

The Cu-Y (Copper-Yttrium) System

63.546 amu

88.9059 amu

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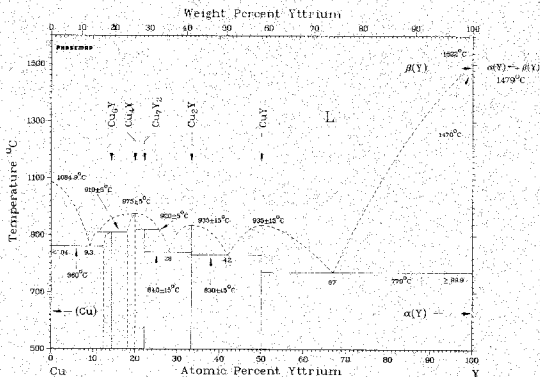
Equilibrium Diagram

The equilibrium phase diagram for the Cu-Y system is presented in Fig. 1. The equilibrium phases in this system are as follows: (1) the liquid; (2) the face-centered cubic terminal solid solution based on copper, with negligible (<0.04 at.%) solubility of Y; (3) the close-packed hexagonal terminal solid solution based on yttrium, with marginal solubility of Cu (maximum between 0.07 and 0.14 at.%) and stable up to 1479 °C; (4) the body-centered cubic terminal solid solution based on Y between the $(\alpha Y) \rightleftharpoons (\beta Y)$ transition temperature at 1479 °C and the melting point of Y at 1522 °C, presumably having negligible solubility of Cu; (5) the compound Cu_3Y , stable up to the peritectic decomposition temperature of 910 ± 5 °C; (6) the compound Cu_4Y , stable over a compositional field whose boundaries are not determined and up to the congruent melting temperature at 975 ± 5 °C; (7) the stoichiometric compound Cu_7Y_2 , stable up to the peritectic decomposition temperature at 920 ± 5 °C; (8) the stoichiometric compound Cu_2Y , stable up to the congruent

melting temperature at 935 ± 15 °C; and (9) the stoichiometric compound CuY , stable up to the congruent melting temperature at 935 ± 15 °C.

The most recent work on this equilibrium diagram is 20 years old. The available information on the system is incomplete with regard to the entire liquidus, and the different transition temperatures are also not accurately determined. Barring these limitations, the diagram is otherwise fairly complete with regard to the establishment of the different coexisting equilibrium phases. The equilibrium diagram shown in Fig. 1 is derived primarily from [1], with several modifications incorporated from [3]. [1] used metallography, X-ray and incipient fusion techniques on arc-melted alloys of 99.99% Cu and 99% Y. The main impurities in Y were 0.25 to 0.50 wt.% Zr, 0.15 to 0.20 wt.% Ti, 0.125 wt.% O, 0.10 wt.% Fe, 0.03 wt.% each of Ni and N and 0.02 wt.% C. Y used by [3] was of much higher purity, namely 99.9 wt.% or 99.5 at.% Y, with impurities 0.24 at.% O, 0.085 at.% C, 0.075 at.% F, 0.03 at.% Fe and 0.0035 at.% N.

Fig. 1 Cu-Y Phase Diagram



D.J. Chakrabarti and D.E. Laughlin, 1981.

Considering the low purity of the Y used, the results of [1] are in fair accord with those of [2] with regard to both the number and the stoichiometry of the compounds, with the exception that the compound Cu₄Y is indicated by [2] to be formed by syntectic rather than by congruent reaction as found by [1]. The purity of Y used by [2] is not reported but, in all likelihood, may not be much different from that of [1], considering the contemporary nature of the two works.

The occurrence of the compound Cu₄Y₂ was missed by both [1] and [2]. The thermal arrest at the peritectic decomposition temperature of the compound at 920 °C, noticed by [2], was misinterpreted to represent the syntectic reaction for the formation of Cu₄Y. The clarification of this point came from the careful DTA studies in this composition region by [3], who also confirmed that Cu₄Y is formed by congruent rather than by syntectic reaction. The uncertainty in the recorded temperatures by [1] is rather large, which is further augmented by the large interstitial impurity content in Y. Even if the distribution of the equilibrium phases remains unaltered, the temperature scales in the diagram are expected to undergo some revision in future studies using higher purity Y metal. Some of these changes have been incorporated from [3], in view of the better temperature accuracy (± 5 °C) and the use of higher purity material.

Liquidus, Solidus and Solvus. The liquidus, shown by dashed lines in Fig. 1, is tentative because the incipient fusion technique used by [1] is suitable only for determining the solidus accurately. The compositions at the various invariant points are, however, reasonably well determined by suitable selection of alloy com-

positions [1]. Four eutectic reactions that occur in the system are enumerated below. Details of the composition and temperature data from different authors are shown in Table 1. All the liquid composition data are accepted from [1], in view of their selection of closely spaced alloy compositions near the incongruent points. The eutectics are:

- The liquid of composition, 9.3 at.% Y, in equilibrium with (Cu) and Cu₄Y at 860 °C. The temperature datum is taken from [5] because of the accuracy and comparative recentness of measurement and of its reasonable agreement with that of [2].
- The liquid of composition, 28 at.% Y, in equilibrium with Cu₂Y₂ and Cu₂Y at 840 \pm 15 °C. The temperature is taken from [1], because the details of the accuracy of measurement by [2] are not known.
- The liquid of composition, 42 at.% Y, in equilibrium with Cu₂Y and CuY at 830 \pm 15 °C. The same comments apply for the selection of temperature as in above.
- The liquid of composition, 67 at.% Y, in equilibrium with CuY and (Y) at 770 °C. The temperature is taken from [6], because it falls within the scatter limit of the data by [1] and [2].

The accepted melting temperature of Y is 1522 °C [7]. Applying the Clausius-Clapeyron approximation for dilute alloys with negligible terminal solid solubility, the change in the melting point of Y is ~ 23 °C per atomic percent solute. The melting point quoted by [1] for the 99% Y is 1545 \pm 15 °C, approximately 23 °C more than that for Y. This surprising agreement with the calculation is perhaps fortuitous, considering different solutes and their conflicting influence on raising or

Table 1 Eutectic Compositions and Temperatures (a)

Phases in equilibrium with L	Composition, at.% Y [1]	Temperature, °C	Composition, at.% Y [4]	Temperature, °C	Temperature, °C [2]	Temperature, °C [5]
(Cu) Cu ₂ Y	9.3	890 ± 10	8	850	866	860 ± 2.5
Cu ₂ Y-Cu ₂ Y	28	840 ± 15	25.0	...	842	...
Cu ₂ Y-CuY	42	830 ± 15	60	...	836	...
CuY (Y)	67	760 ± 15	68 [6]	770 [6]	782	...

Note: All composition data are taken from [1] for reasons explained in the text.

(a) As cited by various authors.

Table 2 Phase Equilibria and Transformation Characteristics for Cu-Y, Including Intermediate Phases

Temperature, °C	Phases			Composition, at.% Y			Type
860	(Cu)	L	Cu ₂ Y	≤ 0.04	9.3	≤ 14.3	Eutectic
910 ± 5	L	Cu ₂ Y	Cu ₂ Y	?	14.3	~18	Peritectic
975 ± 5	L	Cu ₂ Y	...	20	20	...	Congruent
920 ± 5	Cu ₂ Y	Cu ₂ Y	L	~20	22.2	?	Peritectic
840 ± 15	Cu ₂ Y ₂	L	Cu ₂ Y	22.2	28	33.3	Eutectic
935 ± 15	Cu ₂ Y	L	...	33.3	33.3	...	Congruent
890 ± 15	Cu ₂ Y	L	CuY	33.3	42	50	Eutectic
935 ± 15	CuY	L	...	50	50	...	Congruent
770	CuY	L	(αY)	50	67	≥ 99.9	Eutectic
1470	L	(αY)	(βY)	~97.5	≥ 99.9	≥ 99.9	Metatectic

lowering the fusion point. [3] also observed similar agreement for 1.4 at.% Cu in Y, where the liquidus was depressed to 1495 °C. Likewise, the $\alpha \rightarrow \beta$ transition temperature of Y, presumably of similar purity as in [1], measured by [8], shows close correspondence with the thermodynamic value, being 24 °C lower than the presently accepted value of 1479 °C [9]. At the copper end of the diagram, where a number of intermetallic compounds occur, ideal solution approximation fails to predict the liquidus, which falls at a faster rate with temperature on addition of Y to Cu. There are three congruent points in the liquidus, corresponding to the decomposition of Cu₂Y at 985 ± 15 °C [1] or at 975 ± 5 °C [3], of Cu₂Y at 935 ± 15 °C [1] or at 895 °C [2] and of CuY at 935 ± 15 °C [1] or at 952 °C [2]. The congruent temperature for Cu₂Y is taken from [3] because of better temperature accuracy and higher purity Y used, and those for Cu₂Y and CuY from [1], as the error limits for the data by [2] are not known. In addition, two peritectic invariants occur in the solidus, corresponding to the decomposition of Cu₂Y at 930 ± 20 °C [1] and 910 ± 5 °C [3] and of Cu₂Y₂ at 920 ± 5 °C [3].

The maximum terminal solubility of Cu in Y is between 0.07 and 0.14 at.%, according to the unpublished data of [2], and that of Y in Cu is less than 0.04 at.% [5]. The high temperature $\alpha \rightarrow \beta$ transformation of Y at 1479 °C is difficult to determine because of its proximity to the melting temperature. However, metallographic evidence of precipitation of a second phase in Y solid solution at this temperature has been found in several systems of Y with very limited solubility of solute, suggesting that the transformation takes place by a peritectic or a metatectic reaction [9]. Report of the effect of Cu on $\alpha \rightarrow \beta$ transition in Y comes from [3], who by careful DTA study observed the transition temperature to decrease from 1478 °C for the starting Y metal to 1470 °C for the alloy with 1.4 at.% Cu. Thus,

the transformation of (β Y) to (α Y) and Y-rich liquid apparently occurs by a metatectic reaction at 1470 °C.

Intermetallic Compounds. Of the five intermetallic compounds in this system, CuY, Cu₂Y and Cu₂Y₂ occur at stoichiometry. Cu₂Y is indicated by [1] to exist over a broad composition range; the same also is likely with Cu₂Y.

[3] observed a two-phase structure at Cu₂Y and a single-phase structure at Cu₂Y₂ composition, suggesting a Cu₂Y stoichiometry of the compound, or alternatively, an off-stoichiometric extension of the Cu₂Y phase field to higher Cu. [13] also failed to detect a single-phase compound at Cu₂Y composition; whereas [1] did. The apparent discrepancy of [3] and [13] with [1] may be related to the stabilization effect due to impurity, which is higher in Y used by [1] (1% vs 0.1 wt.% for both [3] and [13]). Therefore, the Cu₂Y phase field is indicated extended on the Cu side, with the boundaries tentatively at Cu₂Y and Cu₂Y₂ compositions.

That Cu₂Y occurs at stoichiometry was confirmed by [1], [3] and [13]. [13] reported the occurrence of another compound, Cu₃Y, of hexagonal CaCu₃ prototype. The thermal decomposition behavior of Cu₃Y is, however, very different from other Cu-R compounds with rare earths, and the composition of Cu-Y also lies at lower than stoichiometric Cu, as noted by [13]. It is likely that Cu₃Y is not a separate compound but results from an extension of Cu₂Y phase field to higher Cu levels, as suggested also by [3]. Accordingly, Cu₂Y phase field is shown with an off-stoichiometric extension on the Cu side to about 12.5 at.% Y.

Table 2 summarizes the different phase equilibria, transformation characteristics and temperatures for the system, including those for the intermediate phases.

Metastable Phase

Although equilibrium solubility of Cu in Y is very restricted, metastable extension of the solid solubility limit up to 20 at.% Cu was obtained by [10] by ultra-rapid quenching of melt at the rate of $\sim 10^4$ °C/s to form foils of 0.1 to 5.0 μm thickness.

The occurrence of the stoichiometric compound of Cu_2Y has been reported by [11] and [12]. Under the rapid solidification conditions of splat cooling, [13] succeeded in synthesizing single-phase Cu_2Y compound at the stoichiometric composition, thus confirming its occurrence as a metastable phase. The d -spacing values for the Cu_2Y structure reported by [11] correspond closely to those for Cu_2Y listed by [1], who confirmed that the compounds Cu_2Y and Cu_3Y occur as equilibrium phases in the composition region of Cu_2Y . [1], however, also reported some difficulty in interpreting X-ray evidence in the vicinity of Cu_2Y composition. Apparently, equilibrium conditions are difficult to attain in this composition range, being strongly sensitive to the thermal history of specimens, and the metastable Cu_2Y phase can precipitate out to coexist with the equilibrium phases.

Y, like the rare-earth elements, is very reactive and may be contaminated by gases, such as H and O [14]. Minor impurities may alter phase equilibria considerably in these systems [15]. Apparently, the presence of impurities and rapid solidification conditions favor the kinetics of the formation of Cu_2Y compound over that of the equilibrium phases Cu_2Y and Cu_3Y . In the two reports, [11] and [12], where Cu_2Y phase was obtained directly in the ingot, neither used Y of the purity (99.9%) employed by [13]; in the work of [12], rapid chilling of the melt on a copper crucible could have further aided the formation of the metastable phase.

The question remains if Cu_2Y is at all an equilibrium phase. Certainly, its composition does not correspond to the stoichiometry, Cu_2Y ; [3] reports it at $\text{Cu}_{1.4}\text{Y}$, and

even [1], who suggested this stoichiometry, observed its occurrence at about 81 at.% Cu (75 wt.% Cu). If the phase is stabilized by impurities at lower than equilibrium Cu levels, as the work of [13] suggests, then the equilibrium occurrence of Cu_2Y is in question (also note, both Cu_2Y and Cu_3Y are reported to have the same crystal structure; see below). Studies using high purity Y between the compositions Cu_2Y and Cu_3Y should help clarify this point.

Crystal Structure and Lattice Parameters

Considerable confusion prevails regarding the crystal structure of two of the highest Cu compounds, i.e., Cu_2Y and Cu_3Y . Both [11] and [12] reported the occurrence of a Cu_2Y compound and identified it as the hexagonal CaCu_2 -type structure. However, as mentioned earlier, Cu_2Y is a metastable compound. Microscopic examination of alloys in the Cu_2Y composition range by [1] left no doubt that the equilibrium phases occurring are the compounds Cu_2Y and Cu_3Y . The d -spacings for Cu_2Y by [1] correspond closely to those for Cu_2Y by [11] and, therefore, [15] attributed the reported CaCu_2 structure for Cu_2Y to Cu_2Y .

Several other Cu_2R compounds, where R is a rare-earth element, are also known to have the CaCu_2 -type structure. To resolve the apparent stoichiometric disagreement, [16] and [17] proposed that the actual composition of the compounds is $\text{R}_{1.2}\text{Cu}_2$, so that the unit cell contains 1.2 formula units and, thus, six atoms. It was proposed that electron transfer between R and Cu atoms leads to the partial equalization of metal valency and atomic radii, and accounts for the 0.2 R atoms, which normally have much larger atomic radii than the Cu atoms, to occupy one of the two copper positions together with the 4.8 Cu atoms. On this basis, the CaCu_2 -type structure may be attributed to the Cu_2Y compound. [13], on the other hand, reported that they did not observe this structure type for the formula composition of the RCu_2 compound ($\text{R} = \text{La, Ce, Nd, Gd, Y}$), thus

Table 3 Crystal Structures

Phase	Approximate composition (at.% Y)	Pearson symbol	Prototype	Space group	a	b	c	Lattice parameters, nm	Comments	Reference
Equilibrium phases										
(Cu)	cF4	Cu	$Fm\bar{3}m$	0.36147	At 18 °C, 0% Y	(b)
Cu_2Y	12.5 to 14.3	?	0.683	...	0.407	...	Hexagonal	[18]
Cu_3Y	18.2 to 20	$hP6$	CaCu_3 ?	$P6_3/mmm$?	0.4994	...	0.4113	...	For 16.7 at.% Y, as explained in text	[12]
Cu_2Y	33.3	$oI12$	CeCu_2	$Imma$	0.4305 ± 0.0005	0.6800 ± 0.0005	0.7315 ± 0.0005	...	Material purity 99.9+ % Y and 99.999 % Cu	[19]
Cu_2Y	50	$cP2$	ClCs	$Pm\bar{3}m$	0.3477	[12]
(aY)	~99.7	$hP2$	Mg	$P6_3/mmc$	0.36496	...	0.57371	...	100% Y; 10^{-6} Torr vacuum annealed filings containing 0.0225 wt.% O	[14]
(βY)	$cI2$	W	$Im\bar{3}m$	0.411	100% Y	(b)
Metastable phase										
Cu_2Y	16.7	$hP6$	CaCu_2	$P6_3/mmm$	0.5005	...	0.4097	...	By splat cooling of 99.9% pure Y alloy	[13]

(a) From the phase diagram. (b) Fessenden [Landolt-Börnstein].

Table 4 Experimental Crystal Structure Data

Phase	Crystal structure	a	Lattice parameters, nm b	c	Reference
Cu ₅ Y	Hexagonal	0.683	...	0.407	[18]
	Hexagonal	0.4940	...	0.4157	[13], reported for Cu ₅ Y
Cu ₄ Y	Hexagonal	0.4984 ± 0.0005	...	0.4117 ± 0.0005	[11], quoted for Cu ₅ Y
	Hexagonal	0.4994	...	0.4113	[12], quoted for Cu ₅ Y
	Hexagonal	0.496	...	0.410	[2]
Cu ₂ Y	Hexagonal	0.749	...	0.609	[4]
	Hexagonal	0.741	...	0.584	[18]
	Orthorhombic	0.4305 ± 0.0005	0.6800 ± 0.0005	0.7315 ± 0.0005	[19]
	Orthorhombic	0.4308 ± 0.0003	0.6891 ± 0.0008	0.7303 ± 0.0007	[20]
CuY	Cubic	0.3474	[1]
	Cubic	0.354	[2]
	Cubic	0.3477	[12]
	Cubic	0.3479	[21]

contradicting [15]. They, however, did suggest the possibility of an off-stoichiometric extension of the homogeneous phase field of the CaCu_5 -type compound and, in fact, proposed such an occurrence between Cu_5Y and Cu_7Y compositions. This hypothesis, although accounting for the observance of the CaCu_5 -type structure at off-stoichiometric compositions, is in serious variance with metallographic evidence of the presence of a two-phase field in the Cu-Y system by [1], who also observed that the X-ray patterns for the Cu_5Y do not correspond to the Cu_5Y -type structure.

On the basis of the above facts and the available information, it is proposed that the metastable compound Cu_5Y and, possibly, compound Cu_4Y , have hexagonal CaCu_5 structures. The Cu_5Y compound also has a hexagonal symmetry.

Lattice parameters for the equilibrium phases, Cu_5Y , Cu_4Y , Cu_2Y and CuY , and for the metastable phase, Cu_5Y , having the hexagonal CaCu_5 prototype structure, are given in Table 3.

A collection of various lattice parameter and crystal structure data for the equilibrium phases obtained by different authors is given in Table 4. Selected values from this table, based on reported accuracy of measurement, consistency with the other results, and purity of the starting material, are incorporated in Table 3.

Thermodynamics

No thermodynamic data are available for this system. For the estimation of change of melting temperature and $\alpha \rightarrow \beta$ transformation temperature of Y, the enthalpy-difference values used in the Clausius-Clapeyron approximation are 11.43 kJ/g-at and 5.0 kJ/g-at, respectively [Hultgren].

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Cu-Y evaluation contributed by D.J. Chakrabarti and D.E. Laughlin, Department of Metallurgical Engineering and Materials Science, Carnegie-Mellon University, Pittsburgh, PA 15213, USA. Work was supported by the International Copper Research Association, Inc. (ICRRA) and the Department of Energy through the Joint Program on Critical Compilation of Physical and Chemical Data coordinated through the Office of Standard Reference Data (OSRD), National Bureau of Standards. Literature searched through 1980. Prof. Laughlin is the ASM/NBS Data Program's Category Editor for binary copper alloys.