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PROPERTIES AND HANDLING PRACTICES FOR MAGNESIUM:
A LITERATURE SURVEY

by

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March, 1958

Operated by The University of Chicago
under
Contract W-31-109-eng-38

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PROPERTIES AND HANDLING PRACTICES FOR MAGNESIUM:
A LITERATURE SURVEY

INTRODUCTION

In the high-temperature program for melt refining of uranium and its alloys, a number of operations involving the handling of magnesium were proposed. Accordingly, an extensive literature survey on magnesium was made. This survey covered the cost and availability of various grades of high-purity magnesium, safety considerations in handling magnesium, presently used materials of construction and industrial handling procedures, methods of production and distillation of magnesium, physical and thermodynamic properties of magnesium, and a survey of the binary and ternary alloys of magnesium. This over-all information was assembled as a background for procuring, testing and handling magnesium.

Magnesium is a silvery white metal which is the lightest (sp.g. 1.74) structural metallic base material. Magnesium in its various compounds is widespread in nature; its principal ores are dolomite ($(\text{CaMg})\text{CO}_3$), magnesite (MgCO_3), and carnallite ($\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$). Magnesium also occurs as the chloride in underground natural brines and in sea water. Magnesium is produced either by the thermal reduction of the oxide, using carbon, ferro-silicon, or other reducing agents, or by the electrolysis of magnesium chloride in mixtures of molten salts (principally chlorides).

I. PHYSICAL PROPERTIES AND THERMODYNAMICS

The physical and thermodynamic properties of magnesium are here presented. The material includes crystallographic data, data of density versus temperature, surface tension, coefficient of thermal expansion, electrical resistivity, nuclear properties of magnesium isotopes, vapor pressure data, thermodynamic data, thermal conductivity, thermal diffusivity, viscosity, magnetic properties, and flammability.

Atomic No. 12
Atomic Wt. 24.32

A. Crystallography(1,2)

1. Crystal Structure	Close-packed hexagonal
2. Space Group	D_{6h}^{14} (C6/mmc)
3. Lattice Parameters (at 25 C)	$a = 3.2094 \text{ \AA}$
(for magnesium of ~99.99% purity)	$c = 5.2103 \text{ \AA}$
4. Axial Ratio	$c/a = 1.6234$
5. Atomic Coordinates	(000) $(1/3 \ 2/3 \ 1/2)$
6. Minimum Interatomic Distance* (at 25 C)	$3.197 \text{ \AA}$
7. Atomic Volume* (at 25 C)	$14.00 \text{ cm}^3/\text{gram atom}$
8. The primary slip plane (0001) is operative between 20 C and 225 C, and the secondary slip plane (1011) is operative above 225 C. The twinning plane is (1012). The cleavage plane is (0001).(2)	

*Calculated from the lattice parameters.

B. Density(3-10)

C	Experimental, ^a g/cu cm	Calculated, ^b g/cu cm	C	Experimental, ^a g/cu cm	Calculated, ^b g/cu cm
20	1.7388		755	1.570	
25		1.737 ^a	755	1.562	
650*		1.666 ^a	760	1.563	1.569
650**		1.590 ^a	770	1.564	1.567
672	1.584		770	1.568	
675		1.584	780		1.565
680	1.586	1.583	790	1.565	1.563
690	1.581	1.581	795	1.560	
700		1.579 ₅	795	1.563	
705	1.580		800		1.561 ₅
710	1.582	1.578	805	1.559	
720		1.576	810		1.560
728	1.575		820	1.558	1.558
730	1.568	1.574	830	1.557	1.556
732	1.576		840	1.555	1.554
740	1.575	1.572	850	1.555	1.552
750	1.569	1.570 ₅			

^aThe experimental values from 672-850 C, inclusive, have been taken from reference 3. The density for the liquid at 650 C was obtained by extrapolating the data of Grothe and Mangelsdorff.⁽³⁾ The result is in good agreement with the values reported by references 4 and 5. The liquid density data of reference 4, 5, 6, 7, 8 and 9 were given no weight in the preparation of the table. (The original references to 8 and 9 were not obtained. The data were taken from reference 10.)

The value for the solid at 650 C is an average of the measurements reported by references 4, 5, 6, 7 and 8.

The density at 20 C is an experimental value reported by reference 6 on a sample of 99.99 per cent magnesium. The density of 25 C was calculated from X-ray diffraction data (see page 1).

^bThese values were calculated from the following formula, which is given in reference 3,

$$D_{675-850 \text{ C}} = 1.584 - 0.00018 (t - 675)$$

*Solid

**Liquid

C. Surface Tension⁽¹¹⁾

C	dynes/cm	
650	559	The temperature coefficient of surface tension (in dynes/cm/C) was observed, to vary from a minimum of -0.14 to a maximum of -0.50, with an average value of -0.35.
700	542	
800	508	

(Reference 12 reports 563 dynes/cm at 681 C and 502 dynes/cm at 894 C, and claims that there is a linear decrease in surface tension between these two temperatures.)

D. Coefficient of Linear Thermal Expansion (polycrystalline)^(10,13,14)

The changes in dimension of cast and extruded magnesium between 20 C and 500 C can be expressed by the following equations:⁽¹³⁾

Cast: $L_t = L_0 [1 + (24.94 t + 0.00946 t^2) 10^{-6}]$ (99.99 per cent pure Mg)

Extruded: $L_t = L_0 [1 + (24.66 t + 0.00976 t^2) 10^{-6}]$ (99.98 per cent Mg)
(Average)

Average: $L_t = L_0 [1 + (24.80 t + 0.00961 t^2) 10^{-6}]$

where L_0 = length at 0 C
and L_t = length at t C

The average coefficients of expansion listed below were computed from these three equations.

Temperature Range, C	Average Coefficients of Expansion, inches/inch/C		
	Cast Magnesium	Extruded Magnesium	Average
20-100	26.1×10^{-6}	25.8×10^{-6}	26.0×10^{-6}
100-200	27.8	27.6	27.7
200-300	29.7	29.5	29.6
300-400	31.6	31.5	31.5
400-500	33.5	33.4	33.4
20-200	27.0	26.8	26.9
20-300	28.0	27.8	27.9
20-400	28.9	28.8	28.8
20-500	29.9	29.7	29.8

References 2 and 10 note the dependence of the coefficient of expansion on the orientation of the crystal lattice. Reference 59 reports on a high-temperature X-ray study and presents data for the linear thermal expansion of magnesium in directions perpendicular and parallel to the axis of six-fold symmetry. The calculated average linear expansion of a polycrystalline mass of the metal is given as follows:

Temp Range, C	Expansion, inches/inch/C
0-160	27.3×10^{-6}
160-310	27.6
310-455	31.0
455-600	39.6

E. Electrical Resistivity (polycrystalline)^(10,14-18)

C	u, ohm-cm	
20	4.4611	(99.99 per cent Mg) ⁽¹⁵⁾
300	10	(99.9 per cent Mg) ⁽¹⁴⁾
650 (solid)	~19*	(99.95 per cent Mg) ⁽¹⁶⁾
650 (liquid)	~29*	
700	28.8	(99.975 per cent Mg) ⁽¹⁷⁾
750	28.6	
800	28.4	
850	28.2	
900	28.0	

At the melting point the ratio of electrical resistivity of liquid to solid (ρ_e/ρ_s) is 1.63 for pure Mg (99.95 per cent).⁽¹⁶⁾

Constant Mass Temperature Coefficients of Electrical Resistance^(15,18)

$$[R_t = R_0 (1 + \alpha t)]$$

Temp, C	α , per C	
0	0.0038	(These values are the results of several investigators. Reference 10 reports 0.00386 as an average value for the temperature range 0-100 C.)
20	0.0040	
25	0.0050	
100	0.0045	
500	0.0036	
600	0.0100	

*Values taken from a graph.

Mass Conductivity at 20 C	= 197.71 per cent that of annealed copper	} {	Extruded Magnesium, 99.99 per cent pure	} 15)
Volume Conductivity at 20 C	= 38.65 per cent that of annealed copper (International Copper Standard)			

Reference 10 contains a graph showing the electrical conductivity of magnesium as a function of temperature in the range 0-600 C. The reference also discusses and gives data (in graphical form) for the dependence of electrical resistance on the orientation of the lattice, the degree of purity of the magnesium, and the nature of the impurities.

F. Nuclear Properties

Isotopic Data

Isotope (Isotopic Mass)(19)	Abundance,(21)* (per cent)	Type of(23) Decay	Half-life(23)	Method of Production and Genetic Relationships(23)
Mg^{23} (23.002) (Ref. 20)		β^+	11.9 sec 13.2 sec 11.6 sec	Na (p,n) Mg (γ ,n)
Mg^{24} (23.9924)	78.60 $\pm$ 0.13			
Mg^{25} (24.9938)	10.11 $\pm$ 0.05			
Mg^{26} (25.9928)	11.29 $\pm$ 0.08			
Mg^{27} (26.9928)		β^-	9.45 min 9.6 min 10.0 min 10.2 min	Mg (d,p) Mg (n, γ) Al (n,p)
Mg^{28}		β^-	21.2 hr 21.3 hr	Si (γ , 2p) Mg (α , 2p) spall. Cl parent of Al ²⁸

*Reference 22 reports 78.98 ± 0.04 , 10.05 ± 0.02 and 10.97 ± 0.04 , respectively, for Mg^{24} , Mg^{25} and Mg^{26} .

NUCLEAR REACTIONS(23)

NEUTRON CROSS SECTION DATA(24-27)

Isotope (Target)	Thermal Neutrons			Total Cross Section (σ_T)(26)			Reaction Cross Section(25) for 14.5-Mev Neutrons	
	Reaction Cross Section(24) (2200 m/sec) ^a		Scattering(25) Cross Section σ coherent					
	σ absorption	σ activation ^b		14.1 Mev	16.0 Mev	18.0 Mev	Half-Life ^c	σ (n,p)
Normal Mg	59 ± 4 mb		3.6 ± 0.1 ^b (hard sphere scattering)	1.74 ± 0.05 ^b 1.75 ± 0.03 ^b Refs 25, 27	1.72 ± 0.05	1.69 ± 0.05		
Mg ²⁴	33 ± 10 mb						15 hr	190 ± 30 mb
Mg ²⁵	270 ± 90 mb						60 sec	45 ± 20 mb
Mg ²⁶	60 ± 60 mb			9.6 mc 50 ± 10 mb				

Reference 24 has total cross section data (in graphical form) as a function of neutron energy. The energy ranges covered for magnesium are 2×10^{-2} to 300 eV and 10^{-2} MeV to 100 MeV.

^aThe "Reaction Cross Section" refers to all cases in which the neutron is not re-emitted. The data presented here are for (n,γ) reactions.

^bThe activation cross sections, σ_{act} , are those determined from the radioactivity of the product nucleus. In this case an (n,γ) reaction has occurred.

^cThe half-life is that of the product nucleus.

G. Vapor Pressure(28-38)1. Solid Magnesium

Temp. °C	Vapor Pressure, mm					
	Coleman and Egerton(28) (Doubly Sublimed Magnesium)		Reviews			
	(Observed)	(Calculated) ^a	Ref. 29	Ref. 30	Ref. 31	Ref. 53
377				10 ⁻³ (extrap.)		
382						7.6 x 10 ⁻⁴
426.8	6.90 x 10 ⁻³	6.87 x 10 ⁻³				
432.0	8.22 x 10 ⁻³	8.25 x 10 ⁻³				
432.1	8.23 x 10 ⁻³	8.28 x 10 ⁻³				
437				10 ⁻²		
442						7.6 x 10 ⁻³
444.7	1.28 x 10 ⁻²	1.27 x 10 ⁻²				
461.5	2.30 x 10 ⁻²	2.21 x 10 ⁻²				
461.6	2.25 x 10 ⁻²	2.22 x 10 ⁻²				
463.2	2.26 x 10 ⁻²	2.33 x 10 ⁻²				
465.3	2.47 x 10 ⁻²	2.50 x 10 ⁻²				
516			0.076	10 ⁻¹		0.076
608			0.76			0.76
614				1		
621					1	

^aThe values in this column have been calculated by means of the equation

$$\log p = - \frac{7527.0}{T} + 8.5899 \text{ (for the temperature range } T = 700\text{-}739 \text{ K)}$$

which has been derived by the method of least squares from the best straight line through the experimental points.

2. Liquid Magnesium

Temp, C	Ref. 32 (Experimental)	Vapor Pressure, mm			
		Reviews			
		Ref. 29	Ref. 30	Ref. 31	Ref. 53
702				5	
725		7.6			
727					7.6
739	10		10		
743				10	
750	12				
789				20	
805	27				
838				40	
851	50				
868				60	
874	67				
876	70				
883	76				
886		76			
887	80				
890	84				
898	91				
899	94				
905			100		
908	104				
909				100	
942	153				
963		190			
967				200	
998	274				
1006	300				
1030		380			
1034				400	
1103			760		
1107	760 (extrap.)	760		760	
1126					760
1137			1000 (extrap.)		

The measurements of Hartmann and Schneider⁽³²⁾ appear to be the best experimental data available for the vapor pressure of liquid magnesium. Coleman and Egerton⁽²⁸⁾ state that their vapor pressures for solid magnesium are in good agreement with those of Hartmann and Schneider on the liquid.

References 29, 30, 31 and 53 are reviews of the data in the literature and include, in addition to Hartmann and Schneider's data, the measurements reported in references 33, 34 and 35. (The data of reference 35 is not included in the compilations of references 29 and 31.)

3. Vapor Pressure Equations:

Eucken⁽³⁶⁾ has derived the following vapor pressure equations for magnesium:

$$\left\{ \begin{array}{l} \text{Solid Magnesium} \\ T = 573 - 924 \text{ K} \end{array} \right\} \log p = - \frac{7636}{T} + 2.500 \log T - 0.00295 T + 0.874 \times 10^{-6} T^2 + 3.27$$

$$\left\{ \begin{array}{l} \text{Liquid Magnesium} \\ T = 924 - 1400 \text{ K} \end{array} \right\} \log p = - \frac{7610}{T} - 1.020 \log T + 11.61$$

where, in each case, p is the pressure in millimeters of mercury and T is the absolute temperature.

The vapor pressures calculated from these equations are in good agreement with the measurements of Coleman and Egerton (about 1.5 per cent average deviation) and those of Hartmann and Schneider (about 5 per cent average deviation). The boiling point calculated from the second equation (1104 C) is also in good agreement with other measurements.

Lumsden,⁽³⁷⁾ using calorimetric data available for magnesium together with Coleman and Egerton's vapor pressure data, has derived an expression for the vapor pressure of liquid magnesium. Vapor pressures calculated from the expression are of the order of 13 to 30 per cent higher than the experimental data of Hartmann and Schneider. A recalculation of Lumsden's equation, using some recent calorimetric data, results in only slightly better agreement with the experimental vapor pressures.

4. Spectroscopic Studies on Magnesium Vapor:

Reference 39 and 40 discuss the existence of the Mg_2 gas molecule. Its dissociation energy has been estimated⁽³⁹⁾ as 7.2 ± 0.2 kcal/mole.

H. Thermochemical Data

Process	Temperature	ΔH (cal/mole)	ΔS [cal/(deg)/ (mole)]
1. Fusion ^a [Mg(s) $\rightarrow$ Mg(l)]	648.7 $\pm$ 0.2 C (Ref. 41,b)	2,140 ⁹ (Ref. 42,b)	2.32 ^d
2. Vaporization ^a [Mg(l) $\rightarrow$ Mg(g)]	1103 $\pm$ 5 C (Ref. 45) (normal boiling point ^c)	32,000 $\pm$ 500 (Ref. 42)	23.26 ^d
3. Sublimation a. [Mg(s) $\rightarrow$ Mg(g)] ⁽²⁸⁾ b. [Mg(s) $\rightarrow$ Mg(g)] ⁽⁴⁷⁾ c. [Mg ₂ (s) $\rightarrow$ Mg ₂ (g)] ⁽⁴⁷⁾	446 C 298 K 298 K	34,436 35,600 $\pm$ 300 63,400 $\pm$ 700	47.89 ^d 119. $\pm$ 1. ^d 213. $\pm$ 2. ^d
4. Combustion ⁽⁴⁸⁾ in 25 atm oxygen	24.6 C	-143,380 $\pm$ 120	
5. Solution ⁽⁴⁹⁾ in 1 N HCl (at a dilution of 1 mole of reacting substance in 77.2 HCl $\cdot$ 4,190 H ₂ O)	298.16 K	-111,322 $\pm$ 41	
6. Critical Temperature = 1867 C ⁹ (Ref. 32) (calculated estimate)			
7. Flame Temperature = 4850 C(Ref. 14) (theoretical)			

^aNote that for processes 1 and 2 (fusion and vaporization) the ΔH value and the temperature for the phase change have been taken from different references.

^bThe melting point listed here was determined by means of inverse-rate cooling curves. Reference 41 also reports 648.5 $\pm$ 0.5 C as determined by an electrical resistance technique. Reference 43 gives 2.00 $\pm$ 0.12 kcal/g. atom for the heat of fusion at 649.5 C.

^cLietgebel⁽⁴⁶⁾ reports 1097 $\pm$ 3 C for the boiling point of magnesium. See also the vapor pressure data in Section VII for other estimates of of the boiling point.

^dCalculated from the relationship $S = \frac{\Delta H}{T}$.

I. Molal Thermodynamic Functions of Magnesium⁽⁴²⁾

Temp, K	C_p° cal/(deg) (g-atom)	S° , cal/(deg) (g-atom)	$(H^\circ - H_{298}^\circ)$, cal/g-atom	$(H^\circ - H_{298}^\circ)/T$, cal/(deg) (g-atom)	$-(F^\circ - H_{298}^\circ)/T$, ^b cal/(deg) (g-atom)
298.16	5.953 ± 0.002^c (5.941) ^d	7.81 ± 0.01^c			7.81
300	5.960^c (5.948) ^d	7.85 ^c	11.	0.04	7.81
400	6.29 (6.241) ^d	9.61	623.	1.56	8.05
500	6.58 (6.493) ^d	11.04	1267.	2.53	8.51
600	6.84	12.27	1939.	3.23	9.04
700	7.09	13.34	2635.	3.76	9.58
800	7.42	14.31	3360	4.20	10.11
900 (solid)	7.81	15.20	4121.	44.58	10.62
1000 (liquid)	7.88	18.35	7041.	7.04	11.31
1100	8.14	19.11	7842.	7.13	11.98
1200	8.40	19.83	8669.	7.22	12.61
1300	8.66	20.51	9522.	7.32	13.19
1400 (gas)	4.968	44.30	42322.	30.23	14.07
1500	4.968	44.64	42819.	28.55	16.09
1600	4.968	44.96	43316.	27.07	17.89
1700	4.968	45.26	43813.	25.77	19.49
1800	4.968	45.54	44309.	24.62	20.92
1900	4.968	45.81	44806.	23.58	22.23
2000	4.968	46.07	45303.	22.65	23.42
2100	4.968	46.31	45800.	21.81	24.50
2200	4.968	46.54	46296.	21.04	25.50
2300	4.968	46.76	46793.	20.34	26.42
2400	4.968	46.97	47290.	19.70	27.27
2500	4.968	47.18	47786.	19.11	28.07
2600	4.968	47.37	48283.	18.57	28.80
2700	4.968	47.56	48780.	18.07	29.49
2800	4.968	47.74	49277.	17.60	30.14
2900	4.968	47.91	49773.	17.16	30.75
3000	4.968	48.08	50270.	16.76	31.32

^aActually is 298.16.

^bCalculated from the relationship $-(F^\circ - H_{298}^\circ)/T = S^\circ - (H^\circ - H_{298}^\circ)/T$.

^cThese values were obtained by correcting the data in reference 50 for a mistake which appears therein. As a result of this correction the data of reference 42 was adjusted very slightly. All of the $(H^\circ - H_{298}^\circ)$ values were increased by 1 calorie and the entropy values above 300 C were increased by 0.04 e.u.

^dWallace, W. E., Craig, R. S., Saba, W. G., and Sterrett, K. F., "The Heat Capacities of Magnesium and Cadmium Between 20 and 270 C," NYO-6334.

J. Molal Thermodynamic Functions of Magnesium Gas

	298.16 K	500 K	1000 K	1500 K	2000 K
Heat of Formation, ΔH_f° (kcal/mole) ⁽⁵²⁾	35.9				
Free Energy of Formation, ΔF_f° (kcal/mole) ⁽⁵²⁾	27.6				
Heat Capacity, C_p [cal/(deg)(mole)] ⁽⁵²⁾	4.9680				
Entropy, S [cal/(deg)(mole)] ⁽⁵³⁾	35.504 ⁽⁵²⁾	38.08	41.52	43.54	44.97
$H_T - H_{298.16}$ (kcal/mole) for Gaseous Alkaline Earth Metal ⁽⁵³⁾		1.003	3.49	5.97	8.45
$(H_T - H_{298.16})/T$ [cal/(deg)(mole)] for Gaseous Alkaline Earth Metal		2.01	3.49	3.98	4.23
$-(F - H_{298.16})/T$ [cal/(deg)(mole)] ^{(53)*}	35.504	36.07	38.03	39.56	40.74
$-(F^\circ - H_0^\circ)/T$ [cal/(deg)(mole)] ^(54,55) For values at other temperatures, [$(F - H_0^\circ)/T$] _T = -6.8635 log M - 11.4392 log T + 7.2820 where M is the atomic weight of magnesium (24.32) and T is the absolute temperature.	30.534	33.104	36.548		39.992

*Calculated from the entropy and heat content data by means of the relationship
 $-(F - H_{298.16})/T = S - (H - H_{298.16})/T$.

K. $\frac{\text{Thermal Conductivity at } 20^\circ\text{C}^{(14)}}{(99.9\% \text{ pure Mg})} = 0.376 \frac{\text{cal}/(\text{sq cm}) (\text{C}/\text{cm})}{(\text{sec})}$
 $[1090 \text{ BTU}/(\text{sq ft}) (\text{F}/\text{in.}) (\text{hr})]$

L. $\frac{\text{Thermal Diffusivity}^{(14)}}{(99.9\% \text{ pure Mg})} = 0.868 \frac{\text{sq cm}/\text{sec}}{[0.135 \text{ sq in.}/\text{sec}]}$

M. Viscosity⁽⁵⁶⁾

Temp, C	Viscosity, Centipoises
650	1.32 (extrapolated)
700	1.10
800	0.84
900	0.67

N. Magnetic Properties^(2,10)

Magnetic Susceptibility (specific) = 0.55×10^{-6} cgs

Magnetic Permeability = 1.000012 cgs

Magnesium, like aluminum, belongs to the weakly paramagnetic metals. Reference 10 presents a graph showing the magnetic susceptibility as a function of temperature, at $H = 10.5 \times 10^3$ Gauss, for magnesium sheet containing 0.0235 per cent iron. The magnetic susceptibility has been found to decrease with reduced intensity of the magnetic field.

O. Flammability

1. Ignition temperature in oxygen at atmospheric pressure is $623 \text{ C} \pm 0.5$. In an 80 per cent nitrogen, 20 per cent oxygen mixture the results were 638, 613, 624, and 635 C for the ignition temperatures.⁽⁵⁷⁾

2. Minimum value for the autoignition temperature of magnesium powder, less than 40μ in diameter, and a concentration in air of 0.058-0.110 gram/liter, is 504 C.⁽⁵⁸⁾

3. The lower concentration limit beyond which magnesium dust will not explode is about 30 mg/liter, which is similar to that for aluminum.⁽¹⁰⁾ Reference 10 further discusses the spontaneous combustion of magnesium powder and the flammability of swarf and solid.

P. Miscellaneous

Information on the following topics is presented in References 2,10, and 15.

1. Electrochemical Properties^(2,10,15)
2. Thermoelectric Power^(10,15)
3. Reflecting Power^(2,10,15)

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II. PRODUCTION AND DISTILLATION OF MAGNESIUM

A survey of the literature has been conducted to determine methods and materials used in the production and distillation of magnesium. Information gained through this survey will be applied to the design of extraction and distillation equipment required initially to extract plutonium from uranium with magnesium and then further to separate the plutonium from magnesium by distillation.

A. Production of Magnesium

1. Electrolytic Process

a. Dow Process

The Dow Chemical Company produces magnesium by an electrolytic reduction process using slightly hydrated chloride obtained by the chemical treatment of sea water.⁽²²⁾ Magnesium from the reduction cells has a purity of over 99.9 per cent. The metal is usually remelted under carefully controlled conditions to remove some of the more volatile elements and is then poured into ingots. Information on the final purification procedure was not divulged. The Dow process as developed for the sea-water plants located in Freeport and Velasco, Texas, is considered the most economical and most important methods of producing magnesium in the United States.

b. Basic Magnesium, Inc. Process

During World War II, Basic Magnesium Incorporated at Henderson, Nevada, utilized anhydrous magnesium chloride in electrolytic cells for the production of magnesium. In this process, magnesite, MgCO_3 , was calcined to form MgO . Magnesium oxide, mixed with coal tar and peat, was formed into pellets which were loaded into a chlorinator maintained at a temperature of 1100 C to produce molten anhydrous magnesium chloride according to the reaction: $\text{MgO} + \text{Cl}_2 + \text{C} \longrightarrow \text{MgCl}_2 + \text{CO}$. The electrolysis took place in ceramic-lined steel cells, and magnesium metal of 99.95 per cent purity was produced.

2. Ferrosilicon (Pidgeon) Process

The ferrosilicon process⁽²²⁾ or Pidgeon process was developed for the Dominion Magnesium Company of Canada and is being used at the present time in Haley, Ontario. Ford Motor Company and Union Carbide and Carbon Research Laboratory used the Pidgeon process during World War II. This process was the first large-scale metallurgical process ever undertaken under vacuum.

At pressures of less than 0.2 mm Hg and controlled condenser temperatures, a good grade of magnesium deposit is obtained. The reaction is as follows:

The reaction units, ten inches in diameter and ten feet in length, are made of 25-15 or 28-12 nickel-chromium steels. These units are part of a horizontal, gas-fired furnace, with about two feet of the tube ends protruding from the furnace. The ends of the tubes are water jacketed to act as condensers, and the inner wall of the condenser consists of a removable steel lining upon which the magnesium condenses in crystalline form.

An early furnace used in the ferrosilicon process was the Blackwell-Turner furnace in which an induction heater was used, a pressure of 2 mm Hg being maintained over the melt. The magnesium distilled and collected on a water-cooled steel dome or cupola of the furnace. The dome would be hoisted out after the end of a run and the crystals collected and remelted.

At the end of the run, the magnesium is removed from the condenser lining by partly cooling the furnace with a resulting differential contraction between the magnesium and the steel. The magnesium is also collected by pressing it out of the linings, melting under flux and then casting into ingots.

The magnesium produced in the Pidgeon process has a purity of 99.982 per cent. Batches normally run from 30 to 50 pounds in weight, but one plant using large retorts was able to produce 500-lb batches. Retorts tend to collapse after long runs, but are put back into operation by heating to 1170 C, applying a pressure of 70 psi, and then allowing to cool at this pressure.

3. Thermal Reduction Processes

a. Murex Process

The Murex process was used in England for some time and was based on the following reaction:

This reaction was carried out under vacuum at temperatures between 1200 C and 1600 C, with the magnesium being distilled off and collected.

b. Aluminum Reduction Process

Another thermal reduction reaction is as follows:

This reaction was carried out in retorts under vacuum and the magnesium distilled and condensed.

4. Carbothermic Process

The carbothermic process developed by Hansgirg in Austria utilized the following reaction:⁽²⁷⁾

The magnesium vapor was shock cooled with a blast of hydrogen at 200 C to form a fine solid powder. Upon exhausting the powder from the furnace, it was briquetted and redistilled under vacuum.

The vapor condensed on a vertical, oil-cooled tube, forming liquid metal which was recovered in an oil well protected by an air trap. This resulted in a product of 99.97 per cent purity. The main drawbacks to this process are the explosive characteristic of hydrogen and the highly pyrophoric character of the distilled magnesium.

The carbothermic process was used to produce magnesium during World War II by the Permanente Metal Corp. in California. An arc furnace maintained at 2100 C was fed magnesia and coke, and the resulting magnesium vapor and carbon monoxide were drawn through a valve at the top of the furnace. The magnesium vapor was then shock cooled with natural gas or hydrogen.

5. Bureau of Mines Process

Using a modification of the Hansgirg carbon reduction process, the U.S. Bureau of Mines, Boulder City, Nevada, used a spray of mineral oil to shock cool the magnesium vapor.⁽¹²⁾ Only a small volume of oil was needed to cool the hot metal vapor; as a result of this modification the danger of fire and explosion was curtailed. The mixture of oil and metal is passed through a centrifugal scrubber and then into a two-stage still where first the lighter oils and next the magnesium metal are vaporized. The vapor is condensed, remelted, and cast into ingots. A distillation rate of 1 lb/hr was attained at 1000 C with a pressure slightly above atmospheric. A 24-12 chromium-nickel alloy was used in the construction of a major portion of the components of this pilot plant.

6. Sublimation Processes

a. Bakken Process

A method often used for purification of magnesium metal is sublimation. In the Bakken process, a retort of steel is mounted in a firebrick structure at an angle of 30°. The tube is charged from the top, covered and sealed; a vacuum is applied and heat applied to the lower end. The upper inside end of the tube is provided with a loosely fitting

liner and the outside portion of the tube is water jacketed to act as a condenser. Thermocouples are located at both ends of the tube and careful control of temperature and residual pressure are maintained. The absolute pressure in the retort is maintained below the vapor pressure of magnesium at the temperature selected. Sublimed magnesium is press extruded from the condensers and is of 99.98 per cent purity. Bakken reported 150 lb of magnesium were sublimed in 5 to 6 hours at a temperature of 600 C at pressures of 0.5 to 0.15 mm Hg.

b. Herenguel Process

The Herenguel process developed in France uses a higher vacuum than the Bakken process and a residual argon atmosphere free of oxygen, nitrogen, and carbon. Vertical, cylindrical, cast steel retorts having calorized surfaces to prevent release of occluded oxygen and nitrogen from the retorts are used in this sublimation process. The lower zone is heated by an electric resistance winding, and a water-cooled cylindrical condenser somewhat smaller than the retort extends down from the top about one-third the depth of the retort. A series of horizontal baffle plates surround the condenser to reduce the velocity and turbulence of the vapor. Condensation under these conditions take place rapidly and results in large dendritic crystals.

c. Dow Chemical Research

Under an AEC contract, the Dow Chemical Company conducted a research and development program on the preparation of high-purity magnesium by sublimation.⁽¹³⁾ A sketch of the initial vacuum sublimation furnace is shown in Figure 1. The charge was vaporized at 670 C at a pressure of 0.001 mm Hg and then passed through multi-layer screens which acted as entrainment barriers, on which manganese, the predominant impurity deposited. The metal was condensed in the area adjacent to the subliming zone at a temperature of 300 C. The product was of high purity but of high porosity, which made it readily subject to oxidation.

To overcome this objectionable feature, a vacuum sublimation - argon casting furnace was designed as shown in Figure 2. In this furnace, it was possible to sublime the magnesium and cast under an argon atmosphere to produce a nonporous billet.

A graphite lining covers the interior walls of the cylinder, because early work showed it was necessary to prevent the magnesium from contacting

FIGURE 2
SUBLIMATION-ARGON CASTING FURNACE

the chrome steel shell. The graphite lining was coated with acetylene black to enable ease of billet removal without damage to the liner. After loading the furnace with magnesium and evacuating the system, the system was outgassed at 500 C for 3 to 4 days. At this temperature, the sublimation rate was very low. After this preliminary outgas period, the furnace went through a short final outgas at an elevated temperature at pressures of 0.0005 to 0.001 mm Hg. The temperature

was then raised to 600-700 C for sublimation to proceed. The resulting sublimate was melted in the condenser under an atmosphere of argon with melt-out efficiencies of 80 per cent of the charge metal. Graphite entrainment barriers and charge cradles were used to eliminate further sources of iron contamination.

The condensed magnesium vapor took various crystalline forms, depending on the sublimation conditions. With a rapid condensation at about 300 C and 0.01 mm pressure, droplet-type crystals were formed. Single magnesium crystals were formed with slow condensation at approximately 600 C and 5 to 10 mm pressure. Layered crystals appeared as a result of slow condensation at 640 C under an argon pressure of one atmosphere. At 600 C under the same pressure, dendritic crystals were formed.

Spectrographic analysis of the magnesium showed only a few parts per million of Fe, Ca, K, Na and only traces of Al, Cu, and Pb (see Table 1).

Table 1

IMPURITIES OF SUBLIMED MAGNESIUM (ppm)

	Al	Ba	Ca	Cu	Fe	K	Mn	Na	Ni	Pb	Si	Sn	Sr	Zn
<u>Steel Unit</u>														
Single Sublimed	3.5	2.0	12	<1	7	15	18	6	3	5	<100	<10	<5	<100
Triple Sublimed	<1	<1	11	<1	<4	12	<2	6	<3	<5	<100	<10	<5	<100
Graphite-Lined Sublimers	<1	<1	6	<10	<4	<5	<2	7	<4	<10	<10		<1	2

Spectroscopically pure magnesium, except for approximately 10 ppm Na and Ca, can be produced by multiple sublimation of commercially pure magnesium billets or ingots if suitable vapor filters are used (see Table 1).

At the present time, Dow Chemical Company produces singly, doubly, and triply sublimed magnesium in a sublimator similar to that shown in Figure 1. This unit is 12 in. in diameter and about 10 feet long, with a water-cooled condensing area at each end. Removable steel liners are provided for ease of removal of the sublimed magnesium. The sublimations are run at about 600 to 700 C under a vacuum of 5 microns. To process an 80-lb batch of magnesium, a total of 8 days are required, which amounts to a rate of 10 lb/day.

Traces of aluminum may be removed by supplementing the triple layer of screens used in the sublimation unit with a 1/2-in. layer of graphite granules to react with aluminum to form aluminum carbide.

B. Distillation of Magnesium

1. Titanium Metals Corporation Experience

In the production of titanium and zirconium sponge metal, the chlorides of these metals are reduced with liquid magnesium. Titanium Metals Corporation of America, Henderson, Nevada, charges retorts with magnesium metal. After assembly and leak testing, the temperature is raised to 850 C. Titanium chloride is fed into the molten magnesium, and the interior of the retort is maintained under a positive pressure of helium.⁽²⁵⁾ An excess of magnesium over tetrachloride is used in this step of the process. The magnesium chloride formed is intermittently drained from the bottom of the retort in order to make the best usage of reaction pot volume and keep residual magnesium available for the reaction to continue. The retorts produce about 500 lb of spongy titanium, magnesium, and magnesium chloride per batch.

The titanium is separated from the excess magnesium and magnesium chloride by vacuum distillation at a temperature of 800 to 900 C. The magnesium and magnesium chloride distill off and condense in a cooled portion of the reaction vessel. After the distillation, the reaction vessel is removed from the furnace and placed in a cooling station. When the temperature has been reduced sufficiently so that the reactor may be disassembled without oxidation of the product, the titanium sponge is removed. A sketch of the reaction vessel is shown in Figure 3.

2. Carborundum Metals Company Experience

In the production of zirconium, the Carborundum Metals Company, Akron, New York, reduces pure zirconium tetrachloride to sponge metal with molten magnesium.⁽⁴⁾ This is accomplished by the use of an electric furnace which is located with two drums, one located above the other. The upper drum holds the zirconium chloride crystals, and the lower, of Inconel, contains bars of magnesium. The stacked drums, separated by a

FIGURE 3
MAGNESIUM - MAGNESIUM CHLORIDE DISTILLATION FURNACE

spacer, are raised into the furnace by a hydraulic lift, after which the bottom of the furnace is sealed off and the air is displaced by argon. Heat from electric coils vaporizes the zirconium chloride and melts the magnesium. Zirconium chloride vapor finds its way to the surface of the molten magnesium, where it reacts to form metallic zirconium and magnesium chloride. Magnesium chloride and magnesium are separated from the zirconium by vacuum distillation.

A survey of recent patent literature on the distillation of metals revealed the design of some interesting distillation apparatus.

3. Patent Literature on Distillation of Magnesium

(1) U.S. Patent 2, 386, 189, by G. G. Bagley, describes an apparatus for producing magnesium from magnesium oxide, calcium oxide, and ferrosilicon. The mixture is heated under vacuum at temperatures of 1100 to 1250 C. Magnesium vapors produced are condensed in a removable condenser. The apparatus is a pressure-resistant, airtight outer steel shell, lined with a heat-insulating material and adapted to be evacuated. Electrical-heating elements and a charge-supporting structure are located within the outer shell. A section of the charge-supporting structure is constructed so as to be removed from the shell upon completion of a magnesium-producing operation, and the residue may be discharged by gravity.

(2) U.S. Patent 2, 387, 677, by L. M. Pidgeon, describes the apparatus used by Dominion Magnesium Company of Canada for the production of magnesium by the ferrosilicon process. Chrome-nickel alloy tubes, 10 in. in diameter, are placed horizontally in gas-fired furnaces. Each end of the tube projects out of the furnace and has a cooling section for the condensation of magnesium vapor. The retorts of furnace tubes contain two removable sleeves in the condenser to facilitate removal of the crystalline magnesium, sodium, and calcium. The metals of higher vapor pressure are condensed on one sleeve while the magnesium condenses on the other section. The furnace is operated at a temperature of 1160 to 1200 C at a pressure of less than 0.25 mm Hg.

(3) F. J. Hansgirg's U.S. Patent 2, 391, 156 describes an apparatus for refining sublimable materials. This unit is especially adaptable for refining crude, alloyed, or impure magnesium by sublimation and to process magnesium dust obtained as an intermediate product in the carbothermic reduction of magnesium oxide.

(4) An apparatus for metals distillation is described in U.S. Patent 2, 458, 253 by D. S. Chisholm and Thomas Griswold, Jr. It was specifically designed for distillation of magnesium from a lead-magnesium mixture. The still pot was operated at 550-600 C and the column at 950-1100 C. The condenser was held at about 655 C, which is slightly above the solidification temperature for magnesium, and the entire apparatus was maintained at a pressure of about 0.25 mm Hg. Liquid metal was pumped from the still pot into the top of the column, which contained a spiral graphite pillar. As the metal ran down the graphite spiral, the magnesium would distill and condense in the upper part of the still.

One-inch thick type 430 steel was used in the construction of the still, which was 16 in. in diameter. A life of 100 hours was reported for the apparatus when operated at temperatures of 950 to 1100 C. It is believed that if the furnace had been graphite lined the life of the unit would have been greatly increased.

(5) U.S. Patent 2, 389, 307 by H. M. Griffoul describes a gas-fired magnesium melting furnace in which the air in the furnace may be replaced with an inert gas during melting, and a rotating or rocking motion may be imparted to the melting pots.

(6) U.S. Patent 2, 684, 898 by James Barton describes a simple apparatus for the distillation of calcium or magnesium which basically appears to operate on the same principle as that used in the Pidgeon process.

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III. MATERIALS OF CONSTRUCTION AND HANDLING PROCEDURES

A. Introduction

One of the proposed steps in the purification of PBR spent fuel elements involves removal of plutonium by contacting with molten magnesium. Such a process must involve the selection of materials which will not be attacked by the molten metals. Likewise, the development of satisfactory methods of handling these materials is also of primary importance. Accordingly, a survey was made of current industrial and experimental techniques and materials which are used in the handling of molten magnesium.

B. Materials of Construction^(7,9)

1. General

Magnesium is less corrosive to container materials than aluminum, antimony, tin, or zinc and can be contained satisfactorily in certain materials and under temperature conditions that would prove unsatisfactory in the case of the latter liquid metals. Information concerning the attack on engineering metals and alloys by liquid magnesium is largely qualitative in nature and, for the most part, is the result of experience in the manufacturing and casting of this metal and its alloys.

2. Ferrous Metals

Cast iron and low-carbon steel have good resistance to magnesium at its melting point (651 C), and limited resistance up to 800 C or higher.

Cast iron and low-carbon (SAE 1010) steel are most frequently used for handling magnesium, but low-carbon steel in particular is best suited for temperatures up to 900 C. Centrifugal pumping units fabricated from cast Meehanite iron, Graphitar, and low-carbon steel are reported to give satisfactory service under erosive conditions up to 760 C. Attack occurs by dissolution of iron, which at 651 C corresponds to an apparent solubility of 0.0025 per cent by weight. Both cast iron and low-carbon steel have limited resistance at and above 800 C where the solubility of iron in magnesium increases beyond 0.1 per cent by weight. In the continuous casting of magnesium at temperatures ranging to about 760 C precipitation of iron in the cooler zones has never been observed. High-chrome stainless steel is more resistant to attack than cast iron and low-carbon steel. Austenitic stainless steel is attacked by magnesium at its melting point, 651 C. Heat-resistant steel⁽¹¹⁾ containing manganese, wolfram, chromium, vanadium or molybdenum can be used to advantage when greater strength or oxidation resistance is required.

High-chromium stainless steel possesses as good resistance as that exhibited by cast iron and low-carbon steel; it has the added advantage of being resistant to oxidation. Under the added condition of erosion the attack is no more severe than it is in the case of cast iron and low-carbon steel.

The attack on austenitic stainless steel (18 Cr - 8 Ni) at 651 C is attributed to its nickel content and the fact that liquid magnesium can dissolve 23.5 per cent by weight of nickel at 507 C. The use of such materials as containers would result in contamination of the melt and deterioration of the steel.

The observations concerning the relative resistance of low-carbon steel and high chrome stainless steel are further confirmed by some unpublished tests made at Argonne in which molten magnesium was contained in bombs of 1020 steel⁽¹³⁾ and 446 stainless at 1150 C for various times and the penetration measured:

Table 2

PENETRATION OF IRON-BASE ALLOYS BY MAGNESIUM AT 1150 C

Run and Capsule No.	Metal	Exposure Time	Total Penetration, mils		
			Liquid Phase	Interface Maximum	Vapor Phase
46-33	1020 steel	3 days	3.5	10.5	4.5
49-31	1020 steel	6 days	8.5	16.5	3.5 - 6
50-32	1020 steel	14 days	3.5 - 7.5	45	4.5 - 7.5
58-45	Type 446 stainless	24 hours	2.5	8.5	0.5 - 1.5
59-46	Type 446 stainless	6 days	8.5	77	2.5 - 8.5
60-47	Type 420 stainless	24 hours	2.5 - 6.5	18	4.5 - 6.5

3. Refractory Metals

Titanium has good resistance to attack by magnesium up to 250 C, and limited resistance to 850 C. Zirconium probably has limited to poor resistance to attack at any temperature above the melting point of magnesium. Niobium, wolfram, tantalum, molybdenum, and chromium have been suggested for use with liquid magnesium. Beryllium has good-to-limited resistance to attack by magnesium at 800 C, although available solubility data are not in complete agreement.

Titanium appears to have good resistance to attack by magnesium up to 750 C, where the reported solubility is approximately 0.01 per cent, and limited resistance up to 850 C, where the solubility increases to 0.015 per cent.

Wolfram is reported to be insoluble in both liquid and solid magnesium.

The general belief that chromium cannot be alloyed with magnesium seems to be substantiated by the inactivity of chrome plate to liquid magnesium at 651 C, and its low solubility (0.008 per cent by weight) in magnesium at 734 C.

The appreciable solubility of zirconium in magnesium indicates it would have poor resistance to liquid magnesium at any temperature.

There is disagreement in the literature on the solubility of beryllium in magnesium. Attempts to alloy the two metals have indicated complete insolubility to a maximum solubility of beryllium in magnesium of approximately 0.05 per cent by weight.

4. Other Metals

Because of their appreciable solubility in liquid magnesium at low temperatures, as indicated by the phase diagrams, aluminum, silver, gold, barium, bismuth, calcium, cadmium, cobalt, copper, gallium, lithium, nickel, lead, palladium, platinum, antimony, silicon, tin, thallium, and zinc are excluded from consideration as container materials.

Practical experience has demonstrated that brass and bronze fittings are dissolved by magnesium at its melting point, and that most of the other metals are dissolved up to 10 per cent by weight, when added to liquid magnesium at 734 C.

5. Non-Metals and Oxides

Liquid magnesium does not attack alumina, graphite, magnesia, or silicon carbide at temperatures near its melting point; although quantitative data are lacking in the case of beryllia, calcium oxide, thorium and zirconia, there is some doubt that these materials would be attacked under similar conditions. Most other oxygen-containing compounds, such as quartz and silicates, are attacked by liquid magnesium at this temperature. When graphite is used with molten magnesium containing magnesium oxide, attack is not likely to occur below 2000 C, but above this temperature carbon has been reported capable of reducing magnesia, and attack can be expected to occur, depending largely on the amount of magnesia present.

Experimental results of tests in static magnesium at 900 C have shown that alundum, beryllia, magnesia, porcelain, quartz and zirconia are strongly attacked in 2 to 3 hours. It is probable that thoria would also show strong attack by magnesium at this temperature, in view of the thorium magnesium compound (Mg_2Th_x) that is formed on heating magnesium powder with thorium oxide.

Much of the above information is confirmed in an extensive series of tests carried out by The Dow Chemical Company.⁽²⁰⁾ These tests were made in order to find suitable crucible materials for containing highly purified molten magnesium without contamination from the crucible. A summary of these results is given in Table 3.

Table 3

MELTING AND ATTACK OF METALS AND REFRACTORIES
BY MOLTEN MAGNESIUM

Material	Melting Temp, C	Time, hr	Melting Method	Wetting	Attack by Magnesium	
					From Analysis of Melt	From Metallograph
Niobium	750	6	graphite under argon	Yes	No	Yes
Tantalum		6	↓	↓	No	No
Molybdenum		6	↓	↓	No	No
Kennometal		7	↓	↓	Yes	?
Titanium (oxidized)		6	↓	No	No	Yes
18-8 Steel		6	↓	Yes	Yes	Yes
MgO		1	argon	↓	Slight	-
Zirconium		1	↓	↓	Yes	-
ThO ₂		1	↓	↓	↓	-
Titanium		6	graphite under argon	↓	↓	Yes
Graphite (spec. pure)		2	argon	No*	Slight	-
Wolfram		6	graphite under argon	Yes	No	No
430 Steel		15	argon	↓	Yes	-
Graphite	825	16	argon	↓	Slight	-

*Some oxide present.

C. Handling Procedures

1. Foundry Practice⁽¹⁵⁾

The successful application of magnesium alloys to any casting operation requires properly refined metal, so poured or cast as to insure the transfer of clean metal into the mold cavities. Molten magnesium is highly reactive chemically and readily reacts with oxygen from the atmosphere or any available moisture. Its reaction with water or moist objects may be quite violent, and it is necessary that the utmost care be taken in its handling. Oxide inclusions are detrimental to the finished product. Flux inclusions resulting from improper refining may not only cause castings of low strength characteristics, but will result in low qualities, of corrosion resistance which may make the castings entirely unsuited for any reasonable application.

a. Use of Fluxes^(2,12,14,17,18)

All melting and refining processes for magnesium and its alloys require the use of fluxes or similarly acting materials. These fluxes serve the double purpose of refining the metal and of reducing oxidation while the metal is in the molten state. The "cover" fluxes have a magnesium chloride base plus other halide salts or oxides to give a density or behavior exactly suited to the particular melting practice; the "alloy" fluxes are characterized by the presence of manganese chloride. Table 4 lists the compositions and main applications of the Dow Chemical Company fluxes.

Specifically, the charge of mixed ingot and scrap, the latter consisting of gates and sprues returned from the foundry floor, is charged into a bath of molten flux. In American practice, the latter may amount to as much as 30 per cent of the entire charge at the outset, although cold metal is added from time to time. In European practice a much smaller proportion of flux is used, but it is generally cleaned out at the end of a heat and a fresh charge is introduced. In any event, the flux used is proportional to the amount of scrap and its condition. The flux is very fluid and has a low melting point. The principal constituent, magnesium chloride, tends, in the molten state, to thicken of its own accord; this effect is increased by the addition of calcium fluoride. It forms a sludge with the oxides and nitrides present; the sludge sinks to the bottom, allowing the purified metal to be poured off the top. Stirring and thickening is carried out at 650 to 700 C. The surface is protected from oxidation by a "cover" flux.

Table 4

COMPOSITION AND CHARACTERISTICS OF FLUXES FOR MELTING
AND REFINING MAGNESIUM, DOW CHEMICAL COMPANY

Flux No.	Composition (per cent)	Use	Amount of Flux Present in Pot during Operation (per cent)	Approximate ^a Net Consumption of Flux (per cent)	Characteristics and Remarks
220	57.0 KCl 28.0 CaCl ₂ 12.5 BaCl ₂ 2.5 CaF ₂	Die-casting	0	1-3	A heavy bottom flux used for refining metal in a covered pot provided with SO ₂ surface protection. Flux is removed after refining. Used where dipping is so frequent that open-pot operation is impractical. Preparation of rare-earth alloys.
230	55.0 KCl 34.0 MgCl ₂ 9.0 BaCl ₂ 2.0 CaF ₂	Sand and permanent mold casting Premelting Alloy Production Scrap recovery Flux pots	10-20 5-10 10-20 10-20 100	4-6 2-4 3-6 4-15 0.5	Characterized by high fluidity of surface film protection, alloying parting and recovering for ladling operations. High refining qualities. General <u>open-pot</u> flux.
232	37.5 KCl 42.0 MgCl ₂ 7.5 MgO 4.5 BaCl ₂ 8.5 CaF ₂	Similar to No. 230	-	-	In general, similar to No. 230, but presence of MgO increases the viscosity.
250	23.0 KCl 72.0 MnCl ₂ 2.5 BaCl ₂ 2.5 CaF ₂	Alloying	0	Variable	Used for introducing manganese into alloys made by open-pot process with No. 230 flux. Reaction products approximate No. 230 flux behavior. Flux contains 31.7 <u>per cent manganese</u> by weight.
310	20.0 KCl 50.0 MgCl ₂ 15.0 CaF ₂ 15.0 MgO	Sand and permanent mold foundry Crucible alloying Die-cast scrap refining	1-3 2-5 2-5	3 2-5 2-5	Crucible-type flux characterized by being fluid at start for melting and refining, then drying out to crust that can be removed or held back for direct pouring
320	76.0 MnCl ₂ 13.0 CaF ₂ 11.0 MgO	Crucible alloying	0	Variable	Used for introducing manganese into alloys produced by the crucible process with No. 310 flux. Reaction products approximate No. 310 flux behavior. Flux contains 33.5 <u>per cent manganese</u> by weight.

^aBased on weight of metal poured from a given operation.

b. Use of Protective Atmospheres(1,3,6)

Molding sands for magnesium alloys contain inhibitors that generate a protective atmosphere within the mold. However, these protective vapors do not operate by preventing reaction between metal and mold atmospheres; rather, they operate by the formation of protective films. When a protective film forms on a freshly exposed liquid metal surface, it protects the metal beneath from further reaction. If, however, the protective film is promptly stirred into the body of the liquid metal, exposing fresh surfaces for reaction, as in the case where flow turbulence is involved, severe drossing of the metal will occur.

Thus there are two basic approaches to the prevention of dross inclusions in the casting:

- (1) Complete suppression of dross formation in the transfer from pouring crucible to casting cavity. This is accomplished either by totally avoiding turbulence during the pouring operation, or by protecting the stream of molten metal from oxidation during pouring by dusting such materials as powdered sulfur, boric acid, ammonium fluoride, or a mixture of them on the stream and the surface of the mold. Such materials are used when pouring at higher temperatures than normally employed. Under normal pouring conditions (~700C) the magnesium chloride in the flux decomposes to give chlorine, which is sufficient to prevent reaction of the magnesium with air.
- (2) The separation of the dross from the stream of the melt prior to its entry into the casting cavity. Filters, placed at the bottom of the sprue in such a way that the metal flows through them on its way to the mold cavity, are effective. Steel wool and a perforated skim gate⁽³⁾ are effective filters.

c. Methods of Melting

There are four standard methods of melting in use today.

(1) Open-Pot Method^(3,18,19)

Open pots, varying in capacity from 100-500 pounds of magnesium depending on the amount of production to be handled, are constructed of heavy-walled cast steel. It is recommended that the nickel content be held to a maximum of several tenths of 1 per cent and the copper content to less than 1 per cent. This same type of pot, with a capacity of from 400 to 600 lb of magnesium, is also used for flux pots and is filled with No. 230 flux for cleaning ladles, tools and other utensils. This prevents undue splashing and agitation in the regular casting pot and prevents the carryover of excessive oxide or other impurities into the pot and thus into the castings.

The open-pot method makes use of No. 230 flux in relatively large amounts (10 to 20 per cent of metal weight). This provides protection during melting and a molten pool of flux into which the solid magnesium melts. The flux is stirred through the molten bath and agglomerates oxide or similar foreign bodies; on quiet standing, it floats away, leaving the refined metal ball floating in an encircling layer of molten flux. It forms only a thin fluid film over the surface of the molten metal, which may be

parted for hand-ladling processes and tends to cover the metal again after the ladle is removed. A very light dusting of the pot surface with fresh flux immediately after the ladle is removed is desirable. Ladles hold up to twenty-five pounds of magnesium.

The open-pot method is used generally in the following processes:

- (a) Alloying of small quantities and secondary melting for the production of ingots.
- (b) In sand foundries for the premelting and, to a smaller extent, for the production of small castings requiring hand lading.
- (c) Melting for the production of permanent mold castings.
- (d) Continuous melting methods for the production of cast slabs and billets to be used for the fabrication of wrought products, such as sheet, plate and extrusions.
- (e) General scrap recovery.

(2) Crucible Method(3,16,18)

The crucible method of melting magnesium is considered the best practice for the production of magnesium sand castings. Its advantages over the open-pot process include less waste of metal, less use of flux, and a single cycle of operating steps. The process is adapted to the melting of virgin ingot and foundry scrap, including sprues, risers, gates, scrapped castings, etc.

Crucibles are made of welded boiler plate, usually with extra thick bottoms to resist heat corrosion. This welded-on bottom section can be cut off and a new one welded into place, when such a procedure is economically desirable, particularly on large sizes. Although nickel-steel alloys cannot be used, high chromium (28 per cent) steels are used to some extent and are satisfactory from a scaling standpoint. However, such steels are probably not economically justified in view of the re-welding technique previously mentioned, or the use of a calorizing or aluminum spraying or dipping technique applied to the surface of the crucible to control scale. Such processes increase the life of a crucible to 250-300 heats, representing a three or four-fold increase in life over that obtained with ordinary steel crucibles. Crucibles vary in size from 20-2000 pounds of magnesium.

The standard crucible process makes use of No. 310 flux, which has the property of being thinly fluid at the start in order to provide protection and refining qualities. It then dries out and thickens with time, leaving a protecting crust on the pot surface until the time of casting. At that time it can be readily skimmed off or held back, thus allowing the contents of the crucible to be poured out directly into castings without fear of contamination by the flux. Number 310 flux is not self-healing in its film protection; hence it is not suitable for hand-ladling operations.

After the metal is melted (at a temperature not exceeding 700 C) the melt is stirred. This operation is performed with a one-inch iron rod bent in the form of an "ell" with the short leg in the depth of the crucible. This stirring rod is moved in the crucible in such a manner as to give a rotational motion to the melt. During the stirring operation, flux is added in sufficient quantity to form a fairly heavy coating on top of the melt. The stirring causes the flux to wet the oxide particles in the melt, thereby making them heavier and causing them to separate and sink to the bottom of the crucible. If the stirring and fluxing have been properly done, the metal surface will have a clear, silvery luster.

The fluxing technique is currently being supplanted by the use of chlorine, which is a superior means of removing non-metallic impurities. The magnesium chloride formed by the reaction of chlorine with magnesium is similar in its action to that of No. 310 flux; it is used primarily to remove dissolved hydrogen gas from molten alloys.

The crucible method is used principally: (1) in sand and permanent-mold founding as a single-step melting, refining and pouring operation, or more commonly as a second-step following the transfer to a casting crucible of molten metal from premelting units such as large open pots or tilting crucibles, (2) in batch melting, alloying and pouring of billets or ingots from which wrought products are fabricated, and (3) in the refining of die-casting scrap.

(3) Reverberatory Process^(3,18)

The reverberatory process was first thought to be unsuitable for the melting of magnesium, owing to the large surface of melt as well as to the contact between the gases and the metal or flux. Preliminary experiments showed this untrue and furnaces with a capacity of 6 to 10 tons of magnesium were operating satisfactorily in 1941.

Below the metal line these furnaces were lined with a refractory that is relatively nonreactive with the fluxes and magnesium; possibly magnesite was used. They were heated either electrically or by indirect gas firing.

In operation, the solid charge was fed mechanically into one end of the furnace onto a preheating shelf, from which it was pushed into the bath by the introduction of the next charge. Metal was dipped or pumped out of a well at the opposite end of the furnace.

Protection during melting and holding was provided by No. 230 or a similar type of open-pot flux. Consumption of flux in these units was slightly greater than in open-pot operation; however, some developments showed promise. Sulfur dioxide, at a concentration of ~ 0.5 per cent, proved a satisfactory inhibitor for surface oxidation. The melting loss closely paralleled that obtained in the more conventional methods of melting. Fuel efficiency was much better, being approximately one-half that of open-pot melting.

The outstanding feature was very high melting capacity (up to 5000 lb metal/hr). The combination of this high melting capacity and the ease and control with which magnesium alloys can be pumped to other pots or directly to molds is highly developed in the production of alloy ingots and offers great possibilities in foundry fields.

Safety of operation was another notable feature, since the charging and preheating were all automatic and splatterings could not reach the operators. Furthermore, the likelihood of a run-out was remote, because the refractory construction was cold on the outside.

The field of use was in large-scale continuous melting of magnesium or alloy ingot or heavy scrap. Such a process operated as a premelter for alloying or foundry operations. This method was considered unsuitable for the melting of fine magnesium or light scrap, because of the difficulty in applying adequate mechanical puddling and the development of the large amounts of sludge or dross that accompany the processing of these materials.

A feature of this type of melting was that alloys of controlled purity could be handled without danger of contamination by iron.

In attempting to bring this information up to date, a check of magnesium refiners^(4,8) and local furnace manufacturers^(21,22) failed to locate a single reverberatory furnace currently being used for magnesium refining.

(4) Die-Casting Process⁽¹⁸⁾

The die-casting process makes use of No. 220 flux, which gives no surface protection, but is used only for refining the metal. Surface protection in this method comes from the use of sulfur

dioxide, which is maintained in a closed dome over the pot. Only a very little flux is used as protection during melting down and this is stirred thoroughly through the metal for refining. After a few moments of quiet standing, this flux, together with agglomerated oxides and dross, sinks to the bottom of the pot and is removed with the sludge.

2. High-Temperature Processes^(2,14)

Some of the production methods for the manufacture of magnesium necessitate handling the metal at elevated temperatures. Table 5 lists the maximum temperature in representative processes. The chemical reaction in which the magnesium is formed is also listed.

Table 5

HIGH-TEMPERATURE PROCESSES

Process	Maximum Temperature (C)	Reaction
Electrothermic (Hansging)	2000	$\text{MgO} + \text{C} \rightleftharpoons \text{Mg} + \text{CO}$
Ferrosilicon ^a (Pidgeon)	1170	$2\text{MgO} \cdot \text{CaO} + \text{Si}(\text{Fe}) \rightarrow 2\text{Mg} + (2\text{CaO})\text{SiO}_2 + \text{Fe}$
Electrolytic ^b	750	$\text{MgCl}_2 \rightarrow \text{Mg} + \text{Cl}_2$

^aRetorts constructed of 35-15 and 28-12 nickel-chrome steels. Steel condensers used.

^bBoth Dow and Basic Magnesium, Inc. use this process in which the bath temperature is 750 C and steel cathodes and graphite anodes are used.

Because of the temperatures involved, the electrothermic process and an experimental sublimation process will be discussed in greater detail:

a. Electrothermic Process⁽⁵⁾

As indicated in Table 5 the electrothermic or carbothermic process depends upon the reduction of magnesium oxide by carbon:

This reaction reverses whenever the temperature of the reaction products drops below 1800 C; however, a rapid rate of reaction is not obtained below 2000 C. If reversal does occur, magnesium oxide and carbon will be deposited upon any relatively cool surface by the gaseous products of the reaction. This fact has an important influence on the design and operation of the reduction furnace.

The reaction chamber must be enclosed in a gas-tight bell lined with a suitable refractory and insulating material. As the reaction exceeds 2000 C, the number of satisfactory refractories is limited. Satisfactory refractories are graphite, carbon and magnesia.

A satisfactory lining can be made of carbon blocks insulated with lampblack. As carbon is a good electrical conductor, the electrodes must be insulated from such a lining. No ordinary insulating material is satisfactory, so there must be free space between the electrode and the lining. In practice, a rapid inflow of cold hydrogen through that space excludes the conductive vapors and prevents deposition of carbon.

The insulating problem is much simpler if the furnace is lined with magnesia. Even with such a lining, a small flow of hydrogen may be required to prevent a deposit in the space between the electrode and its port. The magnesia lining must be made of high-grade electrically fused magnesia to prevent fusion or excessive shrinkage at the operating temperature.

The inner wall of the furnace is constructed of pressed magnesia brick in special shapes. The space between this wall and the outer steel shell is packed with pulverized metal of the same composition as the shell.

b. Sublimation Vacuum Casting(5,20)

An extension to this process involves sublimation vacuum casting as developed on a pilot plant basis by the U.S. Bureau of Mines and on an experimental basis by the Dow Chemical Company in order to obtain pure magnesium for corrosion studies.

The Bureau of Mines unit consists of a two-stage continuous distillation unit. This unit occupies a space approximately 15 feet long, 4½ feet wide and 10 feet high. Both retorts are heated by electric resistance elements with automatic temperature control. All heated portions of the metal-distillation retort, flux, dust trap, condenser and cages are constructed of 24-12 chromium-nickel alloy. The oil and metal are distilled at approximately 500 C and 1000 C, respectively. The metal is condensed just above its melting point, and, as it has considerable vapor pressure at that temperature, some solid metal inevitably condenses in the upper part. The solid condensate can be melted down in one leg of the condenser, while the flow of gas is directed to the other leg.

Each distillation system is virtually gas-tight and operated at a pressure slightly above atmospheric. Thermal decomposition of hydrocarbons during both steps produces ample hydrogen to effect loss by leakage or diffusion. The excess is released through a liquid seal.

In the Dow Unit, magnesium is sublimed at 0.0005 mm Hg and condensed in a graphite-lined condenser. After sublimation is complete, the condensed magnesium is vacuum melted in situ and vacuum cast as a billet.

In this unit the condenser area can be heated above the melting point of magnesium so as to allow the melted sublimate to run into a pot at floor level. The entire melting operation is carried out under an argon atmosphere. The condenser is graphite-coated in order to prevent contact of the molten magnesium with the chrome-steel condenser shell. By coating the graphite condenser lining with acetylene black, it is possible to remove the solidified billet from the unit with very little damage to the lining. Melt-out efficiencies of 80 per cent of the charge metal are obtained using the above procedure.

Sublimation with or without filters has been shown to be an effective method of purifying magnesium, although the highest purity metal is only obtainable through the use of baffles and multiple sublimation.

3. Transfer by Pumping^(10,11)

Examination of recent developments will reveal the amazing ease of handling magnesium in the molten state. One of the most striking of these developments, and one which is having far reaching effects in the industry, is the pumping of the molten metal. Pumping is the simplest and most advantageous method of liquid transfer, and the adaptability of magnesium to the process is unique among the common structural materials.

The two properties of magnesium which contribute most to its ability to be pumped are its relatively low melting point, and its inertness to iron and steel at the operating temperatures. Pumping has made large-scale alloy production a continuous operation, has greatly increased capacity, has greatly decreased the manpower requirements, has improved working conditions, and has increased the quality of the product through good mixing of the alloying elements during the flux refining operations.

a. Centrifugal Pumps⁽¹¹⁾

When first experiments were begun at Dow about 1935 on transfer of molten metal through pipes, difficulties were expected with distortion and warpage of the steel pumps due to the effect of heat and oxide build-up on moving parts. The first attempt to provide a solution was the use of a siphon, since it involves no moving parts. It was soon found that the rate of metal flow was difficult to control and starting and stopping of the siphon were decidedly impractical. Both mechanical and displacement pumps resulted in intermittent metal flow; however, centrifugal pumps, with proper modifications, have been adopted as best fitting the needs for pumping molten magnesium.

Contrary to other applications in which efficiency is of first importance, efficiency is a minor consideration in centrifugal pumps for molten metal. The characteristics most desirable in this case are ease and simplicity of operation and cost economy. Piston pumps can be used successfully, but centrifugal pumps are easier to control, have higher capacity and require a minimum outlay of equipment. Several centrifugal pump designs are being used, depending on the specific application. Pumps constructed of cast iron or mild steel perform satisfactorily for this service when due allowance is made for the effect of operating temperature on their properties. Construction details may be obtained from the Dow Chemical Company.

b. Electromagnetic Pumps⁽¹⁰⁾

As long ago as July 6, 1938, the idea of pumping molten Dowmetal (~90 per cent magnesium) by making it a liquid conductor of an electric current in a magnetic field was conceived by F. H. Justin of The Dow Chemical Company. Such a pump would have the particular advantage of eliminating all moving parts. It could also be used as a valve to control the flow of molten Dowmetal.

The pump consists of a throat containing a liquid conductor through which current is passed. A piece of iron (the field core) placed around the conductor causes the field of the conductor to be passed through the conductor instead of around it. Due to its magnetic properties, cobalt is used as the field core for temperatures greater than 700 C. The force thereby exerted in the conductor, which is in this case the liquid magnesium, causes it to flow.

From the standpoint of materials, the most important is the use of chrome steel in the throat carrying the magnesium. Ordinary steel sheet oxidizes at 700 C and the scale flakes off on cooling. There would also be deterioration of the outside surface in contact with air. Chrome steel does not scale, nor alloy with magnesium. Its oxidation temperature is around 870 C; its magnetic properties are unknown at this temperature.

The field core surrounding the conductor is made of sheet steel lamination. Quartz is used electrically insulate the field core from the chrome steel throat. Power is supplied through a transformer, the liquid conductor being part of the circuit of the single turn secondary winding. The transformer core is separated from the secondary winding by several inches of thermal insulation to cut heat losses, thus enabling operation near room temperature. The variation of head from zero to maximum is accomplished by placing a variac on the primary side of the pumps. Efficiency is estimated at 15 to 30 per cent.

Experiments were carried out on pumps activated by two different, but similar types of, electrical systems. The first is known as the separate field pump, conceived by F. H. Justin, and the other is described as the E. T. Bainbridge circuit described in an M.I.T. master's thesis in 1926. Other electrical systems are possible.

The following experimental conclusions apply to both investigated electrical systems:

- (1) It is possible to make an electromagnetic pump to pump 60 pounds per minute of Dowmetal at a viscosity of 2 centipoises a height of 8 to 13 feet; at a viscosity of 50 centipoises, the head is reduced to 5 to 10 feet. For these experiments the temperature did not exceed 700 C.
- (2) The pressure developed is limited by the current only.
- (3) The pump or pressure unit can be used to give valve action. The full pressure of the pump is available the instant the current is turned on. The flow of metal can be regulated closely from a minute stream to the full stream available.
- (4) As a corollary, it is recommended that heating of the metal be accomplished by using the resistance of both the pipe and the molten metal as part of a separate electrical circuit.

No current reference whatever has been located concerning the use of electromagnetic pumps with magnesium.

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IV. SAFETY PRECAUTIONS IN HANDLING MAGNESIUM

The following procedures for storing, melting, machining, and handling magnesium are taken from a safety manual⁽¹⁾ written for machine shop and manufacturing operations. Consequently some of the safety rules are carried to the "nth" degree; also, a broader range of operations is covered than is contemplated for high-temperature operations. These, however, are included for the sake of completeness.

A. Engineering Control

To date the available literature regarding the industrial health aspects of magnesium seems to indicate that, if this substance is used with the generally accepted controls, it in itself should prove to be no more dangerous than other common metals.

Several potential exposures connected with foundry and fabrications operations are of importance. The major problems and control are discussed herein.

1. Foundry Operations:

During pouring operations, magnesium oxide is liberated. Controls indicated are enclosure of the pouring area and a well-ventilated area. Other precautionary measures recommend having employees stay to the lee side of fumes and wear approved respiratory protection.

Magnesium dust is generated when castings are cleaned or sandblasted as well as in such operations as grinding, sawing, filing, and buffing. These operations should be conducted in a well-ventilated enclosure.

a. Melting Magnesium

It is of prime importance to avoid oxidizing the melting magnesium and, consequently, burning. The following rules should therefore be observed:

- (1) Crucibles for preheating or superheating metal must be thoroughly cleaned and inspected for imperfections.
- (2) All scrap must be sand blasted and cleaned of all sand before processing.
- (3) Any operation which is likely to result in the accidental introduction of impurities into the melt (such as dumping in metal by inverting a container) should be avoided.

- (4) The amount of Dow 230 flux used for the purpose of avoiding oxidation or burning should not exceed 10% of the weight of the total melt.⁽⁴⁾ Pagonis⁽¹⁾ states that flux should not exceed 5 per cent of the total melt. In any case, it is important that the flux be dry, since most fluxes are hygroscopic.
- (5) Thermocouple sheaths, stirring bars, or skimmers must be heated before they are used in the melt to drive off moisture and must be thoroughly cleaned and free from dross or scale.
- (6) Gas-introduction tubes to be inserted into the melt must be clean and dry, and the gas should be flowing before the tubes are inserted.
- (7) Valves and switches for shutting off power in case of accident should be readily accessible.

The following rules (8-10) apply to furnaces operating with an air atmosphere. Under such conditions, it is important to operate as near to the melting point of magnesium as possible in order to reduce the possibility of vapor ignition. In the absence of oxygen, no such restriction would apply.

- (8) Furnaces should be provided with an outlet at the lowest level so that metal run-out cannot accumulate inside the furnace.
- (9) A receptacle must be kept clean and filled with fresh flux daily.
- (10) The furnace should be equipped with a hinged cover, because such a cover could be easily slammed shut in case a leak or "burn" develops in the furnace.
- (11) In case of accidental spilling of molten magnesium, cover it immediately with dry magnesium molding sand (see composition on page 55) to prevent metal from burning or exploding.

b. Magnesium Castings - Grinding and Buffing Operations

It is during the grinding and buffing operations that sparking may occur. Ignition sparks can be caused by accidental contact of a revolving wheel and a ferrous material; by the impact of loose flying portions of the grinding compound on the protective hoods; by the tearing of the abrasive paper backing, and flapping against metal guards or metal guides;

by undue pressure of the casting part against buffing or grinding wheels; by dressing grinding wheels while mounted on grinders, by careless grinding of tools on magnesium grinding or buffing machines, with the result that sparks set fire to wet pack dust in the lines and may cause explosions in the ducts and lines leading to dust collecting systems.

Magnesium dust is a dangerous substance. Vigilance and good housekeeping are imperative. The following precautionary rules apply:

- (1) Magnesium dust must be swept regularly and often from the floor, rafters and other locations where it might accumulate.
- (2) Dust-collecting vacuum machines attached to grinders or buffers must be built with short and straight ducts and lines.
- (3) Dust-collecting equipment, as well as the ducts and lines leading from grinders or buffers, must be cleaned, regularly and often, of wet dust pack or sludge.
- (4) Never grind or buff tools or other sparking metals on the same machines where magnesium has been used.
- (5) Never dress grinding wheels while mounted on grinders. Remove them for dressing to a separate maintenance room or other safe place.
- (6) Avoid any friction with sparking metal, as with the bandsaw, abrasive wheels, abrasive belts and buffing. Guides used on these machines must be made of wood, plastic or any other non-sparking material.
- (7) Workers doing grinding or buffing or other dust-producing operations should keep their clothing free from dust by blowing the dust off with compressed air. Personnel engaged in this type of work should wear hard-finished clothing, free of folds, pockets, and cuffs. Hats or caps should be worn to protect the hair and head. Shoes should be of the boot type.
- (8) Containers used to store the collected dry magnesium dust should be clean, dry, and free from any waste materials and should be kept covered.

- (9) Drinking water or water containers should not be permitted in the same room where magnesium dust is stored or likely to accumulate.

2. Fabrication Operations:

In the machining of magnesium alloy parts, finely divided particles may be generated where rotary files, band saws, or buffers are used. Where such operations are conducted, mechanical exhaust ventilation (with approved respiratory protection over the face) should be provided. Good housekeeping and personal hygiene should be enforced.

It might be well, however, to emphasize that, associated with foundry and fabrication operations with magnesium, there are numerous other materials used which require specific control measures. Such incidental potential exposures are toxic fumes (sulphur dioxide, fluorides, chlorides) produced as result of flux decomposition; toxic materials (fluoride or fluo-borate incorporated with sand) used in preparation of molds and cores; toxic gases and fumes (fluorides, steam, aldehydes, sulphur dioxide, hydrogen sulphide, boron) liberated at shakeout area; and sulphur dioxide in heat treatment.

a. Storage

Ingots should be placed on pallets and kept under cover (shelter). The metal must be kept dry and away from combustible materials. Water in pipes or water containers should not be present in the same room.

b. Machining Magnesium

It is difficult to ignite a cross section of magnesium during the normal process of proper machining operations, especially with the correct tools of the proper angles, correct feed, speed and clearance.

(1) Tool Angles:

Lathe Tools - Grind with 10° to 20° top rake, 10° to 15° clearance, 0 to 10° side rake.

Broad Nose Tools - Reduce the top rake to 3° to 8° to prevent clattering. For parting tools use extra large side clearances.

Drills - For holes less than 5 in. diameter, drill with 10° twist; for deep holes, 40° twist, with frequent lifting for chip removal. Lands should be extra narrow and the chip clearance extra deep.

Milling Cutters - For plain-type cutters, use coarse-tooth milling with $1/3$ to $1/2$ the number of blades customary for cutting steel. Rake should be about 10° to 15° ; on form cutters about 5° to 8° . Peripheral clearance should be about 10° , followed by 20° secondary clearance. Lands should be narrow and the chip clearance extra large. The same recommendations apply to other types of milling cutters and countersinks.

(2) Dry or Wet Machining

The question of dry or wet machining of magnesium cannot be approached by the same rules that govern the use of wet or dry vacuum dust collectors, used in the grinding and buffing operations, since these machines are supplied with special equipment for dust.

(a) Wet Machining

If wet machining is undertaken, the liquid is usually crude petroleum, which requires equipment for exhausting fumes. Water can also be used but only with an addition of soda. If other cutting oils are used, they must be absolutely acid free and must have a high flash point. Oil-water emulsions (water-soluble oils) should be avoided as they react with the fine particles and shreds and under certain conditions may form an explosive gas mixture.

Wet-Machining Recommendations

Use heavy feeds to produce thick chips.

Do not allow fine particles or shreds to accumulate on machine bed or clothing.

Keep on hand an adequate supply of G-1 powder (product of Pyrene Manufacturing Co., Newark 8, New Jersey); also chemically treated sand:

FORMULA FOR CHEMICALLY TREATED SAND FOR MAGNESIUM FIRES

Natural or synthetic foundry molding sand	100 parts
Powdered sulphur	10 parts
Boric Acid (commercial)	6 parts
Graphite (low grade)	8 parts
Diethylene Glycol	2 parts
Water	2 parts

Mix all dry ingredients first, then add glycol and water.

(b) Dry Machining

If dry machining is to be undertaken it becomes necessary to use compressed air directed at the cutting edge; this will help to dissipate the heat developed during machining operations, and it will disperse the fine shreds and particles from the tool, thereby eliminating the danger of flash. The flashpoint of fine shreds or particles is 215 F.

B. Applications to ANL Work

The following practices should be observed in handling magnesium at ANL:

- (1) Because moisture coming into contact with molten magnesium can result in serious accidents, all equipment which comes into contact with molten magnesium should be thoroughly cleaned and dried (crucibles, thermocouples, gas introduction tubes, etc.).
- (2) For large-scale operations, it is advisable that operations involving the handling of molten magnesium be conducted in rooms with concrete or dirt floors.
- (3) Workers should wear appropriate safety clothing (face shields, asbestos-type gloves, and hats).
- (4) There should be on hand adequate supplies of G-1 powder and chemically treated sand (see above for composition) in well-marked containers for extinguishing fires. Never use water to put out a magnesium fire.
- (5) Good housekeeping is essential. Magnesium powder or chips should not be allowed to accumulate.

C. Extinguishing Magnesium Fires

- (1) In case of magnesium fires, close all doors and windows immediately. Exhaust fans should be set in motion to disperse the accumulated hazardous gases.
- (2) Remove all non-burning castings or magnesium parts from the burning pile. Place (do not throw) chemically treated sand on the burning parts or castings in sufficient quantities to cover them completely (sand formula as in machining). Sand of such composition acts very rapidly and effectively in solidifying burning magnesium.

- (3) Never use water on a magnesium fire unless magnesium is first completely covered with chemically treated sand.

D. Medical Aspects

No known cases of deleterious systemic effect among the workers exposed to magnesium have been noted in the literature.

However, in addition to the usual hazards involved in the production and fabrication of commercial metals, there exists a small group of potential dangers which have been acknowledged as being peculiar to the handling of magnesium and magnesium alloy.

The most important are:

- (1) Burns - Because most of the companies are aware of the ready combustibility of magnesium, the problem of burns had been fairly well controlled or avoided.
- (2) Foreign Bodies - In the alloy and fabrication departments, magnesium alloy slivers are common. At the site of the magnesium sliver, there may be - according to the amount of surface involved - an evolution of hydrogen gas and an area of tissue reaction which may progress to local death (necrosis) of the tissue (chemical in nature). Therefore, it is important that these foreign bodies be immediately removed in which case magnesium may be said to be no more harmful than foreign bodies of other material.
- (3) Magnesium Dust - It is acknowledged by most writers that magnesium dust is definitely irritating to the mucous membrane, particularly of the nose, resulting in frequent nose bleeds. There have been remarkably few cases of dermatitis in workers employed in the handling of this metal.
- (4) Metal Fume Fever - Doctors P. Drinker and K. Lehmann have been able experimentally to induce metal fume fever with magnesium oxide (electric or acetylene welding in a confined space may generate magnesium metal fume concentration in excess of those used by Drinker and Lehmann in their study). At present, there are not data on the effects of breathing dense concentration for prolonged periods.
- (5) Complications from production and fabrication of magnesium - Hazards associated with the production and fabrication of magnesium but not directly due to magnesium

have been mentioned in the discussion of these processes. They constitute hazards from bacterial contamination of wounds from cutting oils, from the evolution of toxic fumes and dusts, and from high temperature, etc.

Medical Control - Medical vigilance of all workers.

Preplacement and periodic medical examinations complement the engineering control of the working environment. Prompt medical attention to all foreign bodies will contribute markedly to reduce man-hour loss.

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V. AVAILABILITY, GRADES, AND COST OF HIGH PURITY MAGNESIUM

The sole major producer of commercial magnesium metal in the United States is the Dow Chemical Company. Dominion Magnesium, Ltd. and Johnson, Matthey Company are two Canadian firms producing spectrographically pure (99.95 per cent) magnesium. The primary magnesium, produced by an electrolytic process, is furnished in one grade conforming to ASTM B92-52, having a minimum purity of 99.8 per cent. A typical analysis of this grade of magnesium is as follows:

Element	Per Cent
Aluminum	0.003
Copper	0.003
Iron	0.03
Manganese	0.08
Nickel	0.001
Silicon	0.005
Magnesium (by difference)	99.878

The primary magnesium is available in either pig form, sticks, turnings, or four-notched ingots. Data concerning these forms are listed in the following table:

Form	Size		Weight (pounds)	Cost (1956 data)
	Diameter (inches)	Length (inches)		
Round rods	1.3	24	2	Base price is \$0.46/lb. For lots under 100 lb add \$0.10 per pound.
	1.3	12	1	
	0.92	12	1/2	
	0.65	12	1/4	
Notched ingots (4 pc)	4 $\frac{1}{4}$ x 4 $\frac{3}{8}$ x 28 in.		20	\$0.56/lb
Turnings	0.010 x 1/8 to 3/16 x 1/2 in. (coiled)		100 or 200 lb drums	\$0.27/lb
Interlocking self-palletizing	3 $\frac{5}{8}$ x 8 $\frac{1}{4}$ x 32 $\frac{1}{2}$ in.		42	\$0.27/lb

Dow also produces very high-purity magnesium by repeated sublimations of the commercial grade. This grade is not a general production item but is usually produced in quantities suitable for fundamental research work. It is available, however, to AEC installations upon their request as a special material. A typical analysis of impurities in this material is as follows:

Element	Parts per million	Element	Parts per million
Al	1-4	Zn	2-4
Cu	1-5	Ba	1-2
Fe	4-7	Ca	10-20
Mn	2-10	K	5-20
Ni	2-4	Sr	5
Pb	5-10	Cl	2
Si	10	P	2
Sn	10	B	1

A small amount of oxygen will be present in the form of MgO film formed on the surface of the sublimed crystals upon exposure to the atmosphere.

This grade of magnesium can be supplied in the form of crystals in seventy-five-pound batches of uniform quality at a cost of \$2.00 per pound. One hundred to two hundred-pound quantities are generally on hand and orders of this magnitude can be filled within thirty days. Larger orders may require as long as three months to fill.

Recommended methods for the chemical analysis of magnesium and its alloys are to be found in the Dow Chemical Company publication, Bulletin DM 41, "Magnesium Laboratory Methods." The general limits of elements for which the methods of analysis are applicable are as follows:

Element	Per Cent	Element	Per Cent
Aluminum	0.0 to 12	Manganese	0.0 to 2
Beryllium	0.01 to 5	Nickel	0.0 to 5
Cadmium	0.0 to 5	Rare earth metals	0.02 to 10
Calcium	0.02 to 1	Silicon	0.0 to 0.8
Cerium	0.02 to 1	Tin	0.0 to 6
Copper	0.0 to 1	Zinc	0.0 to 5
Iron	Less than 0.04	Zirconium	0.01 to 5
Lead	0.0 to 0.5		

This bulletin also contains a discussion of the spectrographic methods used by the Dow Company for the analysis of magnesium and magnesium alloys for impurities and alloying constituents.

Activation analysis has been investigated as a means of determining concentrations of certain trace impurities in highly purified experimental magnesium metal.* For many elements the technique of neutron activation analysis is more sensitive than conventional methods of analysis.

*Atchison, G. J. and Beamer, W. M., "Determination of Trace Impurities in Magnesium by Activation Analysis," Anal. Chem. 24, 1812 (1952.)

VI. BINARY AND TERNARY PHASE DIAGRAMS OF MAGNESIUM

This section presents a compilation of the binary phase diagrams of magnesium, the liquidus surfaces of the ternary phase diagrams, and a description of the information available on quaternary, quinary and senary systems.

Whereas a considerable body of complete data is available for the binary systems, the available information on ternary phase diagrams is considerably less complete. The main reasons for this are the much larger number of possible systems with three components and the larger number of alloy compositions that must be investigated for the construction of a ternary phase diagram. Even the liquidus surface, which is easiest to obtain, is known completely for only a few systems. Thus for most ternary systems for which information was found, only part of the system was covered or only very sketchy data were obtained. Information on systems of more than three components is very rare indeed.

Sources

The principal sources for the phase diagrams of binary systems have been the 1948 edition of the Metals Handbook,⁽¹⁾ Hansen's compilation⁽²⁾ and Gmelin's Handbuch der anorganischen Chemie⁽³⁾ (volumes on magnesium and the platinum metals). Occasional use was made of a bibliography by Haughton^(4a) on metallurgical phase diagrams.

Ternary phase diagrams were found accessible through Gmelin⁽³⁾ (volumes on magnesium and aluminum), Hanemann and Schrader's "Ternäre Legierungen des Aluminums,"⁽⁵⁾ and Haughton's bibliography.^(4a)

The Metals Handbook covers the literature to 1947, but many systems are not included. Comments on the printed phase diagrams are scant.

Hansen's compilation covers the literature to 1936, but omits mention of systems for which no data were available. A second edition is in press and will be published shortly by an American publishing house.

The issuance of the various sections of Gmelin was interrupted towards the middle of World War II. As a result, the literature for the binary systems with Si, Sb, Bi, Li, Na, K, Rb, Cs, Be, Ca, Sr, Ba, Ra, Po, As, N, and P is covered only to 1942, and for the remaining systems to 1952. Ternary Mg-Al-X systems are covered in the volume on aluminum as follows. For X being

Sb, Si, Bi to 1936;
Zn, Cd, Ga, Ge, Pb to 1937;
Mn, Ni, Ag to 1939;
Fe to 1941.

Hanemann and Schrader's book covers the information to about 1950.

Haughton's bibliography and its supplement covers the literature to 1944. Recently a new edition under the co-authorship of Haughton and Prince has appeared, covering the literature to the end of 1954.^(4b) This edition has been the source of references for systems with more than three components.

Coverage not included in the above mentioned references was augmented by a search of Metallurgical Abstracts.⁽⁶⁾

Choice of Reference Material

In general, the most recently published phase diagrams or portions of phase diagrams were used, including solid solubility data. In some instances a choice was made on the basis of the purity of the components, preference having been given to experimental data obtained with the purest starting materials.

In the case of ternary systems modifications have sometimes been introduced into the phase diagrams when later information on the binary systems warranted this. No use was made of information concerning crystal structures, theoretical and thermodynamic relations in ternary systems, lattice parameters, metallography and mechanical properties, except when used for solubility determinations or phase identification. Russian and Japanese journals were generally not consulted directly, only through Metallurgical Abstracts.⁽⁶⁾

Construction of the Phase Diagrams

The phase diagrams were generally copied from the corresponding figures in the reference used, often without use of actual experimental data. It is a criticism of German publications that the experimental points are hardly ever shown with sufficient precision in the figures. British publications do not share this defect. The exact shape of the solidus and liquidus lines is, therefore, not necessarily accurate. Since eutectic melting points and compositions and the melting points of intermediate compounds are nearly always given separately, the accuracies of these points are determined by the accuracies of the original investigations.

In all binary phase diagrams the melting point of magnesium was taken as 649 C. The scale of reproduction of the phase diagrams permits temperatures to be read with a precision of ± 3 C and compositions with a precision of ± 0.5 weight per cent (w/o).

The solid solution phase fields have been labeled with lower case Greek letters, with that phase richest in magnesium being designated α . Succeeding solid solution phases of lower magnesium content have been designated β , γ , etc. If two such phases appear to differ only as a result

of an order-disorder transformation, the disordered (high-temperature) modification was designated by a prime (e.g., β and β'). If an intermediate compound or the terminal element undergoes a solid state transition, the high-temperature and low-temperature modifications have been labeled in the order β , γ .

This does not follow the customary practice of designating the lowest temperature modification of an element as α and successive higher temperature modifications as β , γ , etc.

Intermediate compounds and terminal phases for which no range of homogeneity is shown are designated by formulae or chemical symbols, respectively. This does not necessarily mean that a range of homogeneity for such phases does not exist; either the range of homogeneity (or solid solubility) is very small, or no data on its extent are available.

On the ternary diagrams, eutectic valleys and peritectic folds are shown as heavy solid lines with double arrows indicating the direction of the temperature gradient. The boundaries of miscibility gaps are similarly indicated. Lines indicating the composition of terminal solid solutions in equilibrium with solutions along a eutectic valley are shown as heavy lines with a single arrow pointing in the direction of the temperature gradient. Isotherms are shown by lightly drawn lines.

Tie lines are not shown since as a rule they are not given in the literature consulted.

The following symbols have been used:

E denotes a ternary eutectic point
 P denotes a ternary peritectic point
 e denotes a binary or quasi-binary eutectic point
 p denotes a binary or quasi-binary peritectic point
 K denotes a consolute point on the boundary of a liquid miscibility gap.

In the figures only the isotherms are labeled with their corresponding temperatures. Melting points of compounds, eutectic and peritectic temperatures are tabulated separately. Invariant points with unknown temperatures are not tabulated. Often, however, such temperatures can be estimated from the isotherms. Temperatures of points on the binary system are listed to ± 5 C.

All temperatures are given in degrees Centigrade, all compositions in weight per cent (w/o). The symbol a/o is used for atom per cent where required. The symbol % is used when there was uncertainty as to whether a/o or w/o was meant.

Compositions can be read to ± 0.5 w/o abs, but the lines are drawn with an accuracy of not better than ± 2 w/o abs, except at points where compositions were given separately in the literature and where reference could be made to binary systems.

End points of eutectic valleys and peritectic folds, and of isotherms, have been checked against the binary diagrams and adjusted from the originals whenever required to make binary and ternary phase diagrams mutually consistent.

It is suspected that in many instances eutectic valleys and peritectic folds are drawn by the original author(s) from a very small number of points. Similarly many isotherms are likely to be the result of conjecture and reasonable guesses. It was usually not possible, however, to recognize where this occurred and, as a result, an uncertainty is introduced as to the exact location of the projections of the above lines.

Organization of Information

The information is presented in three sections. Section B deals with binary phase diagrams, Section C with ternary phase diagrams, and Section D with multicomponent systems. Sections C and D are subdivided in Subsections 1 and 2. Sections C1 and D1 deal with those systems for which no phase diagrams were found and Sections C2 and D2 with those systems for which phase diagrams were available. Section D1, however, does not list the possible ternary systems for which no data at all could be found.

The discussion of the information is preceded by a Section 2 containing tables in which all systems considered are listed in alphabetical order of the symbol of the alloying element(s). References to the appropriate figure and literature are included in the tables. A compilation of the figures and the bibliography can be found at the end of this chapter.

A. A Tabular Survey

Table 6

BINARY SYSTEMS FOR WHICH NO PHASE
DIAGRAMS ARE AVAILABLE

Alloying Element	Literature Ref.	Remarks
Ac	3(27A-602)*	No data
Am	-	No data
As	2(185)	-
B	7, 8	-
Be	1(1177),** 3(27A-456)	-
C	2(372)	-
Cf	-	No data
Cm	-	No data
Cr	3(27A-658) 9, 10	-
Cs	3(27A-456)	No data
Dy	3(27A-602)	-
Er	3(27A-602)	-
Eu	3(27A-602)	-
Fr	-	No data
Gd	3(27A-602)	-
Hf	3(27A-613), 9	-
Ho	3(27A-602)	-
Ir	3(68A-732)	-
K	3(27A-453), 2(832)	-
Lu	3(27A-602)	-
Mo	3(27A-658), 9, 11	-
N	2(860)	-
Na	2(861), 3(27A-450)	-
Nb	3(27A-657)	-
Nd	3(27A-601)	-
Np	-	No data
Os	3(68A-720), 9	-
P	2(863)	-
Pa	3(27A-658)	No data
Pd	3(68A-581)	-
Pt	2(867), 3(68A-749), 12	-
Ra	3(27A-482)	No data
Rb	3(27A-456)	No data
Re	3(27A-759)	-
Rh	3(68A-552)	No data
Ru	3(68A-536)	-
Sc	3(27A-584)	No data
Se	2(869)	-
Si	13	-
Sm	3(27A-602)	-
Ta	3(27A-658)	-
Tb	3(27A-602)	-
Tc	3(27A-759)	No data
Te	2(874), 13	-
Tm	3(27A-602)	No data
V	3(27A-657)	No data
W	2(877), 3(27A-659), 9, 10, 11	-
Y	9	-
Yb	3(27A-602)	-

* Ref. 3, vol. 27A, p. 602

**Ref. 1, p. 1177

Table 7

BINARY SYSTEMS FOR WHICH PARTIAL OR COMPLETE
PHASE DIAGRAMS ARE AVAILABLE

Alloying Element	Figure	Literature Ref.
Ag	4	1(1150), 3(27A-724)
Al	5	14, 15
Au	6	2(233), 3(27A-754), 16
Ba	7	17, 18
Bi	8	1(1179), 3(27A-420)
Ca	9	17, 19
Cd	10	1(1188), 3(27A-532)
Ce	11	3(27A-589), 20, 21
Co	12	3(27A-691), 22
Cu	13	1(1197), 3(27A-702)
Fe	14	3(27A-695), 23, 24, 25
Ga	15	3(27A-571), 26, 27
Ge	16	3(27A-615), 28, 29
H	17	30, 31
Hg	18	2(786), 3(27A-559), 32
In	19	33, 34, 35
La	20	3(27A-584)
Li	21	36, 37
Mn	22	1(1225), 3(27A-659), 25, 38
Ni	23	1(1225)
Pb	24	1(1226), 3(27A-637), 34, 39
Pr	25	3(27A-599)
Pu	26	40, 41
Sb	27	2(869), 39
Si	28	1(1226)
Sn	29	1(1227)
Sr	30	17
Th	31	42, 43
Ti	32	44, 45
Tl	33	2(876), 46
U	34	47, 48
Zn	35	1(1227), 2(878), 3(27A-483), 49, 50
Zr	36	51, 52

Table 8

TERNARY SYSTEMS WITH INCOMPLETE DATA FOR LIQUIDUS SURFACES

Alloying Elements	Literature references	Alloying Elements	Literature references
Ag-As	3(27A-743)	Bi-Pb	60
Ag-Bi	53	C-Fe	85
Ag-Cd	3(27A-746), 54(78)	C-Ni	86
Ag-Cu	3(27A-753)	Ca-Si	54(p 89)
Ag-Li	3(27A-743)	Cd-Li	3(27A-555)
Ag-Sb	3(27A-743), 55	Ce-Zn	87
Ag-Sn	3(27A-751), 56	Cr-Li	3(27A-658)
Ag-Tl	3(27A-748), 54(79)	Cr-Zn	3(27A-658)
Ag-Zn	3(27A-745), 54(79), 57	Cu-Sn	3(27A-722)
Al-Be	3(35A-678), 58, 59	H-Zn	30
Al-Ca	60	In-Sn	84
Al-Ce	61	Li-Mn	3(27A-672)
Al-Co	62, 63	Li-Mo	3(27A-658)
Al-Cr	64, 65, 66, 67	Li-Pb	88
Al-Fe	3(36A-1175), 68, 69, 70, 71	Li-U	3(27A-659)
Al-Ge	72	Li-W	3(27A-659)
Al-H	30	Li-Zn	89
Al-La	73	Mn-Zn	3(27A-673)
Al-Li	74, 75	Mn-Zr	3(27A-679)
Al-Mn	3(36A-929), 68, 71, 72, 76, 77, 78, 79, 80, 81	Na-Pb	3(27A-654)
Al-Ni	3(36A-1001), 82	Ni-Zn	90
Al-Pb	3(36A-863), 5(p 122), 72, 79, 83	Ni-Sb	91
Al-Sn	60, 72, 84	Ni-Sn	91
As-Cu	3(27A-716)	Pb-Sb	3(27A-653)
Be-Cu	3(27A-718)	Pu-U	92
Be-Ni	3(27A-689)	Sb-Zn	93
Bi-Cd	3(27A-555)	Th-Zn	3(27A-614)
Bi-Cu	53, 54(p 89)	Th-Zr	94

Table 9

TERNARY SYSTEMS FOR WHICH PARTIAL OR COMPLETE
LIQUIDUS SURFACES ARE KNOWN

Alloying Elements	Figure	Literature references
Ag-Al	37	3(35A-1079), 95, 96, 97, 98
Al-Bi	38	99, 100
Al-Cd	39	101, 102, 103, 104
Al-Cu	40	5(73), 105 thru 114
Al-Sb	41	3(35A-665)
Al-Si	42	1(1246), 3(35A-667), 115
Al-Tl	43	116
Al-Zn	44	1(1247), 117 thru 126
Bi-Ca	45	127
Bi-Zn	46	3(27A-524), 54(89)
Ca-Zn	47	3(27A-527), 54(89), 128
Cd-Pb	48	3(27A-655), 54(91)
Cd-Tl	49	3(27A-582)
Cd-Zn	50	3(27A-555)
Cu-Ni	51	3(27A-722), 129, 130
Cu-Sb	52	3(27A-716), 5(125), 131(491)
Cu-Si	53	3(27A-714)
Cu-Zn	54	3(27A-719), 129, 132
Fe-Mn	55	3(27A-701), 23, 25
Fe-Si	56	85
Hg-Mn	57	3(27A-676)
Pb-Sn	58	3(27A-657), 54(95), 131(458), 133
Si-Zn	59	3(27A-520), 54(97)
Sn-Zn	60	3(27A-635), 54(97), 134
Th-U	61	48
Tl-Zn	62	3(27A-581), 54(98), 135

Table 10

MULTICOMPONENT SYSTEMS FOR WHICH PHASE
INFORMATION HAS BEEN FOUND

Alloying Elements	Literature References
Al-Cr-Zn	136
Al-Cu-Fe	137
Al-Cu-Mn	137
Al-Cu-Ni	138
Al-Cu-Si	137, 139, 140, 141, 142, 143
Al-Cu-Zn	144, 145
Al-Mn-Fe	137
Al-Fe-Si	137, 146, 147, 148
Al-Mn-Si	137, 149, 150, 151
Al-Mn-Zn	152, 153, 154, 155
Al-Si-Zn	150, 151
C-Fe-Ni	85
C-Fe-Si	85
Cr-Pu-U	92
Cu-Ni-Zn	156
Al-Cu-Fe-Mn	137
Al-Cu-Mn-Si	137
Al-Cu-Fe-Si	137
Al-Fe-Mn-Si	137
Al-Cu-Fe-Mn-Si	137
Pu-U-Fission Products	157

B. Binary Systems

1. Systems for Which No Phase Diagrams Are Available.

Mg-As

Only the non-metallic compound, Mg_2As_2 , is known.⁽²⁾

Mg-B

The compound MgB_2 is known.⁽⁷⁾ There is evidence for the existence of a second compound, MgB_4 .⁽⁸⁾

Mg-Be

Attempts to prepare Mg-Be alloys have failed. The solubility in magnesium is at most 0.05 w/o beryllium; there is no agreement regarding the exact value.^(1,3)

Mg-C

Two non-metallic compounds, Mg_2C_3 and MgC_3 , are known.⁽²⁾

Mg-Cr

Magnesium and chromium do not appear to form alloys.⁽⁹⁾ The solubility of chromium in magnesium has been given as 0.008 w/o at 734 C.⁽¹⁰⁾ Gmelin, however, lists a reference in which supposedly Mg-Cr alloys were obtained by reduction of Cr_2O_3 by magnesium, with the possible existence of the compounds MgCr , Mg_3Cr_2 , Mg_3Cr , and Mg_4Cr . It is not impossible, however, that mixed oxides were obtained.

Mg-Dy

In view of the miscibility of magnesium with La, Ce, Pr, Nd, and Gd, it is likely that liquid miscibility also exists between magnesium and the remaining rare earths. Some caution should be exercised, however, in view of the fact that hafnium and zirconium appear to differ widely in their behavior toward magnesium.

Mg-Er

See Mg-Dy.

Mg-En

See Mg-Dy.

Mg-Gd

Alloys containing up to 10.5 w/o gadolinium or 10.8 w/o neodymium have been made.

Mg-Hf.

Hafnium does not alloy with magnesium.

Mg-Ho

See Mg-Dy.

Mg-Ir

Certain patents suggest the existence of alloys of magnesium with Ir, Pd, and Ru. These may, however, be very intimate mixtures of magnesium and these elements.

Mg-K

The Mg-K and Mg-Na systems form two almost completely immiscible liquids in the molten state. The mutual liquid and solid solubility of potassium and magnesium is very small. According to Mathewson (cf 2-861), magnesium and sodium form a monotectic at 638 C and 2 w/o sodium and sodium dissolves about 1.5 w/o magnesium at this temperature. The phase diagrams for the Mg-K and Mg-Na systems are not shown in the next section, because the numerical data are in doubt. The work was carried out in glass equipment which was heavily attacked by the melts.

Mg-Lu

See Mg-Dy.

Mg-Mo

The resistance of certain metals to attack by liquid magnesium has been discussed in the Liquid Metals Handbook⁽¹⁾ and in ANL-4417.⁽¹⁰⁾ Beryllium has good to limited resistance to attack by magnesium at 800 C. Titanium has good resistance to attack by magnesium up to 750 C and limited resistance at 850 C. Tantalum is attacked only intergranularly at 1170 C but may be suitable at lower temperatures.

Brewer⁽¹¹⁾ suggests that the following metals (in order of decreasing preference) would contain liquid magnesium: Fe, Co, Cr, Nb, W, Ta, Mo, Re. His suggestion is partially based on theoretical considerations, primarily the differences between the melting points of these elements and of magnesium. Such reasoning is not necessarily correct. Thus, cobalt is known to form alloys with magnesium. More experimental data on the behavior of the above-mentioned metals with magnesium are required before any conclusion can be drawn regarding their suitability as container materials under specified conditions.

Mg-N

Only the non-metallic compound, Mg_3N_2 , is known.⁽²⁾

Mg-Na

See Mg-K.

Mg-Nb

See Mg-Mo.

Mg-Nd

See Mg-Gd.

Mg-Os

Osmium alloys readily with magnesium and forms a eutectic.^(3,9)

Mg-P

Only the non-metallic compound, Mg_3P_2 , is known.

Mg-Pd

See Mg-Ir.

Mg-Pt

Alloys are known to be formed with platinum. Platinum is heavily attacked by magnesium vapor. An unproven claim has been made regarding the existence of Mg_2Pt .⁽²⁾

Mg-Re

See Mg-Mo.

Mg-Ru

See Mg-Tr.

Mg-Se

The non-metallic compound, MgSe, is known.⁽²⁾

Mg-Si

Busk has found no change in the axial ratio and unit cell dimensions of "alloys" of Mg with Si, Te, and W and has concluded that the solid solubility of these elements in Mg is vanishingly small.⁽¹³⁾

Mg-Sm

See Mg-Dy.

Mg-Ta

See Mg-Mo.

Mg-Tb

See Mg-Dy.

Mg-Te

The non-metallic compound, MgTe, is known.⁽²⁾ See also Mg-Si.

Mg-W

See Mg-Mo and Mg-Si.

Mg-Y

Yttrium and magnesium alloy readily. Alloys with 3 w/o yttrium have been made.⁽⁹⁾

2. Systems for Which Partial or Complete Phase Diagrams are Available

Mg-Ag

Most phase boundaries are experimentally well defined. Numerical data are presented fully in the Gmelin reference.⁽³⁾

Mg-Al

In the system Mg-Al the solid phase relations between 42 and 67 w/o aluminum are not entirely clear yet. Eickhoff and Vosskühler⁽¹⁴⁾ have given a critical evaluation of the entire phase diagram.

Recent work by Clark and Rhines⁽¹⁵⁾ has shown Eickhoff and Vosskühler's evaluation to be essentially correct in the solid region between 45 and 70 w/o aluminum, with the exception that the γ phase decomposes eutectoidally somewhere below 335 C. The eutectoid horizontal is drawn arbitrarily at 250 C.

Mg-Au

The solid solubility of gold in magnesium is of the order of 0.8 w/o at the eutectic temperature (576 C).⁽¹⁶⁾

Mg-Ba

Earlier results by Grube and Dietrich⁽¹⁸⁾ do not agree with those by Klemm and Kinkelacker⁽¹⁷⁾ for compositions containing more than 25 w/o barium; there is no obvious reason for the discrepancy. Grube and Dietrich's results have been drawn in as a broken line between 25 and 77 w/o barium. It is more than likely, however, that Klemm and Dinkelacker's diagram is correct. The existence of a low-melting eutectic on the barium-rich side has been confirmed in this laboratory.

Mg-Bi

No remarks.

Mg-Ca

Burke⁽¹⁹⁾ has redetermined the solid solubility of Ca in Mg, and finds, e.g., at 516 C 0.93 w/o and a negligible solubility at 300 C.

Mg-Cd

Stepanov and Kornilov (cited in Gmelin⁽³⁾) found liquidus and solidus curves touching at the composition MgCd and assumed the existence of this compound. In some instances the nature of the phases involved in the solid state reactions is not accurately known.

Mg-Ce

The Ce-rich portion (more than 60 w/o cerium) is from Vogel and Heumann;⁽⁹⁾ see also Gmelin. The solidly drawn liquidus for compositions containing less than 60 w/o cerium is according to Weibke and Schmidt (cited in Gmelin⁽³⁾). The broken liquidus is drawn according to Haughton and Schofield.⁽²¹⁾ Vogel and Heumann used 99.7 per cent pure cerium; Haughton and Schofield used 97.7 per cent pure cerium.

The phase designated as γ is a high-temperature modification of cerium.

Mg-Co

Only the Mg-rich portion with less than about 3.5 w/o (8.1 a/o cobalt) may be considered as reasonably well established.⁽²²⁾ Halts in the thermal analysis curves of alloys containing between 3.5 and 6 w/o (8.1 - 13.4 a/o) cobalt have not been interpreted with certainty, but suggest a peritectic involving the compound Mg_2Co . Similarly the interpretation of the photomicrographs is incomplete.

The solid solubility of Co in Mg is extremely small.

Mg-Cu

No remarks.

Mg-Fe

No remarks.

Mg-Ge

No remarks.

Mg-Ga

No remarks.

Mg-H

Sauerwald⁽³⁰⁾ determined the solubility of hydrogen in magnesium at 760 C to be 41 cc of hydrogen per 100 grams of magnesium. Ellinger and co-workers⁽³¹⁾ have determined the decomposition pressures of MgH_2 between 350 C and 475 C.

Mg-Hg

Brauer and Rudolph⁽³²⁾ claim to have identified the compounds Mg_3Hg , Mg_5Hg_2 (?), Mg_2Hg , Mg_5Hg_3 , MgHg , and MgHg_2 . Mg_5Hg_3 was included in the phase diagram shown in Gmelin, but is omitted in Figure 18 (taken from Hansen⁽¹²⁾). It is felt that the portion between 75 and 85 w/o Hg needs confirmation. A metastable eutectic point may exist at 435 C ($\text{Mg-Mg}_3\text{Hg}$) and 508 C ($\text{MgHg-Mg}_2\text{Hg}$).

Mg-In

The composition of any intermetallic compounds is in doubt. Using X-ray methods Hancke⁽³⁵⁾ claims to have identified Mg_5In_2 , Mg_2In , and either MgIn_2 or MgIn_3 . The peritectic point in the phase diagram lies at a lower composition than required by Mg_5In_2 . According to Raynor,⁽³⁴⁾ the β phase does not correspond with Mg_5In_2 either. The γ phase may be Mg_2In , but contains slightly more indium than the stoichiometric amount. The remaining two compounds were not identified. An alloy containing 98.44 w/o indium melted at 175-180 C, consistent with a steady fall of the solidus curve to the melting point of indium (155.4 C) and suggesting that the β phase extends to 100% In.

Between 300 C and 350 C (depending upon composition) and compositions above 60 w/o indium, the β phase undergoes an order-disorder transformation, which involves a change in crystal structure between 72 and 85 w/o (36 and 50 a/o) indium.

Mg-La

The Mg-rich portion of the Mg-La system needs further confirmation. The solid line is according to Weibke and Schmidt (Gmelin⁽³⁾), the broken line according to Canneri (Gmelin⁽³⁾). The phase boundary is still in doubt.

Mg-Li

Boundaries of the α phase are from reference 37; the remainder is from reference 36.

Mg-Mn

The liquidus shown in Figure 22 is that given in reference 1. Other investigators (e.g., Siebel⁽²⁵⁾) find a linear increase in the solubility of manganese between 2 w/o (649.5) and 7.8 w/o (950 C) manganese.

Schneider and Stobbe-Scholder⁽³⁸⁾ have redetermined the liquidus at 700, 750, 800, and 900 C by a study of the reaction

They found solubilities of Mn in Mg somewhat less than those shown in reference 1 (1225) and given in Figure 22.

Temperature (C)	700	750	800	900
Solubility (w/o Mn)	2.6	3.5	4.4	5.9

The peritectic was found to be at 653.5 instead of at 651.2 C.

Mg-Ni

No remarks.

Mg-Pb

No remarks.

Mg-Pr

The praseodymium-rich side (more than 65 w/o praseodymium) of the Mg-Pr system needs reinvestigation in the light of the different and apparently well-established phase relations in the Mg-La and Mg-Ce systems, which suggest the possible existence of the compound Mg_2Pr . The vertical line, presumably representing a phase called (MgPr_4) , may correspond to the $\epsilon + x/x$ boundary of the Mg-La and Mg-Ce systems. The confusion, perhaps, may have arisen as a result of an expanded x-field with a very narrow two phase $x\text{-Pr} + \beta\text{-Pr}$ region.

Mg-Pu

Coffinberry and Ellinger⁽⁴¹⁾ have found two intermetallic compounds, Pu_2Mg and PuMg_2 . The composition of the latter, however, is considered questionable.

Mg-Sb

The exact homogeneity range of Mg_3Sb_2 is not known. For solid solubility data, see W.R.D. Jones and L. Powell.⁽³⁹⁾

Mg-Si

No remarks.

Mg-Sn

No remarks.

Mg-Sr

The phase designated as Mg_4Sr may contain more magnesium than indicated by the stoichiometric composition based on Mg_4Sr .⁽¹⁷⁾

Mg-Th

The phase diagram shown in Figure 31 has been taken from reference 42. During final editing of this chapter, reference 43 was revised; a revised phase diagram for the region 0-75 w/o magnesium was constructed. The α phase boundaries were determined more accurately. The eutectic was placed at 582 C and 42 w/o Th. The first intermediate phase was inferred to be Mg_5Th rather than Mg_3Th , Mg_5Th melting incongruently at 772 C. The peritectic lies at ~ 53 w/o Th. It cannot be inferred with certainty that the Mg_3Th phase does not exist, since the data from reference 43 are insufficient in the region above 50 w/o thorium.

Mg-Ti

According to Aust and Pidgeon the solubility of Ti in Mg is 0.0025 w/o at 650 C and 0.015 w/o at 850 C. Frederickson⁽⁴⁵⁾ finds a solubility of 0.003 w/o at 650 C and 0.064 w/o at 760 C. The solubility is affected by the presence of hydrogen. If all hydrogen is removed from the melt, 0.115 w/o Ti dissolves in Mg at 800 C. Of the remainder of the phase diagrams, only the effect of up to 1.8 w/o Mg on the solid state transition in Ti has been investigated.⁽⁴⁵⁾

Mg-Tl

Boundaries of the α phase are from reference 46; the remainder is from 3-876.

Mg-U

The solubility of uranium in magnesium as shown in reference 17 has been revised recently.⁽⁴⁸⁾ These new data have been incorporated in Figure 34.

The solubility of Mg in U is 0.004 w/o at 1150 C and 3 atm.

Mg-Zn

The region between 50 and 54 w/o zinc is not reliably established. Recent work by Clark and Rhines⁽⁴⁹⁾ give credence to the existence:

- (1) of a simple eutectic at about 52 w/o zinc.
- (2) of an intermediate phase of composition Mg_7Zn_3 stable over only a very short temperature interval. Mg_7Zn_3 decomposes at the lower temperature eutectoidally into solid solution and MgZn, and at the higher temperature peritectoidally into L and MgZn.

Adenstadt and Burns⁽⁵⁰⁾ have determined the solidus on the Mg-side of the diagram by dilatometry. According to this work the solidus is convex rather than concave as shown in Figure 35:

Composition (w/o Zn)	4.5	6	6.3
Solidus Temp. (C)	545	475	465

Mg-Zr

The work of Schaum and Burnett⁽⁵¹⁾ appears to be the most reliable. The solubility of zirconium in magnesium just below the melting point has been determined by Sauerwald⁽⁵²⁾ as 4-4.5 w/o Zr.

C. Ternary Systems1. Systems with Incomplete Data for Liquidus Surfaces.Mg-Ag-As

The compound MgAgAs is known.

Mg-Ag-Bi

A ternary compound MgAgBi does not exist.

Mg-Ag-Cd

Mg and $AgCd_3$ form a complete series of solid solutions.

Mg-Ag-Cu

The sections Mg_3Ag - $MgCu_2$ and $MgCu_2$ - Ag are possibly quasi-binary. The phase boundaries at room temperature have been determined. The solid solubility of Ag in $MgCu_2$ is very small.

Mg-Ag-Li

Isothermal sections through the Mg-corner have been constructed for 421, 321, and 205 C. The behavior of the solid solubilities in the binary systems by ternary additions is discussed.

Mg-Ag-Sb

The ternary compound MgAgSb is known. Isothermal sections have been determined at 550 and 450 C.

Mg-Ag-Sn

Isothermal sections are shown at 550 and 450 C for compositions with 0.47 w/o Mg (80 a/o) and 0-32 w/o Sn (30 a/o). The 550 C section shows the line of intersection with the liquidus surface to run from 23 w/o Sn (22 a/o), 0 w/o Mg to 29.5 w/o Mg (65 a/o), 0 w/o Sn.

Mg-Ag-Tl

A eutectic valley originates at 469 C in the Mg-Ag system and drops to 432 C at 30 w/o Tl. The solubility of Ag in Mg at 380 C is decreased by the addition of Tl.

Mg-Ag-Zn

Liquidus and solidus curves of the section MgZn_2 - ($\text{Mg/Ag} = 1/2$) with 40-100 w/o MgZn_2 have been determined. The section appears to be quasi-binary.

Isothermal sections through the Ag-corner have been determined at 650, 450 and 250 C for compositions with up to 45% Mg. The 650C isotherm lies considerably above the $\text{L} + \beta \rightleftharpoons \text{Mg}_3\text{Ag}$ peritectic in the Mg-Ag system, but the solute rich boundary of the ternary phase in equilibrium with the melt has not been investigated.

Mg-Al-Be

No compounds have been found in the Al-corner. Pereslegin⁽⁵⁸⁾ has made alloys containing 0.1 - 0.5% Be, but these alloys were non-uniform. There is probably a ternary eutectic near the Al-Mg side at 449 C, with 34.45 w/o Mg, 65.50 w/o Al, ~ 0.04 w/o Be.⁽⁵⁹⁾

Mg-Al-Ca

The section Mg-Al₂Ca is quasi-binary with a eutectic at 535 C.

Mg-Al-Ce

Investigation of the triangle Al₃Mg₄-Mg-Mg₉Ce. The section Mg-Al₂Ce is quasi-binary. A ternary compound (m.p. ~ 1465 C) exists. Ternary eutectics exist at 435 C, 561 C, and 588 C. Ternary peritectic points exist at ~ 575 C and 625 C. The solid solubility of Al and Ce in Mg has been determined at 580, 500, 420 and 25 C.

Mg-Al-Co

The solubility of Co_2Al_9 in liquid Mg is 0.24% at 840 C and 0.021% at 650 C. Reference 63 shows projected surfaces of primary separation at co-concentrations up to 4 w/o and isothermal section at 400 C.

Mg-Al-Cr

There exists a ternary solid species, T, of about 17 w/o Cr, 9 w/o Mg, 74 w/o Al. A ternary eutectic at 447.4 C with 31.1 w/o Mg, 1.7 w/o Cr, 67.2 w/o Al involves the reaction:

Two ternary peritectics have been found:

P_1 at 632.7 C with 12.8 w/o Mg, 1.7 w/o Cr, 85.5 w/o Al
and P_2 with 12.6 w/o Mg, 2.3 w/o Cr, 85.1 w/o Al.⁽⁶⁴⁾

The ternary compound is designated as $\text{Mg}_{1.5}\text{Al}_{12}\text{Cr}$.⁽⁶⁶⁾ Reference 65 shows the liquidus surface in the Al-corner (0-5 w/o Cr, 0.35 w/o Mg) and an isothermal section at 400 C (0-25 w/o Cr, 0.35 w/o Mg). The solid solubility of Cr in Al is reduced by the addition of Mg.⁽⁶⁴⁾ Little and co-workers⁽⁶⁷⁾ have determined the 460 C isothermal in the range 0-20 w/o Mg, 0-10 w/o Cr.

Mg-Al-Fe

Hanemann and Schrader⁽⁶⁸⁾ who investigated the Al-corner (0-40% Fe, 0-35% Mg) report a ternary eutectic at 68% Al, 3% Fe, 29% Mg at 445 C, and no sign of a peritectic reaction despite the fact that Al_3Fe decomposes peritectically. Barnick and Hanemann⁽⁶⁹⁾ report that the Al- FeAl_3 eutectic valley runs almost parallel to the Mg-Al face. According to Phillips,⁽⁷⁰⁾ however, who investigated the Al- FeAl_3 eutectic valley up to 30 per cent Mg, the ternary eutectic contains less than 0.5 per cent Fe and melts at 451 C. Reference 70 also shows the liquidus and solidus surfaces and the surface of secondary separation in the Al-corner (0-2% Fe, 0-5.0% Mg). The addition of Al decreases the solubility of Fe in Mg.⁽⁶⁸⁾

Mg-Al-Ge

The solid solubility of Mg_2Ge in Al has been determined.⁽⁷²⁾

Mg-Al-H

Sauerwald found the solubility of hydrogen in two magnesium-aluminum alloys at 760 C to be:⁽³⁰⁾

37 ml H_2 /100 g metal in Mg-9 w/o Al

22 ml H_2 /100 g metal in Mg-35.7 w/o Al

A solid Mg-8.5 w/o Al alloy may dissolve between 21.8 and 30.4 ml H_2 /100 g metal.

Mg-Al-La

Al does not change the solubility of La in Mg appreciably.

Mg-Al-Li

MgAl_2Li exists with a small range of homogeneity. MgAlLi_2 is a non-equilibrium structure at all temperatures studied. Isothermal sections are shown at 400, 300, 200, 100 C and at 375, 200, 100 C.⁽⁷⁵⁾

Mg-Al-Mn

A eutectic valley runs from the Mg-Mn eutectic (or peritectic: see Figure 22 and page 74 of this report) through a ternary eutectic at 437 C with 71.25 per cent Al, 26.40 per cent Mg, 2.35 per cent Mn ($\text{L} \rightleftharpoons \text{Al}_4\text{Mn} + \text{Al}_3\text{Mg}_2 + \text{Al}$) which may be metastable.^(69,72,78) A further metastable system involving a peritectic reaction is postulated.⁽⁷⁸⁾ Note that a peritectic point exists in the binary Mg-Mn system at about 2.1 w/o Mn. Isothermal sections through the Al-corner at 630,⁽⁷⁹⁾ and at 495 and 400 C.⁽⁸¹⁾

Phase fields and solidus isothermals are shown in references 79 (Al-corner) and 80 (Mg-corner).

A ternary compound (Mg , $\text{Mn}_3\text{Al}_{10}$, or nearly $\text{Mg}_2\text{MnAl}_{10}$ appears to exist.⁽⁸¹⁾ Al decreases the solubility of Mn in Mg. Further solubility data are in reference 77.

Mg-Al-Ni

Boundaries of primary crystallization of Al, between Al_3Ni and Al_2Ni phases and between Al_2Ni and AlNi have been determined. According to Chao⁽⁸²⁾ there is a ternary eutectic at 449 C at 32 w/o Mg, 1.7 w/o Ni, 66.3 w/o Al.

Mg-Al-Pb

The liquid miscibility gap in the Pb-Al system is closed by addition of about 28 per cent Mg. At low Mg-concentrations and at 725 C the distribution ratio for Mg is about 1.0 (concentrations in w/o). The section Al_2Mg_3 - Mg_2Pb is pseudo-binary, with a eutectic at 439 C and about 45 per cent Al_2Mg_3 . In the triangle Mg- Al_2Mg_3 - Mg_2Pb there is a ternary eutectic at 405 C with 50 per cent Mg, 16 per cent Al, 34 per cent Pb ($\text{L} \rightleftharpoons \text{Mg}$ (solid solution) + Mg_3Al_2 + Mg_2Pb).⁽⁷⁹⁾ Westlinning and Klemm have determined the solid solubility of Mg_2Pb in Al.⁽⁷²⁾ There is another ternary eutectic close to the Mg_2Pb -Pb eutectic at 252.3 C and a composition of 2.5 w/o Mg, 0.5 w/o Al, 97 w/o Pb.⁽⁵⁾

Mg-Al-Sn

The solid solubility of Mg_2Sn in Al is small. Mg_3Al_2 - Mg_2Sn is quasi-binary with a simple eutectic at 455 C and 4-6 w/o Mg_2Sn .⁽⁶⁰⁾

Mg-Be-Cu

Isothermal sections through the Cu-corner (0-2.8 w/o Mg, 0-2.5 w/o Be) have been determined at 800, 725, 650, 500, and 250 C. In the Mg-corner the addition of Cu increases the solubility of Be in liquid Mg:

w/o Cu	1.5	3.5	5.0	10.0
w/o Be	<0.15	0.20	0.40	1.40

The solid solubility of Be in Mg also increases with increasing Cu-content.

Mg-As-Cu

The ternary compound MgCuAs is known.

Mg-Be-Ni

Solubility of Be in Mg-Ni melts:

w/o Ni	1.5	3.5	5.0	10.0
w/o Be	0.40	1.20	1.50	2.20

The solid solubility of Be also increases with increasing Ni content.

Mg-Bi-Cd

The field of primary crystallization of Mg_3Bi_2 extends far into the diagram.

Mg-Bi-Cu

A ternary compound MgBiCu exists. There is also a ternary peritectic point.

Mg-C-Fe

C appears to increase the solubility of Mg in Fe.

Mg-Bi-Pb

The section Mg_3Bi_2 - Mg_2Pb is quasi-binary with a eutectic close to Mg_2Pb , and a peritectic somewhere between 60-100 per cent Mg_3Bi_2 .

Mg-C-Ni

The Ni-corner has been investigated up to 15 w/o Mg and 8 w/o C. A ternary carbide with a wide range of homogeneity was found. The eutectic valleys were determined. A possible ternary eutectic was not found.

Mg-Ca-Si

An alloy with 13.8 per cent and 2.0 per cent Si contains Mg_2Si and the Mg- Mg_2Ca eutectic.

Mg-Cd-Li

Solid solubility data of Cd in β Mg-Li are given.

Mg-Ce-Zn

The liquidus surface in the Mg-corner is given. A ternary eutectic point exists at 341-343 C, at 50 per cent Mg, 47.5 per cent Zn, 2.5 per cent Ce. Ce reduces the solid solubility of Zn in Mg.

Mg-Cr-Li

Cr is almost insoluble in β Mg-Li.

Mg-Cr-Zn

A ternary eutectic exists at 369.25 C with 3.12 w/o Mg, 0.02 w/o Cr, 96.86 w/o Zn.

Mg-Cu-Sn

The section Cu-Mg₂Sn, which is quasi-binary, contains a eutectic at about 22 w/o Mg₂Sn and 690 C. Between the eutectic and the Mg₂Sn axis there exists a ternary compound of unknown composition.

Mg-H-Zn

A Mg-57 w/o Zn alloy will dissolve 8.7 ml H₂/100 g metal.⁽³⁰⁾

Mg-In-Sn

Mg₂Sn forms little or no ternary solid solution with In.

Mg-Li-Mn

Mn is almost insoluble in β Mg-Li.

Mg-Li-Mo

Mo is almost insoluble in β Mg-Li.

Mg-Li-Pb

The mutual solid solubility of Li₄Pb and Mg₂Pb has been determined.

Mg-Li-U

U is almost insoluble in β Mg-Li.

Mg-Li-W

W is almost insoluble in β Mg-Li.

Mg-Li-Zn

Isothermal sections have been determined at temperatures between 400 and 100 C. A ternary intermediate phase exists. MgLi₂Zn was found only as a non-equilibrium structure. A peritectic point exists at 317 C.

Mg-Mn-Zn

A ternary eutectic was found at 369.25 C with 3.20 w/o Mg, 0.07 w/o Mn, 96.73 w/o Zn. The solubility of Mn in melts of 94 w/o Mg - 6 w/o Zn is

at 800 C: 3.0 w/o Mn
at 720 C: 1.7 w/o Mn.

Mg-Mn-Zr

When excess Mn is added to a Mg-Zr melt with about 0.6 w/o Zr, 0.17 w/o Zr is left in the melt and 1.44 w/o Mn goes into solution.

Mg-Na-Pb

The compound $\text{Mg}_4\text{Pb}_3\text{Na}_4$ melts congruently at 600.7 C, MgNaPb melts incongruently.

Mg-Ni-Zn

The section MgNi_2 - MgZn_2 is quasi-binary with a peritectic at about 37 w/o MgZn_2 and 992 C, and a second peritectic at about 95 w/o MgZn_2 at 688 C. A ternary eutectic exists at 751 with a composition probably near 58 w/o Zn, 35 w/o Ni, 7 w/o Mg. Another ternary eutectic has been found in the triangle Mg - MgNi_2 - MgZn_2 .

Mg-Ni-Sb

MgSbNi_2 may be a ternary solid rather than a compound.

Mg-Ni-Sn

MgSnNi_2 may be a ternary solid solution rather than a compound.

Mg-Pb-Sb

The triangle Pb - Mg_3Sb_2 - Sb has been investigated. The section Pb - Mg_3Sb_2 is quasi-binary, with a eutectic at 248 C, the same temperature as the Pb - Sb eutectic. There is also a ternary eutectic at 248 at a composition of about 88.5 w/o Pb , 2.5 w/o Mg , and 9 w/o Sb .

Mg-Pu-U

The distribution of plutonium between magnesium and uranium at 1190 C has been investigated by Feder and co-workers.⁽⁹²⁾ The molar distribution ratio $(N_{\text{Pu}})_{\text{Mg}}/(N_{\text{Pu}})_{\text{U}}$, is 0.20 at a Pu/U ratio of about 0.01.

Mg-Sb-Zn

A ternary eutectic was found at 369.75 C with 3.12 w/o Mg , 0.02 w/o Sb , 96.86 w/o Zn .

Mg-Th-Zn

Some information about the magnesium-rich corner has recently been published.⁽⁹⁴⁾ Liquidus isothermals are shown in the region containing 0 - ~70 w/o Zn, 0-50 w/o Th. No eutectic valleys or peritectic folds are drawn. Also given in Ref. 94 are the solidus surface, terminal solid solubilities between 250 and 350 C, and isothermal sections at 300 and 400 C. There is evidence of a ternary phase.

Mg-Th-Zr

Additions of up to 1 w/o Zr reduce the thorium content of the Mg-Th eutectic. A tentative vertical section at 1 w/o Zr is shown.

There are no ternary intermediate phases. The peritectic reaction $L + Zr \rightleftharpoons Mg(Zr)$ of the Mg-Zr system moves toward the eutectic $L \rightleftharpoons Mg$ Mg_5Th in the Mg-Th system. The ternary invariant reaction is probably eutectic.

2. Systems with Partial or Complete Liquidus Surfaces

Mg-Ag-Al

Mg-Ag - See Figure 4.

Mg-Al - See Figure 5.

Ag-Al - See Ref. 2, p. 1.

Figure 4 is taken from Haughton.⁽⁹⁶⁾ The temperature of the ternary eutectic (403 C) agrees with that found by Nishimura and Sawamoto.⁽⁹⁵⁾ The composition is 28.2 w/o Mg, 52.8 w/o Ag, 19 w/o Al. Kuznetsov and coworkers^(97,98) agreed with Haughton, except that an additional solid phase formed by a peritectic reaction originating from the Mg_3Ag peritectic was found. The temperature of the ternary peritectic point is given as 501 C. The section Mg_3Ag - Mg_4Al_3 is probably quasi-binary. Surfaces of secondary separation, solidus surfaces, solid solubility curves and various vertical sections are given in Ref. 96, isothermal sections at 405, 380, 300, 200 C in Ref. 98.

Mg-Al-Bi

Mg-Al - See Figure 5.

Mg-Bi - See Figure 8.

Al-Bi - See Ref. 2, p. 85.

The composition of the ternary eutectic is 88 w/o Mg, 10 w/o Al, 2 w/o Bi.

Mg-Al-Cd

Mg-Al - See Figure 5.

Mg-Cd - See Figure 10.

Al-Cd - See Ref. 2, p. 90.

The diagram shown is basically according to Riederer.⁽¹⁰²⁾ Jänecke's diagram⁽¹⁰³⁾ shows a consolute point at 510 C, but the limits of the miscibility gap in the Al-Cd system do not agree with those shown in Hansen.⁽²⁾ It is also unlikely that the eutectic valley e_1 - E_1 extends all the way across to the Al-Cd side, since the solubility of Al in molten Cd is almost nil. Mikheeva and co-workers⁽¹⁰⁴⁾ determined the ternary eutectic E_1 to be at 396 C with a composition of about 54 w/o Mg, 32 w/o Cd, 14 w/o Al and claim the existence of two ternary peritectics, interpreted here as the points P_1 and P_2 .

Riederer⁽¹⁰²⁾ has determined the 230 C isothermal section and Mikheeva⁽¹⁰⁴⁾ also determined solid phase boundaries.

Mg-Al-Cu

Mg-Al - See Figure 5.

Mg-Cu - See Figure 13.

Al-Cu - See Ref. 2, p. 98.

The Al-corner of this system has been the subject of many investigations. Only one or two investigators have extended their work into the Mg-corner.

There are still a number of points which need elucidation. There is no doubt about the relations around the point E_1 , although small variations in its composition and temperature have been reported.^(5,112,113) The point E_2 has been reported as a eutectic (445 C),⁽¹⁰⁵⁾ and as a peritectic (451 C).⁽⁵⁾ Around P_1 and P_2 there is some confusion which originates in Mirgalovskaya's phase Q.⁽¹⁰⁵⁾ This phase has not been reported by others. As a result P_1 and P_2 are usually reported as a single peritectic point with composition somewhere between P_1 and P_2 . P_3 has been reported by Urazov and Petrov⁽¹¹²⁾ and by Mirgalovskaya.⁽¹⁰⁵⁾ E_3 is reported by Mirgalovskaya.⁽¹⁰⁵⁾

The relations around E_4 suffer from the same uncertainty as those around P_1 , viz. the existence of Q and hence the line P_4 - P_2 . The relations shown are according to Mirgalovskaya.⁽¹⁰⁵⁾ Hanemann⁽¹⁰⁸⁾ reports only E_4 , but a peritectic must be present, either as P_5 to connect with P_3 or as P_4 to connect with E_3 in which case E_4 connects with P_3 .

Mg-Al-Cu (Cont'd.)

The ternary phases have most likely the following compositions:

The composition of S appears to be well established. In general, however, the ranges of homogeneity are rather large and the phases have been reported with different compositions by different authors.^(106-109,111,114)

Isothermal sections have been determined by Kuznetsov and Guseva⁽¹⁰⁷⁾ (445, 400, 300, 200 C, 0-50 w/o Cu, 0-50 w/o Mg), phase fields by Guerther and Rassmann⁽¹¹⁰⁾ (room temperature after slow cooling) and Brommelle and Phillips,⁽¹¹³⁾ (just below the liquidus surface).

Isotherms have been drawn in figures by Brommelle and Phillips⁽¹¹³⁾ and by Mirgalovskaya.⁽¹⁰⁵⁾ They have not been reproduced here because of their limited extent in relation to the section drawn in Figure 40.

Mg-Al-Sb

Mg-Al - See Figure 5.

Mg-Sb - See Figure 27.

Al-Sb - See Ref. 2, p. 144.

The following sections are quasi-binary: Mg_3Sb_2 -AlSb; Mg_3Sb_2 -Al (eutectic at 658 C); Mg_3Sb_2 - Al_3Mg_2 ; Mg_3Sb_2 - Al_3Mg_4 . There are two ternary eutectics E_1 with 0.35 w/o Mg, 1.7 w/o Sb, 98 w/o Al and E_2 with 34.5 w/o Mg, 0.1 w/o Sb, 63.4 w/o Al.

There is still some doubt regarding the exact boundaries of the miscibility gap.

The solid solubility of Mg_3Sb_2 in Al is very low.

Mg-Al-Si

Mg-Al - See Figure 5.

Mg-Si - See Figure 28.

Al-Si - See Ref. 2, p. 149.

Mg-Al-Si (Cont'd.)

The sections Al-Mg₂Si, Al₃Mg₂-Mg₂Si and Al₂Mg₃-Mg₂Si are quasi-binary. E₄ has the composition 5 w/o Mg, 80.5 w/o Al, 14.5 w/o Si, E₃ the composition 34 w/o Mg, 64.5 w/o Al, 1.5 w/o Si. Ref. 1 shows the solvus surface in the Al-corner, Ref. 115 gives extensive data on the solid solubility of Mg₂Se in Al.

Mg-Al-Tl

Mg-Al - See Figure 5

Mg-Tl - See Figure 33

Al-Tl - See Ref. 2, p. 160

The section Mg₅Tl₂-Al₃Mg₄ (or Al₂Mg₃ ?) is quasi-binary.

Mg-Al-Zn

Mg-Al - See Figure 5.

Mg-Zn - See Figure 35.

Al-Zn - See Ref. 2, p. 162

The sections Al-MgZn and Mg₃Al₂-MgZn are quasi-binary. The diagram is taken from Ref. 1. Hamasumi⁽¹²²⁾ also shows a complete diagram. Butchers and Hume-Rothery⁽¹²⁰⁾ determined liquidus isothermals in the Al-corner. Isothermal sections have been determined as follows:

330, 295, 260 C near the Al-Zn side by Köster⁽¹²¹⁾

440, 200 C near the Al-Zn side (0-40 w/o Mg, (-100 w/o Zn) by Fink and Willey.⁽¹¹⁹⁾

The ternary phase has a widely varying composition. It has been referred to as Mg₃Al₂Zn₃.⁽¹¹⁸⁾ According to Mikheeva and Kryokova⁽¹²⁴⁾ a ternary phase Mg₄Al₃Zn₃ is stable at room temperature but changes into Mg₃Al₂Zn₃ just below the solidus temperature.

Sergeev⁽¹²⁵⁾ has determined the limits of the Mg-rich solid solutions and Siebel the solid solubility of Mg₂Zn in Al. Mikheeva⁽¹²⁶⁾ has published a survey of previous work and of her own research up to 1956.

Mg-Bi-Ca

Mg-Bi - See Figure 8.

Mg-Ca - See Figure 9.

Bi-Ca - See Ref. 2, p. 293.

The sections Mg₂Ca-Bi₂Ca₃, Mg-Bi₂Ca₃, Mg-Mg₂CaBi₂, Bi-Mg₂CaBi₂, Mg₃Bi₂-Bi₂Ca₃, are quasi-binary. The ternary eutectics are all close to the binary eutectics in the binary systems.

Mg-Bi-Zn

Mg-Bi - See Figure 8.

Mg-Zn - See Figure 35.

Bi-Zn - See Ref. 2, p. 348

Mg-Bi-Zn (Cont'd.)

The line U_1-U_2 indicates the alpha-beta transformation of Mg_3Bi_2 (designated as $\beta-\gamma$ in Figure 46). The location of the consolute point K is not exactly known.

Mg-Ca-Zn

Mg-Ca - See Figure 9.

Mg-Zn - See Figure 35.

Ca-Zn - See Ref. 2, p. 412.

The sections T-Mg; T- Mg_2Ca ; T- Mg_2Zn_2 ; T- $CaZn_4$; T- Ca_2Zn_3 ; $Mg_2Ca-Ca_3Zn_2$; $Mg_2Ca-Ca_5An_2$; $MgZn_2-CaZn_4$; $MgZn_2-CaZn_{10}$ and $MgZn_5-CaZn_{10}$ where T is the ternary compound $Mg_5Zn_5Ca_2$, are quasi-binary. There may be some doubt about the nature and composition of e_1 and e_4 . A similar situation as in the Mg-Zn system appears to prevail in Ca-Zn system. E_2 may have to be resolved in a ternary eutectic and a ternary peritectic point (see Figure 60).

Mg-Cd-Pb

Mg-Cd - See Figure 10

Mg-Pb - See Figure 24.

Cd-Pb - See Ref. 2, p. 439.

Because the Mg-Cd phase diagram (Figure 10) is shown without peritectic points, the ternary diagram shown in Gmelin has been reproduced without the peritectic folds originating from the Mg-Cd side. However, the isotherms reproduced here show a reversal of their curvature on either side of a composition corresponding to Mg_2Cd . This would indicate the existence of a peritectic fold with a transition to a eutectic valley originating at Mg_2Cd , or what is not unlikely either, the original author did a considerable amount of guess work in determining the curvature and location of the isotherms between end points.

Mg-Cd-Tl

Mg-Cd - See Figure 10

Mg-Tl - See Figure 33.

Cd-Tl - See Ref. 2, p. 460.

The point p, originating at the Mg-Cd side and corresponding to $MgCd_2$, is in doubt (cf. Mg-Cd).

Mg-Cd-Zn

Mg-Cd - See Figure 10

Mg-Zn - See Figure 35.

Cd-Zn - See Ref. 2, p. 462.

The diagram is reproduced in accordance with Figure 10. The situation around e_1 is uncertain (cf. Figure 35).

Mg-Cu-Ni

Mg-Cu - See Figure 13
 Mg-Ni - See Figure 23.
 Cu-Ni - See Ref. 2, p. 585.

There appears to be no ternary eutectic. The section $\text{MgNi}_2\text{-MgCu}_2$ is quasi-binary, showing complete solid solubility and a possible quasi-binary peritectic point 930 C and about 54 w/o MgCu_2 . The solid solubility of Cu and Ni in Mg is very small.

Mg-Cu-Sb

Mg-Cu - See Figure 13
 Mg-Sb - See Figure 27.
 Cu-Sb - See Ref. 2, p. 614.

The quasi-binary sections have been drawn in this diagram in order to show the extent of the investigation. It appears that only isolated points of the eutectic valleys have been determined, and straight lines drawn. According to the diagram reproduced by Gmelin several quasi-binary eutectics do not lie in the ternary eutectic valleys. This has been disregarded in Figure 52. From the data and the three known binary phase diagrams Jänecke⁽¹³¹⁾ has tried to complete the liquidus surface. The result is open to some question, however. The quasi-binary section $\text{SbCu}_2\text{-MgCuSb}$ may contain a peritectic point.

Mg-Cu-Si

Mg-Cu - See Figure 13
 Mg-Si - See Figure 28.
 Cu-Si - See Ref. 2, p. 621.

Two intermetallic compounds have been identified: $\text{Mg}_2\text{Cu}_3\text{Si}$ and $\text{Mg}_6\text{Cu}_{16}\text{Si}_7$, the latter in particular having a very narrow homogeneity range. The sections $\text{Mg}_2\text{Cu-Mg}_2\text{Si}$, $\text{Mg}_2\text{Cu}_3\text{Si-Mg}_2\text{Cu}$, $\text{Mg}_2\text{Cu}_3\text{Si-MgCu}_2$, $\text{Mg}_2\text{Cu}_3\text{Si-Cu}_3\text{Si}$ and $\text{Mg}_2\text{Cu}_3\text{Si-Si}$ are quasi-binary. In Gmelin the section $\text{MgCu}_2\text{-MgSi}_2$ (0-70 mol per cent) is reproduced and appears to be quasi-binary. MgSi_2 does not exist as an independent compound, however.

Mg-Cu-Zn

Mg-Cu - See Figure 13.
 Mg-Zn - See Figure 35.
 Cu-Zn - See Ref. 2, p. 652.

The sections $\text{MgCu}_2\text{-MgZn}_2$ and Mg (39 w/o Cu, 61 w/o Zn) are quasi-binary. The liquidus lines of these two sections must intersect at an invariant point. The temperature of this point is a maximum on both liquidus lines. On the $\text{MgCu}_2\text{-MgZn}_2$ section there is a peritectic point at 716 C and about 77 w/o MgZn_2 (about 16 w/o Mg - 43 w/o Zn - 41 w/o Cu). The composition of E_2 is given as 6 w/o Mg, 45 w/o Cu, 49 w/o Zn.

Mg-Fe-Mn

Mg-Fe - See Figure 14.

Mg-Mn - See Figure 22.

Fe-Mn - See Ref. 2, p. 676.

The curves show the solubility of Fe in molten Mg with various additions of Mn. The curves for 0, 1.2, and 2.2 w/o Mn are according to Siebel,⁽²⁵⁾ the curves for 1 and 2 w/o Mn according to Fahrenhorst and Bulian.⁽²³⁾

Mg-Fe-Si

Mg-Fe - See Figure 14.

Mg-Si - See Figure 28.

Fe-Si - See Ref. 2, p. 732.

The temperature at the ternary eutectic point is not exactly known, but is probably about 940-950 C. The temperature of the ternary peritectic is about 1000 C, the peritectic fold starting close to Mg_2Si . The temperature of E is not exactly known. The construction of the portion Mg-FeSi-Fe is mainly guesswork. The homogeneity range of FeSi extends deep into the ternary system.

Mg-Hg-Mn

Mg-Hg - See Figure 18.

Mg-Mn - See Figure 22.

Hg-Mg - See Ref. 2, p. 789.

There is a ternary eutectic at about 445 C between Mn, Mg, Hg and Mg-rich α -solid solution. Note that the triangle which is reproduced in Figure 57 extends only to 20 w/o Hg and 20 w/o Mn.

Mg-Pb-Sn

Mg-Pb - See Figure 24.

Mg-Sn - See Figure 29.

Pb-Sn - See Ref. 2, p. 992.

Figure 58 is reproduced from Gmelin; von Vegesack⁽¹³³⁾ shows a perspective drawing of the entire diagram. Jänecke⁽¹³¹⁾ shows a diagram supposedly obtained from Vegesack's work, but claims a ternary eutectic, rather than peritectic at P, and a quasi-binary eutectic at p. According to Jänecke, there is likely to be a ternary eutectic near the Pb-Sn side (166 C, about 58 w/o Sn, 11 w/o Mg, 31 w/o Pb) and another ternary eutectic in the Pb-corner (about 4 w/o Sn, 8 w/o Mg, 88 w/o Pb). The section Mg_2Pb - Mg_2Sn and probably also Pb- Mg_2Sn are quasi-binary.

Mg-Si-Zn

Mg-Si - See Figure 28.

Mg-Zn - See Figure 35.

Si-Zn - See Ref. 2, p. 992.

The sections $\text{Mg}_2\text{Si-MgZn}_2$ and $\text{Mg}_2\text{Si-Zn}$ are quasi-binary. The exact nature of the points e_2 and E is uncertain.

Mg-Sn-Zn

Mg-Sn - See Figure 29.

Mg-Zn - See Figure 35.

Sn-Zn - See Ref. 2, p. 1080.

The sections $\text{Mg}_2\text{Sn-MgZn}_2$ and $\text{Mg}_2\text{Sn-Zn}$ are quasi-binary. According to Gmelin the entire diagram has been worked out by Otani⁽¹³⁴⁾ but the original was not available. Although there is still some doubt about the nature of the liquidus curve in the Mg-Zn system around 55 w/o Zn, the relations as reproduced in Figure 27 are likely to be closer to reality than a binary eutectic and a ternary eutectic alone.

Mg-Th-U

Mg-Th - See Figure 31.

Mg-U - See Figure 34.

Th-U - See Ref. 42, p. 56.

Chiotti and Shoemaker⁽⁴⁸⁾ have recently determined the solubility of uranium in the Mg-Th eutectic alloy (35 w/o Th) and Mg-16 w/o Th alloy.

Mg-Tl-Zn

Mg-Tl - See Figure 33.

Mg-Zn - See Figure 35.

Tl-Zn - See Ref. 2, p. 1087.

The section $\text{Mg}_5\text{Tl}_2\text{-MgZn}_2$ is quasi-binary with just a eutectic.

4. Magnesium Alloys with More than Three Components

Most investigations of systems containing magnesium and three or more elements have been limited to those alloys which are based on aluminum. Often only the solid phase relations have been determined, since the driving force for the work was usually the study and explanation of the hardening characteristics of commercial aluminum alloys.

Mg-Al-Cr-Zn with 0.20 w/o Mg, 0-10 w/o Cr, and 0-10 w/o Zn. Isothermal sections at 400 C have been determined and a section with 8 w/o Zn is shown.⁽¹³⁶⁾

Mg-Al-Cu-Fe - No quaternary phases have been found. Phragmén⁽¹³⁷⁾ gives a table of liquid state equilibria and their relationships. Corresponding compositions are shown in an $\text{Al}_2\text{Cu}-\beta \text{AlMg}-\text{Al}_3\text{Fe}$ triangle.

Mg-Al-Cu-Mn - One unstable quaternary phase of unknown composition has been found. Phragmén⁽¹³⁷⁾ gives a table of liquid state equilibria and their relationships. Corresponding compositions are shown in an $\text{Al}_2\text{Cu}-\beta \text{AlMg}-\text{Al}_3\text{Mn}$ triangle.

Mg-Al-Cu-Ni with 1 w/o Mg, 0-2 w/o Ni and 0-6 w/o Cu. Isothermal sections at 500 and 200 C have been determined.⁽¹³⁸⁾ In this particular investigation, the author dealt in reality with the quinary Mg-Al-Cu-Ni-Si system because of the appreciable Si impurity of the Al.

Mg-Al-Cu-Si - There is a quaternary phase $\text{Al}_5\text{Cu}_2\text{Mg}_8\text{Si}_6$.⁽¹³⁷⁾ Phragmén gives a table of liquid state equilibria and a corresponding composition triangle $\text{Al}_2\text{Cu}-\beta \text{AlMg}-\text{Si}$. Crowther⁽¹³⁹⁾ found two and possibly four quaternary eutectics melting at 447 and 510-520 C. In this paper, sections with 4 w/o Mg, 4 w/o Ti, 4 w/o Cu and with 2 w/o Mg, 2 w/o Si, 4 w/o Cu are shown. Axon⁽¹⁴⁰⁾ determined isothermal sections at 400 C with 0-7 w/o Mg, 0-7 w/o Cu and with 0.6 w/o Si, 1.2 w/o Si and 2.0 w/o Si. Dix and co-workers⁽¹⁴¹⁾ determined liquidus and solidus surfaces of the section Al-Cu-MgSi₂ with 0-6 w/o Cu and 1.3 w/o Mg₂Si. Gayler⁽¹⁴²⁾ shows isothermal sections at 400 and 200 C of Al-Cu-Mg-MgSi₂. Sections with 92 w/o Al, 96 w/o Al and 98 w/o Al and a table with equilibrium relations are given by Schrader⁽¹⁴³⁾ who confirmed Crowther's quaternary eutectics.⁽¹³⁹⁾

Mg-Al-Cu-Zn with 0-30 w/o Mg, 0-8 w/o Zn and 0-55 w/o Cu. Isothermal sections at 460 C with 4 w/o Zn, 6 w/o Zn, 8 w/o Zn and 6.5 w/o Cu are shown.⁽¹⁴⁴⁾ A perspective sketch shows the disposition of the single phase regions in the quaternary model.⁽¹⁴⁴⁾ In another investigation a series of solid solutions between MgZn_2 and the composition MgCuAl has been found.⁽¹⁴⁵⁾

Mg-Al-Mn-Fe - There are no quaternary phases. Phragmén gives a table of liquid state equilibria and their relationships. Compositions are shown in a $\text{Mg}-\beta \text{AlMg}-\text{Al}_3\text{Fe}$ triangle.

Mg-Al-Fe-Si - Phillips⁽¹⁴⁶⁾ has investigated the range 0-14 w/o Si, 0-12 w/o Mg and 0-2.5 w/o Fe rather exhaustively as regards to both liquid and solid phase relations. Phragmén⁽¹³⁷⁾ found one quaternary phase $\text{Al}_8\text{Mg}_3\text{FeSi}_6$ and gives a table with liquid state equilibria. Compositions are shown in a $\text{Si}-\beta \text{AlMg}-\text{Al}_3\text{Fe}$ triangle. Schrader⁽¹⁴⁷⁾ shows a cut through 93 w/o Al at 500 C and also gives a table of reactions. There are three quaternary eutectics in the Al-corner, one at 558 C.

There is a region of solid solutions in the quasi-ternary section Al-Fe-Mg₂Si according to 450 C and room temperature sections.⁽¹⁴⁸⁾

Mg-Al-Mn-Si - There are no quaternary phases. Phragmén⁽¹³⁷⁾ gives a table of liquid state equilibria. Compositions are shown in a Si- β AlMg-Al₃Mn triangle. Jan and co-workers⁽¹⁴⁹⁾ determined the 500 C isothermal for the range 0-12 w/o Mg, 0-9 w/o Mn, 0-16 w/o Si and found a peritectic 5-phase equilibrium at 586 C and a quaternary eutectic at 558 C. There may be one more eutectic near the ternary $\alpha + \beta + \text{Mg}_2\text{Si}$ and $\alpha + \beta + \text{Al}_6\text{Mn}$ eutectics. Axon and co-workers^(150,151) determined the solidus for the range 0-7 w/o Mg, 1 w/o Si, with 1 w/o Mn and 2 w/o Mn.

Mg-Al-Mn-Zn - Butchers and co-workers⁽¹⁵²⁾ gave equations for the α -liquidus (Al-corner) and the MnAl₆ liquidus for the range 0-5 w/o Mg, 0-2 w/o Mn, 0-9 w/o Zn. Raynor and Hume-Rothery⁽¹⁵³⁾ determined the composition of the MnAl₆ phase in the same range. Little and co-workers⁽¹⁵⁴⁾ determined the 500 and 400 C isothermals in the same range. Butchers and Hume-Rothery⁽¹⁵⁵⁾ determined the solidus in the same range.

Mg-C-Fe-Ni - A section (15 w/o Mg, 85 w/o Ni) - 95.7 w/o Fe, 4.3 w/o C) has been determined. The following phases appear: Mg₂Ni, MgNi₂, Fe-Ni solid solution, solid solutions of a Mg-C-Ni ternary carbide, graphite and Fe₃C.⁽⁸⁵⁾

Mg-C-Fe-Si - No ternary Mg-C-Si carbide is formed as in Mg-C-Fe-Ni (see below). As a result the Mg losses during melting were high and no satisfactory alloys were obtained.⁽⁸⁵⁾

Mg-Cr-Pu-U - The distribution of 1-2 w/o Pu between Mg and α w/o Cr - 95.5 w/o W was found to be 0.38 at 930 C and 0.19 at 1190 C by Feder and co-workers.⁽⁹²⁾

Mg-Cu-Ni-Zn - Doering found a series of solid solutions between MgCu₂ and the composition MgNiZn.⁽¹⁴⁵⁾ Lieser and Witte determined some characteristics of the quasi-ternary system MgNi₂-MgCu₂-MgZn₂.⁽¹⁵⁶⁾

Concerning quinary and senary systems, with one exception, only the work of Phragmén is relevant.⁽¹³⁷⁾ Phragmén's paper shows sectional composition diagrams, and tables of equilibria of the following systems:

Mg-Al-Cu-Mn-Fe
Mg-Al-Cu-Mn-Si
Mg-Al-Cu-Fe-Si
Mg-Al-Fe-Mn-Si
Mg-Al-Cu-Fe-Mn-Si

No new phases were found in these systems. The solid solubilities of three of four elements in Al is little or not affected by the fifth element.

The system Mg-Al-Mn-Si-An has been given some attention by Axon and co-workers^(150,151) who determined the 460 C isothermal and the solidus for the range 0-6 w/o Mg, 0-8 w/o Zn, 0-4 w/o Mn, 1 w/o Si.

Mg-Pu-U-Fission Products - A formally more complicated system which has received attention recently is the system Mg-Pu-U-Fission Products.⁽¹⁵⁷⁾ The distribution of Pu and several fission products in the concentration range 0-100 ppm between a liquid Mg and a liquid U phase at 1150 C has been measured. The following data have been published for the distribution ratios:

$$K = \frac{\text{Concentration of element in Mg-phase}}{\text{Concentration of element in U-phase}}$$

For Pu, $K_{Pu} = 0.23 \pm 0.04$ in the range 0.03-97 ppm. For fission products the following distribution ratios have been found:

Total f p conc. (ppm)	0.03	0.3	23	74	97
f p					
Ce	2.5	3.2	1.4	1.6	2.0
Total Rare Earths	0.46	0.23	0.55	0.97	2.3
Cs	0.019	0.034	0.73	1.3	2.4
Sr	0.029	0.048	0.51	0.76	1.5
Te	1.2	3.2	1.0	2.0	1.6
Ru	0.0011	0.006	0.005	0.004	0.011

The scatter in these data suggest that at this time the numbers given are only orders of magnitude.

FIGURE 4
MAGNESIUM-SILVER

(Data from Metals Handbook, A S M, Cleveland, 1948
and Gmelin's Handbuch der anorganische Chemie, 8th Ed, 1952)

FIGURE 5
MAGNESIUM-ALUMINUM

(Data from Eichoff, K, and Vosskuhler, H, Z Metallkunde, 44, 223 (1953) and
Clark, J B, and Rhines, FN, J Metals, 9, January, 1957)

FIGURE 6
MAGNESIUM - GOLD

(Data from Hansen, M., "Aufbau der Zweistofflegierungen," Springer Berlin, 1936 and Gmelin's Handbuch der anorganische Chemie, 8th Ed., 1952; also Hume-Rothery, W. and Butchers, E., J. Inst. Met., 60, 349 (1937))

FIGURE 7
MAGNESIUM - BARIUM

(Data from Klemm, W. and Dinkelacher, F., Z. anorg. Chem., 255, 2 (1947); Grube, G., and Dietrich, A., Z. Elektrochem 44, 755 (1938))

FIGURE 8
MAGNESIUM-BISMUTH

Data from Metals Handbook, A S M, Cleveland, 1948, p. 1148;
Gmelin's Handbuch der anorganische Chemie, 8th Ed., 1942, p. 27A-420)

FIGURE 9
MAGNESIUM-CALCIUM

(Data from Klemm, W. and Dinkelacker, F., Z anorganische Chemie, 255, 2 (1947);
Burke, E C, Trans. Am Inst Min Met Eng, 203, 285 (1955))

FIGURE 10
MAGNESIUM - CADMIUM

(Data from Metals Handbook, A S M, Cleveland, 1948, p 1188,
Gmelin's Handbuch der anorganische Chemie, 8th Ed, 1942, p 27A-532)

FIGURE 11
MAGNESIUM - CERIUM

(Data from Gmelin's Handbuch der anorganische Chemie, 8th Ed, 1942, p 27A-589,
Vogel, R, and Heumann, F, Metallforschung, 2, 1 (1947), Haughton, J L, and
Schofield, T H, J Inst Met, 60, 339 (1937))

FIGURE 12
MAGNESIUM - COBALT

(Data from Gmelin's Handbuch der anorganische Chemie, 8th Ed., 1942, p 27A-69I, Cramer, E M Nielsen, H P and Schonfeld, F W, Light Metal Age, 5, 6 (September, 1947))

FIGURE 13
MAGNESIUM - COPPER

(Data from Metals Handbook, A S M, Cleveland, 1948, p 1197; Gmelin's Handbuch der anorganische Chemie, 8th Ed., 1942, p 27A-702)

FIGURE 14
MAGNESIUM-IRON

(Data from Gmelin's Handbuch der anorganische Chemie, 8th Ed., 1942, p 27A-695, Bulian, W, and Fahrenhorst, E, Z Metallkunde 33, 31 (1941), Mitchell, D W, AIME Inst Met Div, Met, Techn, 15, No 1, Tech Pub No 2309, Siebel, G, Z Metallkunde, 39, 22 (1948))

FIGURE 15
MAGNESIUM-GALLIUM

(Data from Gmelin's Handbuch der anorganische Chemie 8th Ed, 1942 p 27A-571; Pusin, N A, and Micic, O D, Z anorg Chem, 234, 299 (1937), Hume-Rothery, W, and Raynor, G V, J Inst Met, 63, 201 (1938))

FIGURE 16

MAGNESIUM - GERMANIUM

(Gmelin's Handbuch der anorganische Chemie, 8th Ed., 1942, p. 27A-615,
Klemm, W., and Westlinning, H., Z. anorg. Chem., 245, 365 (1941); Raynor,
G. V., J. Inst. Met., 66, 413 (1940))

FIGURE 17

DISSOCIATION PRESSURE AND DISSOCIATION CONSTANT OF MAGNESIUM HYDRIDE (MgH₂)

(Data from Sauerwald, F., Z. anorg. Chem., 258, 27 (1949);
Ellinger, F.H., Holley, C.E., McInteer, B.B., Pavone, D.,
Potter, R.M., Staritzky, E., and Zachariasen, W.H., J. Am. Chem. Soc.,
77, 2647 (1955))

FIGURE 18
MAGNESIUM-MERCURY

(Data from Hansen, *Aufbau der Zweistofflegierung*, Edwards Bros, Ann Arbor, 1943, P 786, Gmelin's *Handbuch der anorganische Chemie*, 8th Ed, 1942, 27A-599; Brauer, G., and Rudolph, R, *Z anorg. Chem.*, **9**, 308 (1942))

FIGURE 19
MAGNESIUM-INDIUM

(Data from Hume-Rothery, W., and Raynor, G.V., *J. Inst. Met.*, **63**, 214 (1938); Raynor, G.V., *Trans Faraday Soc.*, **44**, 15 (1948); Hancke, W., *Naturwiss.*, **26**, 577 (1938))

FIGURE 20
MAGNESIUM-LANTHANUM
(Gmelin's Handbuch der anorganische Chemie, 8th Ed, 1942, p 27A - 584)

FIGURE 21
MAGNESIUM-LITHIUM
(Data from Freeth, W E, and Rayner, G V, J Inst Met, 82, 575 (1954),
Hume - Rothery, W, Raynor, G V and Butchers, E, J Inst Met, 71, 589 (1956))

FIGURE 22
MAGNESIUM - MANGANESE

(Data from Metals Handbook, ASM, Cleveland, 1948, p.1225;
Gmelin's Handbuch der anorganische Chemie, 8th Ed., 1942,
p. 27A - 659; Siebel, G., Z. Metallkunde, 39, 22 (1948);
Schneider, A., and Stobbe - Schelder, H., Metall. 4, 178 (1950))

FIGURE 23
MAGNESIUM - NICKEL

(Data from Metals Handbook, ASM,
Cleveland, 1948, p. 1225)

FIGURE 24
MAGNESIUM-LEAD

(Data from Metals Handbook, ASM, Cleveland, 1948, p 1226, Gmelin's Handbuch der anorganische Chemie, 8th Ed, 1942, p 27A-637, Raynor, G V, Trans Faraday Soc, 44, 15 (1948), Jones, WRD, and Powell, L, J Inst Met, 57, 177 (1941))

FIGURE 25
MAGNESIUM-PRASEODYMIUM

(Data from Gmelin's Handbuch der anorganische Chemie, 8th Ed, 1942, P 27A-599)

FIGURE 26
MAGNESIUM-PLUTONIUM

(Data from Schonfeld, F.W., "Phase Diagrams Studied at Los Alamos," Paper presented at 2nd World Metallurgical Congress, Chicago, Ill., Nov. 2-8, 1957, Coffinberry, A.S., and Ellinger, F.H., Proc. Int. Conf. Peaceful Uses Atomic Energy, Geneva, 1955, Vol. 9, paper 826, p.138, New York, 1956).

FIGURE 27

MAGNESIUM - ANTIMONY

(Data from Hansen, M., Aufbau der Zweistofflegierungen, Edwards Bros., Ann Arbor, 1943, p 869, Jones, W.R.D., and Powell, L., J. Inst. Met., 57, 177 (1941))

FIGURE 28
MAGNESIUM - SILICON

(Data from Metals Handbook, ASM, Cleveland, 1948, p1226)

FIGURE 29
MAGNESIUM - TIN

(Data from Metals Handbook, ASM, Cleveland, 1948, p 1227)

FIGURE 30
MAGNESIUM-STRONTIUM
(Data from Klemm, W, and Dinkelacker, F, Z anorganische Chemie, 255,2 (1947))

FIGURE 31
MAGNESIUM-THORIUM
(Data from Saller, H A and Rough, F A, Compilation of U S and U K Uranium and Thorium Constitutional Diagrams, BMI-1000, p III, Yomamoto, A S, Klimek, E J, and Rostoker, W, WADC-56411, February, 1957)

FIGURE 32
MAGNESIUM-TITANIUM
Data from Aust, K T, and Pidgeon, L M, J Met, 1, Trans,
P 585 (1949), Fredrickson, W, J Met, 7, 368 (1955))

FIGURE 33
MAGNESIUM-THALLIUM
(Data from Hansen, M, Aufbau der Zweistofflegierungen, Ann Arbor, 1943, P876,
Hume-Rothery, W, and Raynor, G V, J Inst Metals, 63, 219 (1938))

FIGURE 34
MAGNESIUM-URANIUM

(Data from Saller, H A and Rough, F A , *op cit* ,
BMI-1000, p 39, Chiotti, P, and Shoemaker, H E ,
Ind Eng Chem 50, 137-140 (1958)

FIGURE 35
MAGNESIUM - ZINC

(Data from Metals Handbook, ASM, Cleveland, 1948, p 1227, Hansen, M , *Aufbau der Zweistofflegierungen*, Edwards Bros, Ann Arbor, 1943, p 878; Gmelin's *Handbuch der anorganische Chemie*, 8th Ed, 1942, p 27A-483, Clark, J B , and Rhines, F N ,
J Metals, 9, 425 (1957), Adenstadt, H and Burns, J R ,
Trans Am Soc Met , 43, 873 (1951))

FIGURE 36
MAGNESIUM-ZIRCONIUM
(Data from Schaum, J B, and Burnett, H C, J Res
Nat Bur Stand, 49, 155 (1952); Sauerwald, F,
Z anorg Chem, 255, 212 (1947))

FIGURE 59

MAGNESIUM-SILICON-ZINC

(Data from Gmelins Handbuch der anorganischen Chemie, 8th ed., 1942, p. 27A-520, Beck, A., The Technology of Magnesium and Its Alloys, P.A. Hughes & Co., Ltd., London, 1943, p. 97)

Mg	650°C	e ₁	637°C
Si	1410	e ₂	-345
Zn	419	E	335
Mg ₂ Si	1100		
MgZn ₂	590

FIGURE 60

MAGNESIUM-TIN-ZINC

(Data from Gmelins Handbuch der anorganischen Chemie, 8th ed., 1942, p. 27A-635; Beck, A., The Technology of Magnesium and Its Alloys, P.A. Hughes & Co., Ltd., London, 1943, p. 97; Otani, B., Tetra to Hagane (Japan), 19, 556 (1939))

Mg	650°C	e ₁	560°C
Sn	232	e ₂ , P	-345
Zn	419	E	340
Mg ₂ Sn	750	P	351

FIGURE 61
SOLUBILITY OF URANIUM IN MAGNESIUM-THORIUM ALLOYS
(Data from Chiotti, P., and Shoemaker H.E., "Pyrometallurgical Separation
of Uranium from Thorium," Ind. Eng. Chem., 50, 137-140 (1958))

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