The Cu-Ho (Copper-Holmium) System

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Equilibrium Diagram

[63Wun] investigated the solid solubility of Ho in Cu in the range 500 to 1000 °C with metallographic methods. They observed that the solid solubility did not show any appreciable temperature dependence in this range, and that the maximum solid solubility of Ho in Cu is ~0.02 at.% Ho (0.06 wt.% Ho) at the eutectic temperature. Differential thermal analysis (DTA) studies on alloys containing ~4.1 at.% Ho (10 wt.% Ho) revealed the Cu-rich eutectic temperature to be 868 °C, and the corresponding liquidus temperature to be 1025 °C. [65Wun] redetermined the eutectic temperature in the Cu-rich region and found it to be 864 °C. There is no other experimental phase diagram information on the Cu-Ho system, and therefore, the assessed equilibrium diagram of Fig. 1 is derived from thermodynamic considerations, as well as the systematics of Cu-lanthanide systems (see "Thermodynamics"). The melting points of pure Cu and Ho are accepted as 1084.87 °C [Melt] and 1474 °C [78Bea, 86Gsc], respectively. Table 1 shows the various invariant temperatures that are expected to occur in the Cu-Ho system. In Fig. 1, the existence of Cu_9Ho_2 and Cu_7Ho_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. Also, there is a possibility that Cu_7Ho exists. A similar phase is found in the Cu-Dy system, but not in the Cu-Er system, and because Ho lies between Dy and Er in the lanthanide series, it is difficult to assess whether this phase will exist in the Cu-Ho system.

Metastable Phases

[79Mcg] prepared amorphous thin films with the composition $Cu_{0.56}Ho_{0.44}$ by sputtering from arc-melted specimens, and by thermal evaporation from Cu and Ho targets, followed by condensation on liquid nitrogen-cooled sapphire substrates. The resultant films were 500 to 1000 nm thick.

Crystal Structures and Lattice Parameters

Crystal structure data for the Cu-Ho system are listed in Tables 2 and 3. [61Dwi] reported the formation of

Fig. 1 Calculated Cu-Ho Phase Diagram

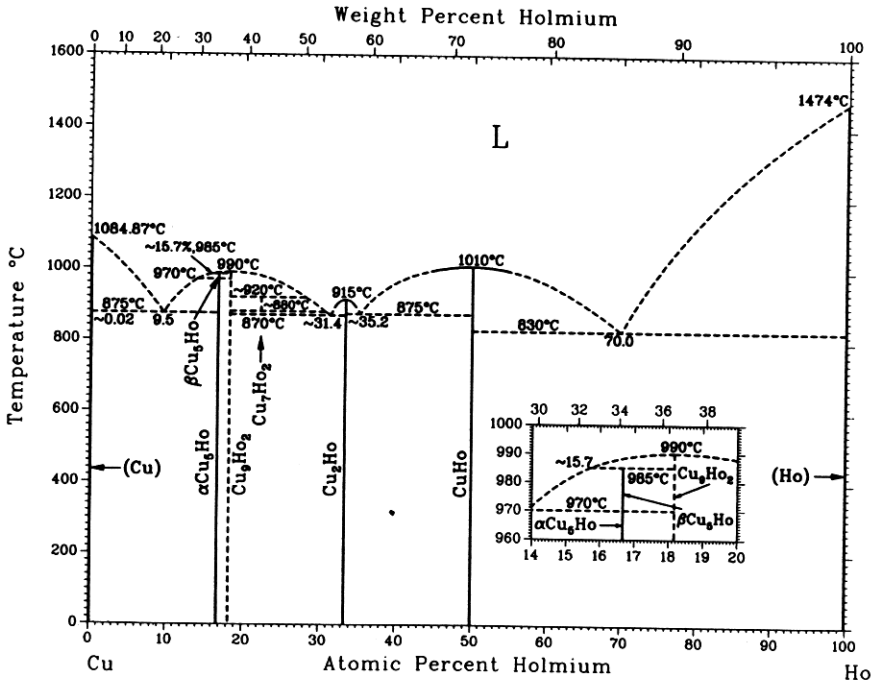

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Table 1 Special Points of the Assessed Cu-Ho Phase Diagram

Reaction		Compositions of the respective phases, at.% Ho		Temperature, °C	Reaction type	Reference
(Cu) ↔ L		0.0		1084.87	Melting point	[Melt]
L ↔ (Cu) + Cu_5Ho	9.5	~0.02	16.67	875	Eutectic	(a), (b)
L + Cu_9Ho_2 ↔ Cu_5Ho	~15.7	18.18	16.67	985	Peritectic	(b)
L ↔ Cu_9Ho_2		18.18		990	Congruent	(b)
L ↔ Cu9Ho_2 + Cu_2Ho	~31.4	18.18	33.33	870	Eutectic	(b)
L ↔ Cu_2Ho		33.33		915	Congruent	(b)
L ↔ Cu_2Ho + CuHo	~35.2	33.33	50.0	875	Eutectic	(b)
L ↔ CuHo		50.0		1010	Congruent	(b)
L ↔ CuHo + (Ho)	70.0	50.0	~100	830	Eutectic	(b)
(Ho) ↔ L		100		1474	Melting point	[78Bea, 86Gsc]

(a) Terminal solid solubility is from [63Wun]. (b) Compositions and temperatures were estimated from the systematics of Cu-lanthanide systems, in conjunction with thermodynamic modeling (see text).

Table 2 Cu-Ho Crystal Structure Data

Phase	Composition, at.% Ho	Pearson symbol	Space group	Strukturbericht designation	Prototype
(Cu)	0	*cF*4	$Fm\bar{3}m$	*A*1	Cu
Cu_5Ho(HT)	~16.67	*hP*6	*P*6/*mmm*	$D2_d$	$CaCu_5$
Cu_5Ho(LT)	~16.67	*cF*24	$F\bar{4}3m$	$C15_b$	$AuBe_5$
Cu_2Ho	~33.3	*oI*12	*Imma*	...	$CeCu_2$
CuHo	~50	*cP*2	$Pm\bar{3}m$	*B*2	CsCl
(Ho)	100	*hP*2	$P6_3/mmc$	*A*3	Mg

Cu_5Ho with the hexagonal $CaCu_5$-type structure, with lattice parameters $a = 0.4960$ nm and $c = 0.4016$ nm. In contrast, [69Bus] reported the occurrence of the cubic $AuBe_5$-type structure in alloys with the stoichiometry Cu_5Ho. This was based on X-ray intensity measurements on alloys annealed for 2 to 3 weeks in the temperature range 700 to 800 °C. For the Cu-Gd, Cu-Tb, 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_5Ho is also present in two allotropic modifications, with the hexagonal form reported by [61Dwi] as the stable phase at elevated temperatures, and the cubic form reported by [69Bus] as the stable phase at lower temperatures. The temperature range of stability of the hexagonal Cu_5Ho is expected to be limited. [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_5RE]/T_m[RE]) vs atomic number with that for the reduced transformation temperature (T_{Tr}[Cu_5RE]/T_m[RE]) vs atomic number shows that the cubic → hexagonal transformation temperature for Cu_5Ho should lie close to 970 °C.

[63Sto] determined that Cu_2Ho crystallizes with the orthorhombic $CeCu_2$-type structure; lattice parameters reported by [63Sto] and [86Sme] are in good agreement. The equiatomic phase CuHo forms with the cubic CsCl structure, and lattice parameter data reported by [64Cha] and [65Ian] are in good accord.

Thermodynamics

No thermodynamic data are available for the Cu-Ho system. Eutectic and melting temperatures in the Cu-lanthanide systems have been shown to vary systematically across the lanthanide series (see "The Copper-Rare Earth Systems," in this issue). On this basis, the terminal eutectic temperatures at the Cu- and Ho-rich ends were estimated to be 875 and 830 °C, respectively. The eutectic compositions at the Cu-rich end and the Ho-rich end were assumed to be ~9.5 and ~70 at.% Ho, respectively. These compositions were inferred from experimental data for the Cu-Gd [83Car], Cu-Dy [82Fra], and Cu-Er [70Bus] systems. The integral Gibbs energy of mixing of the liquid phase was derived from the interpolated eutectic data (9.5 at.% Ho, 864 °C and 70 at.% Ho, 830 °C), with the assumptions that mutual solid solubilities are negligible and that the liquid behaves like a subregular solution. The equilibrium temperatures of known Cu-Ho intermediate phases were obtained by interpolation of corresponding data for other known Cu-lanthanide systems. The Gibbs energies of formation of the Cu-Ho

Table 3 Cu-Ho Lattice Parameters

Phase	Composition, at.% Ho	Lattice parameters,nm a	b	c	Comment	Reference
(Cu)	0	0.36146	...	...	At 25 °C	[Massalski]
Cu_5Ho(Ht)	~16.67	0.4960	...	0.4016	...	[61Dwi]
Cu_5Ho(Lt)	~16.67	0.7016	...	...	...	[69Bus]
Cu_2Ho	~33.3	0.6759	0.7280	0.4280	...	[63Sto, 86Sme]
CuHo	~50	0.3446	...	...	...	[64Cha, 65Ian]
(Ho)	100	0.35778	...	0.56178	At 25 °C	[78Bea, 86Gsc]

Table 4 Cu-Ho 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 Ho(b)

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

$G^0(Ho, cph) = -16\,900 + 9.673\,T$

Integral molar Gibbs energies(c)

$G(L) + X(1-X)(-86\,738 + 38\,480\,X) + RT[X \ln X + (1-X) \ln (1-X)]$

$\Delta_f G(Cu_5Ho) = -20\,284 + 3.50\,T$

$\Delta_f G(Cu_9Ho_2) = -33\,551 + 13.23\,T$

$\Delta_f G(Cu_2Ho) = -17\,526 + 4.37\,T$

$\Delta_f G(CuHo) = -37\,431 + 10.26\,T$

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

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

Phase	Enthalpy of formation, kJ/mol Present modeling	Miedema model
Cu_5Ho	-20.3	-31.9
Cu_9Ho_2	-33.6	-33.5
Cu_2Ho	-17.5	-45.6
CuHo	-37.4	-46.6

Note: Standard states are liquid Cu and liquid Ho. From [83Nie].

phases were next determined at the various interpolated invariant temperatures from the Gibbs energy of mixing of the liquid. In all instances, the phases were treated as line compounds. Table 4 shows the values of the various thermodynamic parameters. The calculated Cu-Ho phase boundaries are shown in Fig. 1.

The enthalpies of formation from the present thermodynamic modeling are compared in Table 5 with the enthalpies evaluated with the Miedema model [80Mie, 83Nie]. With the exception of Cu_9Ho_2, the Miedema values are more exothermic than the values from the present evaluation.

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

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The Cu-Lu (Copper-Lutetium) System

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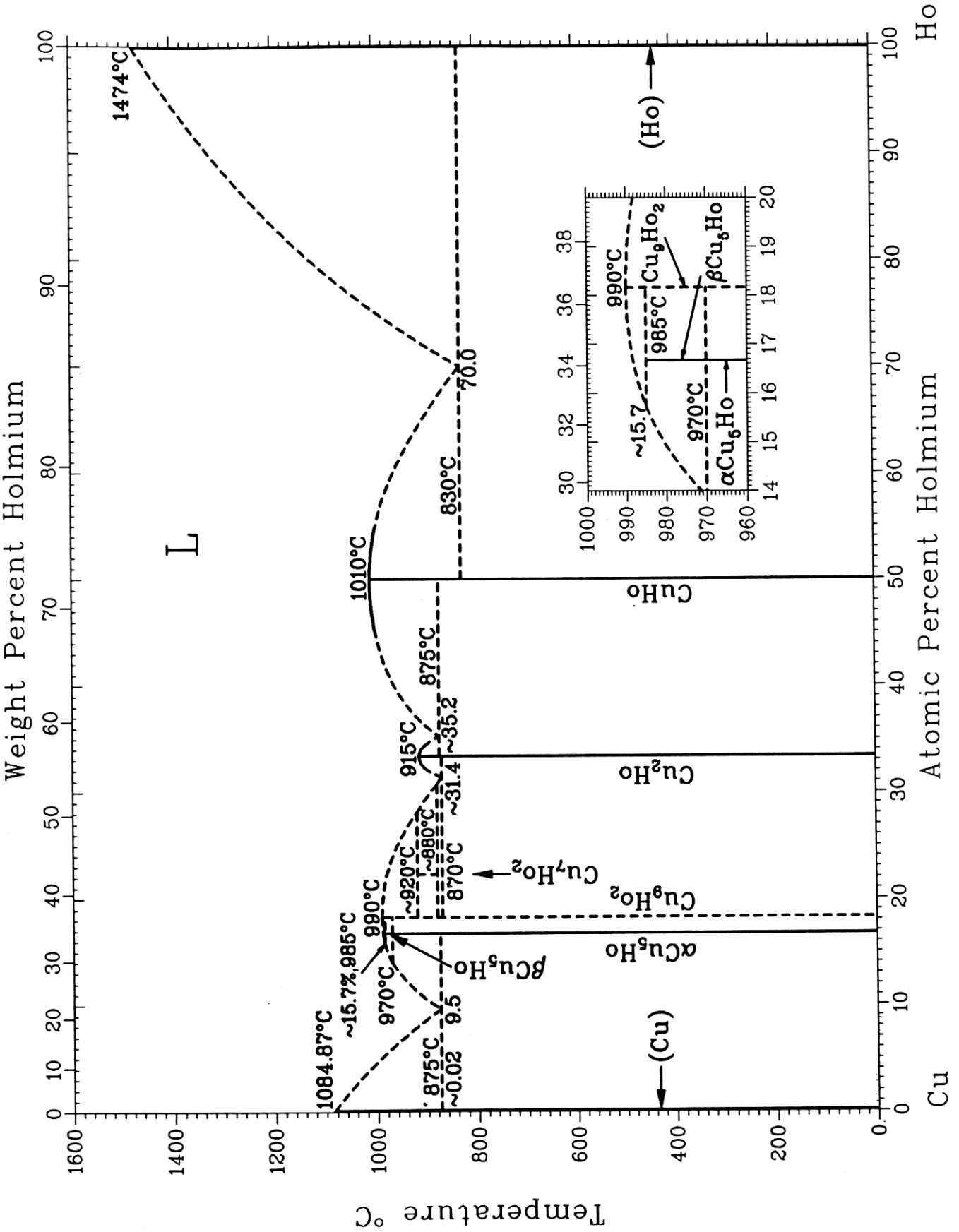
Equilibrium Diagram

No equilibrium diagram is available for the Cu-Lu system. However, the general features of the Cu-Lu 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-Lu intermediate phases were estimated by extrapolation of corresponding data for those Cu-lanthanide systems for which experimental phase diagrams are already known, using the systematic methods described by [83Gsc]. The Cu-Lu equilibrium diagram was then determined from the extrapolated invariant temperatures, in conjunction with thermodynamic considerations (see "Thermodynamics"). Figure 1 shows the schematic Cu-Lu equilibrium diagram. The melting points of pure Cu and pure Lu are accepted as 1084.87 °C [Melt] and 1663 °C [78Bea, 86Gsc], respectively. In Fig. 1, the existence of Cu_9Lu_2 and Cu_7Lu_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 reactions that are expected to occur in the Cu-Lu system.

Crystal Structures and Lattice Parameters

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

[71Ian] reported the cubic $AuBe_5$-type structure for Cu_5Lu. [63Sto] reported the formation of Cu_2Lu with the orthorhombic $CeCu_2$-type structure, and [60Dwi]



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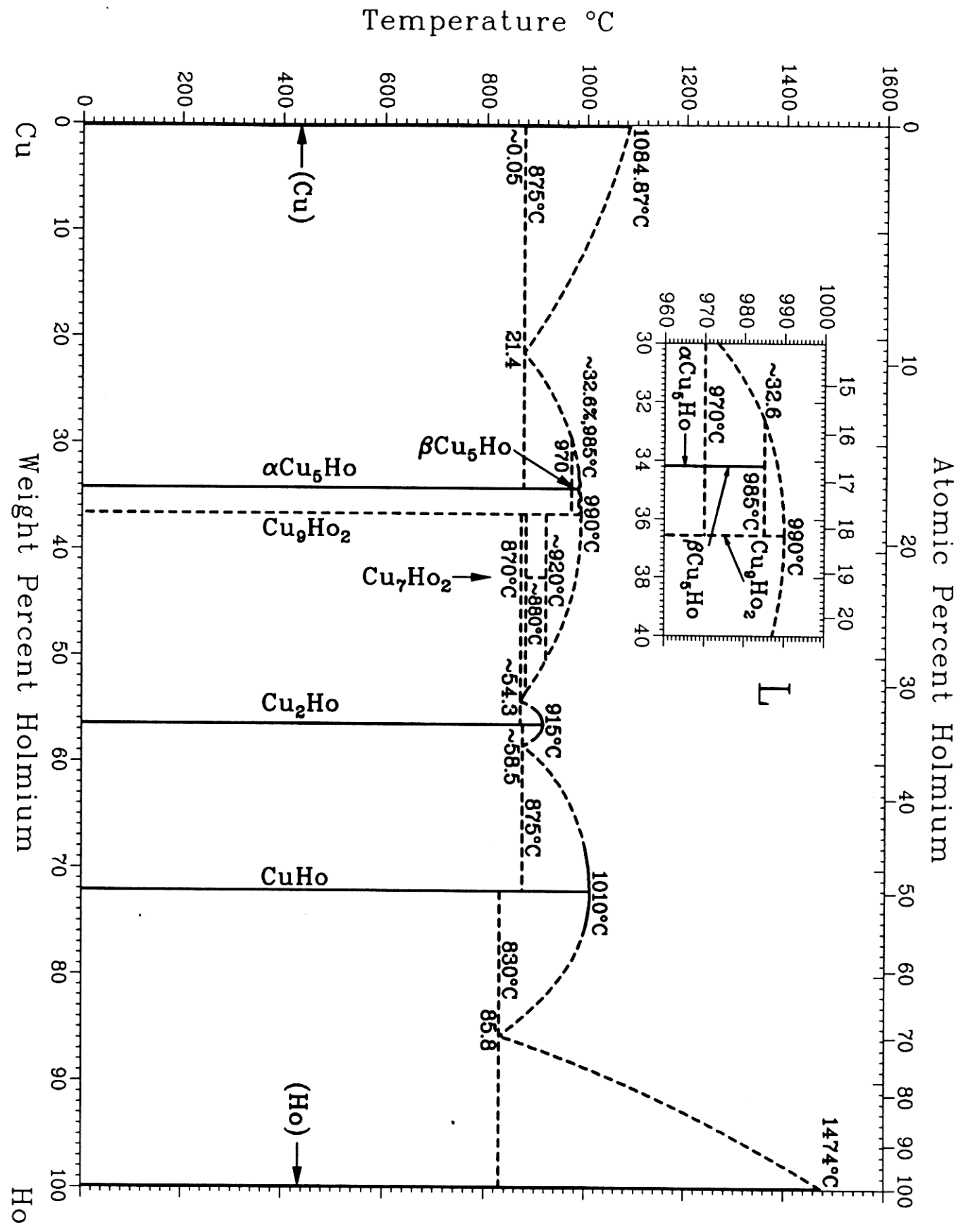

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