The Cu-Er (Copper-Erbium) System

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Equilibrium Diagram

The Er-rich region of the Cu-Er system was investigated by Love (as reported in [Elliott]) and by [64Cop]. Both investigations proposed the formation of a eutectic between CuEr and (Er). According to Love, the eutectic was found to occur at 75.5 at.% Er and 860 °C, whereas [64Cop] found the eutectic to occur at 71.8 at.% Er and 845 °C. [64Cop] estimated the solubility of Cu in (Er) to be <0.2 wt.% Cu (<0.53 at.% Cu).

[70Bus] investigated the Cu-Er system by means of X-ray diffraction, differential thermal analysis (DTA), and metallography. Alloys were prepared by arc melting appropriate amounts of 99.99% pure Cu and 99.9% pure Er (the elemental purities are probably in wt.%), followed by vacuum annealing in sintered alumina crucibles sealed into silica tubes. Differential thermal analysis was performed under both heating and cooling conditions. [70Bus] observed the peritectic formation of Cu_5Er and the congruent formation of Cu_2Er and CuEr. Moreover, thermal analysis indicated the existence of two additional phases occurring near 20

Table 1 Cu-Er Experimental Liquidus Data

Composition, at.% Er	Temperature, °C	Composition, at.% Er	Temperature, °C
5.0	1021	23.5	988
8.0	926	25.0	971
10.0	912	30.0	885
11.2	926	33.3	935
14.3	986	37.0	914
17.4	1006	41.5	964
18.2	1010	50.0	1055
18.8	1010	60.0	1014
20.0	1005	66.2	924
21.0	1000	75.0	1143
22.2	995		

From [70Bus].

Fig. 1 Assessed Cu-Er Phase Diagram

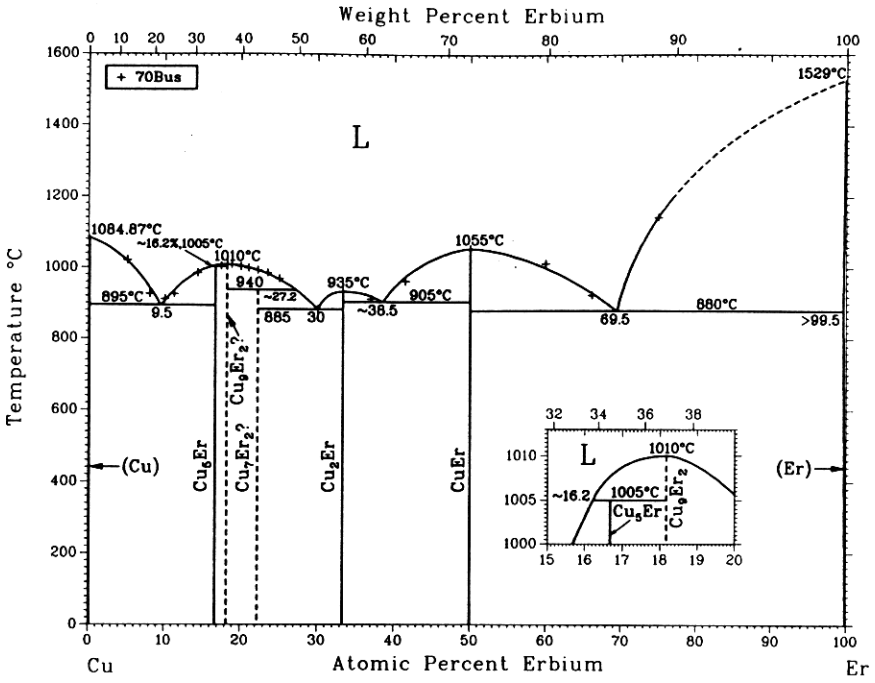

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Table 2 Special Points of the Assessed Cu-Er Phase Diagram

Reaction	Compositions of the respective phases, at.% Er			Temperature, °C	Reaction type	Reference
(Cu) ↔ L		0.0		1084.87	Melting point	[Melt]
L ↔ (Cu) + Cu_5Er	9.5	~0	16.67	895	Eutectic	[70Bus]
L + Cu_9Er_2 ↔ Cu_5Er	~16.2	~18.2	16.67	1005	Peritectic	[70Bus](a)
L ↔ Cu_9Er_2		~18.2		1010	Congruent	[70Bus]
Cu_9Er_2 + L ↔ Cu_7Er_2	~18.2	~27.2	~22.2	940	Peritectic	[70Bus](a)
L ↔ Cu_7Er_2 + Cu2Er	30.0	~22.2	33.33	885	Eutectic	[70Bus]
L ↔ Cu_2Er		33.33		935	Congruent	[70Bus]
L ↔ Cu_2Er + CuEr	~38.5	33.33	50.0	905	Eutectic	[70Bus](a)
L ↔ CuEr		50.0		1055	Congruent	[70Bus]
L ↔ CuEr + (Er)	69.5	50.0	~100	880	Eutectic	[70Bus]
(Er) ↔ L		100		1529	Melting point	[78Bea, 86Gsc]

(a) Liquidus composition was obtained by interpolation of experimental data in Fig. 1.

at.% Er, which [70Bus] designated as Cu_xEr and Cu_yEr, respectively, without giving their exact stoichiometries. These phases are very close to the stoichiometries of Cu_7RE_2 (22.2 at.% RE) and Cu_9RE_2 (18.2 at.% RE), respectively, which have been observed to form for RE ≡ Gd [83Car], RE ≡ Dy [82Fra], and RE ≡ Yb [71Ian] systems. [70Bus] reported that the phase lower in Er forms congruently at 1010 °C, and the other phase forms peritectically at 940 °C. Again, this pattern is consistent with the melting types reported for Cu_9RE_2 (congruent) and Cu_7RE_2 (peritectic), where RE ≡ Gd, Dy, and Yb. As such, the phases Cu_xEr and Cu_yEr have been tentatively assigned the stoichiometries Cu_7Er_2 and Cu_9Er_2, respectively. Metallographic investigation by [70Bus] indicated the occurrence of four eutectics: Cu-Cu_5Er (895 °C, 9.5 at.% Er); Cu_xEr-Cu_2Er (885 °C, 30 at.% Er); Cu_2Er-CuEr (905 °C, 40 at.% Er); and CuEr-(Er) (880 °C, 69.5 at.% Er). Mutual solid solubilities were reported to be negligible, because elemental lat-

Table 3 Cu-Er Crystal Structures

Phase	Composition, at.% Er	Pearson symbol	Space group	Strukturbericht designation	Prototype
(Cu)	0	*cF*4	$Fm\bar{3}m$	*A*1	Cu
Cu_5Er	~16.67	*cF*24	$F\bar{4}3m$	$C15_b$	$AuBe_5$
Cu_2Er	~33.3	*oI*12	*Imma*	...	$CeCu_2$
CuEr	~50	*cP*2	$Pm\bar{3}m$	*B*2	CsCl
(Er)	100	*hP*2	$P6_3/mmc$	*A*3	Mg

Table 4 Cu-Er Lattice Parameter Data

Phase	Composition, at.% Er	Lattice parameters, nm *a*	*b*	*c*	Comment	Reference
(Cu)	0	0.36146	...	...	At 25 °C	[Massalski]
Cu_5Er	~16.67	0.7003	...	...	...	[69Bus]
Cu_2Er	~33.3	0.4274	0.6733	0.7266	...	[63Sto, 70Bus]
CuEr	~50	0.3431	...	...	...	(a)
(Er)	100	0.35592	...	0.55850	At 25 °C	[78Bea, 86Gsc]

(a) [59Dwi, 65Ian, Shunk, 70Bus].

Table 5 Thermodynamic Properties of Cu-Er Phases

Lattice stability parameters for Cu(a)

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

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

Lattice stability parameters for Er(b)

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

$G^0(Er, cph) = -19\,900 + 11.043\,T$

Integral molar Gibbs energies(c)

$G(L) = X(1-X)(-74\,531 + 25\,165X) + RT[X \ln X + (1-X)\ln(1-X)]$

$\Delta_f G(Cu_6Er) = -17\,976 + 2.67\,T$

$\Delta_f G(Cu_9Er_2) = -26\,791 + 8.83\,T$

$\Delta_f G(Cu_7Er_2) = -20\,116 + 2.14\,T$

$\Delta_f G(Cu_2Er) = -17\,341 + 3.10\,T$

$\Delta_f G(CuEr) = -34\,576 + 8.65\,T$

Note: Standard states: pure liquid Cu and pure liquid Er. Gibbs energies are expressed in J/mol, and temperatures are in K. *X* is the atomic fraction of Er. 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].

tice parameters did not change significantly on alloying. From X-ray analysis of CuEr samples annealed at various temperatures between 500 and 1000 °C, [70Bus] inferred that CuEr decomposes partially into Cu_2Er and (Er) at lower temperatures. According to [70Bus], this decomposition is expected to be sluggish because of the large concentration difference between Cu_2Er and (Er).

The assessed Cu-Er phase diagram, shown in Fig. 1, is drawn from the report of [70Bus]. Minor modifications have been made in the liquidus between Cu_2Er and CuEr, so that the slope of the liquidus at the congruent melting point of Cu_2Er conforms to the Gibbs-Konovalov criterion [81Goo]. This involved a shift in the estimated value of the Cu_2Er-CuEr eutectic composition from 40 at.% Er (estimated by [70Bus]) to 38.5 at.% Er. The Er-rich liquidus above 75 at.% Er was shown with dashed lines in the diagram of [70Bus], and is indicated in the same manner in Fig. 1, where the melting point for pure Er has been raised to 1529 °C to conform to the accepted value listed in [78Bea] and [86Gsc]. Similarly, the melting point of pure Cu is accepted from [Melt] as 1084.87 °C.

Table 1 lists the experimental data for the Cu-Er liquidus boundaries from [70Bus]. The various invariant reactions occurring in the Cu-Er system are summarized in Table 2. The eutectic and melting temperatures of [70Bus] are in good agreement with the systematics observed for the corresponding temperatures in the other Cu-lanthanide systems (see "The Copper-Rare Earth Systems," in this issue).

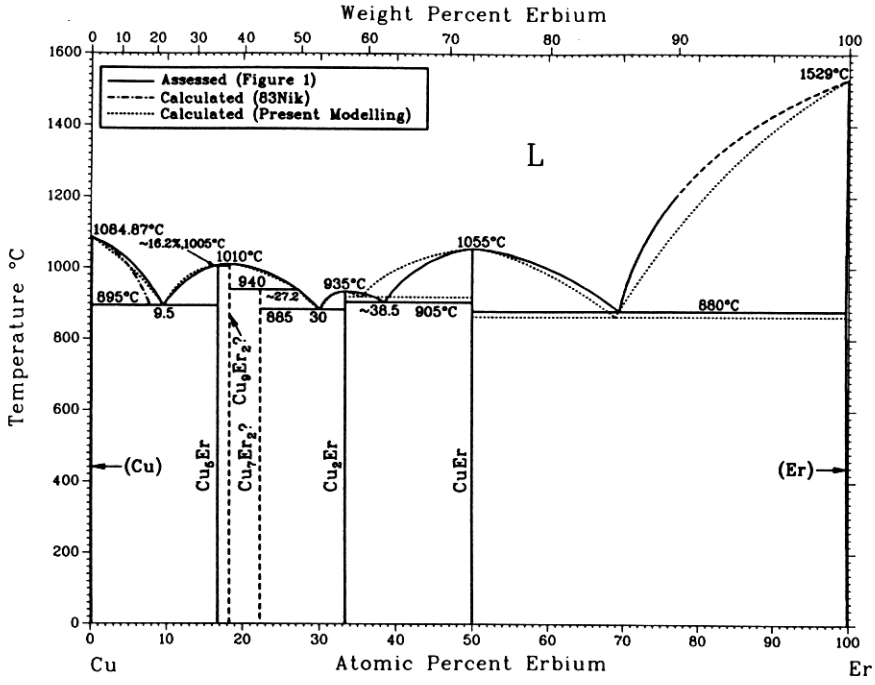
Metastable Phases

Amorphous thin films with the composition $Cu_{0.49}Er_{0.51}$ were prepared by [79Mcg] by sputtering from arc-melted specimens, and by thermal evaporation from Cu and Er targets, followed by condensation on liquid nitrogen-cooled sapphire substrates. The resultant films were 500 to 1000 nm thick.

Crystal Structures and Lattice Parameters

[69Bus] observed the occurrence of the cubic $AuBe_5$-type structure in as-cast as well as annealed samples of Cu_5Er, and reported a lattice parameter of $a = 0.7003$

Fig. 2 Assessed vs Calculated Cu-Er Phase Diagram



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nm. [70Bus] could not identify the crystal structures of the two adjacent phases Cu_xEr and Cu_yEr, because the X-ray patterns corresponding to these two phases were complex. [63Sto] determined that Cu_2Er crystallizes with the orthorhombic $CeCu_2$ structure, and lattice parameters reported for this phase by [63Sto] and [70Bus] are in fairly good accord. The equiatomic phase CuEr forms with the cubic CsCl structure, and lattice parameter data reported by the various authors are in good agreement.

Crystal structures, accepted lattice parameter data, and related parameters for the various phases are summarized in Table 3. Data for the pure elements are also listed in Table 3, and these were taken from [Massalski] for Cu and [78Bea] and [86Gsc] for Er.

Thermodynamics

Thermodynamic Data

[83Nik] determined the enthalpies of dissolution of solid Er in Cu-Er melts at 1180 °C and in the composition range 0 to 8 at.% Er by calorimetry. They obtained the following expression for the partial molar enthalpy of solid Er in liquid Cu-Er:

$$\Delta H_{Er} = (1-X)^2 (-91\,688 - 283\,939\,X + 3\,840\,269\,X^2) \quad \text{(Eq 1)}$$

where X is the atomic fraction of Er. The partial molar enthalpy of dissolution of liquid Er in liquid Cu-Er alloys at infinite dilution was estimated by [83Nik] to be −112.1 kJ/mol at 1180 °C.

Thermodynamic Modeling

The data of [83Nik] were used in conjunction with a subregular approximation for the liquid to derive the following expression for the excess Gibbs energy of mixing of the liquid:

$$G^{ex}(L) = X_{Er}(1-X_{Er})\,(-111\,473 - 165\,782\,X_{Er} + 1\,290\,376\,X^2_{Er}) \quad \text{(Eq 2)}$$

Based on the above equation, as well as the elemental lattice stability parameters from Table 5, the two terminal eutectic compositions were estimated to be 8.1 and 22.6 at.% Er at 895 and 880 °C, respectively. The latter composition is quite unrealistic because it shows an extremely large deviation from the experimental composition of 69.5 at.% Er. The calculated liquidus in the Cu-rich end, shown in Fig. 2, fits well with experimental data. However, extrapolation of the data of [83Nik] to higher Er content results in a very poor fit, as evidenced by the large discrepancy between the calculated and the experimental eutectic composition at 880 °C. As such, it was deemed inappropriate to use the data of [83Nik] for the entire phase diagram.

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

Phase	Enthalpy of formation, kJ/mol Present modeling	Miedema model(a)
Cu_5Er	−18.0	−33.2
Cu_9Er_2	−26.8	−34.9
Cu_7Er_2	−20.1	−39.3
Cu_2Er	−17.3	−48.1
CuEr	−34.6	−49.7

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

An alternative expression was derived for the integral Gibbs energy of mixing for the liquid phase by optimization of the available experimental eutectic data (9.5 at.% Er, 895 °C and 69.5 at.% Er, 880 °C), with the assumptions that the terminal solid solubilities are negligible and that the liquid behaves like a subregular solution. The Gibbs energies of formation of Cu_5Er, Cu_9Er_2, Cu_7Er_2, Cu_2Er, and CuEr were then derived from the various liquidus 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 Cu-Er phase boundaries, evaluated from the expressions in Table 5, are compared in Fig. 2 with the experimental phase diagram. In general, the calculated phase boundaries are in fairly good agreement with the experimental data. Exceptions are observed in the region between 35 and 75 at.% Er, wherein the calculated Cu_2Er-CuEr and CuEr-(Er) eutectics show a definite shift toward higher Cu content. The temperatures corresponding to these eutectics were estimated to be 917 and 868 °C, respectively, which is assumed to be within experimental uncertainty limits.

The enthalpy data from the present modeling are compared in Table 6 with the enthalpies of formation evaluated with the Miedema model [80Mie, 83Nie]. In all instances, the Miedema model predicts enthalpy values that are much more exothermic than the values obtained in the present calculation.

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*Indicates key paper.

#Indicates presence of a phase diagram.

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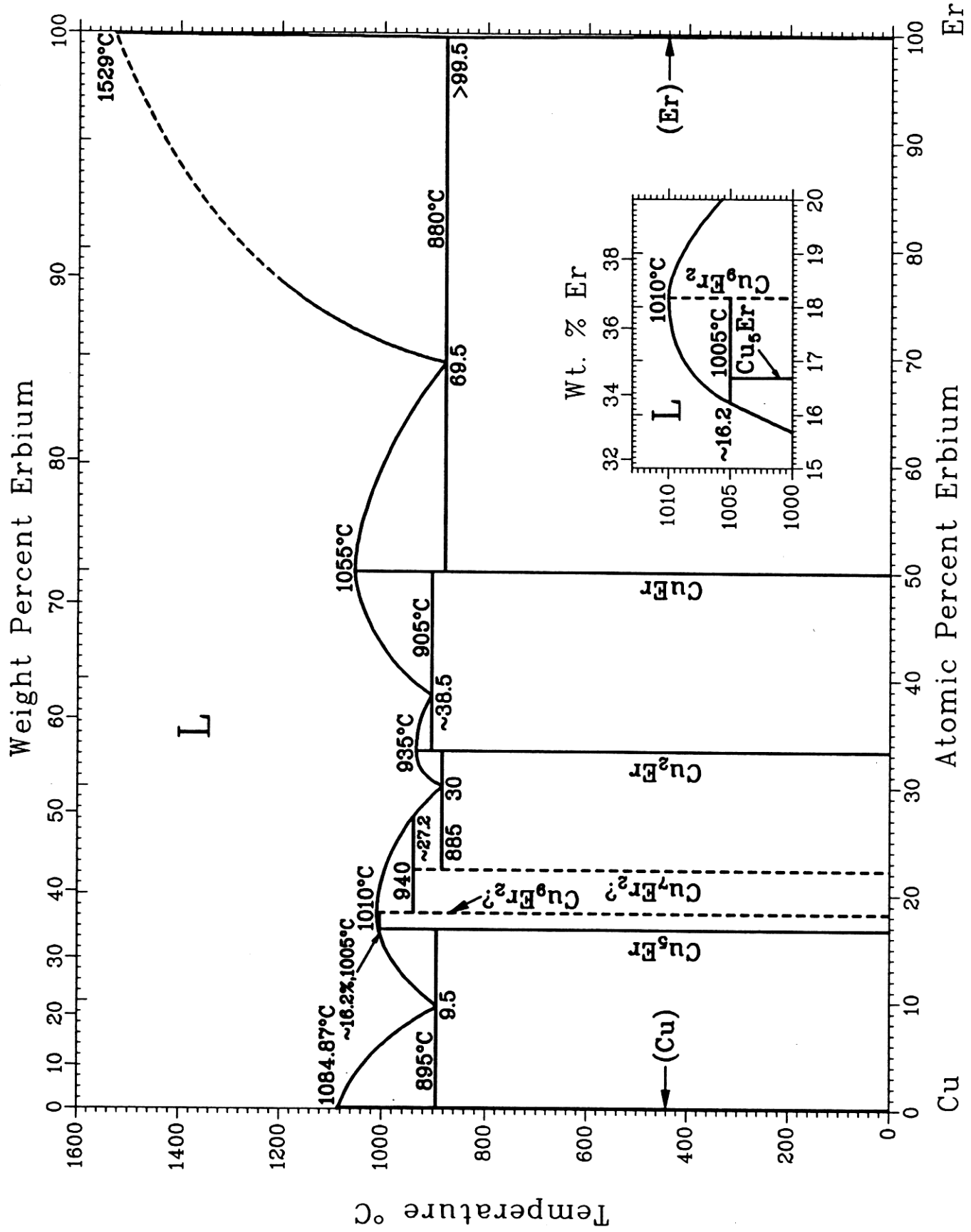

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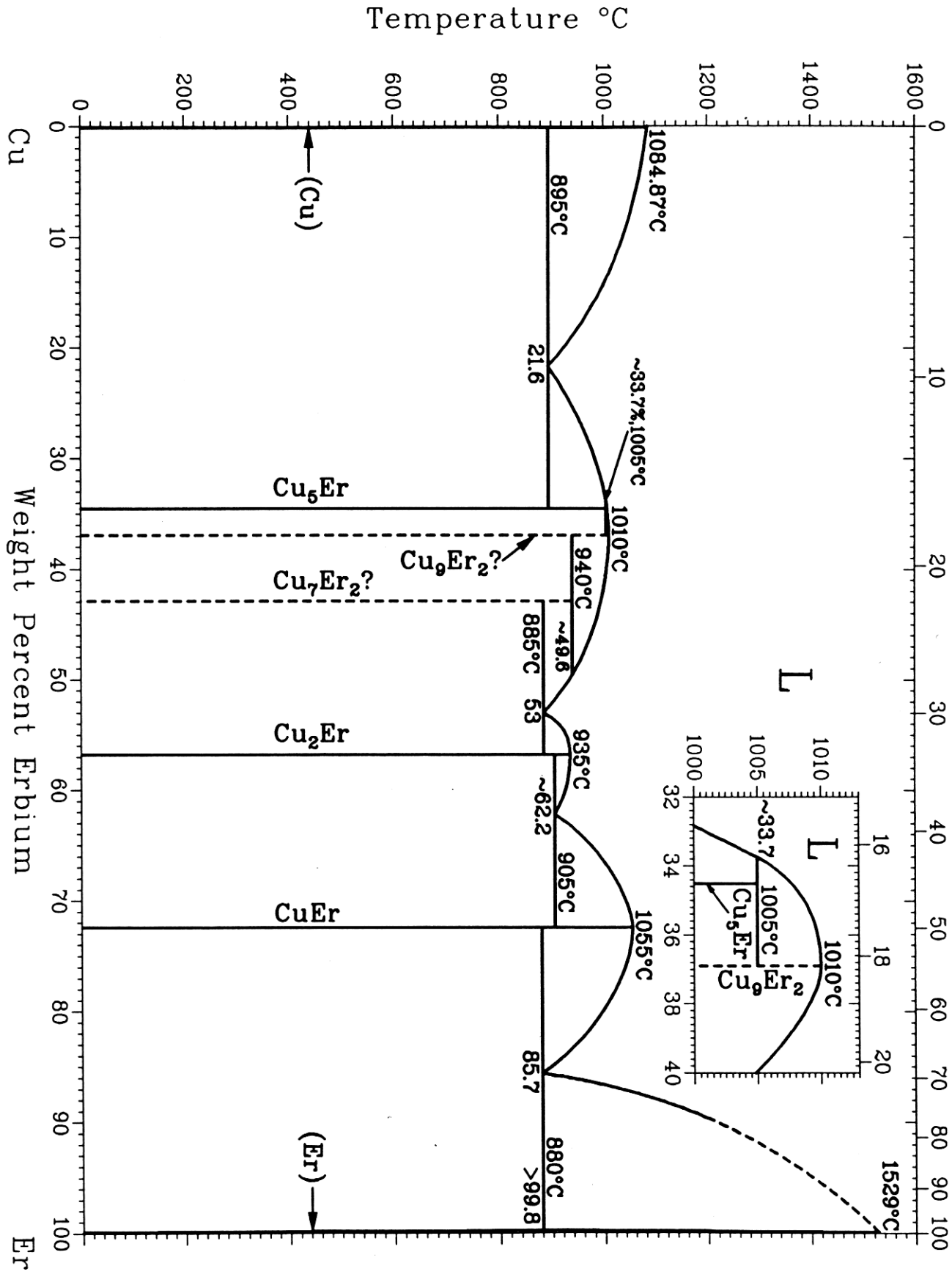

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