The Cu-Tb (Copper-Terbium) System

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Equilibrium Diagram

The equilibrium phases of the Cu-Tb system are: (1) the liquid, L, without any miscibility gaps; (2) the fcc terminal solid solution, (Cu), with negligible solid solubility of Tb in (Cu); (3) the Tb-rich bcc terminal solid solution, (βTb), based on the equilibrium phase of pure Tb between 1289 and 1356 °C; (4) the Tb-rich cph terminal solid solution, (αTb), stable between –53 and 1289 °C; (5) the Tb-rich orthorhombic terminal solid solution, (α'Tb), stable below –53 °C; (6) the hexagonal intermediate phase Cu7Tb, stable only at elevated temperatures; (7) the fcc phase, αCu5Tb, stable up to the allotropic transformation temperature of 895 °C; (8) the hexagonal phase βCu5Tb, stable between 895 °C and the peritectic melting temperature of ~940 °C; (9) the orthorhombic phase, Cu2Tb, stable up to the congruent melting temperature of 870 °C; and (10) the most Tb-rich intermediate phase, CuTb, with a cubic structure and stable up to the congruent melting temperature of 900 °C.

No equilibrium diagram is available for the Cu-Tb system. A calculation of the Cu-Tb phase relationships was, therefore, undertaken. It has been shown that melting and eutectic temperatures in the Cu-lanthanide systems show a systematic variation across the lanthanide series (see "The Copper-Rare Earth Systems," in this issue). This was utilized for the Cu-Tb system, and the invariant temperatures of known Cu-Tb intermediate phases were derived by interpolation of corresponding data for those Cu-lanthanide systems for which experimental phase diagrams are already reported in the literature. The interpolated invariant temperatures were then combined with thermodynamic modeling (discussed in a later section) to derive the Cu-Tb phase diagram. The resulting diagram is shown in Fig. 1, where the melting points of (Cu) and (βTb) are accepted as 1084.87 °C [Melt] and 1356 °C [78Bea, 86Gsc], respectively. In concurrence with the behavior observed for the other Cu-lanthanide systems, mutual solid solubilities are expected to be negligible, except possibly in (βTb). Table 1 shows the various invariant reactions that are expected to occur in the Cu-Tb system. The existence of Cu9Tb2 and Cu7Tb2 is proposed solely on the basis of the presence of similar phases in the Cu-Gd [83Car], Cu-Dy [82Fra], and Cu-Er [70Bus1] systems.

Fig. 1 Calculated Cu-Tb Phase Diagram
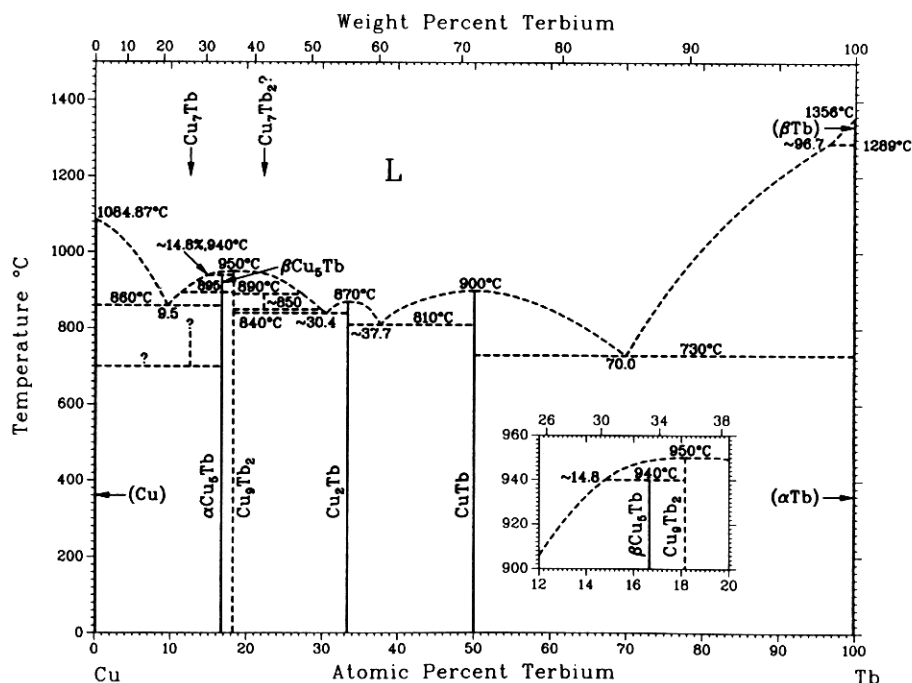
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Table 1 Special Points of the Cu-Tb Assessed Phase Diagram

Reaction	Compositions of the respective phases, at.% Tb			Temperature, °C	Reaction Type	Reference
(Cu) ↔ L............................		0.0		1084.87	Melting point	[Melt]
L ↔ (Cu) + Cu₅Tb............	9.5	~0	16.67	860	Eutectic	(a)
L + Cu₉Tb₂ ↔ Cu₅Tb.......	~14.8	18.18	16.67	940	Peritectic	(a)
L ↔ Cu₉Tb₂......................		18.18		950	Congruent	(a)
L ↔ Cu₉Tb₂ + Cu₂Tb.......	~30.4	18.18	33.33	840	Eutectic	(a)
L ↔ Cu₂Tb		33.33		870	Congruent	(a)
L ↔ Cu₂Tb + CuTb..........	~37.7	33.33	50.0	810	Eutectic	(a)
L ↔ CuTb..........................		50.0		900	Congruent	(a)
L ↔ CuTb + (αTb)............	70.0	50.0	~100	730	Eutectic	(a)
(αTb) ↔ (βTb)...................		~100		1289	Allotropic	[78Bea, 86Gsc]
(βTb) ↔ L........................		100		1356	Melting point	[78Bea, 86Gsc]

Note: From Fig. 1.
(a) Compositions and temperatures have been estimated from systematics of Cu-lanthanide systems, in conjunction with thermodynamic modeling (see text).

Table 2 Cu-Tb Experimental Lattice Parameters

Phase	Crystal structure	Lattice parameters, nm			Reference
		a	b	c	
Cu₇Tb...................	Hexagonal	0.4942	...	0.4164	[71Bus](a)
Cu₆Tb...................	Orthorhombic	0.802	0.501	1.001	[70Bus2](b)
Cu₅Tb...................	Hexagonal	0.496	...	0.415	[60Has](c)
		0.503	...	0.409	[71Bus](d)
Cu₅Tb...................	Cubic	0.7041	...	...	[69Bus](e)
Cu₂₃Tb₆	Cubic	1.22	...	...	[84Tsv](f)
Cu₂Tb...................	Orthorhombic	0.4310	0.6825	0.7320	[63Sto]
CuTb	Cubic	0.348	...	...	[64Cab]
		0.348	...	...	[64Cha]
		0.3479	...	...	[65Ian]
		0.3478	...	...	[65Dwi]
		0.3484	...	...	[67Pie]
		0.348	...	...	[77Bas]

(a) Reported to be stable only at high temperatures. (b) Metastable; observed only in splat-cooled samples of Cu₆Tb. (c) [71Bus] believes that this data is representative of the Cu₇Tb phase, rather than Cu₅Tb. (d) Obtained as single phase only by splat cooling. (e) Sample contained small amounts of the hexagonal Cu₅Tb phase. (f) Formed only at high pressures (7.7 GPa).

Intermediate Phases

[71Bus] reported the high-temperature formation of Cu₇Tb, with its subsequent decomposition to Cu₅Tb and elemental Cu on annealing at temperatures near 700 °C. The decomposition was observed by X-ray diffraction and metallography, and subsequent annealing of the decomposed mixture at 800 °C restored the presence of single-phase Cu₇Tb. X-ray diffraction and density measurements revealed that Cu₇Tb has the actual stoichiometry Cu₅.₄₄Tb₀.₇₈ and that it forms with a hexagonal structure related to that of the CaCu₅ type with 22% of the Ca sites substituted at random by pairs of Cu atoms. [71Bus] did not report the temperature range of existence of Cu₇Tb, although the phase is shown to be unstable below 700 °C.

[70Bus2] observed the formation of Cu₆Tb with an orthorhombic structure in splat-cooled thin foil

samples of Cu₅Tb after vacuum annealing at 700 °C for 4 days. However, [70Bus2] ruled out the existence of Cu₆Tb as a stable phase, because of their inability to obtain it as a single phase through normal melting and annealing techniques. As such, this phase is not shown in the assessed Cu-Tb phase diagram in Fig. 1.

[60Has] reported the formation of Cu₅Tb with a hexagonal structure and with lattice parameters $a = 0.496$ nm and $c = 0.415$ nm. The data of [60Has] were questioned by [71Bus], who observed that the hexagonal CaCu₅ type is formed only in splat-cooled Cu₅Tb alloys. [71Bus] suggested that the data of [60Has] might be ascribed to the Cu₇Tb phase, because the lattice parameter data of [60Has] correspond more closely with the data observed for the hexagonal Cu₇Tb by [71Bus]. [69Bus] observed the occurrence of the cubic AuBe₅-type structure in both as-cast and annealed alloys with the stoichiometry

Table 3 Cu-Tb Crystal Structure Data

Phase	Composition, at.% Tb	Pearson symbol	Space group	Strukturbericht designation	Prototype
(Cu)	0	cF4	$Fm\bar{3}m$	A1	Cu
Cu$_5$Tb(HT)	~16.67	hP6	P6/mmm	D2$_d$	CaCu$_5$
Cu$_5$Tb(LT)	~16.67	cF24	$F\bar{4}3m$	C15$_b$	AuBe$_5$
Cu$_2$Tb	~33.3	oI12	Imma	...	CeCu$_2$
CuTb	~50	cP2	$Pm\bar{3}m$	B2	CsCl
(α'Tb)	100	oC4	Cmcm	...	α'Dy
(αTb)	100	hP2	P6$_3$/mmc	A3	Mg
(βTb)	100	cI2	$Im\bar{3}m$	A2	W

Table 4 Cu-Tb Lattice Parameter Data

Phase	Composition, at.% Tb	Lattice parameters, nm a	b	c	Comment	Reference
(Cu)	0	0.36146	...	...	At 25 °C	[Massalski]
Cu$_5$Tb(HT)	~16.67	0.503	...	0.409	...	[71Bus]
Cu$_5$Tb(LT)	~16.67	0.7041	...	...	(a)	[69Bus]
Cu$_2$Tb	~33.3	0.4310	0.6825	0.7320	...	[63Sto]
CuTb	~50	0.3480	...	...	...	(c)
(α'Tb)	100	0.3605	0.6244	0.5706	At −53 °C	[78Bea, 86Gsc]
(αTb)	100	0.36055	...	0.56966	At 25 °C	[78Bea, 86Gsc]
(βTb)	100	0.402	...	...	(b)	[78Bea, 86Gsc]

(a) Sample contained small amounts of hexagonal Cu$_5$Tb. (b) Determined by extrapolation to 0% solute of a vs composition data for Mg-RE alloys. (c) [64Cab, 64Cha, 65Ian, 65Dwi, 67Pie, 77Bas].

Cu$_5$Tb. However, these alloys did not contain the cubic phase exclusively, and revealed the existence of minor amounts of the hexagonal phase, leading [69Bus] to conclude that both structure types are stable in the Cu-Tb system. For Cu-Gd and Cu-Dy systems, both structure types are present, with the hexagonal type stable at high temperatures and the cubic type stable at lower temperatures. Accordingly, it can be concluded that Cu$_5$Tb is also present in two allotropic modifications, with the hexagonal form reported by [71Bus] as the stable phase at elevated temperatures, and the cubic form reported by [69Bus] as the stable phase at low temperatures. [83Gsc] noted that a plot of the reduced temperature (the melting point of the compound divided by the melting point of the pure lanthanide metal) always results in a straight line that decreases with increase in atomic number. This observation can be extended to include the allotropic transformation temperatures as well. Therefore, a comparison of the trend for the reduced melting temperature (T_m [Cu$_5$RE]/T_m[RE]) vs atomic number with that for the reduced transformation temperature (T_{Tr}[Cu$_5$RE]/T_m[RE]) vs atomic number shows that the cubic → hexagonal transformation temperature for Cu$_5$Tb should lie close to 895 °C.

Metastable Phases

[79Mcg] prepared amorphous thin films with the composition Cu$_{0.507}$Tb$_{0.497}$ by sputtering from arc-melted specimens, and by thermal evaporation from Cu and Tb targets, followed by deposition on liquid nitrogen-cooled sapphire substrates. The resultant films were 500 to 1000 nm thick.

Crystal Structures and Lattice Parameters

There is no ambiguity with regard to the existence as well as the crystal structures of both Cu$_2$Tb and CuTb. Cu$_2$Tb forms with the orthorhombic CeCu$_2$ structure, whereas the equiatomic phase CuTb forms with the cubic CsCl structure.

[84Tsv] reported the synthesis of the phase Cu$_{23}$Tb$_6$ by the application of a pressure of 7.7 GPa at high temperatures to a stoichiometric mixture of the constituent elements. The resulting phase could be indexed on the basis of the cubic Th$_6$Mn$_{23}$ structure with space group $Fm\bar{3}m$, and a lattice parameter a = 1.22 nm.

Table 2 lists the experimental values for the lattice parameters of the various Cu-Tb intermediate phases. Crystal structure information for the Cu-Tb system is summarized in Tables 3 and 4.

Thermodynamics

Because there is no experimental phase diagram information for the Cu-Tb system, the calculation of the Cu-Tb phase relationships involved the following considerations:

- Mutual solid solubilities are negligible.

- The liquid behaves like a subregular solution.

Table 5   Cu-Tb Thermodynamic Properties

Lattice stability parameters for Cu(a)

$G^0(Cu, L) = 0$

$G^0(Cu, fcc) = -13\,054 + 9.613\,T$

Lattice stability parameters for Tb(b)

$G^0(Tb, L) = 0$

$G^0(Tb, bcc) = -10\,800 + 6.629\,T$

$G^0(Tb, cph) = -15\,820 + 9.843\,T$

Integral molar Gibbs energies(c)

$G(L) = X(1-X)(-97\,787 + 46\,267X) + RT[X \ln X + (1-X) \ln (1-X)]$

$\Delta_f G(Cu_5Tb) = -25\,240 + 6.70\,T$

$\Delta_f G(Cu_9Tb_2) = -34\,974 + 13.78\,T$

$\Delta_f G(Cu_2Tb) = -22\,459 + 1.66\,T$

$\Delta_f G(CuTb) = -39\,179 + 11.73\,T$

Note: Standard states: pure liquid Cu and pure liquid Tb. Gibbs energies are expressed in J/mol, and temperatures are in K. X is the atomic fraction of Tb. Mol refers to the atom as the elementary entity.
(a) From [Hultgren,E]. (b) From [83Cha]; melting and transformation temperatures are from [78Bea] and [86Gsc]. (c) From the phase diagram [this work].

- Because eutectic and melting temperatures follow a systematic trend across the lanthanide series [83Gsc], the eutectic temperatures at either end of the Cu-Tb system were estimated by interpolation of experimental data for the other Cu-lanthanide systems (see "The Copper-Rare Earth Systems," in this issue). On this basis, the Cu-Cu5Tb and CuTb-(αTb) eutectic temperatures were obtained as 860 and 730 °C, respectively, and were assumed to occur at 9.5 and 70 at.% Tb, respectively. The eutectic compositions were inferred from experimental data on the Cu-Gd [83Car], Cu-Dy [82Fra], and Cu-Er [70Bus1] systems and the application of systematics [83Gsc].

The integral Gibbs energy of mixing of the liquid was derived from the interpolated eutectic data (9.5 at.% Tb, 860 °C and 70 at.% Tb, 730 °C). The elemental lattice stability parameters used in the calculation are listed in Table 5. The Gibbs energies of formation of Cu5Tb, Cu9Tb2, Cu2Tb, and CuTb were then determined from the interpolated invariant temperatures, as well as the Gibbs energy of mixing of the liquid. In all instances, the phases were assumed to be line compounds. Table 5 shows the values of the various parameters. The calculated phase boundaries, derived from the Gibbs energy functions in Table 5, are shown in Fig. 1.

An alternate calculation was performed using the semi-empirical scheme proposed by [80Mie]. The empirical parameters listed in [83Nie] were used to determine the following excess Gibbs energy of mixing of the liquid:

$G^{ex}(L) = X_{Tb}(1 - X_{Tb}) (-101\,320 + 28\,972X_{Tb})$

Table 6   Calculated Enthalpies of Formation of Cu-Tb Intermediate Phases vs Theoretical Estimates Based on Miedema's Model

| Phase | Enthalpy of formation, kJ/mol | |
	Present modeling	Miedema model(a)
Cu5Tb	-25.2	-32.5
Cu9Tb2	-35.0	-34.2
Cu2Tb	-22.5	-46.5
CuTb	-39.2	-47.0

Note: Standard states are liquid Cu and liquid Tb.
(a) From [83Nie].

Based on the above equation, the eutectic compositions were estimated to be 9.8 and 75.16 at.% Tb at 860 and 730 °C, respectively. The melting temperatures of the intermediate phases were assumed to be the same as those estimated in the earlier approach. The resultant liquidus boundaries were generally compatible with the trends observed for the Cu-heavy lanthanide systems, except in the region close to the stoichiometry of Cu2Tb. The calculated liquidus in this region was unrealistic in that the phase relationship showed a very narrow two-phase field between the liquid and Cu2Tb ($\sim$0.4 at.% Tb). The earlier approach was preferred, and the parameters listed in Table 5 were considered adequate to reproduce the equilibrium phase diagram for the Cu-Tb system.

The empirical parameters of [83Nie] were also used to calculate the enthalpies of formation of Cu5Tb, Cu9Tb2, Cu2Tb, and CuTb. These values are compared in Table 6 with the data obtained in the present modeling. With the exception of Cu9Tb2, the Miedema values are more exothermic than the results of the present thermodynamic analysis.
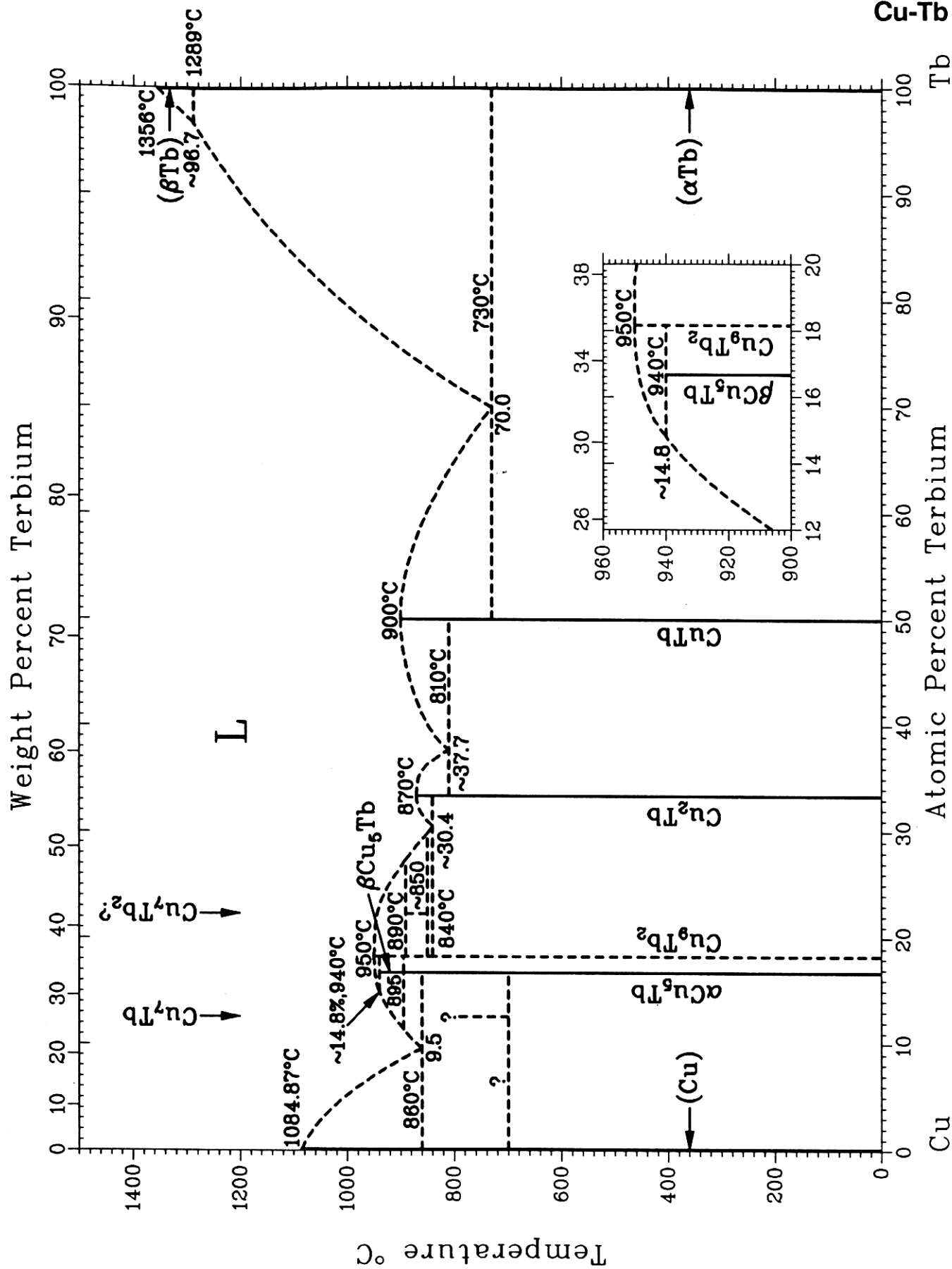
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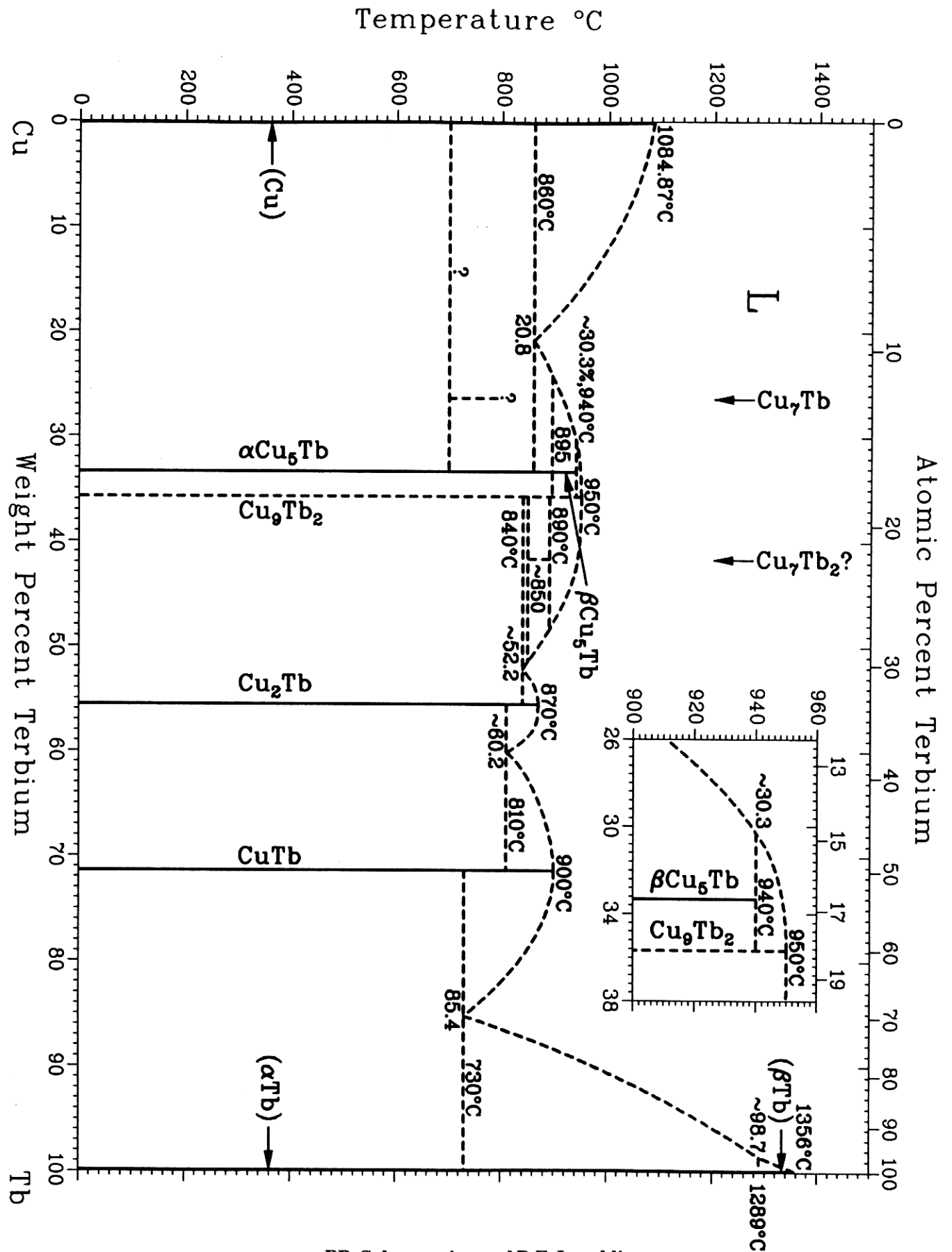
*Indicates key paper.

#Indicates presence of a phase diagram.

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