition, magnesium resists the attack of hydrofluoric acid and its salts by the formation of a complex hydroxide/fluoride film.

In accordance with these basic observations, the corrosion resistance of magnesium is related to the formation of the $Mg(OH)_2$ film. The protective quality depends on the medium in which it is formed and on the alloying elements and impurities in the metal. The importance of alloying elements and impurity levels on the corrosion behavior of magnesium in NaCl solution was demonstrated conclusively by the pioneering work of Hanawalt and Associates. Studies showed that iron, nickel, and copper are very deleterious to corrosion resistance of magnesium. In pure magnesium, the corrosion rate increases rapidly in salt solution as the content of iron, nickel, and copper exceeds 170, 5, and 1300 parts per million, respectively. These values for these three impurities have been designated as "tolerance limits" and are an important technological control of the corrosion resistance of magnesium alloys.

Magnesium has good resistance to both indoor and outdoor atmospheres and, in the absence of galvanic couples, even shows resistance to more aggressive environments such as seawater. Indoor tarnishing is determined largely by relative humidity. In mild marine and in industrial inland atmospheres, the degree of corrosion resistance far exceeds that of mild steel. In stagnant distilled water at room temperature, the $Mg(OH)_2$ film formed is protective.

Most pure magnesium today is extracted by electrolysis of $MgCl_2$ in a fused salt electrolyte and sold as primary magnesium with a minimum purity of 99.8 percent. A typical analysis is given in Table C-2. This grade is sufficiently pure for most chemical and metallurgical applications. For structural applications, magnesium is alloyed with a number of different alloying constituents and several techniques are available for controlling the iron content, the principal contaminant that is introduced by the steel melting pots and equipment. For chemical and metallurgical applications requiring lower levels of specific impurities, special grades of electrolytic magnesium are available or silicothermic magnesium can be used. The latter is produced by direct reduction of magnesium oxide with ferrosilicon. High-purity silicothermic magnesium is also available in limited quantities for research purposes. Typical impurity analysis of all grades is included in Table C-2.

c. Mechanical Properties

Like most unalloyed metals, pure magnesium has relatively low strength. Typical properties of pure magnesium in various product forms are given in Table C-3. Sand cast test bars exhibit the lowest strength that undoubtedly results from the characteristic, coarse columnar grain structure of this form. Extruded and rolled forms show the characteristic lower compressive yield strength associated with the ease of twinning on the $\{10\bar{1}2\}$ planes under compressive loads parallel to the basal plane. The relatively low strength properties are associated with low hardness and not especially high ductility.

TABLE C-2. Typical Chemical Compositions of Commercially Available Pure Magnesium

Designations	Al	Ca	Cu	Fe	Mn	Ni	Pb	Si	Sn	Other Metallics Each	Other Metallics Total	Mg*
Primary Electrolytic	0.005	0.0014	0.0014	0.029	0.06	<0.0005	0.0007	0.0015	<0.0001	<0.05	<0.13**	99.87
Magnesium 2	N.S.	N.S.	<0.02	<0.05	<0.01	<0.001	<0.01	N.S.	<0.01	<0.05	<0.10	99.90
Magnesium 3	<0.004	<0.003	<0.005	<0.03	<0.01	<0.001	<0.01	<0.005	<0.005	<0.01	<0.08	99.92
Magnesium 4	<0.002	<0.003	<0.004	<0.03	<0.004	<0.001	<0.005	<0.005	<0.005	<0.01	<0.07	99.93
Magnesium 5	N.S.	N.S.	<0.003	<0.003	<0.004	<0.001	<0.005	<0.005	<0.005	<0.01	<0.05	99.95
Silicothermic	0.007	0.004	<0.001	0.001	0.002	<0.0005	0.001	0.006	0.001	<0.01	<0.04	99.96
High-Purity Silicothermic	<0.001	<0.001	0.0001	0.0007	0.0005	0.0001	<0.001	<0.001	<0.001	<0.005	<0.01	99.99

N.S. - Not specified.

* Magnesium by difference.

** 0.006 H, 0.0025 N, 0.0022 O; hydrogen, nitrogen and oxygen not reported for other grades.

NOTE: Data by permission from Metals Handbook Volume 1, Copyright, American Society for Metals, 1961, p. 1214.

Specification: Primary electrolytic, silicothermic, high-purity silicothermic, MG-4, and MG-5 are all covered by ASTM Specification B92-67.

Availability: MG-3 and MG-5 are currently unavailable. High-purity silicothermic is available in limited quantities only. All others are regular commercial products.

TABLE C-3. Typical Mechanical Properties of Pure Magnesium at 68° F (20° C)

Form and Section	Tensile Strength (psi)	Yield Strength (psi) Tensile, 0.2% Offset	Yield Strength (psi) Compressive, 0.2% Offset	Elongation (%)	Hardness Rockwell E	Hardness Bhn*
Sand Cast, 1/2 in. diam.	13,000	3,000	3,000	4	16	30
Extrusion, 1/2 in. diam.	27,000	12,000	6,000	6	26	35
Hard Rolled Sheet	29,000	18,000	16,000	6	51	46
Annealed Sheet	26,000	14,000	11,000	9	38	40

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* Brinell hardness using 500-kg load, 10-mm ball.

NOTE: Data by permission from Metals Handbook Volume 1, Copyright, American Society for Metals, 1961, p. 1214.

2. Effects of Alloying Elements

Magnesium must be alloyed with other elements to develop structurally useful properties. These elements, used singly or in combination, profoundly affect magnesium's properties and characteristics. The effects produced by each important alloying element are discussed below:

a. Aluminum

Aluminum is the most widely used alloying element in magnesium. Aluminum is completely miscible with magnesium in the liquid state and is soluble to the extent of 12.6 percent in the solid state at the eutectic temperature. With the aluminum contents normally used in magnesium, the as-cast structure consists of magnesium-aluminum solid solution plus the intermetallic compound $Mg_{17}Al_{12}$. Strengthening is achieved by solid solution hardening and by significant precipitation hardening following a solution heat treatment during which the $Mg_{17}Al_{12}$ phase is dissolved. Aluminum also suppresses the formation of a columnar grain structure. The grain size of the alloys can be refined further by superheating or by carbon innoculation. In general, a good level of strength and ductility is achieved in magnesium-aluminum alloys. The alloys, however, lose their strength rapidly with increasing temperature and do not exhibit good creep resistance.

b. Zinc

Zinc also is completely miscible with magnesium in the liquid state and soluble in the solid state to the extent of 8.4 percent at the eutectic temperature. However, it does not suppress the formation of columnar grains that result in poor castability as demonstrated by a high tendency toward porosity and hot cracking. Zinc contributes significant strength to magnesium by solid solution and precipitation hardening following a solution heat treatment. Zinc also improves corrosion resistance and generally is added to Mg-Al for this purpose. Zinc is added to Mg-RE and Mg-Th alloys to reduce porosity and improve castability.

c. Manganese

Manganese is an important alloying constituent in all Mg-Al and Mg-Al-Zn alloys for improving corrosion resistance. It also contributes to strength and grain size control and plays an important role in the superheating and carbon inoculation grain refining processes. There are no known Mg-Mn intermetallic compounds; manganese is present in binary Mg-Mn alloys in the elemental form. The solid solubility decreases very rapidly with decreasing temperature from a value of approximately 2 percent at the peritectic temperature that exists at only 1° C (34° F) above the melting point of magnesium.

d. Zirconium

Zirconium is a powerful grain refiner of magnesium and magnesium alloys containing zinc, rare earth metals, or thorium; however, the addition of zirconium causes aluminum and manganese, if present, to precipitate from the liquid solution. Zirconium also precipitates iron from liquid magnesium alloys and thus removes the need for the presence of manganese to control the corrosion behavior of the alloys.

The amount of zirconium usually present in magnesium alloys is in the range of 0.5 to 0.75 percent. Larger contents are very difficult to achieve because of the rapid increase in the liquidus temperature above the peritectic temperature that exists at 654° C (1210° F) and at which temperature the liquid solubility is 0.58 percent.

e. Rare Earth Metals

Rare earth metals impart significantly improved and structurally useful strength properties and creep resistance to magnesium at temperatures in the range of 150 to 260° C (300 to 500° F). When used in combination with zirconium, the alloys are easily castable, fine grained, and free of microshrinkage porosity. Although the lighter weight, separated rare earth metals have been investigated as alloying elements, the commercial alloys most generally are produced with the less costly mischmetal (50 percent Ce, 25 percent La, 15 percent Nd, 8 percent Pr, 2 percent other rare earths). Didymium (85 percent Nd, 15 percent Pr) also is used commercially in one alloy for the outstanding properties it imparts to magnesium at room temperature and the good strength and creep resistance it gives at elevated temperatures. The improved creep resistance of the alloys is derived from solid solution hardening and from the presence of excess compound in the grain boundaries. The maximum solid solubility of light rare-earths in magnesium is limited and increases with increasing atomic number of the rare earth achieving a maximum of approximately 2 percent for neodymium. The magnesium-rich intermetallic compound formed by the light rare earths is Mg_9RE that forms an eutectic with magnesium solid solution at a temperature below the melting point of magnesium, approximately 40° C (100° F) for lanthanum to 105° C (120° F) for neodymium.

f. Thorium

Thorium gives magnesium high strength and excellent creep resistance; the result is alloys with structurally useful properties at temperatures as high as 480° C (900° F). Mg-Th alloys require the added presence of zirconium for grain refinement. The alloys are characterized by freedom from porosity and hot cracking and easy castability. Strengthening effects of thorium at room and elevated temperatures result from solid solution hardening and precipitation hardening; the precipitate contributes further to inhibition of grain boundary migration and deformation, which enhances high-temperature strength and creep resistance. The magnesium-rich compound is Mg_4Th that forms an eutectic of 582° C (1080° F) at which temperature the solid solubility is 4.5 percent. The solid solubility decreases rapidly with decreasing temperature.

g. Silicon

Silicon is added to magnesium die casting alloys containing 2 to 4 percent aluminum to improve fluidity and to enhance creep resistance at temperatures between 120 and 190° C (250 and 375° F). The compound Mg_2Si in the magnesium-silicon systems forms an eutectic with magnesium solid solution at 337° C (638° F) and ~ 2 percent silicon. Solid solubility of silicon in magnesium is negligible.

h. Other Elements

The solid solubility of silver is extensive but decreases with decreasing temperature. It imparts significant solid solution and precipitation hardening to magnesium and is used in conjunction with didymium in only one commercial alloy. Yttrium has been investigated extensively as an alloying element and has been found to impart pronounced strengthening in wrought products. In addition, wrought magnesium alloys containing yttrium exhibit equivalent tensile and compressive yield strengths. The present high cost of yttrium precludes its extensive use as a major strengthener for magnesium. Lithium additions in excess of 12.8 percent produce a ductile body-centered cubic lattice of moderate strength. Many combinations of other elements with lithium in magnesium have been investigated and a wide range of strength properties has been observed (up to a compressive yield strength of 100,000 psi). Today, however, no alloy containing lithium is available commercially and it is unlikely that any will become available in the near future.

3. Chemical and Electrochemical Properties of Magnesium Alloys

a. Electromotive Force

Magnesium's theoretical reversible electrode potential is -2.34 volts. This high electronegative solution potential combined with a stability allowing normal handling (compared to sodium, potassium, and calcium) make magnesium and its alloys highly versatile anode materials for both primary batteries and cathodic protection. A voltage of 2.0 volts has been realized in magnesium dry cells while the highest anode voltage obtained in cathodic protection anodes has been about 1.75 volts. For comparison, consider that zinc anodes in batteries produce only 1.5 volts and aluminum and zinc anodes used in cathodic protection have a maximum potential of only 1.10 volts.

b. Electrochemical Equivalent

Theoretically, magnesium can produce almost 1000 ampere hours per pound; however, for various reasons, only about 50 percent anode efficiency (500 ampere hours per pound) is realized in practice. Impurities in the magnesium that are more noble than magnesium act as small cathodes on the metal surface and result in parasitic local cells that remove magnesium from the main circuit, which leads to a lower anode efficiency.

Zinc operates at 335 ampere hours per pound, which is 90 percent of its 372 ampere hours per pound theoretical equivalent. Only aluminum anodes can produce more ampere hours per pound than magnesium (over 1200 ampere hours per pound).

c. Film Forming Characteristics

Magnesium's corrosion resistance is attributed to the rapid film-forming characteristics of the metal. This film is very protective in some environments (e.g., the film formed in hydrofluoric acid provides the metal with complete resistance to attack in this highly acid solution; the film formed in highly alkaline solutions, such as NaOH and KOH solutions, also gives complete protection to the metal). Unfortunately, the films that form in many other environments--in acid solutions except hydrofluoric acid and in highly conductive salt solutions--are porous and allow corrosion to continue.

The film-forming characteristics of magnesium probably account for the lower-than-theoretical solution potential and the delay in the voltage when the circuit is closed on a dry cell battery using a magnesium anode.

The film that forms on magnesium and its alloys contains mostly $Mg(OH)_2$ and therefore is alkaline. Accordingly, chemical treatments that alter this alkaline film are used before painting (paints with alkaline-resisting resins are preferred for the protection of the metal).

Pure magnesium can form a thick porous film, especially in salt solutions. Alloying with aluminum and manganese alters the film significantly, making the film thinner, more dense, and more protective.

d. Corrosion Characteristics

The corrosion characteristics of magnesium alloys are quite complex and related to alloy content, impurity content, metallurgical variables, and corrosive environment. Many alloys, however, exhibit good corrosion resistance.

Alloying elements commonly used with magnesium (aluminum, zinc, manganese, etc.) reduce the electrode activity and improve the resistance to corrosion. However, aluminum, the most extensively used alloying element in magnesium, has the added effect of reducing the tolerance limit for the impurity, iron, from a level of 170 ppm in pure magnesium to 2 ppm in an alloy containing 10 percent aluminum. Fortunately, additions of zinc and manganese to magnesium-aluminum alloys reduce the corrosion rate to acceptable levels even when the iron tolerance limit is exceeded. Thus, by maintaining a careful balance among the alloying ingredients, commercial alloys with varying alloy content, good corrosion resistance, and good mechanical properties are produced in all product forms. In alloys containing zinc, rare earth metals, or thorium, the iron content is controlled at low levels by the addition of zirconium, which precipitates the iron as an iron-zirconium compound from liquid magnesium.

Magnesium alloys, when not galvanically connected to other metals, may be protected satisfactorily with the usual protective methods (chemical treatment or anodizing followed by paint). Magnesium alloys are always anodic to most other structural metals and therefore suffer from galvanic corrosion when electrically connected to other metals in a conductive electrolyte environment. Magnesium alloys are also susceptible to crevice corrosion. Water-absorbing gaskets and designs that allow moisture to pocket next to the metal must be avoided.

e. Resistance to Attack by Specific Agents

Magnesium alloys are attacked to various degrees by solutions of inorganic chemicals with a pH below 7.0 with the following exceptions: chromates, chromic acid, fluorides, and hydrofluoric acid. The lower the pH and the higher the electrical conductivity of the solution, the more rapid is the attack. Magnesium alloys resist highly alkaline solutions with a pH above 8.5, and strong alkaline cleaners containing sodium hydroxide with a pH up to 14 are used on the metal. Solutions of inorganic chemicals with pH values between 7.0 and 8.5 must be tested for compatibility with magnesium alloys. Magnesium alloys are resistant to organic hydrocarbons, alcohols, glycols and other nonconductive solutions. The exception is methanol, which attacks magnesium.

4. Mechanical Properties of Magnesium Alloys

a. General

The marketability of a product depends primarily upon its mechanical properties and cost in relation to competitive materials. One of magnesium's greatest assets is its low density that makes it a preferred material for mobile applications, such as hand tools. Although use of magnesium should increase through greater penetration of these favorable and growing markets, magnesium demand will expand rapidly only when its properties and cost offer advantages over competitive materials (particularly aluminum). Since the properties of magnesium are unlikely to be improved very much, future growth depends primarily on its relative cost. Recent developments, such as increased availability of magnesium, the higher cost of alumina (due to an international cartel or lower grade ores), and the inherent advantage of magnesium in energy conservation, may enhance the competitive position of magnesium in relation to aluminum.

In castings, magnesium alloy properties are very close to those of the most commonly used aluminum alloys and, therefore, castings could be significantly lighter. Wrought magnesium alloys are stronger than the soft aluminum alloys and comparable to aluminum alloys of intermediate strength. Therefore, the properties of magnesium make it competitive with aluminum in a major part of the aluminum market. However, magnesium cannot compete readily with high-strength wrought aluminum alloys, a small part of the total aluminum market. Although the aluminum market is the most logical target for magnesium, its substitution for other materials (e.g., cast iron, steel, zinc, wood) also occurs.

b. Commercial Magnesium Alloys

The commercial magnesium alloys may be classified in the following five systems:

(1) Magnesium-aluminum-zinc
(2) Magnesium-aluminum-silicon
(3) Magnesium-zinc
(4) Magnesium-rare earth metals
(5) Magnesium-thorium

Individual alloys are designated according to the ASTM alloy and temper designation system. In this system, the first two letters represent the two principal alloying ingredients according to the following code and are followed by two numbers representing the nominal content of each alloying ingredient, respectively:

A -- aluminum
E -- rare earth metals
H -- thorium
K -- zirconium
L -- lithium
M -- manganese
Q -- silver
S -- silicon
Z -- zinc

The heat-treated or work-hardened condition of the alloy (commonly referred to as its "temper") is specified by a hyphenated suffix according to the following codes:

F -- as fabricated
T4 -- solution heat-treated
T5 or T51 -- artificially aged (without deliberate solution heat treatment)
T6 -- solution heat treated and artificially aged
T8 or T81 -- solution heat treated, cold-worked, and artificially aged
0 -- fully annealed
H10 or H11 -- slightly strain hardened
H24 -- strain hardened and partially annealed.

The nominal compositions and typical strength properties at room temperature of the important casting and wrought magnesium alloys are given in Tables C-4 and C-5, respectively. A brief discussion of each class of alloys follows.

(1) Magnesium-Aluminum-Zinc Alloys

(a) Casting Alloys

The commercial casting alloys contain 6 to 9 percent aluminum, 0.7 to 3.0 percent zinc, and a few tenths percent manganese. In general, the alloys are easily castable with no hot-cracking problems and the small tendency toward microporosity in AZ63A can be minimized easily by good foundry practices. The strengths of the alloys are enhanced significantly by solution heat treatment followed by an artificial aging treatment. AZ81A generally is used in the T4 temper for its good combination of strength, ductility, and toughness. AZ91C and AZ92A are used most commonly in the T6 temper where the maximum strength is required. AZ91B is the most commonly used for die casting alloy. AM60A, a die casting alloy, is used for automotive wheels where toughness and fatigue strength are the important criteria.

TABLE C-4. Some Commercial Magnesium Casting Alloys

	Nominal Composition (%)						Typical Test Bar Properties		
Alloy	Al	Zn	Mn (Min.)	Zr	Other	Temper	TS (1000 psi)	YS (1000 psi)	% E
Sand Casting and Permanent Mold Alloys									
AZ63A	6.0	3.0	0.15			F	29	14	6
						T4	40	14	12
						T6	40	19	5
AZ81A	7.6	0.7	0.15			T4	40	14	12
AZ91C	8.7	0.7	0.13			F	24	14	2
						T4	40	14	11
						T6	40	19	5
AZ92A	9.0	2.0	0.10			F	24	14	2
						T4	40	14	10
						T6	40	21	2
EZ33A		2.6		0.7	3.2 RE*	T5	23	15	3
HK31A				0.7	3.2 Th	T6	30	15	8
HZ32A		2.1		0.7	3.2 Th	T5	29	14	7
ZE41A		4.2		0.7	1.2 RE*	T5	30	20	4
ZK51A		4.6		0.7		T5	40	24	8
ZH62A		5.7		0.7	1.8 Th	T5	40	25	6
QE22A				0.7	2.2 RE** 2.5 Ag	T6	39	29	4
Die Casting Alloys									
AZ91B	9.0	0.7	0.13			F	39	24	6
AM60A	6.0		0.13			F	38	20	12
AS41A	4.2		0.35		1.0 Si	F	35	20	10
AS21X1	2.0		0.35		1.0 Si	F	--	--	--

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* Rare earth as mischmetal.

** Rare earth as didymium.

NOTE: Data from Roberts, 1960; and Dow Chemical Company.

TABLE C-5. Some Commercial Magnesium Wrought Alloys

	Nominal Composition (%)						Typical Properties (1000 psi)			
Alloy	Al	Zn	Mn (Min.)	Zr	Other	Temper	TS	TYS	CYS	% E
Sheet										
AZ31B	3.0	1.0	0.20			0	37	22	16	21
						H24	42	32	16	15
						H11	37	20	16	20
HK31A				0.7	3.2 Th	H24	37	30	25	9
HM21A			0.80		2.0 Th	T8	36	24	20	11
						T81	37	30	26	6
ZE10A		1.2			0.17 RE*	0	33	20	16	20
						H24	36	26	25	12
Plate										
AZ31B	3.0	1.0	0.20			0	37	22	14	20
						H24	38	24	16	17
						H10	35	20	15	17
HK31A				0.7	3.2 Th	H24	38	30	25	10
HM21A			0.80		2.0 Th	T8	35	26	22	11
Extrusions										
AZ31B	3.0	1.0	0.20			F	38	28	14	15
HM31A			1.20		3.0 Th	F	42	33	27	10
ZK60A		5.5		0.45		F	49	37	27	14
						T5	52	43	31	4
Forgings										
AZ61A	6.5	1.0	0.20			F	43	26	17	12
AZ80A	8.5	0.5	0.12			F	46	31	25	8
						T5	50	34	28	6
						T6	50	34	27	5
ZK60A		5.5		0.45		T5	44	31	28	16
						T6	47	39	25	11
HM21A			0.80		2.0 Th	T5	35	31	26	3

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* Rare earth as mischmetal.

NOTE: Data from Roberts, 1960; and Dow Chemical Company, "Magnesium in Design," 1967.

(b) Wrought Alloys

AZ31B is the major magnesium alloy for wrought products: sheet, plate and extrusions. It derives its strength principally from solid solution hardening, grain size control, and cold working. Accordingly, working temperatures, degree of cold work, and subsequent annealing temperatures are controlled carefully to achieve the optimum combination of strength and ductility. AZ31B must be stress relieved after welding to prevent stress corrosion cracking in service. For high strengths in forgings, AZ61A and AZ80A alloys sometimes are used, but they have been replaced largely by the tougher Mg-Zn-Zr alloys. Although not listed in Table C-5, AZ21A, an important alloy with 0.2 percent Ca and closely controlled manganese content, is produced as an extrusion and used for dry cell anodes. The anodes are thin-walled cans that are produced by impact extrusion of slugs cut from the extruded rod.

(2) Magnesium-Aluminum-Silicon Alloys

Magnesium-aluminum-silicon alloys are used only as die castings. Two compositions, AS41A and AS21, are available today. The addition of silicon imparts improved creep resistance at temperatures up to 190° C (375° F) over that attainable in AZ91B alloy. The alloys are especially useful for automotive engines and power-train components. Silicon, while improving the fluidity, increases the liquidus temperature and necessitates a higher casting temperature.

(3) Magnesium-Zinc Alloys

(a) Casting Alloys

The potent precipitation hardening of Mg-Zn alloys combined with the grain refining effect of Zr yields the high-strength, castable alloy ZK51A. This alloy, however, has serious microporosity and hot-cracking tendencies that are largely eliminated by either the addition of rare earth metals to produce ZE41A or thorium to produce AH62A. The mechanical properties of ZE41A are not quite as high as those of ZK51A or ZH62A. All these alloys lose strength rapidly with increasing temperature. Their creep resistance at moderately elevated temperatures is better than that of Mg-Al-Zn alloys but not even the thorium-containing alloy can be classed as a temperature-resisting alloy.

(b) Wrought Alloys

ZK60A is the important alloy in this group and, in the form of extrusions and forgings, offers the highest commercially available strength and a good combination of toughness and fatigue resistance. The strength properties of ZK60A decrease rapidly with increasing temperature and its creep resistance is low.

The ZE10A alloy(a formable alloy containing 1 percent zinc and 0.17 percent rare earth) has been developed in sheet form and does not require stress relief after welding to prevent subsequent stress corrosion cracking. The presence of rare earth metals in the alloy makes it more expensive than AZ31B. Its availability today is uncertain but, conceivably, a large demand could lead to resumption of its production.

(4) Magnesium-Rare Earth Metal Alloys

Alloys containing rare earth metals as the principal constituent are used only in the form of sand and permanent mold castings for applications requiring good strength and creep resistance at temperatures up to 200 to 260° C (400 to 500° F). The two alloys principally used, EZ33A and QE22A, contain zirconium for grain refinement and improved castability. Rare earth metals are added to EZ33A as mischmetal and to QE22A as didymium. Zinc improves the castability of EZ33A and silver is added to QE22A to achieve higher strength at room temperature, together with good high-temperature strength. QE22A requires a solution heat treatment prior to aging for maximum strengthening. EZ33A does not benefit from such a treatment and is aged artificially directly in the as-cast condition. The addition of zinc and silver impairs the corrosion resistance somewhat.

(5) Magnesium-Thorium Alloys

(a) Casting Alloys

The two important casting alloys in the magnesium-thorium group are HK31A and HZ32A. The alloys have equivalent thorium and zirconium contents; HZ32A also contains 2 percent zinc that improves castability and completely suppresses any tendency towards shrinkage porosity. The zirconium, of course, renders the alloys very fine-grained and decreases iron to a low level. Zinc impairs the corrosion resistance. These alloys are used in applications requiring good creep resistance at temperatures up to 370 to 400° C (700 to 750° F). HZ32A has somewhat higher creep resistance than HK31A at the higher end of the useful temperature range. Care must be exercised in handling the alloys in the molten state because of the high oxidation tendency of thorium.

(b) Wrought Alloys

Three important wrought alloys contain thorium: HK31A for sheet and plate; HM21A for sheet, plate, and forgings; and HM31A for extrusions. The combination of manganese and thorium in the HM alloys results in outstanding creep resistance at temperatures as high as 400° C (750° F) and for short-time applications at even higher temperatures. The best combination of properties is developed in HM21A sheet by a combination of solution heat treatment and warm rolling followed by artificial aging. These conditions are indicated by the temper designations T8 and T81. Special precautions are required in the melting and casting of magnesium-thorium-manganese alloys to assure the production of quality fine-grained ingot for subsequent working operations (rolling, forging, and extrusion).

APPENDIX D

FABRICATING AND FINISHING

1. Molten Metal Preparation

a. Crucibles and Furnaces

Magnesium alloys generally are melted and alloyed in indirect-fired steel crucibles with holding capacities of up to 6,000 pounds. The crucibles are placed in furnaces or settings that are heated generally with natural gas or other fuels such as liquified petroluem gas (LPG), oil, and even electricity. In order to minimize excessive oxidation of the steel crucibles, the furnace temperatures are maintained at 982 to 1093° C (1800 to 2000° F), thus limiting the heat input to about 3 million BTU per hour and the magnesium melting rate to 800 to 1000 pounds per hour. This necessitates the use of a multiple furnace system to provide the required flow of magnesium alloy to the casting machine. As many as 10 crucibles are used in the various process steps involved in preparing the metal for casting--melting, alloying, iron-settling and refining, holding and casting. This operation contrasts with an aluminum D.C. casting plant in which one 90,000 pound reverberatory furnace with a heat input of 20 million BTU per hour can provide 3 million pounds per month to a D.C. machine.

b. Burning Prevention

Molten magnesium must be protected from air to prevent burning. This generally is accomplished by using one of a number of proprietary cover fluxes consisting of mixtures of alkaline and alkaline-earth halides. Care must be exerted to prevent entrapment of flux particles (which have a deleterious effect on the corrosion properties of the product) in the metal.

Recent work (Hanawalt, 1972) shows that molten magnesium can be protected by the introduction of a small concentration of SF_6 in the air over the melt. SF_6 is an odorless, nontoxic, and noncorrosive gas and completely eliminates the flux entrapment and flux pollution problems. This protective agent is gaining acceptance in the industry and is also replacing the use of SO_2 in the D.C. casting mold.

c. Alloying and Alloy Systems

The common alloying elements used in wrought magnesium alloys and the typical mechanical properties of various product forms are given in Tables C-4 and C-5 of Appendix C. Aluminum, zinc, and thorium generally are added in the elemental form. Master alloys (hardeners) of Al-Mn, Th-Mg, and Zr-Mg also are used. Alloying is generally carried out at 704 to 760° C (1300 to 1400° F). Reducible salts, such as $MnCl_2$ and $ZrCl_4$, can be used to add manganese and zirconium to magnesium.

d. Degassing

Hydrogen normally is not a problem in magnesium alloys and degassing is not a required operation in the preparation of metal for D.C. casting. Where degassing might be required for high-aluminum alloys, such as AZ80A, chlorination techniques similar to those used for aluminum-base alloys are applied. Chlorine gas or a chlorine/nitrogen mixture is bubbled through the melt for a period of 5 to 15 minutes.

e. Refining

An important and necessary step in the preparation of magnesium alloys for D.C. casting is the removal of oxide particles, oxide skins, and flux particles. This is accomplished by stirring into the melt a dry, less fluid flux that assists in agglomerating and settling in the undesirable nonmetallic particles. This operation also thickens the less fluid flux used up to that point and the $MgCl_2$ formed when reducible salts are used for alloying. A separate crucible is provided in the melting system for this operation and sufficient time (20 to 60 minutes) must be allowed for the most effective settling action.

f. Pumping

The use of several crucibles in the melting system requires a good method of transferring metal between crucibles. The low solubility of iron in magnesium permits the use of steel pipes and relatively inexpensive centrifugal pumps made of mild steel for this purpose. The same type of pump also is used to deliver metal from the casting pot to the D.C. casting mold. Care must be exercised in this last step to situate the pump in the melt in such a way that neither flux from the surface nor sludge from the bottom of the crucible are drawn to the intake of the pump. The transfer lines are heated either with gas or by electrical resistance heating.

g. Sludge Formation

The fluxes used for protecting molten magnesium are heavier than magnesium and become even heavier when they absorb oxide particles and skins generated during the melting, alloying, and refining operations. Thus, the mixture of spent flux, oxides, and insoluble metallic particles collects at the bottom of the crucible and carries certain amounts of entrapped magnesium with it. This unwanted but unavoidable product of the melting operation is termed "sludge" and must be removed periodically by a scooping or bottom ladling operation. The amount of metal entrapped depends on the fluidity of the sludge, the density of the sludge, the care of the operators, and many other factors. It represents a loss to the operation that can equal 5 percent of the metal melted and is a solid waste disposal problem. Some sludge is collected by secondary processors who recover the metal from it, but only a relatively small amount of the sludge generated by the industry is processed in this way.

h. Metal Recovery

The metal recovery generally realized in the preparation of magnesium alloy billets and slabs, using flux as the protective agent, ranges from 93 to 96 percent. As noted above, a large fraction of the loss is represented by the metal entrapped in the sludge. The industry believes that the use of an air/SF_6 atmosphere in place of the flux will improve metal recovery substantially by minimizing the amount of sludge formed and the loss of metal therein.

2. Billet and Slab Casting

a. Direct-Chill Casting

In the direct-chill casting process, either continuous or intermittent, molten magnesium alloys are pumped directly from the casting pot to a water-cooled copper mold. The metal level in both the mold and the casting pot generally is maintained by the use of spark-gap instruments that control the operation of the casting pump and of the pump feeding metal from the holding to the casting pot.

In the continuous process, the billets and slabs are withdrawn from the mold by a set of rolls that establish the casting rate, support the metal ingot, and guide the product to the flying saw several feet below where it is cut to the desired length for further fabrication. In the intermittent process, the solidified cast is lowered on a hydraulically operated ram. Ingot length obtained is determined by the stroke of the hydraulic cylinder in use, generally 12 to 20 feet. Desired lengths for further fabrication are cut to size by remote control. Casting speeds in both processes range from 2 to 6 inches per minute depending on alloy composition and size of ingot. Round billets for extrusion are cast in sizes from 6 to 36 inches in diameter but the most common sizes are 8 to 16 inches. Rolling slabs range up to 14 x 43 inches in section size. The smaller extrusion billets (6 to 8 inches) usually are cast as twins.

b. Ingot Quality and Inspection Techniques

The principal defects occurring in D.C. cast magnesium alloy ingot are cracks, laps, and inclusions of flux, oxides, and undesirable metallics. Of less frequent occurrence and importance are relatively large grain size and porosity.

The three major factors that affect billet quality are molten metal preparation, casting rate, and control of cooling rate. Great care must be exercised throughout the molten metal handling process but the most critical steps are the refining and settling operations, and the transfer of metal from the casting pot to the mold. The casting speed and the cooling rate are interrelated and must be balanced carefully to avoid premature freezing at the liquid metal/mold interface and causing laps or folds on the surface and to prevent excessive chilling that might lead to severe cracking.

Three techniques are used to inspect the quality of D.C. cast ingot: (1) fracture slice examination, (2) radiographic inspection, and (3) ultrasonic inspection. Slices are removed periodically during the casting operation, fractured in a prescribed manner, exposed several hours in a high-humidity atmosphere, and inspected for inclusions, cracks, porosity, and grain size control. Radiographic examination of slices sometimes is made for more demanding applications where smaller inclusions than those detectable in the fracture test are deemed harmful. These techniques do not yield quality information about specific billets or slabs but they are used as an overall control on the process. For the most critical applications, ultrasonic inspection may be applied to 100 percent of the cast ingot.

c. Scalping

The outer surface of D.C. magnesium alloy ingot usually has a rather heavy MgO and $MgSO_4$ layer resulting from reaction with air and SO_2 during the solidification process. Also, the more highly alloyed compositions may have low melting eutectics on the surface produced by inverse segregation. For these reasons, it is necessary to remove at least 1/4 inch and sometimes as much as 1/2 inch from all surfaces by scalping.

3. Environment Impact

Many sources of undesirable air-born emissions are generated during the molten metal operations for producing D.C. cast magnesium alloys, and they can exceed the levels allowed by present regulatory agencies. The most common emissions and their sources are: (1) MgO from burning magnesium, (2) flux particles from dusting during application on the melt, (3) HCl fumes from hydrolysis of chlorides in the fluxes, (4) SO_2 gas from the protective atmosphere in the mold, and (5) carbonaceous products from decomposition of oil and paint on recycled old scrap. Wet scrubbers and electrostatic precipitators are used to control these emissions to the allowable levels.

Sludge presents a disposal problem. Normal practice is to dump it in a separate area of the plant site, but weathering and leaching can lead to contamination of underground water.

4. Rolling

a. Hot Rolling (Breakdown, Rolling into Re-roll Coil)

Magnesium alloys are rolled from cast ingots or slabs 5 to 11 inches thick. Some alloys have been rolled from extruded slabs 4 to 5 inches thick and 30 inches wide. The cast slabs usually are scalped on the rolling faces as well as on the edges but extruded slabs can be rolled without scalping. The slabs are preheated and soaked thoroughly at temperatures ranging from 316 to 482° C (600 to 900° F) for the breakdown rolling, accomplished in one heating with short times in the mill and with a relatively high degree of metal efficiency. The ratio, weight of slab/weight of usable coil, calculated for a large number of coils, ranges between 95 and 98 percent depending on the type of alloy. These efficiencies are for breakdown rolling on a large 72-inch-wide 4-high mill. However, breakdown rolling also is done at somewhat lower productivity on 3- or 2-high mills. Hot rolling of the cast slabs into coils is the most efficient operation in the entire process of rolling magnesium. Unfortunately, this efficiency and productivity ends at a hot-roll gauge of about 0.10 inch. Further reduction into thinner gauges is more and more cumbersome and costly. The rolling of magnesium to 0.180 inch is essentially comparable on a volume basis with the hot rolling of aluminum slabs to the usual coil gauges. Breakdown hot rolling of magnesium on the 72-inch-wide 4-high mill produces between 10,000 and 20,000 pounds of 0.180 inch gauge re-roll coil per hour depending on the alloy.

b. Cold and Warm Rolling

If sheet thinner than 0.180 inch is required, the coil prepared on the hot-breakdown mill must be processed at either room or elevated temperatures on 2-, 3-, or 4-high mills. If the rolling is at room temperature, the reduction/pass is as low as 2 percent, and annealing of the metal is required after a total reduction of 25 to 30 percent. If the rolling is "warm," 160 to 260° C (300 to 500° F), 30 percent pass reductions are possible but the coil or sheet must be reheated before each pass. Either method is time consuming and conducive to low metal yield (weight of starting slab/weight of finished sheet). This problem results because of the crystal structure of magnesium, and the rolling of magnesium sheet will never approach the efficiency attained in the rolling of aluminum.

Finishing operations, such as straightening, annealing, pickling and surface finishing, are similar to those used for aluminum.

c. Cost and Energy Requirements

Technically, magnesium can be rolled from cast slab to plate as thin as 0.180 inch at the same volume cost as aluminum. In practice, this is not achieved since the market for magnesium plate is insufficient to support the capital investment required to produce plate at these low production costs. However, in looking for areas where magnesium could substitute for aluminum with no penalty in cost or energy consumption, plate should be considered.

For sheet thinner than 0.180 inch, however, the processing required for magnesium is inherently more expensive than that for aluminum. The cost per pound, at best, is between two and three times the cost of aluminum sheet. Energy consumption is about 1.5 times that required for aluminum, compounded by a metal yield of one third to one half that of aluminum. Thus, the total energy requirement to produce a given volume of magnesium sheet is three to five times that required for aluminum.

5. Extrusion

Presses used for extruding magnesium range from 500 to 14,000 tons. While both direct and indirect extrusion are practiced, most extruded magnesium is produced by direct extrusion. For the direct process, the pressure is applied by a solid ram exerting its force against the far end of the billet. For the indirect method, pressure is applied by the extrusion die mounted on a hollow ram. The die, therefore, generates the pressure in the metal without pushing the entire length of the billet along the container wall, thus eliminating friction. The pressure required to flow the metal through the die is reduced by approximately 30 percent when compared with direct extrusion of the same diameter and length of billet.

Either oil hydraulic, direct driven, or water hydraulic with superimposed pressure accumulator driven presses can be used. More accurate speed and pressure control is required for the extrusion of magnesium than for the extrusion of aluminum. Automatic speed control for large volume production will facilitate uniform extrusion speed, avoid hot shorting, and generally result in higher production and better quality. Unit pressures (between ram and billet) of up to 120,000 psi are applied. The harder the alloy and the smaller the cross-sectional area of the shape to be extruded, the higher is the pressure needed to flow the metal. In general, the pressures required for magnesium are approximately the same as those for aluminum alloys.

Magnesium and its alloys can be extruded through dies made from the normal hot work steel that is used for aluminum extrusion dies. Magnesium also can be extruded through the spider, bridge, and porthole dies commonly used for hollow shapes and tubing. Die and mandrel tooling can be used for seamless tubing. Billets for this process usually are bored or a hole is cast and the internal surface reamed to remove the cast surface.

In contrast to aluminum, cast billets of magnesium alloys generally are scalped before extrusion to remove segregated material at the surface. Pre-extrusion of smaller-diameter billets from a large cast billet sometimes is done to minimize the scalping required. Since scalping is required, no "bad" metal accumulates in the container, and continuous extrusion of billets without removal of the butt end is practiced.

Finishing operations following the extrusion itself (straightening, aging, pickling, or oiling) depend upon the extrusion and customer requirements.

6. Forging

Magnesium forgings have the best combination of strength characteristics of all forms of the metal and usually are specified when a higher strength than that attainable with castings is required for a light-weight part of fairly complex shape. Magnesium forgings are used sometimes for pressure tightness and machineability, rather than their higher strengths. Forgings also are used when they are more economical than castings over a long production run.

Alloys AZ31B-F, AZ61-F, AZ80A-F and tempers T5 and T6 are used for applications where service temperatures are expected to be from room temperature up to 150° C (300° F). AZ31B is an easily forged alloy with moderate strength; AZ80A is a high-strength alloy but less forgeable; while AZ61A is intermediate between these two in both strength and forgeability. ZK60A-F alloy in the T5 or T6 temper is used for applications where the service is expected to be at room temperature. HM21A-T5 alloy and temper was developed especially for elevated temperature use and maintains good strength up to about 320° C (700° F). Principal alloying elements and typical mechanical properties of forging alloys are given in Table D-1. The tensile properties obtained in a forged shape depend on factors such as size of forging, amount of working, finishing temperature, and texture variations at different locations in complex forgings.

TABLE D-1. Composition and Mechanical Properties of Magnesium Alloy Forgings

			Typical Mechanical Properties		
Alloy	Temper	Principal Alloying Elements (%)	Tensile Strength (ksi)	Yield Strength (ksi)	Elongation (%)
AZ31B	F	3.0 Al, 1.0 Zn, 0.2 Mn	38	25	9
AZ61A	F	5.5 Al, 1.0 Zn, 0.2 Mn	43	26	12
AZ80A	T5	8.5 Al, 0.5 Zn, 0.15 Mn	50	34	6
HM21A	T5	2.0 Th, 0.8 Mn	35	31	3
ZK60A	T5	5.5 Zn, 0.45 Zr	44	31	16

NOTE: Data from Dow Chemical Company, "Magnesium in Design," 1967.

Magnesium forgings can be produced in the same variety of shapes and sizes as forgings of other metals. The maximum size is limited primarily by the available equipment. Tolerances can be held to the same limits as in normal forging practice with other metals, varying somewhat with size and design.

The easy workability of magnesium greatly reduces the forging operations needed to produce the finished part. Many steps, such as punching, planishing, drawing and ironing, sizing, coining, edging and rolling, that commonly are required on forgings of brass, bronze, and steel are unnecessary on magnesium. Bending, blocking, and finishing are the principal forging steps used for magnesium.

The equipment necessary to forge magnesium alloys is essentially the same as that for aluminum alloys although greater care must be exercised in selecting the type of forge press. Magnesium alloys exhibit much greater hot ductility when deformed at slower strain rates. To minimize cracking, forging usually is performed in hydraulic presses rather than in hammers or fast-acting presses. Alloys ZK60A, AZ31B and HM21A are forged more easily in hydraulic presses than AZ80A, an extremely difficult alloy to forge. Hammer forging usually is limited to alloy AZ31B.

Magnesium forging stock is either cast ingots or billets produced by extrusion. Before homogenizing by the supplier the stock is conditioned and inspected to eliminate surface defects that could open up during forging.

In most instances, the mechanical properties developed in magnesium forgings depend on the strain-hardening and grain size induced during forging. Strain hardening is accomplished by keeping the forging temperature as low as practical; however, if temperatures are too low, cracking occurs. Prior to forging, the stock is raised to temperatures of 330 to 520° C (625 to 950° F), depending on type of alloy, in a preheated oven. Inert or reducing atmospheres are not needed at temperatures below 480° C (900° F). Because magnesium is a good conductor of heat and therefore readily chilled in cold dies, the dies must be heated to from 290 to 480° C (550 to 900° F). Since the forging temperatures are relatively low, conventional low-alloy hot-work tool steels are satisfactory materials for forging dies.

Magnesium alloy forgings are water quenched directly from the forging operation to prevent further recrystallization and grain growth. Forgings of AZ31B and AZ61A always are used in the as-forged condition (F temper). Forgings of AZ80A, ZK60A or HM21A can be used in either the as-forged or the artificially aged (T5) condition. Alloy ZK60A can be solution treated followed by artificial aging (T6 temper).