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The Mg-Nd System (Magnesium-Neodymium)

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Equilibrium Diagram

The Mg-rich region of the Mg-Nd equilibrium phase diagram has been investigated extensively [58Sav, 58Tik, 62Rok, 63Dri]. However, the purity of the starting materials often was quite low, and alumina or corundum crucibles usually were used. Consequently, contamination of the melt by Mg and Nd reduction of the crucible materials could have occurred. For these reasons, the findings of these investigations are open to doubt.

The assessed Mg-Nd phase diagram (Fig. 1 and Table 1) shows only the type and general configuration of the system. Further investigations are needed to establish the phase boundaries shown as dashed lines.

The assessed diagram is compatible with those for the homologous Mg-La, Mg-Ce, and Mg-Pr systems. It includes: (1) the liquid, L; (2) the terminal solid solution of Nd in (Mg); (3) the terminal solid solutions of Mg in (αNd) and (βNd); and (4) possibly five intermetallic compounds with essentially the stoichiometries of $Mg_{12}Nd$, $Mg_{41}Nd_5$, Mg_3Nd, Mg_2Nd, and MgNd.

Liquidus and Solidus

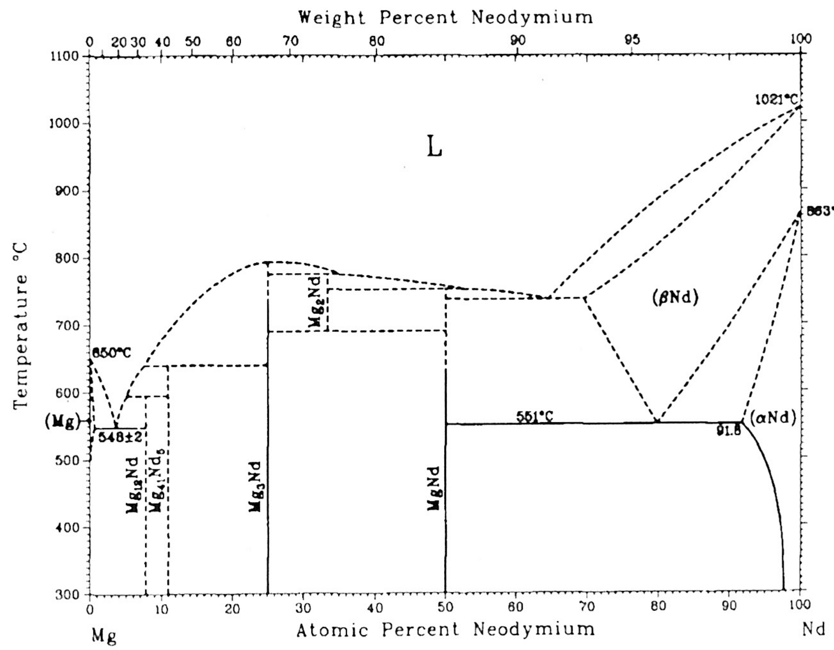
Thermal analysis [57Par] showed that the Mg-rich region is of the eutectic type. The alloys were made of 99.99 wt.% pure Mg and 99.7 wt.% pure Nd (major Nd impurities were oxygen and a few ppm of Mg and Ca) in molybdenum crucibles under a protective argon atmosphere. The melt was stirred with a tungsten rod. According to [57Par], the Mg-rich eutectic point is at

Table 1 Special Points of the Assessed Mg-Nd Phase Diagram

Reaction	Compositions of the respective phases, at.% Nd			Temperature, °C	Reaction type
L ↔ (Mg)	0			650	Melting point
L ↔ (Mg) + $Mg_{12}Nd$	?	?(a)	7.69	548 ± 2	Eutectic
L + $Mg_{11}Nd_5$ ↔ $Mg_{12}Nd$	?	10.87	7.69	?	Peritectic
L + Mg_3Nd ↔ $Mg_{41}Nd_5$	?	25	10.87	?	Peritectic
L ↔ Mg_3Nd	25			?	Congruent
L + Mg_3Nd ↔ Mg_2Nd	?	25	33.33	?	Peritectic
L + Mg_2Nd ↔ MgNd	?	33.33	50	?	Peritectic
Mg_2Nd ↔ Mg_3Nd + MgNd	33.33	25	50	?	Eutectoid
L ↔ MgNd + (βNd)	?	50	?	?	Eutectic
(βNd) ↔ MgNd + (αNd)	?	50	91.8	551	Eutectoid
L ↔ (βNd)	100			1021	Melting point
(βNd) ↔ (αNd)	100			863	Allotropic transformation

(**a**) See "Solid Solubilities."

Fig. 1 Assessed Mg-Nd Phase Diagram



A.A. Nayeb-Hashemi and J.B. Clark, 1988.

Table 2 Reported Solid Solubility of Nd in (Mg)

Composition, at.% Nd	Temperature, °C	Annealing time, h	Composition, at.% Nd	Temperature, °C	Annealing time, h
Parametric method [57Par]					
0.03	500	75 to 1000	0.1	546	75 to 1000
0.07	520	75 to 1000			
Resistivity method [62Rok]					
0.63	552	...	0.12	400	8
0.55	540	5	0.027	300	24
0.37	500	5	0.013	200	100
Metallography method [71Dri]					
0.348	500	50	0.034	250	800
0.088	400	200	0.020	200	800(a)
0.045	300	500			

(a) Specimen annealed at 300 ° for 150 h, then at 250 °C for 250 h, prior to final annealing at 800 °C.

1.7 at.% Nd and 546 °C. The compound involved in the eutectic reaction is of "Mg9Nd" stoichiometry and is formed by a peritectic reaction at 640 °C.

[58Sav] independently determined the Mg-rich region by thermal analysis, metallography, and microhardness measurements. The alloys were made from 99.91 wt.% pure Mg and 95 wt.% pure Nd (major Nd impurities were La, Ce, and Pr) in corundum crucibles. [58Sav] placed the eutectic point at 5.6 at.% Nd and 548 °C. The eutectic temperature of [58Sav] is in agreement with that of [57Par], but the eutectic composition of [58Sav] is over three times higher than that of [57Par]. [58Tik] (see also [59Tik]) reported the eutectic temperature to be "near" 548 to 550 °C. [Elliott] did not accept the (Mg) liquidus curve of [58Sav] and showed it as a dashed line, with the eutectic point at 1.7 at.% Nd and 546 °C, noting that "the constitution diagram must be considered confirmatory as to type, but not quantitative." [61Gsc] preferred the results of [57Par] and showed the eutectic point at 1.7 at.% Nd and 547 °C. For these reasons, the numerical values of the (Mg) liquidus temperatures of [58Sav] are not accepted.

[63Dri] reinvestigated the Mg-rich region by thermal analysis and hardness measurements. The starting materials were 99.99 wt.% pure Mg and 98.7 wt.%

Table 3 Mg-Nd Crystal Structure Data

Phase	Composition, at.% Nd	Pearson symbol	Space group	Strukturbericht designation	Prototype
(Mg)	0 to ?	*hP*2	*P*6$_3$/*mmc*	*A*3	Mg
$Mg_{12}Nd$	7.69	*tI*26	*I*4/*mmm*	*D*2$_b$	$Mn_{12}Th$
$Mg_{41}Nd_5$	10.87	*tI*92	*I*4/*m*	...	$Mg_{41}Ce_5$
Mg_3Nd	25	*cF*16	*Fm*$\bar{3}$*m*	*D*0$_3$	BiF_3
Mg_2Nd	33.33	*cF*24	*Fd*$\bar{3}$*m*	*C*15	Cu_2Mg
MgNd	50	*cP*2	*Pm*$\bar{3}$*m*	*B*2	CsCl
(βNd)	? to 100	*cI*2	*Im*$\bar{3}$*m*	*A*2	W
(αNd)	91.8 to 100	*hP*4	*P*6$_3$/*mmc*	*A*3′	La

Table 4 Mg-Nd Lattice Parameter Data

Phase	Composition, at.% Nd	Lattice parameters, nm *a*	*c*	Temperature, °C	Reference
(Mg)	0	0.32093	0.52107	25	[King1]
$Mg_{12}Nd$	7.69	1.031	0.593	RT	[63Evd]
$Mg_{41}Nd_5$(a)	10.87	...	...	RT	[69Kri](a)
Mg_3Nd	25	0.7410	...	RT	[59Ian]
		0.737	...	RT	[64Kri]
		0.7397	...	RT	[76Bus]
		0.7391	...	RT	[81Gal]
Mg_2Nd	33.33	0.8662	...	RT	[59Ian]
		0.86744	...	RT	[78Bus]
		0.8663	...	RT	[81Loi]
MgNd	50	0.3861	...	RT	[60Ian]
		0.3881(3)	...	RT	[65Ian]
		0.3867	...	RT	[66Cha]
		0.3860	...	RT	[73Bus]
βNd	100	0.413	...	883	[78Bea]
αNd	100	0.36582	1.17966	25	[78Bea]

(a) [Pearson2] did not list this compound.

pure Nd (major Nd impurities were 0.7 wt.% Ca, 0.4 wt.% Pr, 0.1 wt.% Ce, and 0.03 wt.% La). The alloys were made in alumina crucibles, which could introduce Al contamination to the alloys. (Mg reduces Al_2O_3.) [63Dri] placed the Mg-rich eutectic point at 7.66 at.% Nd and 552 ± 2 °C, significantly higher than did [57Par] or [58Sav]. Because [58Sav] and [63Dri] used relatively impure Nd and because of possible contamination of their alloys by Cr or Al from the crucibles, their quantitative results are not reliable.

In the assessed diagram, the Mg-rich eutectic temperature can be placed with confidence at 548 ± 2 °C. The (Mg) liquidus, solidus, and solvus are shown as dashed lines, because the reports vary widely among investigators.

Solid Solubilities

The solid solubility of Nd in (Mg) was determined by [57Par], [58Sav], [62Rok] (also appeared in [63Dri] and [72Rok]), and [71Dri] (Table 2). The discrepancies of the solid solubilities reported in these investigations are so large that a new, independent investigation is needed.

[57Par], using high-purity Mg and 99.7 wt.% pure Nd (with oxygen as the major Nd impurity) and the parametric method, placed the maximum solid solubility of Nd in (Mg) at 0.1 at.% Nd at the eutectic temperature. The alloys were annealed for 75 to 1000 h. [58Sav], by microhardness measurements, placed the maximum solid solubility at 0.33 at.% Nd. As noted above, [58Sav] used relatively impure Nd. [62Rok] determined the (Mg) solvus curve by the conductivity method. The results of [62Rok] showed a solid solubility of Nd in (Mg) six times greater than that of [57Par] and twice that of [58Sav]. However, not only did [62Rok] use relatively impure Nd, but also their alloys were made in alumina crucibles and may have been contaminated with Al.

[71Dri] redetermined the (Mg) solvus curve by the metallographic method. The starting materials were 99.98 wt.% pure Mg (with 0.005 wt.% Si, 0.006 wt.% Mn, 0.002 wt.% Cu, 0.007 wt.% Al, 0.003 wt.% Fe, 0.003 wt.% Cl, and 0.007 wt.% Ni as impurities) and 99.5 wt.% pure Nd (with 0.05 wt.% La, 0.007 wt.% Ce, 0.23 wt.% Pr, 0.05 wt.% Sm, 0.026 wt.% Fe, 0.03 wt.% Ca, and 0.029 wt.% Cu as impurities). However, the results of [71Dri] also are suspect, because their alloys were made in alumina crucibles.

Al dissolves significantly in (Mg), and we suspect that [62Rok] and [71Dri] actually measured the combined

Table 5 Vapor Pressure of Mg over Two-Phase Mg-Nd Alloys

Over phase region	Coefficients $-A$	B	Temperature, K
$(\alpha Nd) + (\beta Nd)$	7762 ± 137	9.683 ± 0.154	822.0 to 934.5
(αNd) + MgNd	8772 ± 114	10.953 ± 0.148	723.0 to 824.3
(βNd) + MgNd	8764 ± 99	10.945 ± 0.114	824.0 to 926.0
MgNd + Mg_2Nd	8719 ± 27	10.972 ± 0.033	700.5 to 925.5
Mg_2Nd + Mg_3Nd	8227 ± 37	10.494 ± 0.045	698.0 to 89.0
Mg_3Nd + $Mg_{41}Nd_5$	8152 ± 30	10.737 ± 0.039	654.5 to 868.0
$Mg_{41}Nd_5$ + $Mg_{12}Nd$	7457 ± 30	10.515 ± 0.041	636.5 to 825.5

Note: From [72Pah].
$\log P = A/T + B$ (P in Pa)

Table 6 Enthalpies, Entropies, and Gibbs Energies of Formation of Mg-Nd Compounds from Pure Solid Elements

Compound	Enthalpy of formation, kJ/mol	Entropy of formation at 773 K, J/mol·K	Gibbs energy of formation at 773 K, kJ/mol
MgNd	13.89 ± 1.55	4.02 ± 2.05	10.79 ± 0.33
Mg_2Nd	18.66 ± 1.42	6.32 ± 1.88	13.81 ± 0.47
Mg_3Nd	18.74 ± 1.42	5.15 ± 1.88	14.77 ± 0.42
$Mg_{41}Nd_5$	17.99 ± 1.34	5.86 ± 1.80	13.47 ± 0.50
$Mg_{12}Nd$	13.93 ± 1.30	4.77 ± 1.76	10.25 ± 0.54

Note: From [72Pah]. The entity for a mol is an atom.

solid solubility of Al and Nd in (Mg). (See [69Pad].) We believe that because of the higher-purity materials and the more reliable method used by [57Par], 0.10 at.% Nd, the true solid solubility of Nd in (Mg) is closer to that reported by [57Par], than to the data of [58Sav], [62Rok], and [71Dri]. (See also [78Rok].

[65Jos], using high-purity Mg and Nd and the parametric method, determined the solid solubility of Mg in (αNd). The maximum solid solubility of Mg in (αNd) at the eutectoid decomposition temperature of (βNd) (551 °C) was shown at 91.8 at.% Nd (8.2 at.% Mg).

Intermetallic Compounds

There is controversy concerning the stoichiometry of the compound in equilibrium with (Mg). [57Par], [61Bel], [63Dri], [66Dri], [69Pad], and [71Svi], based on nonanalytical methods, reported it as Mg_9Nd. [61Bel] reported that Mg_9Nd may have various modifications. ([Pearson2] noted that "the results of [61Bel] are said to be incorrect.") [63Evd], [64Kri], and [64Las], based on X-ray analyses, reported it as $Mg_{12}Nd$, whereas [64Las] reported it as $Mg_{12-x}Nd$ (0 ≤ x). Because the results of [63Evd], [64Kri], and [64Las] are based on X-ray analyses, they are considered to be more reliable than those based on quantitative metallography.

[69Kri] found two Mg-rich compounds, designated $Mg_{12}Nd$ and $Mg_{8+n}Nd$. The latter compound was designated as $Mg_{41}Nd_5$ by [69Kri], based on the existence of a similar compound in Mg-Ce. (See also [72Pah].) [78Dri] reported that the compound in equilibrium with (Mg) is Mg_9Nd and noted that an alloy of Mg_9Nd composition was single-phase, but that an alloy of $Mg_{12}Nd$ composition was multi-phase.

Because the presence of the Mg-rich compounds $Mg_{12}RE$ and $Mg_{41}RE_5$ in the Mg-La, Mg-Ce, and Mg-Pr systems has been established (see the evaluations of those systems in this monograph and [70Joh]), and because of the reliability of the X-ray results of [63Evd], [64Kri], [64Las], and [69Kri], we think there are at least two Mg-rich compounds in the Mg-Nd system—possibly $Mg_{12}Nd$, which is in equilibrium with (Mg), and $Mg_{41}Nd_5$. The designation of $Mg_{12}Nd$ as the compound in equilibrium with (Mg) implies the rejection of the (Mg) liquidus of [63Dri]. We believe this is justified by the argument of contamination of their alloys by Al and the use of relatively impure Nd.

[57Par] placed the peritectic reaction temperature for the formation of the Mg-rich compound, which he designated Mg_9Nd, at 640 °C. [63Dri] reported this peritectic temperature as 560 ± 4 °C and showed Mg_3Nd forming congruently at 744 °C.* However, the reported partial Mg-Nd phase diagram of [63Dri] is open to several criticisms and as we noted above, is not reliable and needs to be confirmed. We rejected the compound Mg_9Nd and designated $Mg_{12}Nd$ as the Mg-

*[Shunk] erroneously reported this temperature as 774 °C.

rich compound. The peritectic temperature of $Mg_{12}Nd$ is not certain and is not given in Table 1. A dashed line is drawn (arbitrarily) at 590 °C in Fig. 1.

Crystal Structures and Lattice Parameters

The crystal structure and lattice parameter data of Mg-Nd phases are shown in Tables 3 and 4. (See also [67Per].)

Thermodynamics

[67Ogr] and [72Pah] determined the Gibbs energy of formation of Mg-Nd compounds from pure solid Mg and Nd by vapor pressure measurements, using the Knudsen effusion method (Tables 5 and 6).

[74Fro] determined the thermodynamic properties of liquid Mg-Nd alloys (8.6 to 76.4 at.% Nd) in the temperature range 1083 to 1133 K by vapor pressure measurements, using the transpiration method. The results of [74Fro] were deposited at the All Union Institute of Scientific and Technical Information (VINITI) (no. 1645-74), but were not available to the present evaluators.

Magnetism

[73Bus] and [76Bus] investigated the magnetic properties of MgRE and Mg_3RE compounds, respectively, in the temperature range 4 to 300 K. According to [73Bus], the temperature dependence of the magnetization of MgNd gives rise to a maximum, indicative of a paramagnetic-antiferromagnetic transition. The temperature of the maximum (T_N of MgNd is 48 K, and the asymptotic Curie temperature (θ_p is −14 K). Whereas [76Bus] found that Mg_3Nd does not show any magnetic ordering, and that θ_P for Mg_3Nd from linear extrapolation is −124 K, [82Gal] reported θ_P as −58 K. (See also [81Gal].)

[78Bus] studied the magnetic properties of Mg_2RE compounds in the temperature range 1.5 to 300 K and the magnetic field up to 18 k Oe. According to [78Bus], most of the Mg_2RE compounds order ferromagnetically at temperatures "well below 100 K," except for Mg_2La, Mg_2Yb, and Mg_2Y, which show Pauli paramagnetism; Mg_2Sm and Mg_2Eu order antiferromagnetically. The Curie temperature (T_C) of Mg_2Nd was found to be 26 K [78Bus], which is in fair agreement with 28.5 K, reported by [81Loi].

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*Indicates key paper.
#Indicates presence of a phase diagram.

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