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Supplemental Literature Review of Binary Phase Diagrams: Ag-Ca, Al-Yb, As-Fe, B-Zr, Co-U, Cu-Se, Cu-Th, La-Mo, Mg-Sn, Mo-Th, Sn-Ta, and Te-Ti

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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 Ag-Ca, Al-Yb, As-Fe, B-Zr, Co-U, Cu-Se, Cu-Th, La-Mo, Mg-Sn, Mo-Th, Sn-Ta, and Te-Ti 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.

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Ag-Ca (Silver-Calcium)

A preliminary form of the Ag-Ca phase diagram prepared by [1988Bar] was shown in [1990Mas]. Problems on the form of liquidus boundaries in this phase diagram were pointed out by [1994Oka], but these problems have already been solved in the final version of [1988Bar]. This revised phase diagram is shown in, e.g., [2010Oka]. The phase diagram was assessed thermodynamically by [2008Hua]. The calculated result shown in Fig. 1 is in good agreement with [1988Bar]. Similar phase diagrams were obtained by [2014Bra] and [2015Wan]. Ag-Ca crystal structure data are updated in Table 1 according to [2007Vil].

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2007Vil: P. Villars and K. Cenzual, *Pearson's Crystal Data CD-ROM*, Release 2007/8, ASM International, OH, 2007

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2010Oka: H. Okamoto, *Desk Handbook, Phase Diagrams for Binary Alloys, 2nd Edition*, ASM International, Materials Park, OH, 2010, p 5

2014Bra: M.H. Braga, A. Dębski, and W. Gasior, Optimization and Assessment of the Ag-Ca Phase Diagram, J. Alloys Compd., 2014, 612, p 280-286

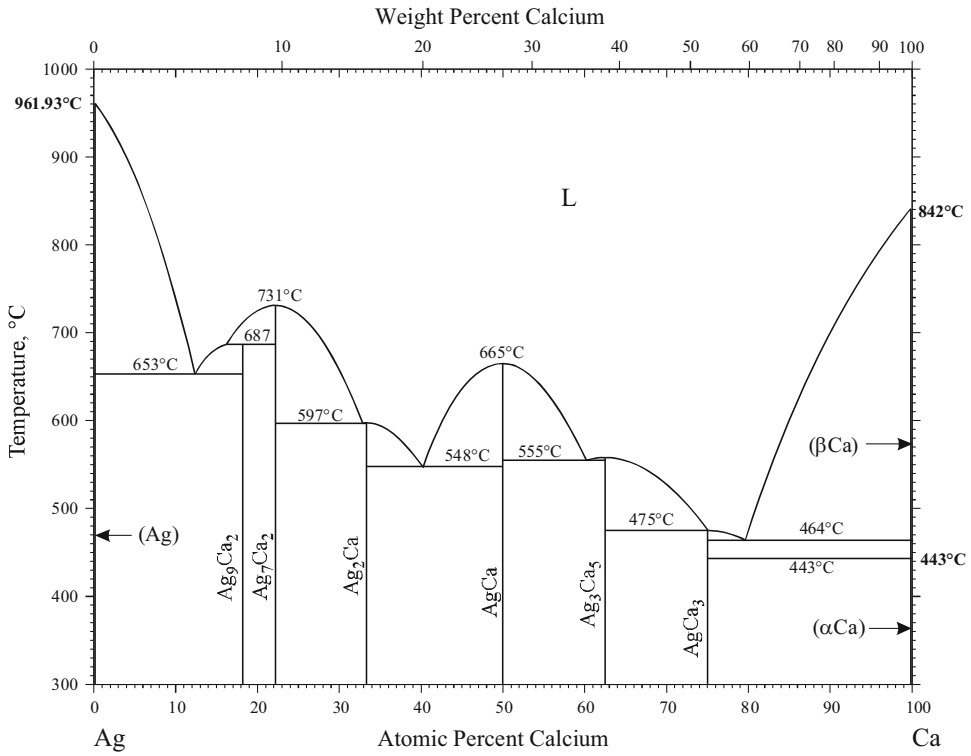

Fig. 1 Ag-Ca phase diagram [2008Hua]

Table 1 Ag-Ca crystal structure data

Phase	Composition, at.% Ca	Pearson symbol	Space group	Strukturbericht designation	Prototype
(Ag)	0	*cF*4	$Fm\bar{3}m$	*A*1	Cu
Ag_9Ca_2	18.2	…	…	…	…
Ag_7Ca_2	22.2	*oS*36	*Cmcm*	…	…
Ag_2Ca	33.3	*oI*12	*Imma*	…	Hg_2K
AgCa	50	*oS*8	*Cmcm*	B_f	CrB
Ag_3Ca_5	62.5	*tI*32	*I*4/*mcm*	$D8_l$	Cr_5B_3
$AgCa_3$	75	…	…	…	…
(βCa)	100	*cI*2	$Im\bar{3}m$	*A*2	W
(αCa)	100	*cF*4	$Fm\bar{3}m$	*A*1	Cu

2015Wan: J. Wang, P. Chartrand, and I.H. Jung, Thermodynamic Description of the Ag-(Ca, Li, Zn) and Ca-(In, Li) Binary Systems, CALPHAD, 2015, 50, p 68-81

Al-Yb (Aluminum-Ytterbium)

The review of the Al-Yb system done by [1989Gsc] was accepted by [1990Mas]. The assessed phase diagram was drawn based on experimental phase boundary data reported by [1971Kul] and [1972Pal]. Figure 2 shows the Al-Yb phase diagram obtained by thermodynamic modeling by [2008Men]. The phase diagram agreed with [1989Gsc] excellently.

[1990Kom] observed approximately 0.2 at.% solubility of Yb in (Al) at the eutectic temperature on the Al side. This is too small to be shown on Fig. 2.

References

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1989Gsc: K.A. Gschneidner, Jr. and F.W. Calderwood, The Al-Yb (Aluminum-Ytterbium) System, Bull. Alloy Phase Diagrams, 1989, 10(1), p 47-49

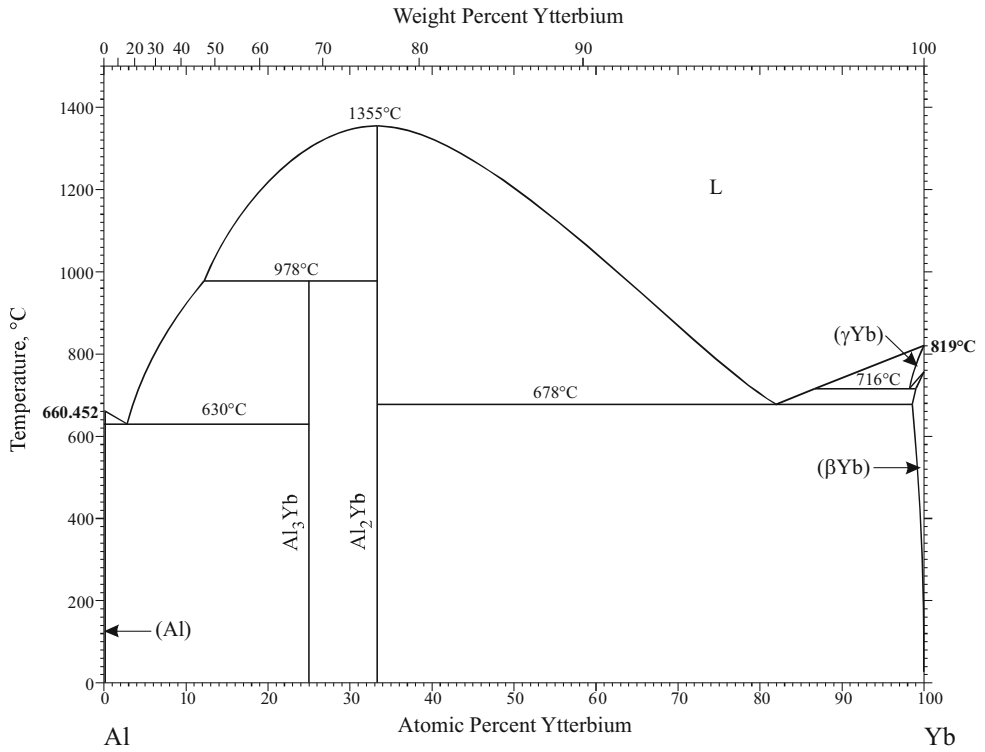

Fig. 2 Al-Yb phase diagram [2008Men]

1990Kom: V.L. Komonenko and S.V. Golubev, Phase Diagrams of Binary Systems of Aluminum with La, Ce, Pr, Nd, Sm, Eu, Yb, Sc and Y, Russ. Metall., Vol., 1990, p 193-195

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2008Men: F.G. Meng, L.G. Zhang, H.S. Liu, L.B. Liu, and Z.P. Jin, Thermodynamic Optimization of the Al-Yb Binary System, J. Alloys Compd., 2008, 452, p 279-282

As-Fe (Arsenic-Iron)

The As-Fe phase diagram in [1990Mas] was redrawn from [1991Oka], which reviewed the As-Fe system based on literature data published before 1986. Experimental data on the As_2Fe liquidus were missing in this review, but they were published later by [1988Uga].

Thermodynamic modeling of this system was attempted by [1994Pei] and [2008Ohn]. The calculated phase diagram of [2008Ohn] (Fig. 3) is in good agreement with the experimental data reported by [1991Oka] and [1988Uga].

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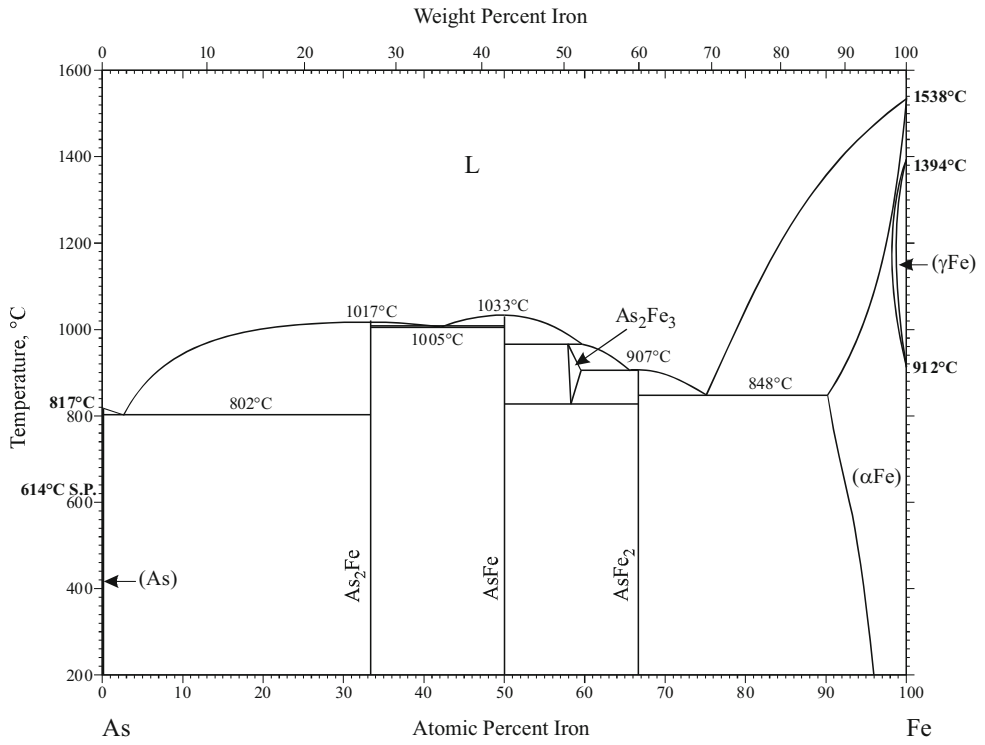

Fig. 3 As-Fe phase diagram [2008Ohn]

B-Zr (Boron-Zirconium)

Th B-Zr phase diagram in [1990Mas] was based on [1970Por]. [1993Oka] updated the phase diagram by integrating information from phase diagrams of [1953Gra] and [1969Rud] as well. The B-Zr phase diagram of [1993Oka] was thermodynamically optimized by [2008Tok], as shown in Fig. 4. Temperature values for invariant reactions were read from the figure.

Reference:

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1970Por: K.I. Portnoi, V.M. Romashov, and L.N. Burobina, Constitution Diagram of the System Zirconium-Boron, Sov. Powder Metall. Met. Ceram., 1970, 9, p 577-580

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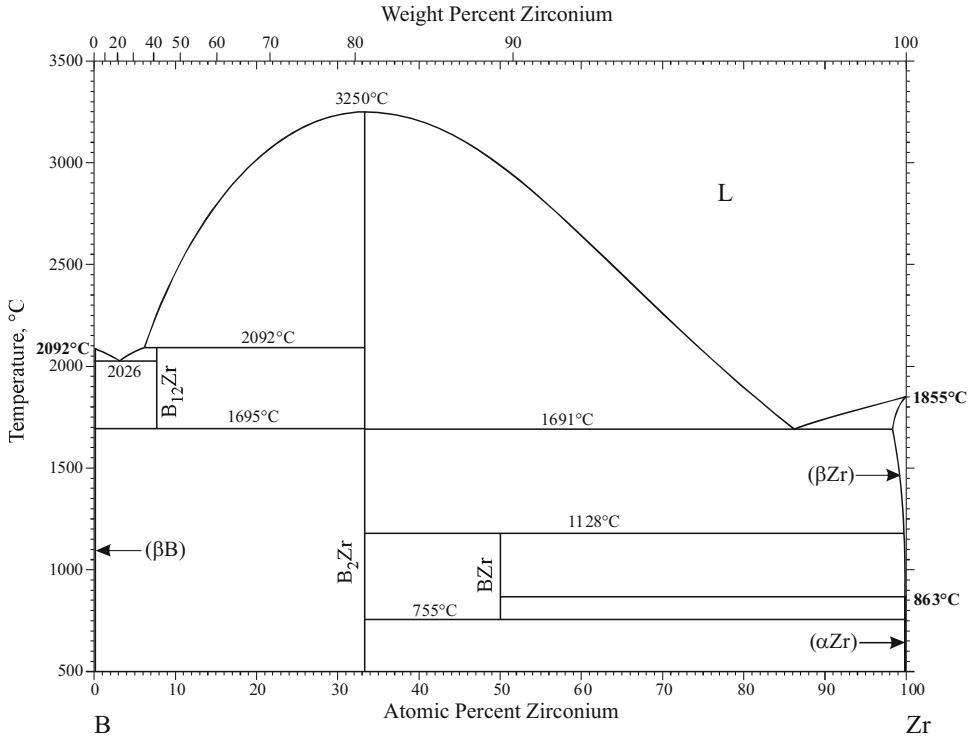

Fig. 4 B-Zr phase diagram [2008Tok]

Co-U (Cobalt-Uranium)

The Co-U system was reviewed by [1990Ish]. The assessed phase diagram was thermodynamically analyzed by [2008Wan]. The calculated phase diagram (Fig. 5) agrees with that of [1990Ish] mostly. However, in view of [1991Oka], the phase diagram of [2008Wan] shows more likely form with regard to the curvatures of liquidus boundaries of intermetallic compounds. On the other hand, [2008Wan] is less likely with regard to the solubility range of Co_2U. This phase is shown to have a constant width below $\sim$ 1100 °C. This phenomenon requires impossibly delicate balance in the temperature dependence of Gibbs energies with neighboring phases. This part of the phase diagram is questionable.

References

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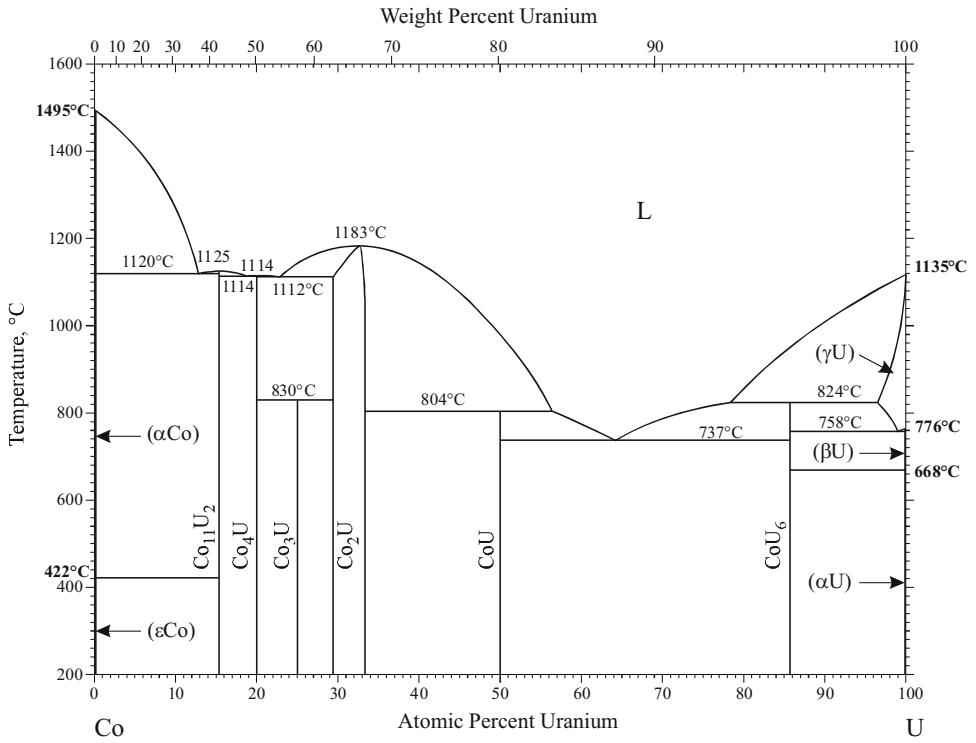

Fig. 5 Co-U phase diagram [2008Wan]

2008Wan: J. Wang, X.J. Liu, and C.P. Wang, Thermodynamic Modeling of the Al-U and Co-U Systems, J. Nucl. Mater., 2008, 374, p 79-86

Cu-Se (Copper-Selenium)

The Cu-Se system was reviewed by [1981Cha]. The assessed phase diagram was accepted by [1990Mas]. Since then, the miscibility gap of the liquid phase on the Cu-rich side was determined by [1990Gla]. Figure 6 shows the Cu-Se phase diagram thermodynamically analyzed by [2008Du]. [1995Coh] observed only two polymorphic forms for CuSe with the transition temperature at 50 °C. Confirmation is needed.

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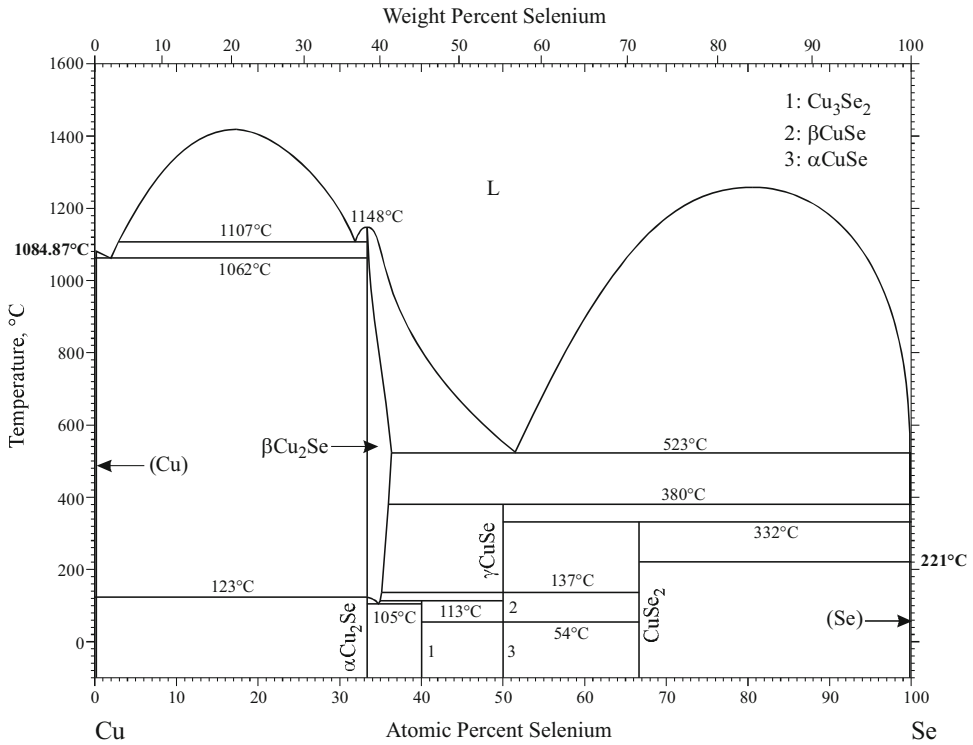

Fig. 6 Cu-Se phase diagram [2008Du]

Cu-Th (Copper-Thorium)

The Cu-Th system was reviewed by [1986Cha]. The assessed phase diagram, primarily based on [1971Sch], was accepted by [1990Mas].

The Cu-Th phase diagram calculated by [2008Wan] (Fig. 7) was in excellent agreement with [1986Cha]. $Cu_{51}Th_{14}$ in Fig. 7 has been treated as $Cu_{3.6}Th$ in both [1986Cha] and [2008Wan]. $Cu_{51}Th_{14}$ is the correct configuration [1972Ber]. Because the compositions of $Cu_{51}Th_{14}$ and $Cu_{3.6}Th$ are very close (the difference is within line width in Fig. 7), the phase diagram has not been modified. However, Cu-Th crystal structure data have been updated in Table 2.

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2008Wan: C.P. Wang, Y.F. Li, X.J. Liu, and K. Ishida Thermodynamic Assessments of the Cu-Th and Mo-Th Systems, J. Alloys Compd., 2008, 458, p 208-213

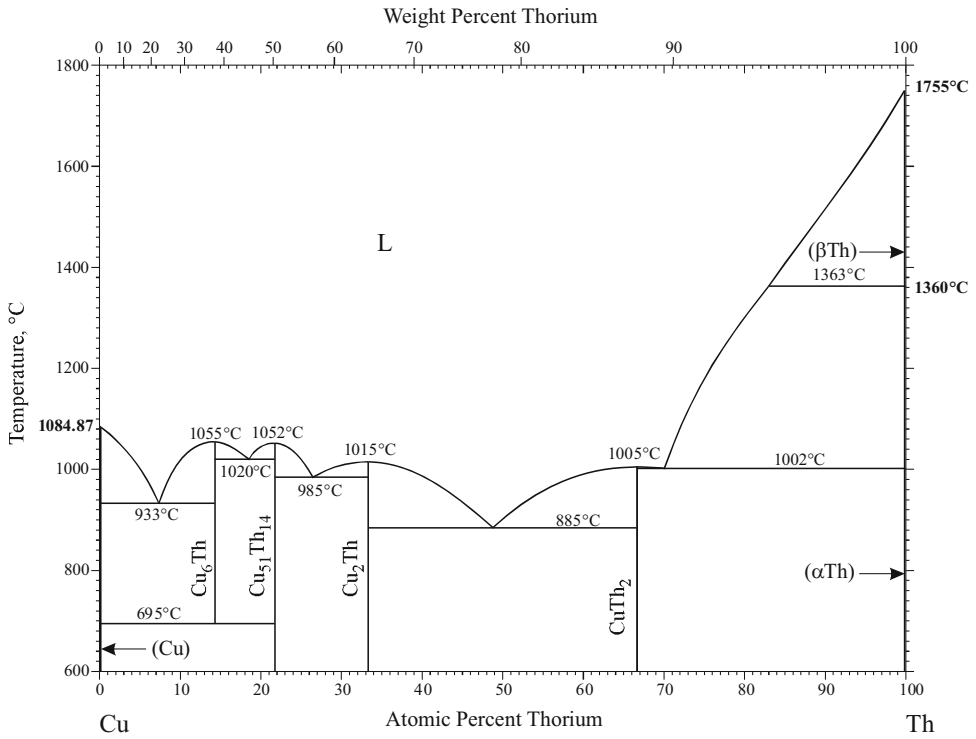

Fig. 7 Cu-Th phase diagram

Table 2 Cu-Th crystal structure data

Phase	Composition, at.% Th	Pearson symbol	Space group	Strukturbericht designation	Prototype
(Cu)	0	*cF*4	$Fm\bar{3}m$	*A*1	Cu
Cu_6Th	14.3	*oP*28	*Pnma*	…	…
$Cu_{51}Th_{14}$	21.5	*hP*68	*P*6/*m*	…	…
Cu_2Th	33.3	*hP*3	*P*6/*mmm*	*C*32	AlB_2
$CuTh_2$	66.7	*tI*12	*I*4/*mcm*	*C*16	Al_2Cu
(βTh)	100	*cI*2	$Im\bar{3}m$	*A*2	W
(αTh)	100	*cF*4	$Fm\bar{3}m$	*A*1	Cu

La-Mo (Lanthanum-Molybdenum)

[1990Mas] introduced the La-Mo phase diagram predicted by [1980Bre]. [2008Wan] optimized this phase diagram by thermodynamic modeling. The result is shown in Fig. 8. The critical temperature of the miscibility gap is estimated to be about 200 °C lower than that of [1980Bre]. The difference must be compromised experimentally.

References

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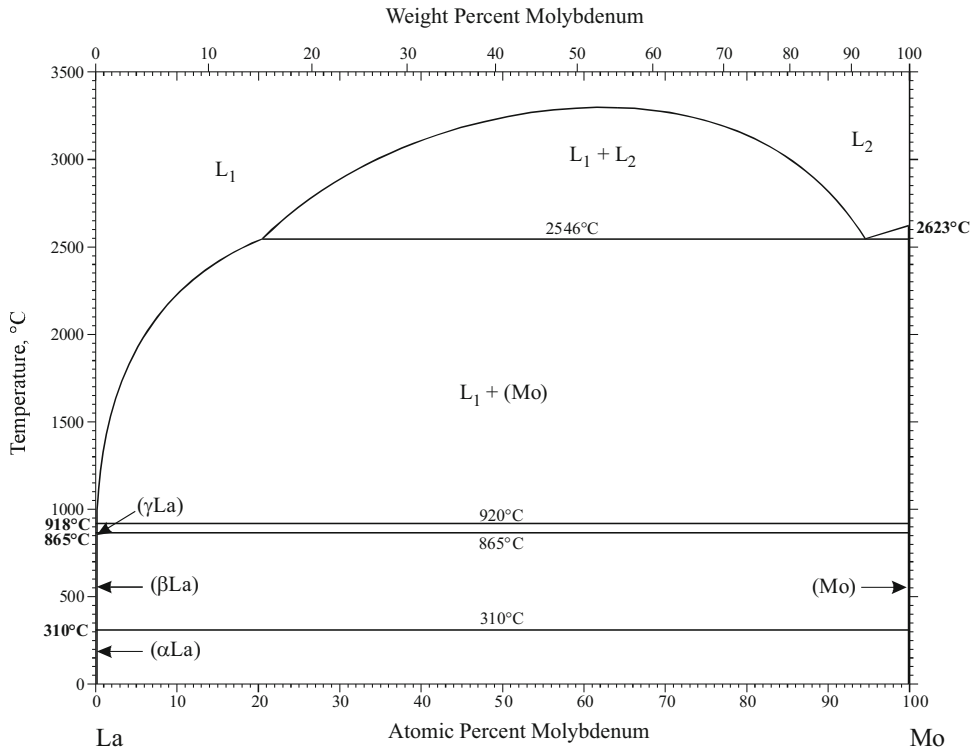

Fig. 8 La-Mo phase diagram [2008Wan]

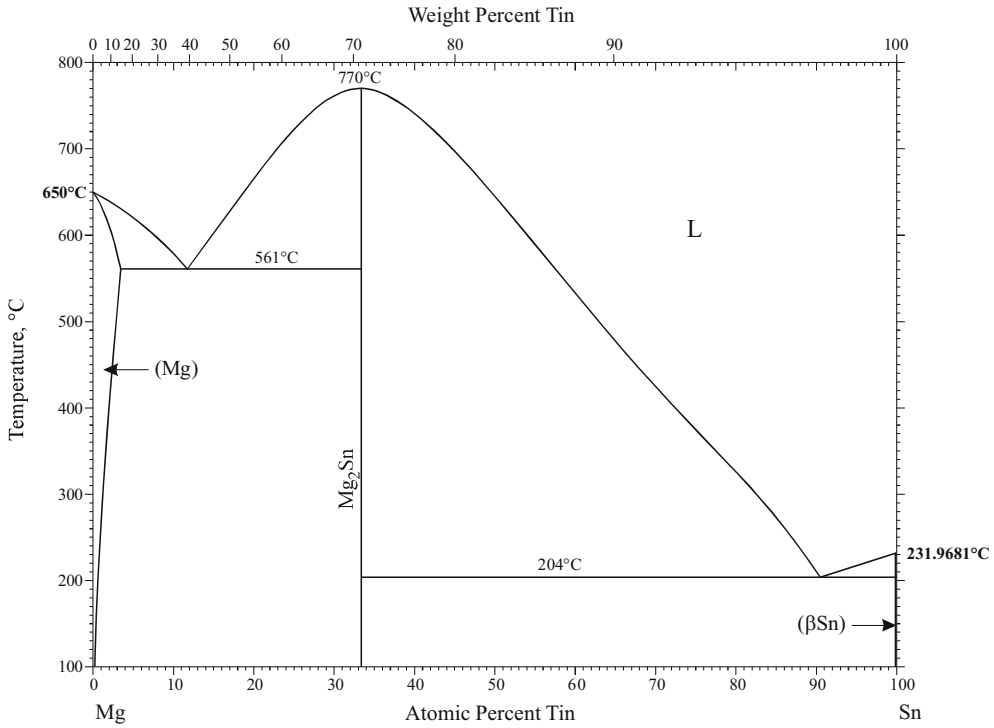

Fig. 9 Mg-Sn phase diagram [2010Kan]

Mg-Sn (Magnesium-Tin)

The Mg-Sn system was reviewed by [1984Nay]. The assessed phase diagram was accepted by [1990Mas].

Since then, this phase diagram has been analyzed repeatedly by [1986Jon], [1991Sri], [1999Mor], [2007Jun1, 2007Jun2], and [2010Kan]. The phase diagram of [2010Kan] (Fig. 9), which takes into account short-range ordering in the liquid phase in the thermodynamic model, appears to represent the experimental phase diagram most adequately.

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Mo-Th (Molybdenum-Thorium)

[1982Chi] introduced the Mo-Th phase diagram determined by [1977Gar] ([1978Gar]). This phase diagram showed the liquidus for only ~ 40-100 at.% Th although the original literature showed the liquidus for the entire composition range. [1990Bre] presented a complete phase diagram based on [1977Gar] and thermodynamic modeling.

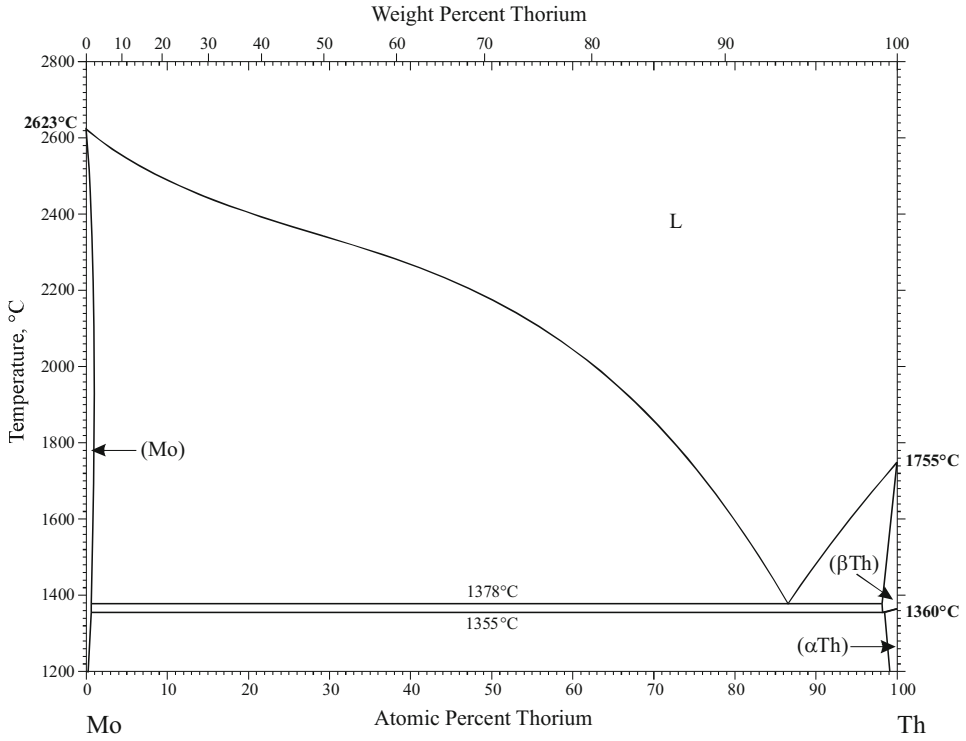

Fig. 10 Mo-Th phase diagram [2008Wan]

This phase diagram was analyzed again by [2008Wan]. In comparison with [1990Bre], the calculated phase diagram shown in Fig. 10 is in better agreement with [1977Gar].

Earlier, [1962Mcm] reported a Mo-Th phase diagram with the same topology as that shown in Fig. 10, but the (Mo) liquidus at 0 at.% Th was too steep in comparison with the slope expected from the van't Hoff law.

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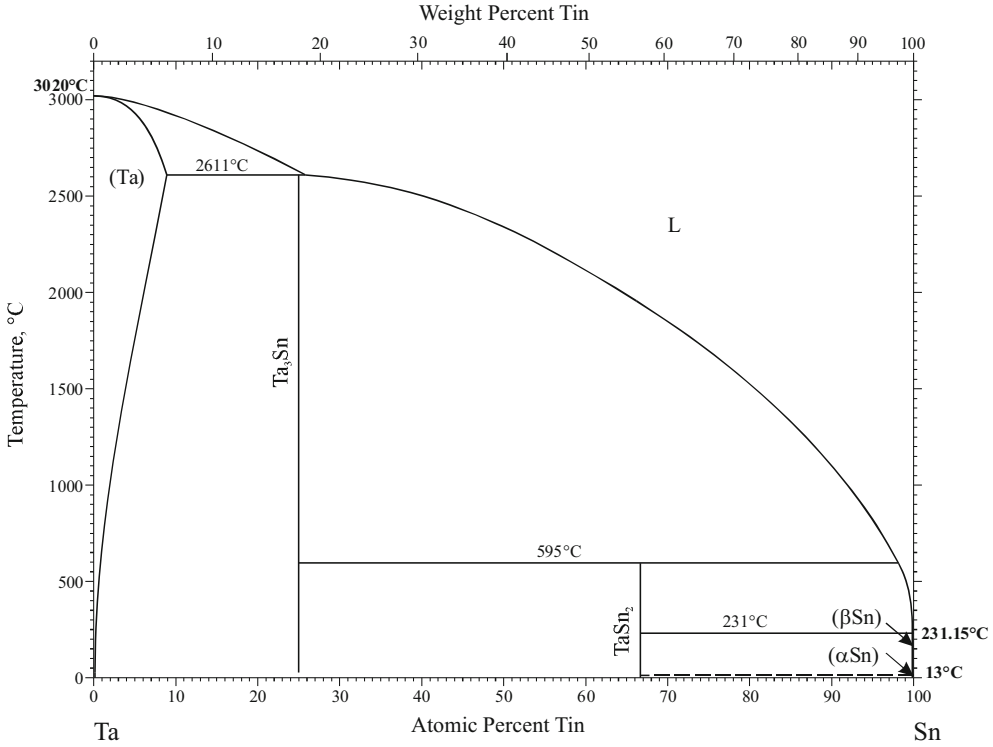

Fig. 11 Ta-Sn phase diagram [2017Mar]

Thermodynamic Properties of Refractory Metal Solutes in

Table 3 Ta–Sn crystal structure data

Phase	Composition, at.% Sn	Pearson symbol	Space group	Strukturbericht designation	Prototype
(Ta)	0-9	*cI*2	$Im\bar{3}m$	*A*2	W
Ta_3Sn	25	*cP*8	$Pm\bar{3}n$	*A*15	Cr_3Si
$TaSn_2$	66.7	*oF*48	*Fddd*	C_b	$CuMg_2$
(βSn)	100	*tI*4	$I4_1/amd$	*A*5	βSn
(αSn)	100	*cF*8	$Fd\ \bar{3}m$	*A*4	C (diamond)

Sn-Ta (Tin-Tantalum)

[2003Oka] introduced the Ta-Sn phase diagram proposed by [2002Stu]. Ta_3Sn and Ta_2Sn_3 existed in this phase diagram. The latter phase was shown to form by a peritectic reaction at 595 °C according to [1971Bas]. The phase diagram was drawn up to 1400 °C, and the melting behavior of Ta_3Sn was unknown.

Figure 11 shows the Ta-Sn phase diagram predicted by [2017Mar] based on first-principles calculations. Ta_2Sn_3 in [2002Stu] was replaced by $TaSn_2$. The crystal structure data ($CuMg_2$ type: Table 3) supports this change. The phase diagram may need fine adjustment due to lack of supporting experimental phase boundary data.

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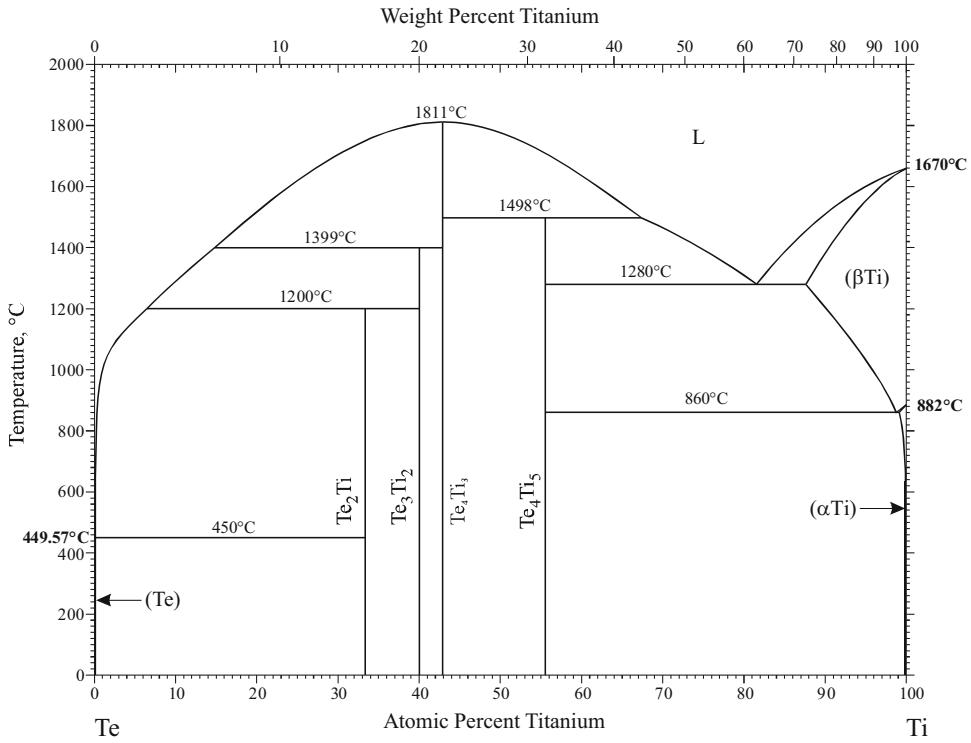

Fig. 12 Te-Ti phase diagram [2008Phi]

Table 4 Te-Ti crystal structure data

Phase	Composition, at.% Ti	Pearson symbol	Space group	Strukturbericht designation	Prototype
(Te)	0	*hP*3	$P3_121$	*A*8	γSe
Te_2Ti	33.3	*hP*3	$P\bar{3}m1$	*C*6	CdI_2
Te_3Ti_2	40	*h***	…	…	…
Te_4Ti_3	42.9	*mS*14	*C*2/*m*	…	Cr_3Se_4
Te_4Ti_5	55.6	*tI*18	*I*4/*m*	…	…
(βTi)	87.7-100	*cI*2	$Im\bar{3}m$	*A*2	W
(αTi)	99.1-100	*hP*2	$P6_3/mmc$	*A*3	Mg

2017Mar: C. Marker, S. Shang, X.L. Liu, G. Lindwall, and Z.K. Liu, First-principles Calculations and Thermodynamic Modeling of the Sn-Ta System, CALPHAD, 2017, 57, p 46-54

Te-Ti (Tellurium-Titanium)

[1996Oka] introduced the Te-Ti phase diagram reported by [1994Cor]. The following intermediate phases existed: Te_2Ti, Te_8Ti_5, Te_3Ti_2, Te_4Ti_3 (dimorphic), and Te_4Ti_5 (dimorphic). Reactions among these phases and terminal phases were mostly unknown or speculative.

Figure 12 shows the Te-Ti phase diagram obtained by [2008Phi] based on thermodynamic data and modeling. Te_8Ti_5 was not found. Confirmation of the phase diagram based on phase boundary data is needed.

Table 4 shows Te-Ti crystal structure data.

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