

Supplemental Literature Review of Binary Phase Diagrams: Al-P, B-Ga, B-Nd, Ba-Ga, Bi-Cs, Ca-Ga, Cd-Gd, Cr-Mo, Gd-Ni, Ni-Pb, Ni-Sc, and Sc-Sn

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Introduction

Binary Alloy Phase Diagrams, 2nd edition, a comprehensive collection of alloy phase diagrams for 2159 binary systems, was published in 1990 (T.B. Massalski, H. Okamoto, P.R. Subramanian, and L. Kacprzak., ASM International, Materials Park, OH [Massalski2]). This review intends to provide more recent information on the binary phase diagrams for the Al-P, B-Ga, B-Nd, Ba-Ga, Bi-Cs, Ca-Ga, Cd-Gd, Cr-Mo, Gd-Ni, Ni-Pb, Ni-Sc, and Sc-Sn systems that have become available after 1990. The criteria for selecting such information for inclusion in this review are (1) systems for which no phase diagram was given in [Massalski2], (2) complete diagrams that are substantially different from the earlier version, and (3) partial diagrams that alter or clarify the earlier version. Thermodynamic consistency of the new phase diagrams was checked based on phase rules and the diagrams were modified

if necessary. However, each updated phase diagram has not gone through the ordinary evaluation process. Accordingly, a newer phase diagram is not always a better diagram, especially when there is too little published data on a system. For convenience, reaction tables and crystal structure data have been added when new information was available.

Al-P (Aluminum-Phosphorus)

The Al-P phase diagram shown in [1990Mas] was assessed by [1985Mac]. The pressure was assumed to be high enough to suppress the gas phase.

The Al-P phase diagram for the ambient pressure condition was calculated by [1994Ans] and [2013Lia]. Figure 1 shows the phase diagram reported by the latter, which is based on more detailed thermodynamic data obtained by the authors.

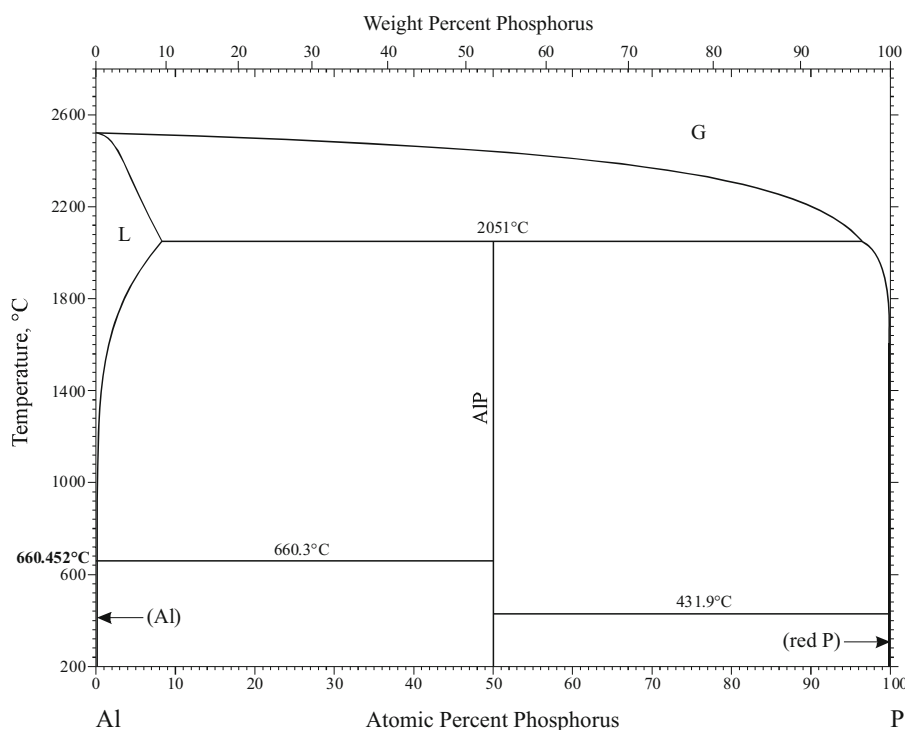


Fig. 1 Al-P phase diagram [2013Lia]

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B-Ga (Boron-Gallium)

The B-Ga phase diagram in [1990Mas] was redrawn from [1991Oka]. The original diagram was proposed by [1976Mof] based on scant information that the B-Ga phase diagram is a monotectic type [1965Wal]. Accordingly the entire phase diagram was speculative.

Figure 2 shows the B-Ga phase diagram proposed by [2013Li] using first-principles calculations. This phase diagram is expected to be better than that shown in [1990Mas], but experimental confirmation is required.

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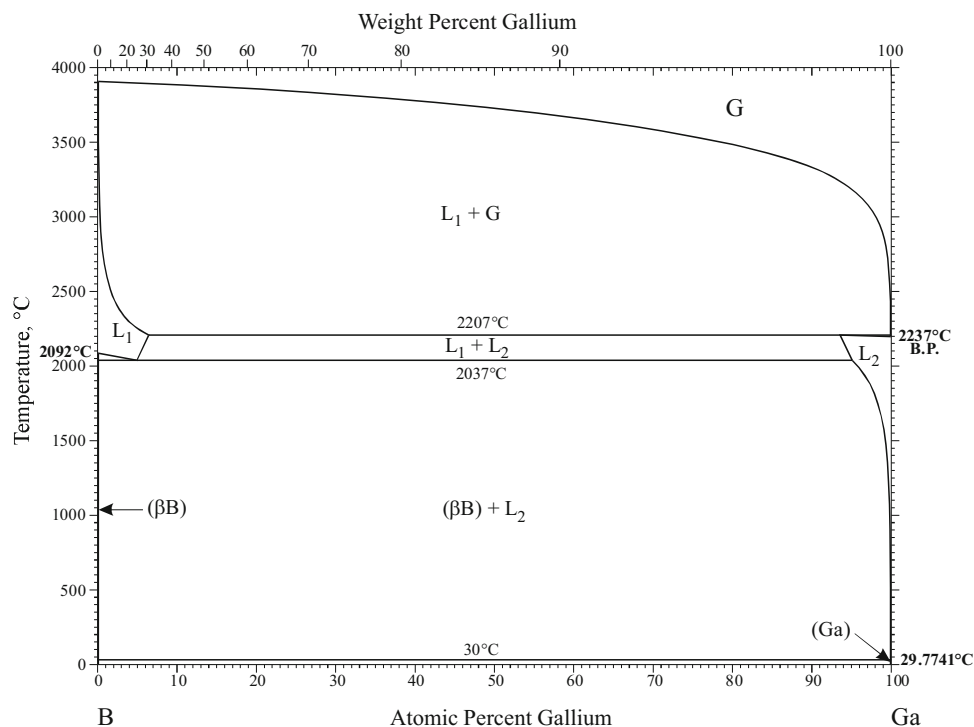


Fig. 2 B-Ga phase diagram [2013Li]

B-Nd (Boron-Neodymium)

The B-Nd phase diagram shown in [1990Lia] was taken from [1976Spe]. This phase diagram was updated by [1996Lia]. The B_5Nd_2 liquidus was drawn almost linearly to the Nd end (see [2010Oka]). Accordingly the phase diagram has become more thermodynamically unlikely by this update in view of [1991Oka].

A more plausible B-Nd phase diagram was reported by [1995Hal] by thermodynamic modeling. However, [2013Van] disclosed that the model proposed by [1995Hal] causes formation of an unlikely inverted miscibility gap in the liquid phase. Figure 3 shows the B-Nd phase diagram calculated by [2013Van] using a problem-free thermodynamic model.

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1995Hal: B. Hallmans, P. Wollants, and J.R. Roos, Thermodynamic Assessment of the Fe-Nd-B Phase Diagram, *J. Phase Equilib.*, 1995, **16**, p 137-149

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Ba-Ga (Barium-Gallium)

The Ba-Ga phase diagram was first reported by [1966Bru]. Five intermediate phases ($Ba_{10-12}Ga$, Ba_3Ga_2 , $BaGa$, $BaGa_2$, $BaGa_4$) were shown in this phase diagram. However, [1991Itk] concluded that there are only four equilibrium intermediate phases ($Ba_{10}Ga$, Ba_8Ga_7 , $BaGa_2$, $BaGa_4$) in this system by reviewing the works of [1979For] and [1983For]. This phase diagram was adopted by [1990Mas].

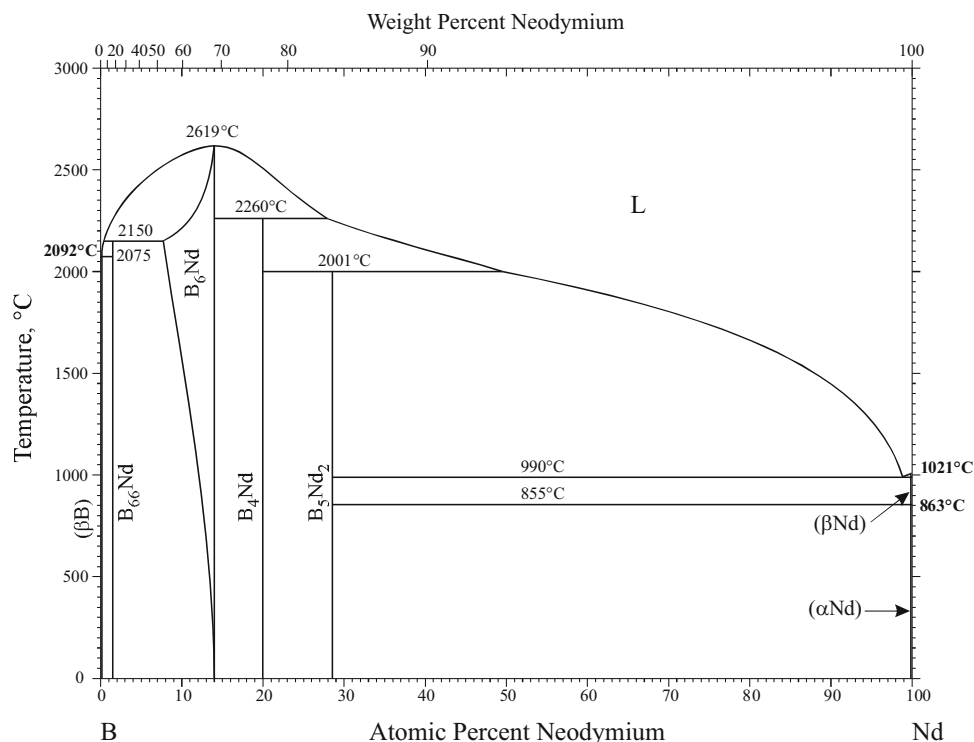


Fig. 3 B-Nd phase diagram [2013Van]

Subsequently, [1994For] discovered a stable phase Ba_5Ga_6 . Figure 4 shows the complete Ba-Ga phase diagram calculated by [2013Li] by taking into account the information described above.

Table 1 shows Ba-Ga crystal structure data.

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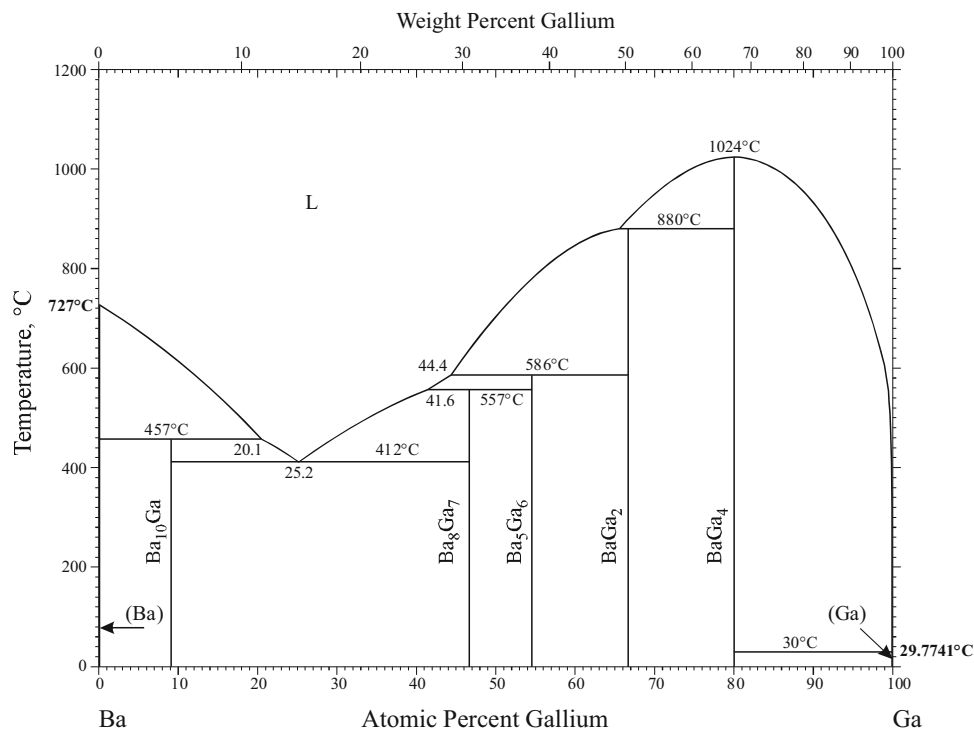


Fig. 4 Ba-Ga phase diagram [2013Li]

Table 1 Ba-Ga crystal structure data

Phase	Composition, at.% Ga	Pearson symbol	Space group	Strukturbericht designation	Prototype
(Ba)	0	<i>cI2</i>	<i>Im</i> $\bar{3}m$	<i>A2</i>	W
$Ba_{10}Ga$	9.1	<i>cF176</i>	<i>Fd</i> $\bar{3}m$...	$Al_{10}V$
Ba_8Ga_7	46.7	<i>cP60</i>	<i>P2</i> ₁ 3	...	Al_7Sr_8
Ba_5Ga_6	54.5	<i>hP24</i>	<i>P</i> $\bar{6}c2$
$BaGa_2$	66.7	<i>hP3</i>	<i>P6/mmm</i>	<i>C32</i>	AlB_2
$BaGa_4$	80	<i>tI10</i>	<i>I4/mmm</i>	<i>D1</i> ₃	Al_4Ba
(Ga)	100	<i>oC8</i>	<i>Cmca</i>	<i>A11</i>	Ga

Bi-Cs (Bismuth-Cesium)

The Bi-Cs phase diagram in [1990Mas] was adopted from [1991San]. The estimated error in the liquidus temperature was ± 30 °C due to uncertainty in the experimental data. Figure 5 shows the Bi-Cs phase diagram obtained by thermodynamic analysis by [2015Dja]. This calculated phase diagram agrees well with the phase boundary data used for determining the phase diagram of [1991San]. However, further refinement of the thermodynamic model may be needed because the BiCs_3 liquidus appears to be too asymmetric according to a criterion given in [1993Oka].

References

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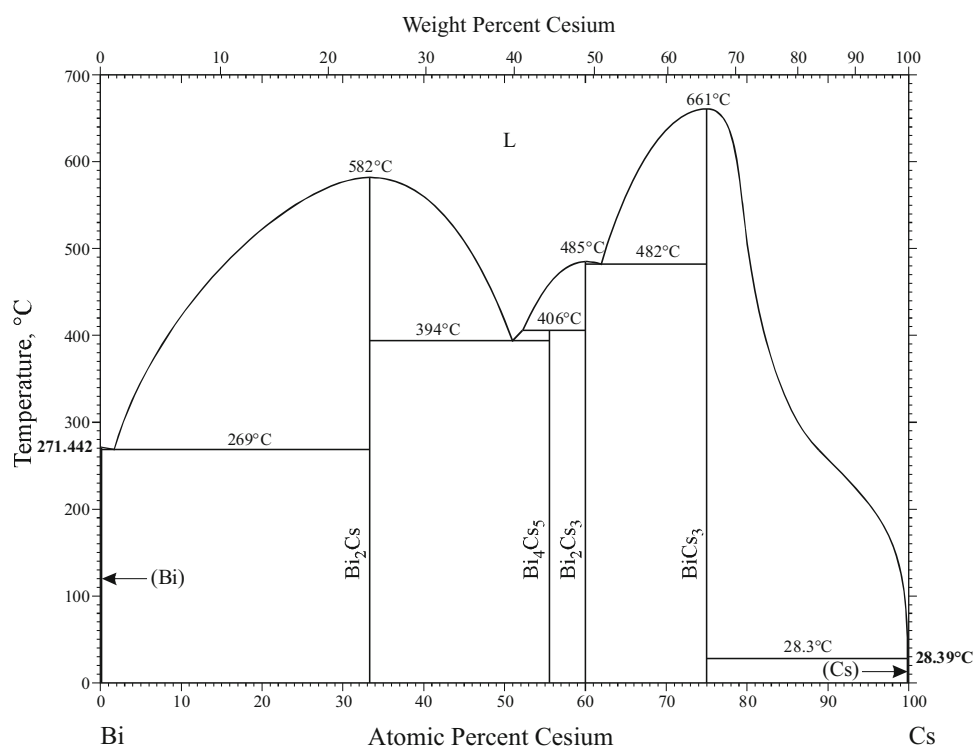


Fig. 5 Bi-Cs phase diagram [2015Dja]

Ca-Ga (Calcium-Gallium)

The Ca-Ga phase diagram originally reported by [1966Bru] was revised by [1989Bru]. [1990Mas] accepted the diagram of [1989Bru].

This system was analyzed thermodynamically by [2013Li]. Figure 6 shows the calculated Ca-Ga phase diagram. The CaGa_{2+x} phase having an unlikely constant width (67.7 to 70.6 at.% Ga below $\sim 900^\circ\text{C}$) in [1990Mas] was modeled as a line compound $\text{Ca}_{25}\text{Ga}_{59}$.

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Cd-Gd (Cadmium-Gadolinium)

[1988Gsc] reviewed the Cd-Gd system and proposed an assessed phase diagram primarily based on [1971Bru]. This phase diagram was accepted by [1990Mas]. Six intermediate phases (one dimorphic) existing in this system were shown as line compounds. [2001Kur] attempted thermody-

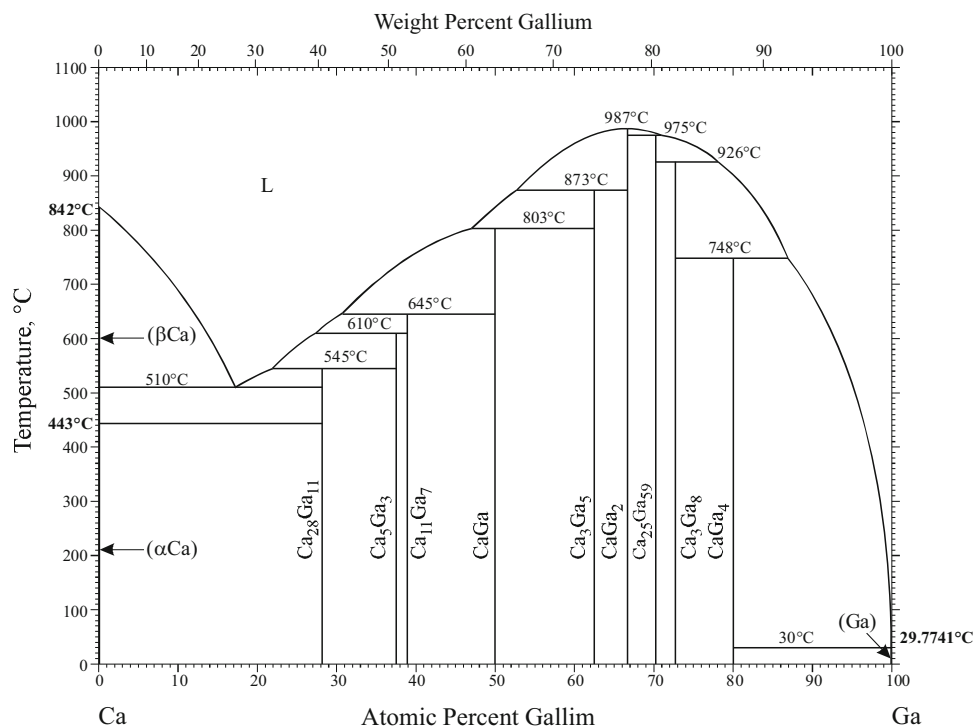


Fig. 6 Ca-Ga phase diagram [2013Li]

dynamic modeling of this phase diagram for the composition range 0 to 60 at.% Gd.

[2014Rei] reinvestigated the Cd-Gd phase diagram by means of powder XRD, SEM, and DTA. The result is shown in Fig. 7. The existence of six intermediate phases was confirmed. In addition, a phase corresponding to Cd_8Gd stoichiometry was found to form by a peritectic reaction at 465 °C. No crystal structure data were available for this phase.

In view of [1991Oka], the following features of this phase diagram may have to be examined further.

- Relationship between the liquidus and the solidus of (βGd): When extended to the Cd-rich direction, they would cross each other unless unlikely bends are introduced.
- Constant solid solution ranges over wide temperature range for $\text{Cd}_{45}\text{Gd}_{11}$, $\alpha\text{Cd}_2\text{Gd}$, and CdGd : Solid solution ranges usually decreases as the temperature decreases.
- Narrow two-phase field over wide temperature range between $\text{Cd}_{58}\text{Gd}_{13}$ and $\text{Cd}_{45}\text{Gd}_{11}$: One of the two phases may be unstable at low temperatures or $\text{Cd}_{45}\text{Gd}_{11}$ may have a narrower solid solution range.

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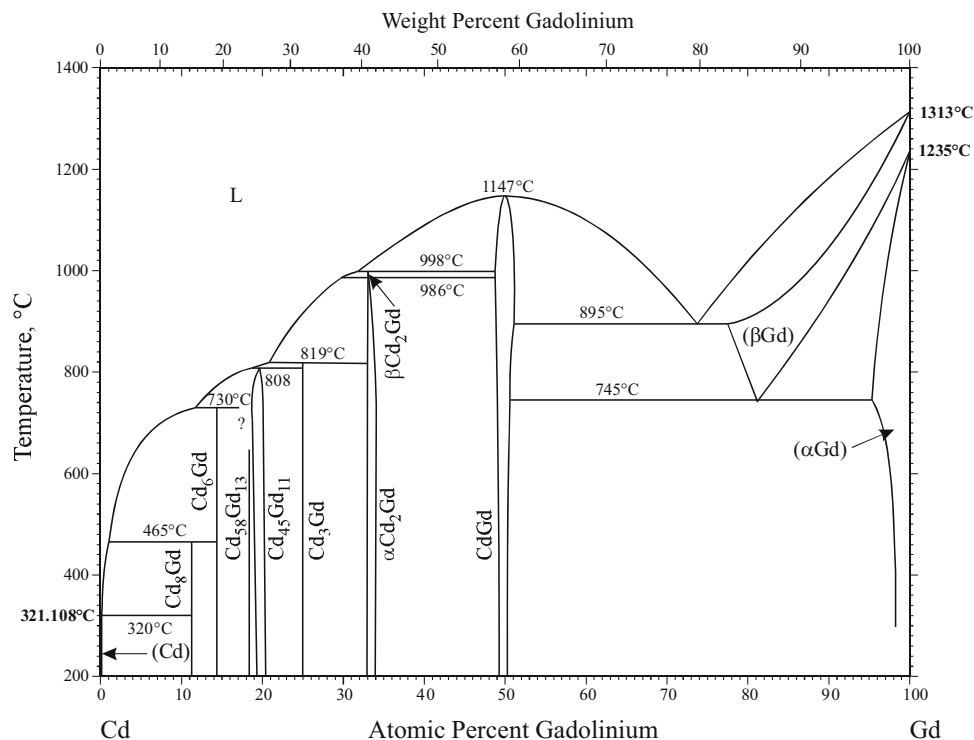


Fig. 7 Cd-Gd phase diagram [2014Rei]

Cr-Mo (Chromium-Molybdenum)

[1987Ven] reviewed the Cr-Mo system. The liquidus and solidus were estimated from numerous data points. The miscibility gap in the solid phase was taken from [1973Kau]. The assessed diagram was accepted in [1990Mas].

Thermodynamic modeling of the complete phase diagram was attempted by [2005Shu], [2006Tur], and [2013Jin]. Table 2 compares the minimum melting point temperature and the critical point temperature of the miscibility gap obtained by these works. It is difficult to select the most likely equilibrium diagram from these

Table 2 Calculated temperatures of characteristic points in the Cr-Mo phase diagram

Reference	Min. melting temp. (°C)	Critical temp. of miscibility gap (°C)
1987Ven	1820 ^a	880
2005Shu	1830	1033
2006Tur	1852	940
2013Jin	1854	908

^a From experimental data points

diagrams because of uncertainty in the experimental data points for the liquidus and solidus and absence of data points for the miscibility gap. Figure 8 shows the Cr-Mo phase diagram published most recently.

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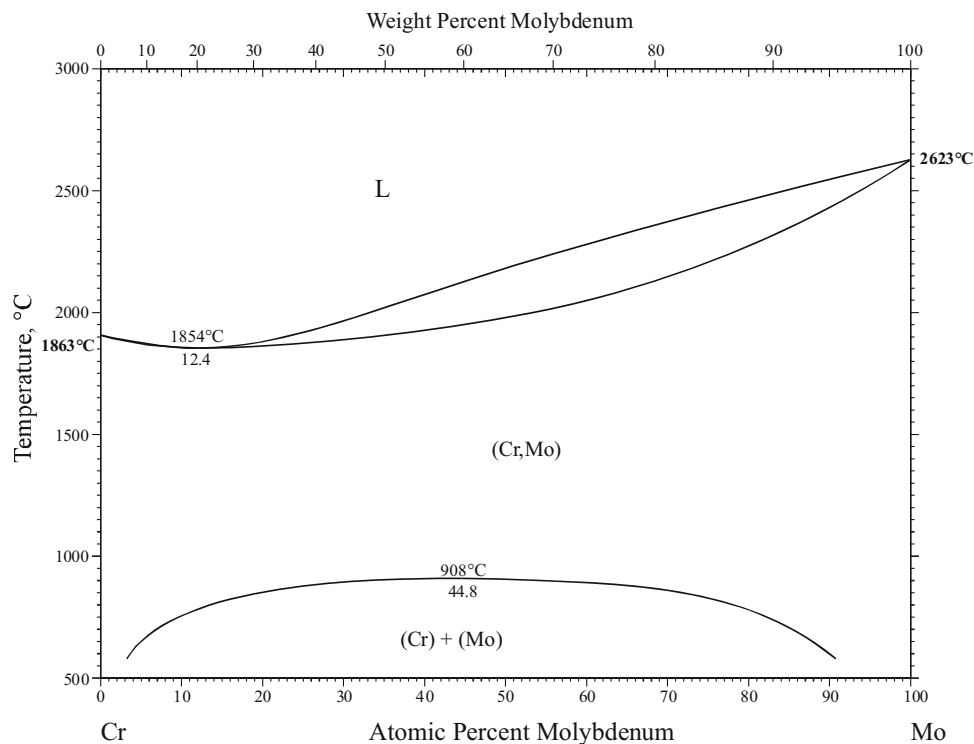


Fig. 8 Cr-Mo phase diagram [2013Jin]

Gd-Ni (Gadolinium-Nickel)

The Gd-Ni phase diagram in [1990Mas] was adopted from [1991Pan]. This assessed phase diagram was essentially identical to the one determined by [1986Pan]. The phase diagram of [1986Pan] in turn was in excellent agreement with [1961Nov]. Nine intermediate phases were shown (Gd_3Ni , Gd_3Ni_2 , $GdNi$, $GdNi_2$, $GdNi_3$, Gd_2Ni_7 , $GdNi_4$, $GdNi_5$, Gd_2Ni_{17}). However, [1994Oka] pointed out that further studies may be needed for this phase diagram because liquidus curves of compounds are unnaturally uneven.

[2012Xu] reexamined the Gd-Ni system and obtained the phase diagram shown in Fig. 9. A major difference from [1991Pan] is the absence of Gd_3Ni_2 and $GdNi_4$. This result is in good agreement with [1961Cop] and the problem pointed out by [1994Oka] has been resolved. The Gd-rich end of Fig. 9 may have to be adjusted because the melting point and allotropic transformation temperatures of pure Gd are shown fairly differently from commonly accepted values of 1313 and 1235 °C, respectively.

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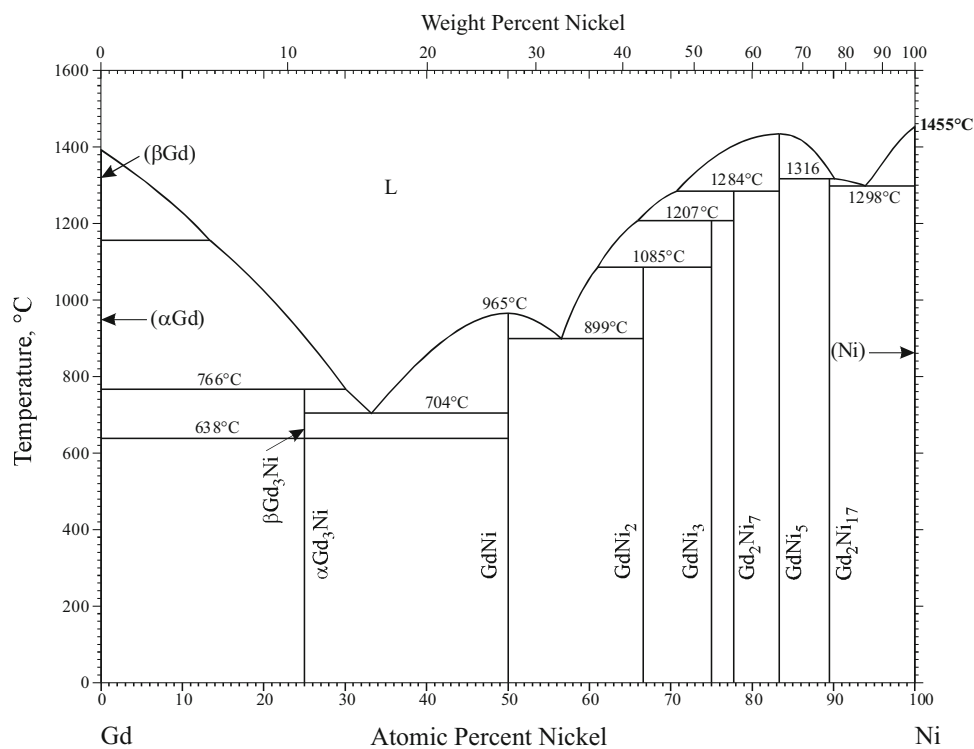


Fig. 9 Gd-Ni phase diagram [2012Xu]

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Ni-Pb (Nickel-Lead)

The Ni-Pb system was reviewed by [1987Nas] and the assessed phase diagram was adopted by [1990Mas]. Due to lack of experimental data, the maximum solubility of Pb in (Ni) was speculated to be ~3 at.% on the phase diagram.

[2014Oka] updated this phase diagram according to [2010Kai]. The maximum solubility was estimated to be 0.13 at.% Pb. [2013Vaa] measured the solubility of Pb in (Ni) by chemical analysis of equilibrated specimens and determined the (Ni) solvus by thermodynamic modeling. The result was quantitatively in agreement with [2010Kai]. Figure 10, 11, and 12 show the complete Ni-Pb phase

diagram, Ni-rich corner, and Pb-rich corner, respectively, calculated by [2013Vaa].

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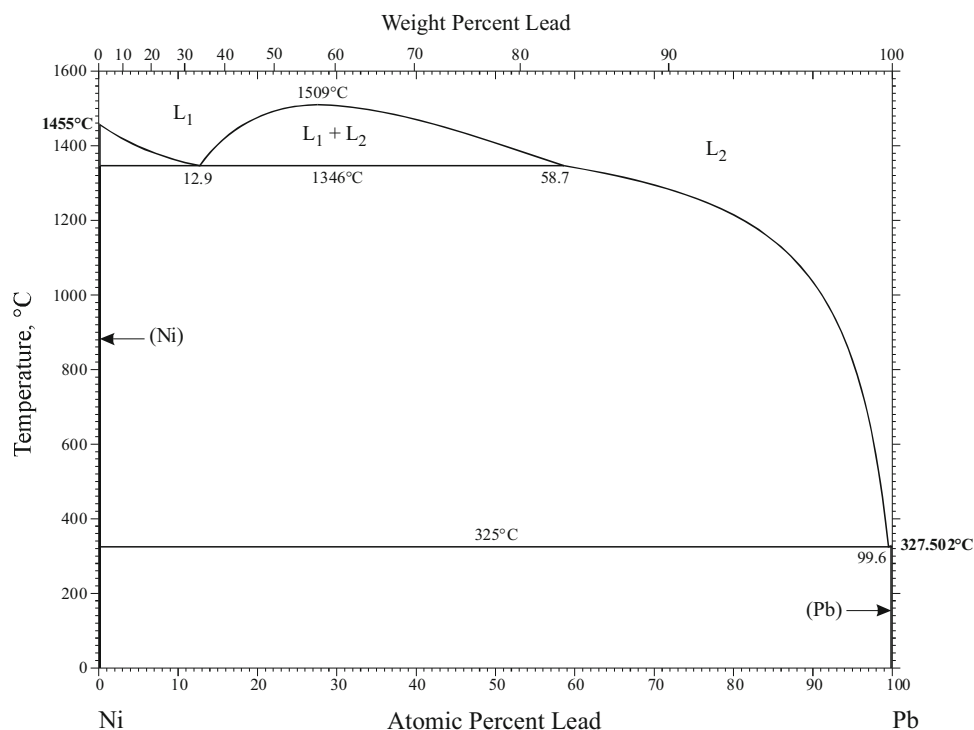


Fig. 10 Ni-Pb phase diagram [2013Vaa]

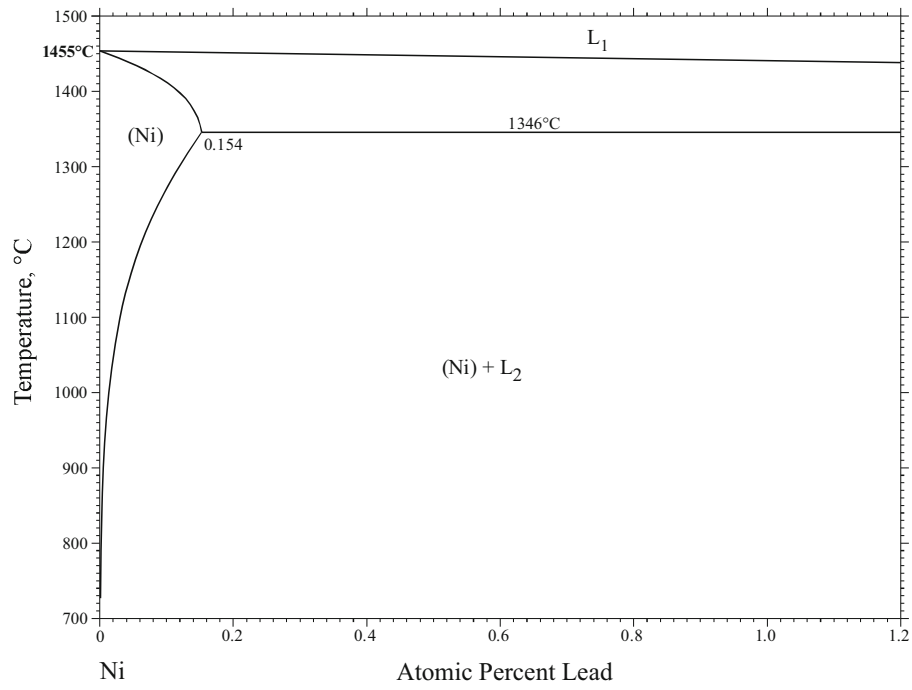


Fig. 11 Ni-rich corner of the Ni-Pb phase diagram [2013Vaa]

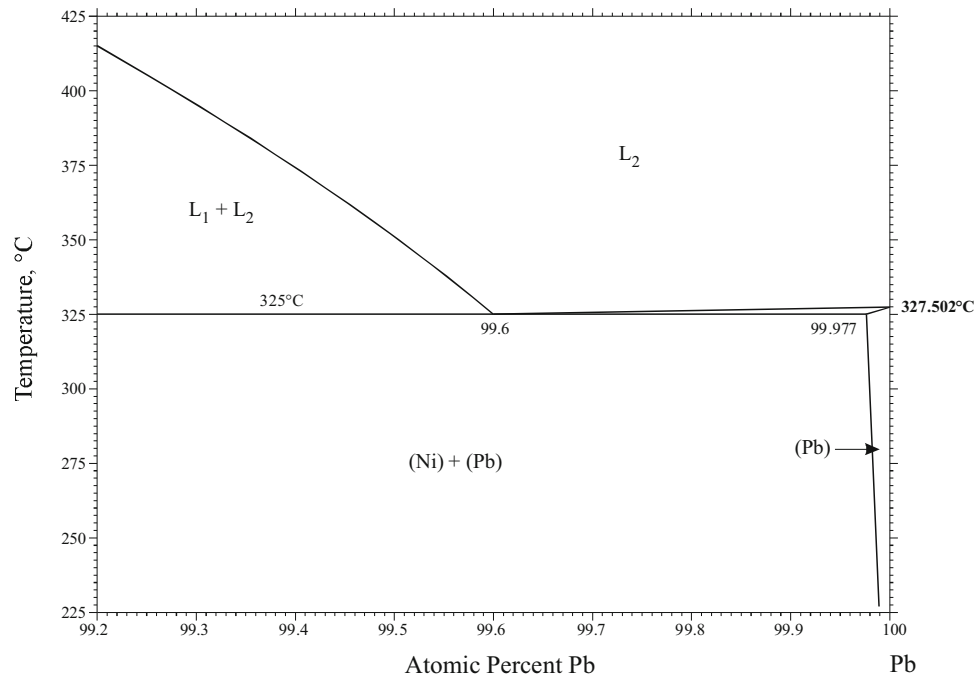


Fig. 12 Pb-rich corner of the Ni-Pb phase diagram [2013Vaa]

Ni-Sc (Nickel-Scandium)

The Ni-Sc phase diagram in [1990Mas] was updated by [2000Oka] based on experimental data reported by [1997Sem]. Thermodynamic modeling of this system was attempted by [2013Kar] and [2015Li]. Figure 13 shows the Ni-Sc phase diagram calculated by [2015Li]. The result of [2013Kar] seems to be less likely because the width of the Ni_2Sc phase field is shown to increase as the temperature decreases, according to the guideline given by [1993Oka].

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Sc-Sn (Scandium-Tin)

The complete Sc-Sn phase diagram was constructed by [2009Oka] by compromising two partial phase diagrams reported by [1995Pal] and [2005Pod].

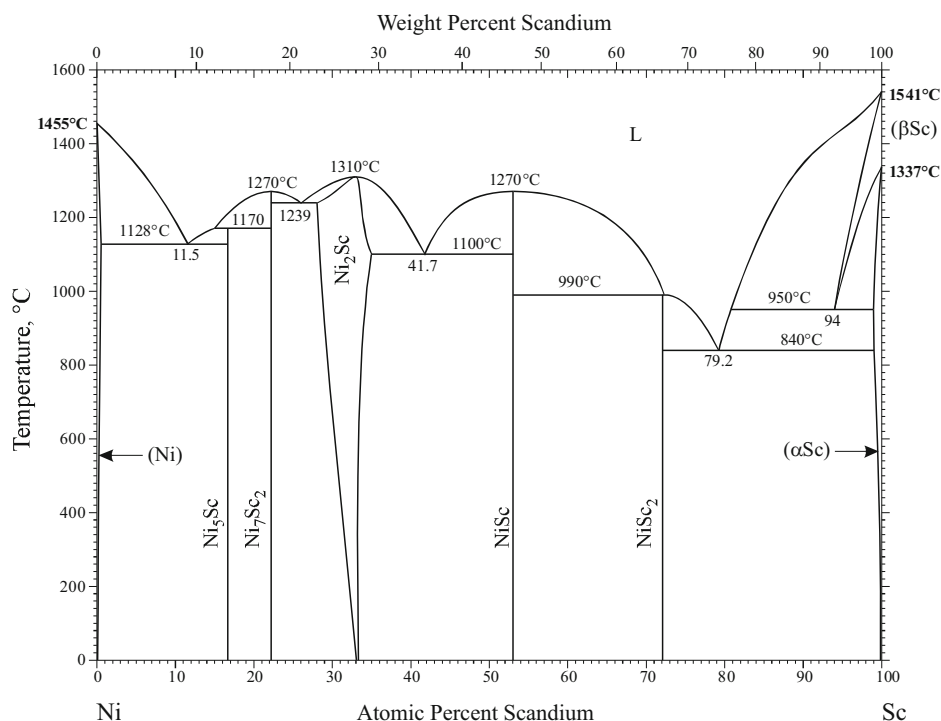


Fig. 13 Ni-Sc phase diagram [2015Li]

This phase diagram was thermodynamically analyzed by [2013ldd]. Figure 14 shows the calculated phase diagram.

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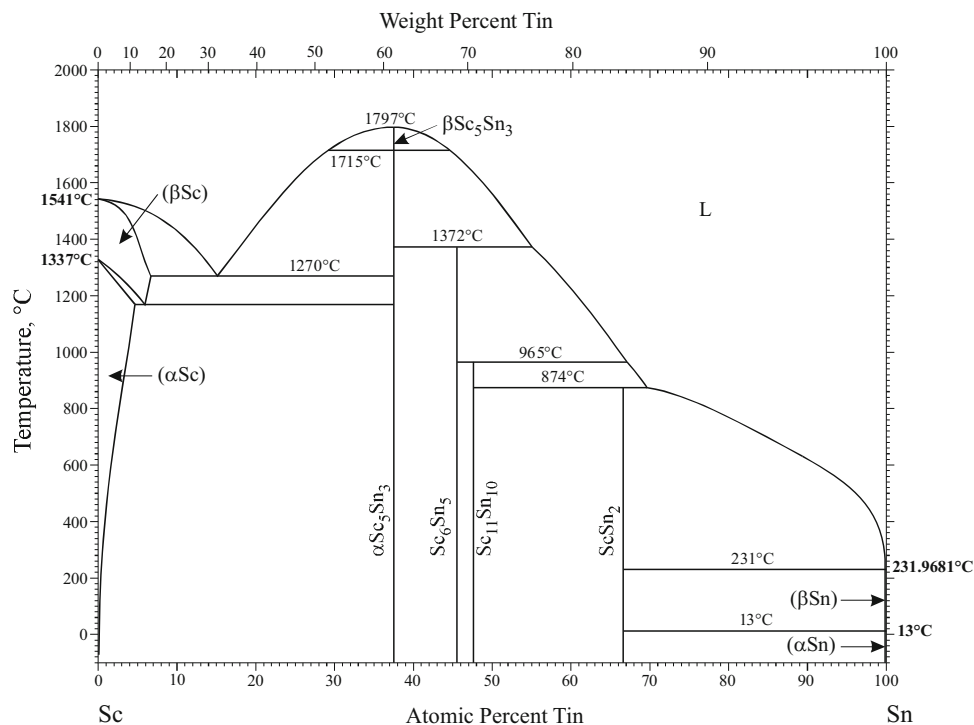


Fig. 14 Sc-Sn phase diagram [2013ldd]