The Cu-Tm (Copper-Thulium) System

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Equilibrium Diagram

[75Boc] studied the solubility of Tm in (Cu) by metallography, electrical resistance, and hardness measurements. They reported a maximum solubility between 0.05 and 0.07 wt.% Tm (0.02 and 0.03 at.% Tm) at the Cu-rich eutectic temperature; the eutectic temperature was reported to lie between 850 and 870 °C. There is no other experimental phase diagram information on the Cu-Tm system. However, the general features of the Cu-Tm phase diagram are expected to be similar to those of the other Cu-heavy lanthanide systems [85Gsc]. Moreover, melting and eutectic temperatures in the Cu-lanthanide systems, in general, are known to vary systematically across the lanthanide series (see "The Copper-Rare Earth Systems," in this issue). Accordingly, the invariant temperatures of known Cu-Tm intermediate phases were estimated by extrapolation of corresponding data for those Cu-lanthanide systems for which experimental phase diagrams are already known, using the methods described by [83Gsc]. The Cu-Tm equilibrium diagram was then determined from the extrapolated invariant temperatures, in conjunction with thermodynamic considerations (see "Thermodynamics"). Figure 1 shows the schematic Cu-Tm equilibrium diagram. The melting points of pure Cu and pure Tm are accepted as 1084.87 °C [Melt] and 1545 °C [78Bea, 86Gsc], respectively. In Fig. 1, the existence of Cu_9Tm_2 and Cu_7Tm_2 is proposed solely on the basis of the presence of similar phases in the Cu-Gd [83Car], Cu-Dy [82Fra], and Cu-Er [70Bus] systems. Table 1 shows the various invariant temperatures that are expected to occur in the Cu-Tm system.

Metastable Phases

Amorphous thin films with the composition $Cu_{0.39}Tm_{0.61}$ were prepared by [79Mcg] by sputtering from arc-melted specimens, and by thermal evaporation from Cu and Tm targets, followed by condensation on liquid nitrogen-cooled sapphire substrates. The resultant films were 500 to 1000 nm thick.

Fig. 1 Calculated Cu-Tm Phase Diagram

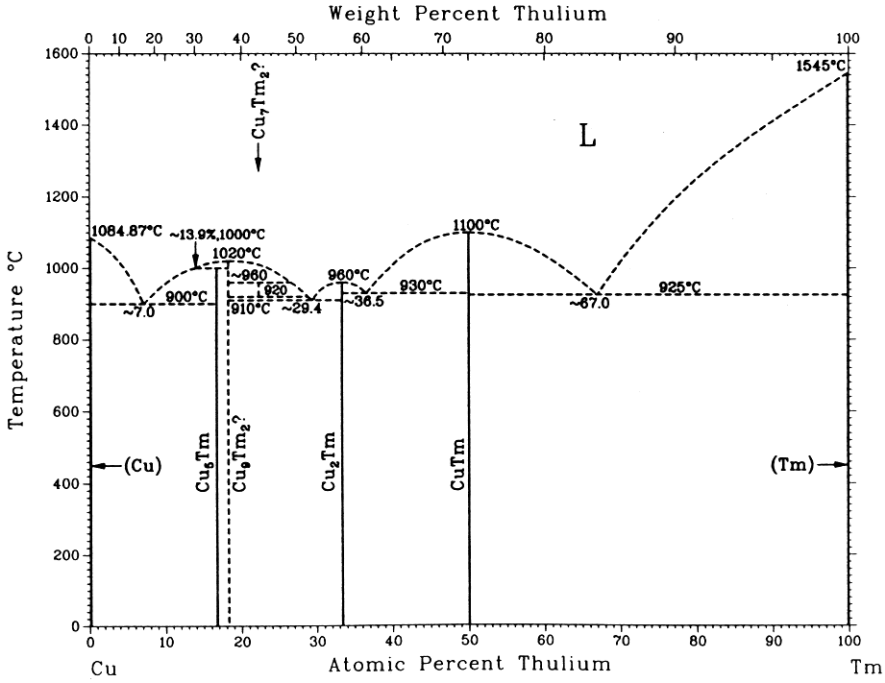

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Table 1 Special Points of the Cu-Tm Assessed Phase Diagram

Reaction		Compositions of the respective phases, at.% Tm		Temperature, °C	Reaction type	Reference
(Cu) ↔ L		0.0		1084.87	Melting point	[Melt]
L ↔ (Cu) + Cu_5Tm	8.0	~0	16.67	900	Eutectic	(a)
L + Cu_9Tm_2 ↔ Cu_5Tm	~13.9	18.18	16.67	1000	Peritectic	(a)
L ↔ Cu_9Tm_2		18.18		1020	Congruent	(a)
L ↔ Cu_9Tm_2 + Cu_2Tm	~29.4	18.18	33.33	910	Eutectic	(a)
L ↔ Cu_2Tm		33.33		960	Congruent	(a)
L ↔ Cu_2Tm + CuTm	~36.5	33.33	50.0	930	Eutectic	(a)
L ↔ CuTm		50.0		1100	Congruent	(a)
L ↔ CuTm + (Tm)	~67.0	50.0	~100	925	Eutectic	(a)
(Tm) ↔ L		100		1545	Melting point	[78Bea, 86Gsc]

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

Table 2 Cu-Tm Crystal Structure Data

Phase	Composition, at.% Tm	Pearson symbol	Space group	Strukturbericht designation	Prototype
(Cu)	0	*cF*4	$Fm\bar{3}m$	*A*1	Cu
Cu_5Tm	~16.67	*cF*24	$F\bar{4}3m$	$C15_b$	$AuBe_5$
Cu_2Tm	~33.3	*oI*12	*Imma*	...	$CeCu_2$
CuTm	~50	*cP*2	$Pm\bar{3}m$	*B*2	CsCl
(Tm)	100	*hP*2	$P6_3/mmc$	*A*3	Mg

Table 3 Cu-Tm Lattice Parameter Data

Phase	Composition range, at.% Tm	Lattice parameters, nm *a*	*b*	*c*	Comment	Reference
(Cu)	0	0.36146	...	...	At 25 °C	[Massalski]
Cu_5Tm	~16.67	0.6991	...	...	...	[69Bus]
Cu_2Tm	~33.3	0.4266	0.6697	0.7247	...	[63Sto]
CuTm	~50	0.34145	...	...	...	[64Cha, 65Ian]
(Tm)	100	0.35375	...	0.55540	At 25 °C	[78Bea, 86Gsc]

Crystal Structures and Lattice Parameters

Crystal structure data for the Cu-Tm system are listed in Tables 2 and 3. Data for pure Cu are taken from [Massalski], and those for pure Tm from [78Bea] and [86Gsc].

[69Bus] reported the formation of Cu_5Tm with the cubic $AuBe_5$-type structure. [63Sto] determined that Cu_2Tm crystallizes with the orthorhombic $CeCu_2$-type structure. Both [64Cha] and [65Ian] reported the formation of CuTm with the cubic CsCl structure, and lattice parameter data reported by the authors are in good accord.

Thermodynamics

No thermodynamic data are available for the Cu-Tm system. The calculation of the Cu-Tm phase relationships, therefore, involved the following assumptions:

- The liquid behaves like a subregular solution.
- Terminal solid solubilities are negligible.
- Eutectic and melting temperatures represent values extrapolated from experimental data for the other Cu-lanthanide systems. On this basis, the Cu-Cu_5Tm and CuTm-Tm eutectic temperatures were estimated to be 900 and 925 °C, respectively, and for a first approximation, the corresponding compositions were assumed to be close to 9.5 and 70 at.% Tm, respectively. These compositions were inferred from experimental data for the Cu-Gd [83Car], Cu-Dy [82Fra], and Cu-Er [70Bus] systems, and the application of systematics of Cu-lanthanide systems [83Gsc]. In the modeling, the terminal eutectic temperatures were kept fixed, but the eutectic compositions were allowed to vary within 3 at.% to provide a good fit.

The integral Gibbs energy of mixing of the liquid phase was derived from the interpolated data, in conjunction

Table 4 Cu-Tm 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 Tm(b)

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

$G^0(Tm, cph) = -16\,840 + 9.262\,T$

Integral molar Gibbs energies(c)

$G(L) = X(1-X)(-98\,730 + 61\,664X) + RT[X \ln X + (1-X) \ln (1-X)]$

$\Delta_f G(Cu_5Tm) = -29\,072 + 9.33\,T$

$\Delta_f G(Cu_9Tm_2) = -33\,474 + 11.88\,T$

$\Delta_f G(Cu_2Tm) = -22\,245 + 1.34\,T$

$\Delta_f G(CuTm) = -32\,418 + 5.48\,T$

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

with the elemental lattice stability parameters listed in Table 4. The Gibbs energies of formation of the Cu-Tm phases were then determined at the various interpolated invariant temperatures from the Gibbs energy of mixing of the liquid. In all instances, the phases were assumed to be line compounds. Table 4 summarizes the various thermodynamic functions. The resultant Cu-Tm phase boundaries are shown in Fig. 1.

The enthalpies of formation from the present modeling are compared in Table 5 with those calculated on the basis of the semi-empirical model of Miedema and co-workers [80Mie, 83Nie]. The two estimates are closely comparable for Cu_5Tm_2 and Cu_9Tm_2. However, the Miedema values are more exothermic for Cu_2Tm and CuTm.

Table 5 Calculated Enthalpies of Formation of Cu-Tm Intermediate Phases vs Theoretical Estimates Based on Miedema's Model

Phase	Enthalpy of formation, kJ/mol: Present modeling	Miedema model(a)
Cu_5Tm	-29.1	-32.4
Cu_9Tm_2	-33.5	-34.1
Cu_2Tm	-22.3	-46.8
CuTm	-32.5	-48.1

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

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Cu-Tm
Cu-Yb

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

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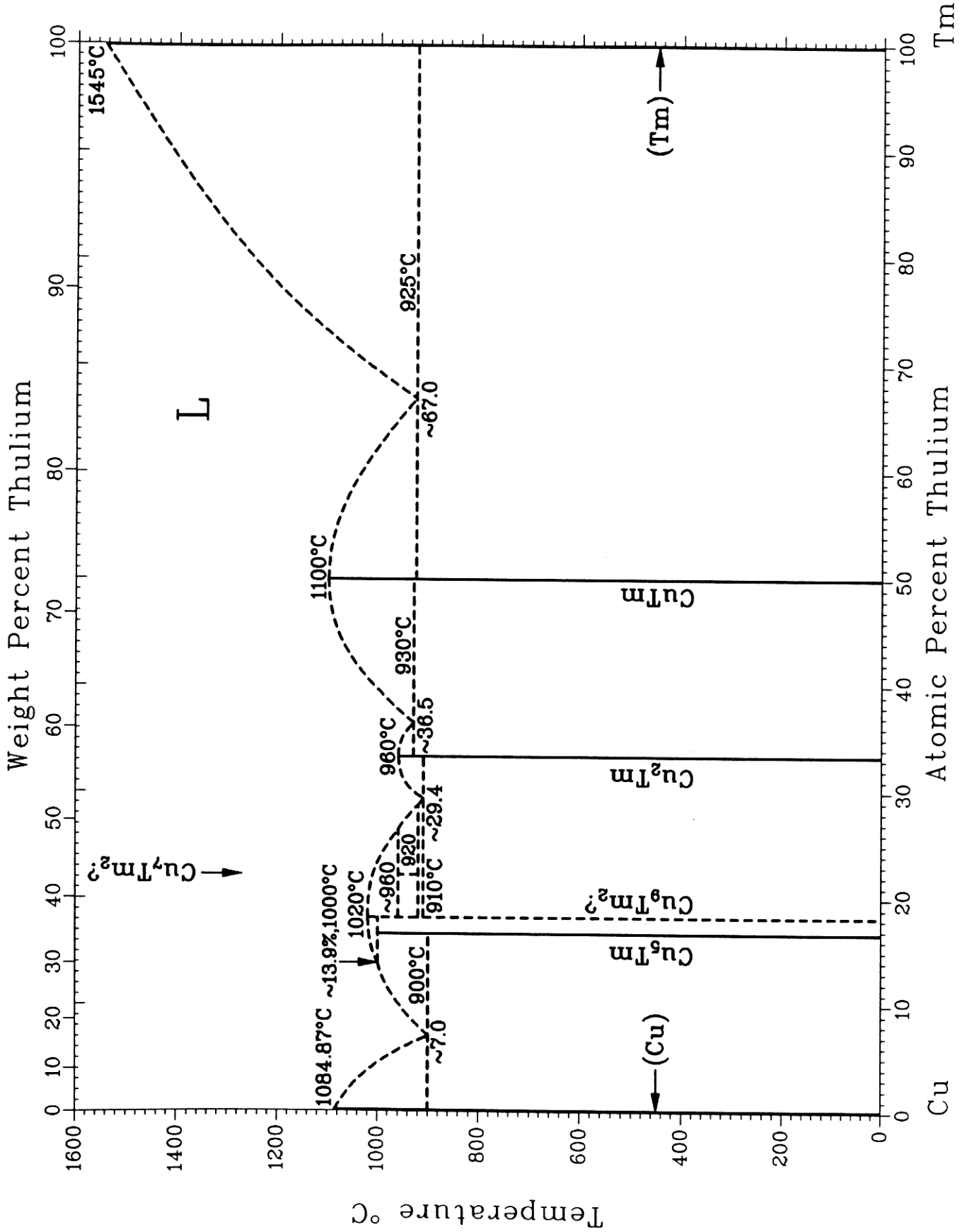

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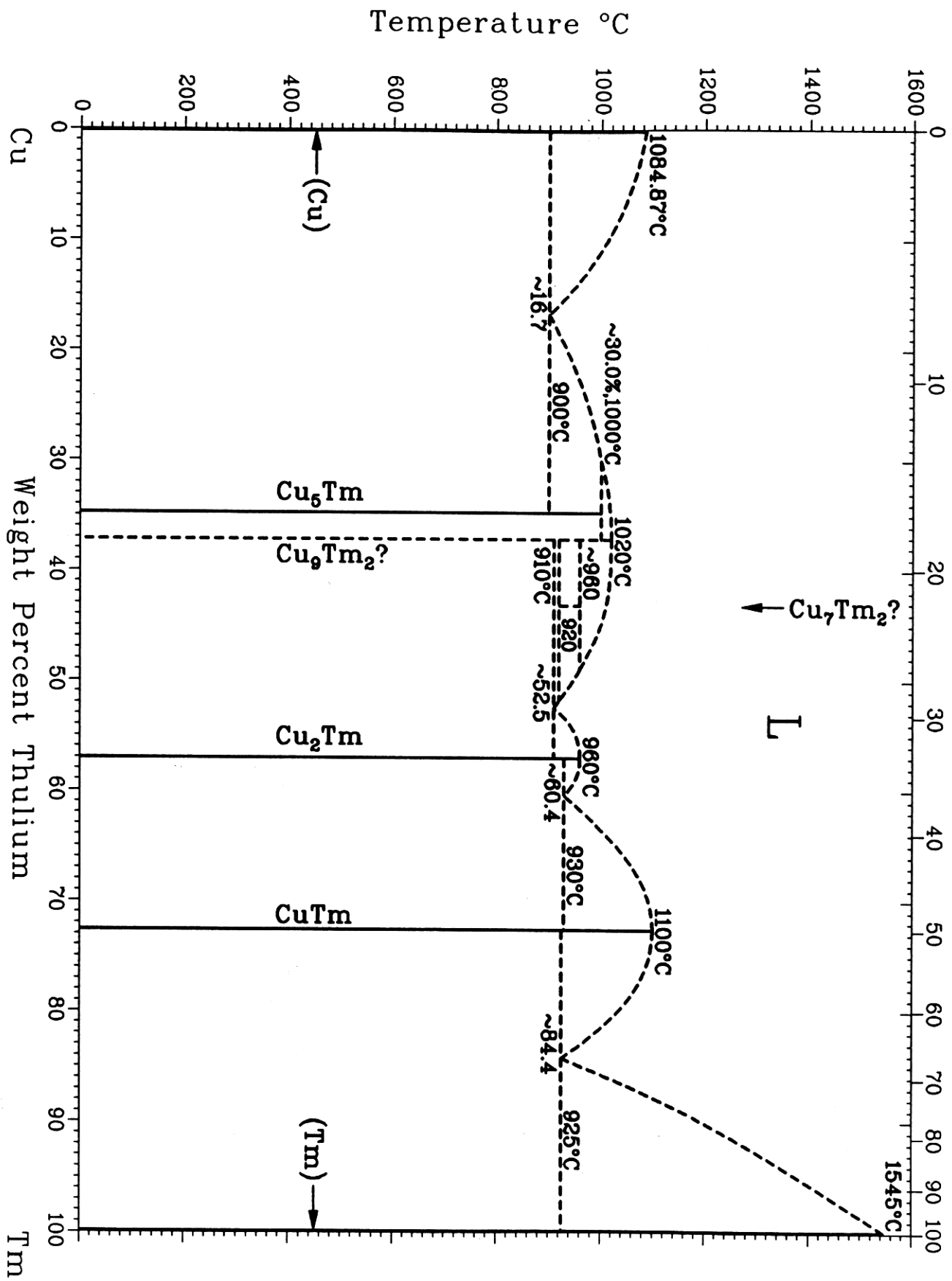

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