

ties of Liquid Alloys in the Systems Mg-Sr and Ba-Mg," *Z. Metallkd.*, 71(2), 120-123 (1980) in German. (Thermo; Experimental)

82Mer: F. Merlo and M.L. Fornasini, "Sr₉Mg₃₆: Structural Redetermination of SrMg₄," *Acta Crystallogr.*, 38B, 1797-1798 (1982). (Crys Structure; Experimental)

82Som: F. Sommer, "Association Model for the Description of Thermodynamic Functions of Liquid Alloys," *Z. Metallkd.*,

73(2), 77-86 (1982) in German. (Thermo; Theory)

83Cha: M.W. Chase, "Heat of Transformation of the Elements," *Bull. Alloy Phase Diagrams*, 4(1), 123-124 (1983). (Thermo; Compilation)

*Indicates key paper.

#Indicates presence of a phase diagram.

Mg-Ba evaluation contributed by A.A. Nayeb-Hashemi and J.B. Clark, Department of Metallurgical Engineering, The University of Missouri-Rolla, Rolla, MO 65401. Thermodynamic calculations were made using the F*A*C*T (Facility for the Analysis of Chemical Thermodynamics) computer program. This work was supported by American Society for Metals. Literature searched through 1983. Professor Clark is the ASM/NBS Data Program Category Editor for binary magnesium alloys.

The Mg-Sr (Magnesium-Strontium) System

24.305

87.62

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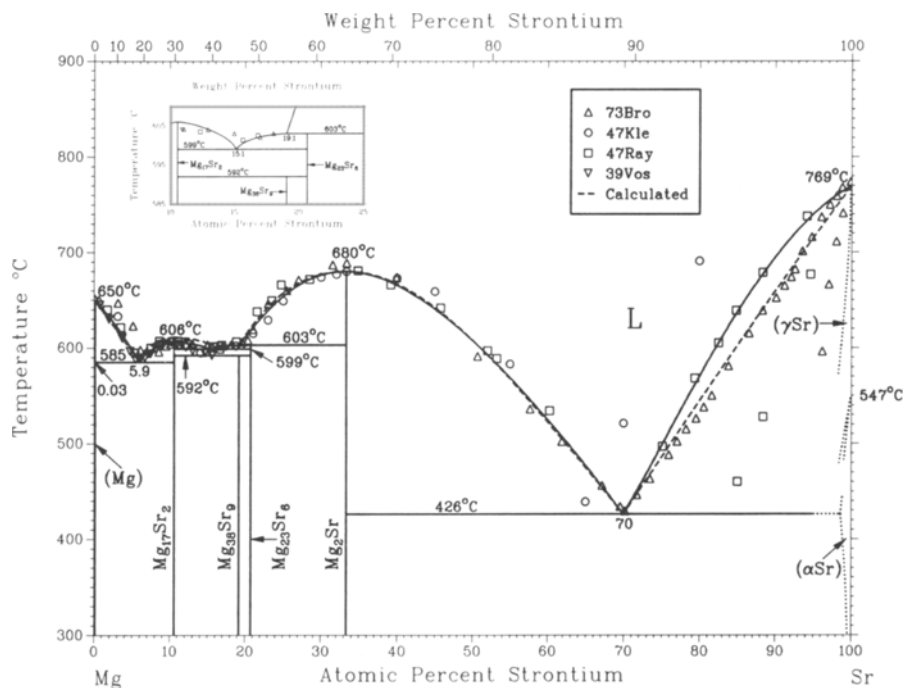
Equilibrium Diagram

[47Kle] and [47Ray] independently determined the Mg-Sr phase diagram. The Mg-rich region was determined earlier by [39Vos]; in the Mg-rich region, the results of these investigations are in good agreement. For compositions higher than 15 at.% Sr, the results of [47Kle] and [47Ray] are significantly different. [73Bro] reinvestigated the system over the entire composition range. The

results of [73Bro] are in qualitative agreement with those of [39Vos], [47Kle], and [47Ray], except for the Sr-rich region, where the cph form of Sr reported by [Pearson1] and [Pearson2] appears to be nonexistent.

The assessed Mg-Sr phase diagram is shown in Fig. 1 and consists of: (1) the liquid, L; (2) the terminal (Mg) solid solution, with maximum 0.03 at.% Sr solid solubility; (3) the compound Mg₁₇Sr₂, which melts congruently at

Fig. 1 Assessed and Calculated Mg-Sr Phase Diagram



Numerical values for [47Ray] and [47Kle] were extracted from graphical results. — Assessed; - - - - - Calculated.

A.A. Nayeb-Hashemi and J.B. Clark, 1986.

Table 1 Invariant Reactions in the Assessed Mg-Sr Phase Diagram

Reaction	Compositions of the respective phases, at.% Sr			Temperature, °C	Reaction type	Reference
$L \rightleftharpoons (Mg)$	0			650	Melting point	[83Cha]
$L \rightleftharpoons (Mg) + Mg_{17}Sr_2$	5.9	0.03	10.53	585	Eutectic	Assessed
$L \rightleftharpoons Mg_{17}Sr_2 + Mg_{23}Sr_6$	15.1	10.53	20.69	599	Eutectic	Assessed
$L + Mg_2Sr \rightleftharpoons Mg_{23}Sr_6$	19.36	33.33	20.69	603	Peritectic	[73Bro]
$Mg_{17}Sr_2 + Mg_{23}Sr_6 \rightleftharpoons Mg_{38}Sr_9$	10.53	20.6	19.15	592	Peritectoid	Assessed
$L \rightleftharpoons Mg_2Sr$	33.33			680	Congruent	[47Ray]
$L \rightleftharpoons Mg_2Sr + (Sr)$	70	33.33	?	426	Eutectic	Assessed
$L \rightleftharpoons (\gamma Sr)$	100			769(a)	Melting point	[Melt]
$(\gamma Sr) \rightleftharpoons (\alpha Sr)$	100			547(b)	Allotropic	[83Cha]

Note: The temperatures are presented as published and have not been corrected to IPTS-68.

(a) [83Cha] placed the melting point at 777 °C. (b) [King2] showed two allotropic transformations, $\gamma Sr(bcc) \rightarrow \beta Sr(cph)$ at 605 °C and $\beta Sr \rightarrow \alpha Sr(fcc)$ at 213 °C, in accordance with [Pearson1] and [Pearson2]. However, [66Pet] showed the hexagonal structure was binary hydride, which exists from 240 to 620 °C. (See also [Hultgren, E] and [83Cha].) [83Cha] showed the $\alpha Sr(fcc) \rightarrow \gamma Sr(bcc)$ transformation at 547 °C.

Table 2 Invariant Reactions Reported in the Mg-Sr System

Reaction	Compositions of the respective phases, at.% Sr			Temperature, °C	Reaction type	Reference	
$L \rightleftharpoons (Mg) + Mg_9Sr$	5.9	0	10	582	Eutectic	[39Vos]	
	6	0	10	585 ± 2		[47Kle]	
	6	0.03	10	586		[47Ray]	
$L \rightleftharpoons (Mg) + Mg_{17}Sr_2$	6.45	0.1	10.53	585	Congruent	[73Bro]	
		10		606		[39Vos]	
$L \rightleftharpoons Mg_9Sr$...		603	Congruent	[47Kle]	
		...		609		[47Ray]	
$L \rightleftharpoons Mg_{17}Sr_2$		10.53		604		[73Bro]	
$L \rightleftharpoons Mg_9Sr + Mg_4Sr$	15.5	10	20	592	Eutectic	[39Vos]	
	15.5	10	20	587		[47Kle]	
	15.1	10	18.18	592		[47Ray]	
$L \rightleftharpoons Mg_9Sr + Mg_9Sr_2$	15.1	10	18.18	592		[47Ray]	
$L \rightleftharpoons Mg_{17}Sr_2 + Mg_{23}Sr_6$	16.6	10.53	20.69	599		[73Bro]	
$L + Mg_2Sr \rightleftharpoons Mg_4Sr$	~17.5	33.33	20	598	Peritectic	[47Kle]	
$L + Mg_3Sr \rightleftharpoons Mg_9Sr_2$	~17.44	25	18.18	599		[47Ray]	
$L + Mg_2Sr \rightleftharpoons Mg_3Sr$	19.1	33.33	25	608		[47Ray]	
$L + Mg_2Sr \rightleftharpoons Mg_{23}Sr_6$	19.36	33.33	20.69	603		[73Bro]	
$Mg_{17}Sr_2 + Mg_{23}Sr_6 \rightleftharpoons Mg_4Sr$	10.53	20.69	20	592	Peritectoid	[73Bro]	
		33.33		680		Congruent	[47Kle]
$L \rightleftharpoons Mg_2Sr$				680	Congruent	[47Ray]	
				689		[73Bro]	
				438		Eutectic	[47Kle]
				426			[47Ray]
				426			[73Bro]
$L \rightleftharpoons Mg_2Sr + (Sr)$	65	33.33	100	438	Eutectic	[47Kle]	
	70	33.33	85.5	426		[47Ray]	
	70.4	33.33	93.7	426		[73Bro]	

Note: The temperatures are presented as published and have not been corrected to IPTS-68.

606 °C; (4) the compound Mg_4Sr (more correctly, $Mg_{38}Sr_9$), which probably forms by a peritectoid reaction at 592 °C; (5) the compound $Mg_{23}Sr_6$, which forms by a peritectic reaction at 603 °C (further investigation is needed to conclusively establish the invariant reactions for the formation of Mg_4Sr ($Mg_{38}Sr_9$) and $Mg_{23}Sr_6$); (6) the compound Mg_2Sr , which melts congruently at 680 °C; and (7) the terminal (Sr) solid solution, with an uncertain maximum solid solubility of Mg in (Sr). The assessed invariant reactions are given in Table 1, and Table 2 lists the experimentally reported reactions.

Liquidus. [39Vos] determined the liquidus temperatures of 18 alloys containing 0 to 15.6 at.% Sr. The starting materials were 99.8 to 99.9 pure Mg and 99.74 pure Sr, with 0.22 wt.% Fe and 0.04 wt.% Si. [47Kle], [47Ray], and [73Bro] determined the liquidus temperatures across the phase diagram (see Table 3). In the composition range 0 to 15 at.% Sr, there is good agreement among the results of [39Vos], [47Kle], and [47Ray]. However, the (Mg) liq-

uidus temperatures of [73Bro] lie at significantly higher temperatures.

For alloys with more than 15 at.% Sr, the liquidus temperatures of [47Kle] differ significantly from those of [47Ray], particularly for the Sr-rich alloys. It appears that [Hansen] drew the liquidus curve of Mg_2Sr by an eyeball fit through the liquidus temperatures of [47Kle] and [47Ray] and took the (Sr) liquidus curve from [47Ray], who examined six alloys, compared to two by [47Kle]. The (Sr) liquidus temperatures of [73Bro] are below those of [47Kle] and [47Ray]. Because there is an indication of hydrogen contamination of the Sr-rich alloys and the formation of strontium hydride in the data of [73Bro], his results, particularly in the Sr-rich region, are less reliable. [73Bro] reported a cph form of pure Sr and showed associated phase reactions and boundaries in his Mg-Sr phase diagram. However, recent compilations [Hultgren, E; 83Cha; 84Cha] reject the cph structure of pure Sr. The cph form of Sr apparently observed by

Table 3 Results of Thermal Analyses in the Mg-Sr System

Composition, at.% Sr	Liquidus temperature, °C	Eutectic temperature, °C	Peritectic temperature, °C	Composition, at.% Sr	Liquidus temperature, °C	Eutectic temperature, °C	Peritectic temperature, °C
From [39Vos], thermal analysis				75.13	496.9
0.59	645	581	...	79.43	568.1
1.85	630	579	...	82.57	605
3.54	612	582	...	84.9	639
3.58	610	579	...	88.43	678.8
4.61	597	582	...	94.3	737.8
5.36	588	583	...	From [73Bro], DTA			
6.60	590	583	...	0	651
7.05	594	583	...	0.5	650	585	...
7.36	594	582	...	3.01	647	585	...
8.05	599	583	...	5.01	623	586	...
8.69	602	582	...	6.01	598	585	...
8.78	604	583	...	8.44	596	585	...
10.17	606	9.45	602	585	...
10.86	604	585	...	10.00	604	585	...
12.08	601	588	...	11.00	604	597 (592)(c)	...
12.97	597	588	...	12.90	604	599 (594)	...
14.56	595	592	...	14.97	603	599 (592)	...
15.51	592	592	...	15.61	601	599 (592)	...
15.59	594	591	...	16.60	599	599 (592)	...
16.71	602	596	...	17.01	602	598 (591)	...
From [47Kle], thermal analysis(a)				18.07	603	601 (592)	...
3	633	585 ± 2	...	19.36	603	601 (592)	...
8.6	602	19.59	606	600 (592)	603
10	607	20.30	608	597 (592)	603
12	602	587	...	21.00	619	...	604
14	595	23.02	646	...	601
18.7	602	25.48	660	...	603
21	615	...	598 (604)(b)	57.03	671	...	603
23	629	31.49	687	...	604
25	649	33.33	689
30	674	39.94	674
32	677	39.9	673	426	...
33.3	680	50.7	591	427	...
40	673	438	...	57.7	536	428	...
45	659	61.9	502	426	...
55	583	67.2	456	426	...
65	439	69.6	434	424	...
70	521	70.2	429	426	...
80	691	71.8	446	425	...
From [47Ray], thermal analysis				73.5	463	426	...
1.62	640	586	...	76.0	488	425	...
3.38	621.2	77.1	502	426	502
5.3	594.7	78.3	515	426	504
7.4	600	79.6	526	426	502
8.53	607	80.6	538	424	500
10.98	607	592	...	81.7	550	426	502
12.29	603.5	83.9	581	426	502
15.65	601.3	86.6	615	425	501
16.83	602.5	88.4	639	426	502
18.78	606.4	...	599	90.2	652	426	502
21.52	637.7	...	508	91.3	665	427	503
23.48	649.4	92.2	674	426	502
24.73	665.9	92.7	682	424	501
28.49	671.7	93.7	701	426	502
34.83	680.7	426	...	94.9	716	...	501
39.13	665.9	96.2	737
45.78	641.6	97.3	750
52	597	98.2	759
53.22	588.8	98.9	768
60.26	534.1	100	774

(a) Numerical values were extracted from graphical results. (b) A second set of thermal arrests near 604 °C were observed only on heating. These arrests were 6 °C higher than those observed on cooling curves for the same compositions. (c) The values in parentheses correspond to the reported peritectoid reaction $Mg_{17}Sr_2 + Mg_{23}Sr_6 \rightleftharpoons Mg_4Sr$ [73Bro].

[73Bro] and others (see [Pearson1]) appears to be a phase stabilized by hydrogen contamination [66Pet].

In the assessed diagram, the (Mg) liquidus is taken from [39Vos] and [47Ray]. The (Sr) liquidus is taken from [47Ray], and the liquidus for the remainder of the system is from [47Kle], [47Ray], and [73Bro] (see Fig. 1).

Solidus. [47Ray] determined the (Sr) solidus by thermal analyses; however, [Hansen] showed it with a dashed line in his assessed Mg-Sr phase diagram, indicating some uncertainty. [73Bro] determined the (Sr) solidus and its allotropic transformations by differential thermal analysis and high-temperature X-ray diffraction analyses. The (Sr) solidus temperatures of [73Bro] are significantly below those of [47Ray]. Both investigations [47Ray, 73Bro] were done in the same lab under supervision of Dr. F. Kanda. From the homologous Mg-Ba system, it appears that the (Sr) solidus temperatures of [73Bro] are more realistic than those of [47Ray], in spite of possible hydrogen contamination effects in the results of [73Bro].

[47Kle] drew a Sr-rich eutectic isotherm that extended from Mg_2Sr to pure Sr. However, in the assessed diagram, the (Sr) solidus is shown by a dashed line.

Solid Solubilities. The thermal analyses of [39Vos], [47Kle], and [47Ray] and metallographic examinations of [39Vos] and [47Ray] indicated a very small solid solubility of Sr in (Mg). The metallographic examinations of [39Vos] and [47Ray] placed the maximum solid solubility of Sr in (Mg) at ~0.03 at.% Sr. Based on his differential thermal analysis, which indicated a eutectic arrest in Mg-0.5 at.% Sr, [73Bro] estimated the maximum solid solubility as 0.1 at.% Sr. The values reported by [39Vos]

and [47Ray] are more reliable and are preferred to those of [73Bro].

The thermal and metallographic analyses of [47Ray] and the differential thermal analysis of [73Bro] showed significant solid solubility of Mg in (Sr). [47Ray] placed the maximum solid solubility of Mg in (Sr) near 85.5 at.% Sr, and [73Bro] placed it near 93.7 at.% Sr. In the homologous systems, Mg-Ca and Mg-Ba, the solubilities of Mg in (Ca) and (Ba) are negligible; consequently, it appears that the reported solid solubilities of Mg in (Sr), (14.5 at.% Mg [47Ray], and 6.3 at.% Mg [73Bro]) are high. The solid solubility of Mg in (Sr) should be reinvestigated.

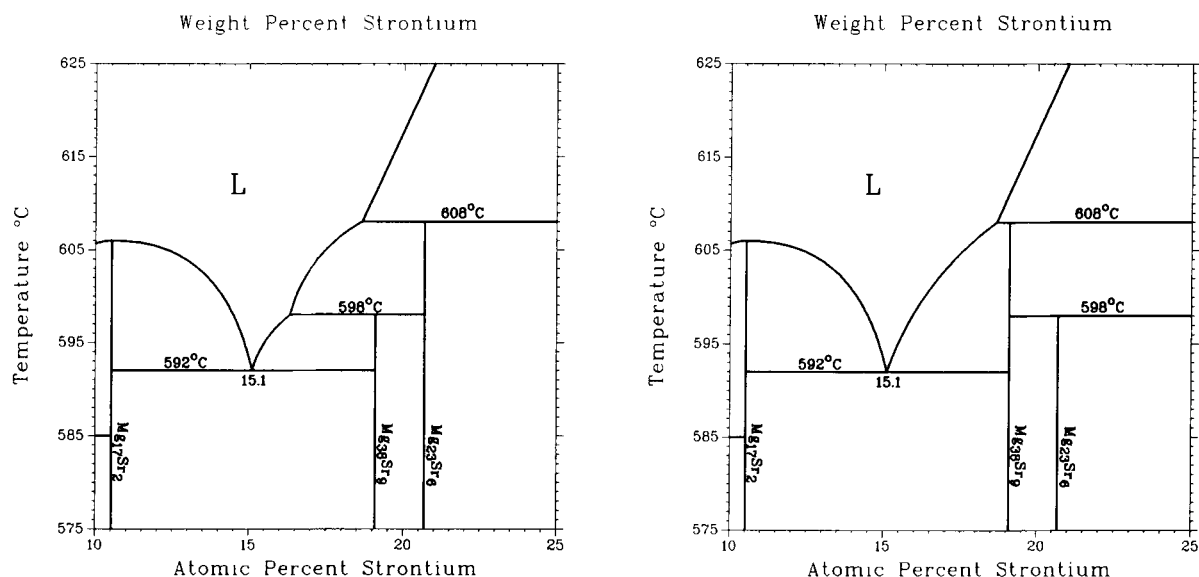
Intermetallic Compounds

Mg₁₇Sr₂. [39Vos] reported the existence of the Mg₉Sr compound melting congruently at 606 °C. [47Kle] and [47Ray] also reported the existence of Mg₉Sr and reported its melting point as 603 and 609 °C, respectively. [61Gla] showed that the compound designated as Mg₉Sr is isotypic with Ni₁₇Th₂ and concluded that its correct formula is Mg₁₇Sr₂.

[62Kri], [63Wan], [65Wan], and [73Bro] confirmed the results of [61Gla]. [63Wan] also noted that, contrary to [48Mis], Mg₁₇Sr₂ and Mg₁₇Ba₂ are not isomorphous. [73Bro] placed the melting point of Mg₁₇Sr₂ at 604 °C. In the assessed diagram, the melting point of Mg₁₇Sr₂ is placed at 606 °C.

Mg₃₅Sr₉ and Mg₂₃Sr₆. [39Vos] reported the existence of a second intermetallic compound in the Mg-rich region, but

Fig. 2 Alternative Mechanisms of the Formation of Mg₃₅Sr₉ and Mg₂₃Sr₆



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Table 4 Mg-Sr Crystal Structure Data

Phase	Homogeneity range, at.% Sr	Pearson symbol	Space group	Strukturbericht designation	Prototype	Reference
(Mg)	0 to 0.03	<i>hP</i> 2	<i>P</i> 6 ₃ / <i>mmc</i>	A3	Mg	[King1]
Mg ₁₇ Sr ₂	10.53	<i>hP</i> 38	<i>P</i> 6 ₃ / <i>mmc</i>	?	Ni ₁₇ Th ₂	[61Gla, 73Kan, 81Mak]
Mg ₃₈ Sr ₉	19.15	<i>hP</i> 94	<i>P</i> 6 ₃ / <i>mmc</i>	?	Mg ₃₈ Sr ₉	[82Mer, 82Nym, 65Wan]
or Mg ₄ Sr		<i>hP</i> 90		?		
Mg ₂₃ Sr ₆	20.69	<i>cF</i> 116	<i>Fm</i> 3 <i>m</i>	D8 _a	Mn ₂₃ Th ₆	[62Gla, 65Wan, 81Mak]
Mg ₂ Sr	33.33	<i>hP</i> 12	<i>P</i> 6 ₃ / <i>mmc</i>	C14	Mg ₂ Zn	[43Hel, 81Mak]
(γSr)	100	<i>cI</i> 2	<i>Im</i> 3 <i>m</i>	A2	W	[King2]
(αSr)	? to 100	<i>cF</i> 4	<i>Fm</i> 3 <i>m</i>	A1	Cu	[King1]

did not specify its formula. [47Kle], in their thermal analyses (cooling curves), found thermal arrests corresponding to an invariant reaction in the composition range ~18 to 33.3 at.% Sr at 598 °C. [47Kle], in their heating curves of the alloys in this composition range, observed second thermal arrests (corresponding to an invariant reaction) at 6 °C above the "peritectic decomposition of Mg₄Sr." [47Kle] speculated on the possible existence of a Mg₃Sr compound, but did not attempt to establish it and did not show it in their phase diagram. However, [47Kle] reported observations of a possible invariant arrest by a dashed line at 604 °C in the composition range of ~20 to 30 at.% Sr. [47Ray] observed thermal arrests at 608 °C (~18 to 33.33 at.% Sr) and 599 °C (~17 to 25 at.% Sr) and assigned these to the peritectic formation of Mg₃Sr (L + Mg₂Sr ⇌ Mg₃Sr) and Mg₉Sr₂ (L + Mg₃Sr ⇌ Mg₉Sr₂). [47Ray] did not show the existence of the Mg₃Sr compound by any other method. [63Kan], [65Wan], and [66Mis] did not find the presence of the Mg₃Sr compound.

Because the Mg₃Sr compound is nonexistent, the two invariant reactions observed in the composition ranges ~20 to 30 at.% Sr (588 and 604 °C) [47Kle] and ~17 to 25 at.% Sr (599 and 608 °C) [47Ray] cannot be explained by the peritectic reactions reported by [47Ray]. [65Wan] and [Shunk] noted that further investigation is needed to explain the thermal arrests reported by [47Kle] and [47Ray].

[62Gla], from powder X-ray diffraction analysis, found that the compound designated "Mg₄Sr" by [47Kle] and Mg₉Sr₂ by [47Ray], is fcc, isotypic with Mn₂₃Th₆ and concluded that its formula is Mg₂₃Sr₆. [63Kan] and [65Wan], from single-crystal X-ray diffraction analyses, confirmed the results of [62Gla]. [65Wan] also found the existence of a new "Mg₄Sr" compound with a complex hexagonal structure.

[82Nym] showed by using "γ brass clusters" that a simple relationship exists between the structure of "Mg₄Sr" and Mg₂₃Sr₆; he found that the crystal structure, atom positions, and density of "Mg₄Sr" can be described consistently by the formula Mg₃₈Sr₉, with *Z* = 2.

[73Bro] reinvestigated the system by differential thermal analysis, using very slow heating and cooling rates. Moreover, the alloys were annealed at a temperature close to the invariant reaction temperatures for at least 1 h before heating or cooling through the invariant reaction. In the composition range ~20 to 33.33 at.% Sr, [73Bro] observed only one thermal arrest (characteristic

of an invariant reaction) and assigned it to the formation of the Mg₂₃Sr₆ compound by the reaction L + Mg₂Sr ⇌ Mg₂₃Sr₆. Contrary to the results of [47Kle] and [47Ray], [73Bro] also found a second thermal arrest below the eutectic isotherm in alloys, in the composition range 10.53 to 20.69 at.% Sr, and assigned it to the peritectoid formation of "Mg₄Sr," i.e., Mg₁₇Sr₂ + Mg₂₃Sr₆ ⇌ Mg₄Sr. No other method was used to confirm the existence of this peritectoid reaction. [73Bro] found the eutectic arrest in this composition range (10.53 to 20.69 at.% Sr) at 599 °C, compared to 592 °C [39Vos, 47Ray] and 587 °C [47Kle]. The results of [73Bro] in the composition range 10.53 to 33.33 at.% Sr, along with assumed deviations from equilibrium conditions in the thermal analyses of [47Kle] and [47Ray], can explain the results of [47Kle] and [47Ray] in this composition range. However, because the results of [73Bro] show possible hydrogen contamination, further investigation is needed to establish the mechanisms for formation of the Mg₃₈Sr₉ and Mg₂₃Sr₆ phases. In the assessed diagram, the invariant reactions for the formation of these compounds are taken tentatively from [73Bro], with minor adjustment based on the results of [82Nym]. Other possible phase topologies that may explain the results of [47Kle] and [47Ray] are shown in Fig. 2.

Mg₂Sr. [43Hel] reported the existence of the Mg₂Sr compound and determined its crystal structure (see Table 4). [47Kle], [47Ray], and [73Bro] confirmed its existence and showed it to melt congruently at 680 °C [47Kle, 47Ray] and 689 °C [73Bro].

The MgSr compound reported by [42Now] was discredited by the studies of [47Kle], [47Ray], [66Mis], and [73Bro].

Crystal Structures and Lattice Parameters

Crystal structure and lattice parameter data for the phases in the Mg-Sr system are shown in Tables 4 and 5. [42Now] reported the existence of the MgSr compound with cubic, CsCl-type structure, space group *Pm*3*m*, *a* = 0.3908 nm. [47Kle] and later investigations showed that this compound does not exist. [King2] and [Pearson2] reported two allotropic transformations for pure Sr, αSr (fcc) ⇌ βSr (cph) ⇌ γSr (bcc). [Pearson2] indicated that the cph form of Sr is an impurity effect. [66Pet] showed that the cph structure of Sr is the result of a hydrogen impurity that forms strontium hydride, which exists between 240 and 620 °C (see also [Hultgren, E], [83Cha], and [84Cha]).

Table 5 Mg-Sr Lattice Parameter Data

Phase	Approximate composition, at.% Sr	Lattice parameters, nm		Comment	Reference
		a	c		
(Mg)	0	0.32093	0.52107	At 25 °C	[King1]
Mg ₁₇ Sr ₂	10.53	1.0533 ± 7 × 10 ⁻⁴	1.0341 ± 7 × 10 ⁻⁴	At RT(a)	[61Gla]
		1.0535 ± 5 × 10 ⁻⁴	1.0356 ± 5 × 10 ⁻⁴		[73Kan]
		1.053	1.0408		[81Mak]
Mg ₃₀ Sr ₉ or Mg ₄ Sr	19.15 20	1.0500	2.8251	At RT	[82Mer]
		1.0546	2.5832	At RT	[82Nym]
Mg ₂₃ Sr ₆	20.69	1.0511 ± 8 × 10 ⁻⁴	2.8362 ± 1 × 10 ⁻³		[65Wan]
		1.491	...	At RT	[62Gla]
		1.4914 ± 1.5 × 10 ⁻³	...		[65Wan]
		1.5000	...		[81Mak]
Mg ₂ Sr	33.33	0.6426 ± 8 × 10 ⁻⁵	1.0473 ± 8 × 10 ⁻⁵	At RT	[43Hel]
		0.6475	1.043		[81Mak]
(γSr)	100	0.487	...	At >605 °C(b)	[King2]
(αSr)	100	0.6084	...	At 25 °C	[King1]

Note: RT = room temperature.

(a) See also [62Kri] for atom positions. (b) See footnote (b) in Table 1.

Table 6 Heat of Mixing of Liquid Mg-Sr at 1080 K

Composition, at.% Sr	Heat of mixing (Δ _{mix} H(L)), J/mol(a)	Composition, at.% Sr	Heat of mixing (Δ _{mix} H(L)), J/mol(a)
10	-2640	46	-5310
13	-2970	52	-4980
17	-4100	61	-3890
25	-4770	70	-3100
30	-5520	75	-2260
35	-5520	86.4	-1260

From [77Som]. (a) The unit for a mole is an atom.

Thermodynamics

[64Kin] measured the heat of formation of solid Mg₂Sr from solid Mg and Sr by tin solution calorimetry as -21.35 kJ/mol.* [64Kin] also calculated the heat of formation of Mg₂Sr from sublimation energies of Mg and Sr as -55.3 kJ/mol.* [77Som] measured the heat of mixing of liquid Mg and Sr by high-temperature calorimetry (see Table 6).

[80Som] determined the thermodynamic activity of Mg and Sr in liquid Mg-Sr alloys at 1054 ± 2 K by vapor pressure measurement (see Table 7).

Thermodynamic Model. [80Som] applied an association model to describe the thermodynamic properties of liquid Mg-Sr alloys (see also [82Som1]). However, no attempt was made to calculate the phase diagram.

In the present evaluation, the experimental thermodynamic data and the assessed phase diagram were used to derive thermodynamic functions of liquid Mg-Sr alloys by using the F*A*C*T program, as follows.

The heat of mixing of liquid Mg and Sr as given in [77Som] can be represented by Eq 1, which was obtained by optimization (increasing the number of parameters did not improve the fit significantly):

$$\Delta_{\text{mix}}H(L) = (-33\,033.988 + 26\,343.152X_{\text{Sr}})X_{\text{Mg}}X_{\text{Sr}} \text{ J/mol} \quad (\text{Eq 1})$$

*The entity for a mol is the formula unit unless otherwise specified.

Table 7 Thermodynamic Activity of Mg and Sr in Liquid Mg-Sr Alloys at 1054 K

Composition, at.% Sr	Mg activity		Sr activity	
	[80Som]	Calculated(a)	[80Som]	Calculated(a)
0	1
10	0.897	0.885	0.033	0.030
19	0.751	0.762	0.067	0.073
30	0.589	0.604	0.133	0.150
37	0.466	0.506	0.233	0.213
45	0.341	0.400	0.350	0.299
56	0.230	0.273	0.483	0.435
65	0.161	0.187	0.617	0.557
80	0.090	0.081	0.783	0.762
90	0.045	0.033	0.893	0.890
100	1.0	...

(a) Calculated by the present evaluators.

where X_{Sr} and X_{Mg} are atomic fractions. The entity for a mol is an atom unless otherwise specified.

The Gibbs energies of fusion of Mg and Sr, using the heat capacity data of [77Bar], heats of fusion data of [Hultgren, E] and [83Cha], and melting points of [Melt], are as follows:

$$T_{\text{fus}} = 923 \text{ K}$$

$$C_p(\text{Mg, cph}) = 26.2094 - 1.0048 \times 10^{-3} T - 159\,098.4 T^{-2} + 8.42 \times 10^{-6} T^2 \text{ J/mol} \cdot \text{K}$$

$$C_p[(\text{Mg, L})] = 34.3318 \text{ J/mol} \cdot \text{K}$$

$$\Delta_{\text{fus}}H(\text{Mg}) = 8477 \text{ J/mol}$$

$$\Delta_{\text{fus}}G(\text{Mg}) = 2931.3541 + 51.6424 T - 5.024 \times 10^{-4} T^2 + 1.4033 \times 10^{-6} T^3 - 8.1224 T \ln T - 79\,549.2 T^{-1} \quad (\text{Eq 2})$$

$$C_p(\text{Sr, fcc}) = 22.23191 + 0.0139 T \text{ (298 to 830 K)} \text{ J/mol} \cdot \text{K}$$

$$C_p(\text{Sr, bcc}) = 12.686 + 26.79552 T \text{ (830 to 1042 K)} \text{ J/mol} \cdot \text{K}$$

$$T_{\text{fus}}(\text{Sr}) = 1042 \text{ K}$$

$$\Delta_{\text{fus}}H(\text{Sr}) = 7431 \text{ J/mol}$$

$$\Delta_{\text{fus}}G(\text{Sr}) = 2913.044217 + 110.383126 T + 13.39776 \\ \times 10^{-3} T^2 - 18.296316 T \ln T \text{ J/mol} \quad (\text{Eq } 3)$$

where T is in K.

From coupled optimization of the experimental thermodynamic activity of Mg of [80Som], the (Mg) liquidus temperatures of [73Vos] and [47Ray], the (Sr) liquidus temperatures of [47Ray], and Eq 1, the excess entropy of liquid Mg-Sr alloys is given by Eq 4:

$$\Delta S^{\text{ex}}(\text{L}) = (-18.496 + 23.215X_{\text{Sr}})X_{\text{Mg}}X_{\text{Sr}} \text{ J/mol} \cdot \text{K} \quad (\text{Eq } 4)$$

and

$$\Delta G^{\text{ex}}(\text{L}) = \Delta_{\text{mix}}H(\text{L}) - T\Delta S^{\text{ex}}(\text{L}) \text{ J/mol} \quad (\text{Eq } 5)$$

From Eq 1 and 4 (or Eq 5) and liquidus temperatures of $\text{Mg}_{17}\text{Sr}_2$, $\text{Mg}_{23}\text{Sr}_6$, and Mg_2Sr , their Gibbs energies of fusion are calculated as:

$$\Delta_{\text{fus}}G(\text{Mg}_{0.895}\text{Sr}_{0.105}) = 6181.08 - 6.999 T \text{ J/mol} \quad (\text{Eq } 6)$$

and

$$\Delta_{\text{fus}}G(\text{Mg}_{0.793}\text{Sr}_{0.207}) = 25\,672.98 - 29.302 T \text{ J/mol} \quad (\text{Eq } 7)$$

and

$$\Delta_{\text{fus}}G(\text{Mg}_{0.667}\text{Sr}_{0.333}) = 12\,336.03 - 12.950 T \text{ J/mol} \quad (\text{Eq } 8)$$

The calculated liquidus curves, using Eq 1 to 8, are shown by dashed lines in Fig. 1. All the characteristic points of the assessed diagram are reproduced very closely. The calculated liquidus temperatures are within 5 °C of the assessed values, except for (Sr) liquidus temperatures, where the calculated values are in close agreement with those of [73Bro]. The calculated activities of Mg and Sr are compared with those of [80Som] in Table 7 and show negative deviation from Raoult's law in all compositions, in accordance with the results of [80Som]. The heats of fusion of the compounds taken from Eq 6 to 8 are:

$$\Delta_{\text{fus}}H(\text{Mg}_{0.895}\text{Sr}_{0.105}) = 6.181 \text{ kJ/mol}$$

and

$$\Delta_{\text{fus}}H(\text{Mg}_{0.793}\text{Sr}_{0.207}) = 25.673 \text{ kJ/mol}$$

and

$$\Delta_{\text{fus}}H(\text{Mg}_{0.667}\text{Sr}_{0.333}) = 12.336 \text{ kJ/mol}$$

Assuming $\Delta C_p = 0$ and using the calculated heat of fusion of Mg_2Sr , the heat of mixing (Eq 1), and the heats of fusion of Mg and Sr, the heat of formation of Mg_2Sr is estimated as -29.35 kJ/mol (the entity for a mol is a formula unit). This is within the experimental (-21.35 kJ/mol) and calculated (-55.3 kJ/mol) values of [64Kin], indicating that the model closely reproduces the phase diagram as well as the experimental data.

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Mg-Sr S-Ti

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

Mg-Sr evaluation contributed by A.A. Nayeb-Hashemi and J.B. Clark, Department of Metallurgical Engineering, The University of Missouri-Rolla, Rolla, MO 65401. Thermodynamic calculations were made using the F*A*C*T (Facility for the Analysis of Chemical Thermodynamics) computer program. This work was supported by American Society for Metals. Literature searched through 1983. Professor Clark is the ASM/NBS Data Program Category Editor for binary magnesium alloys.

The S-Ti (Sulfur-Titanium) System

32.06 47.88

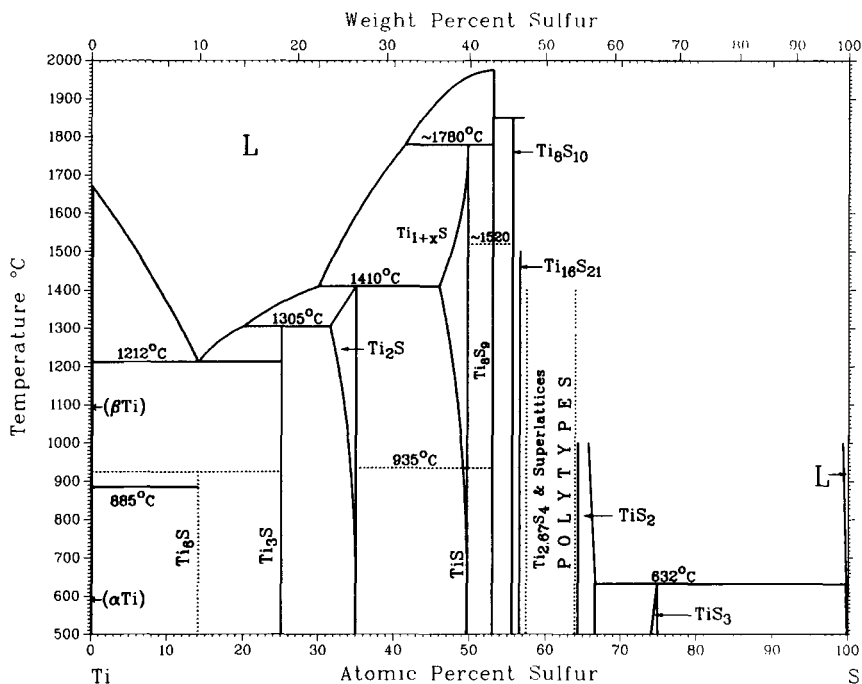
By J.L. Murray
National Bureau of Standards

Equilibrium Diagram

The Ti-S system is very complex and requires further experimental study before a complete phase diagram can be constructed. The sulfides generally are prepared by direct reaction of the elements in sealed silica tubes at one or two elevated temperatures; quenched samples are exam-

ined by X-ray diffraction. Commonly used preparation techniques can introduce significant contamination; the predominant use of X-ray diffraction also creates an uncertainty as to whether apparently single-phase material is actually so. Systematic studies have not been performed on the temperature range of stability of phases in the TiS to TiS_2 region.

Fig. 1 Assessed Ti-S Phase Diagram



The phase diagram is extremely uncertain. Most solid lines have been used to enhance the clarity of the figure rather than to indicate the accuracy of the phase boundary. In the region between 58 and 64 at.% S, many structurally similar phases have been observed, and equilibrium relations are unknown. See text and tables for descriptions of these structures.
J.L. Murray, 1986.