The B-Cu (Boron-Copper) System

10.81   63.546

By D. J. Chakrabarti and D. E. Laughlin
Carnegie-Mellon University

Equilibrium Diagram

The equilibrium phases in the Cu-B system are: (1) the face-centered cubic terminal solid solution based on Cu with limited solubility of B amounting to ~0.29 at.% maximum; (2) the terminal solid solution based on B, having several allotropic modifications with the β-rhombohedral form dominant at elevated temperatures, and the β-tetragonal and, possibly, α-rhombohedral and α-tetragonal forms stable at low temperatures. The stability ranges for these are not well defined. The maximum recorded solubility of Cu in B is between 3.65 and 4.17 at.%, with retrograde characteristics at elevated temperatures.

The Cu-B phase diagram displayed in Fig. 1 is of the simple eutectic type with no intermediate phases present. The high melting point of B and its strong affinity for oxygen in the liquid state presented difficulties in alloy preparation and in identification of equilibrium phases in earlier studies [Hansen]. The occurrence of a eutectic reaction between the Cu-rich terminal solid solution and the compound, CuB$_{22}$, was earlier reported by [54Lih] by means of thermal, X-ray, microscopic, electrical conductivity, and hardness measurements. The study, however, extended up to ~11 at.% (2 wt.%) B. Subsequent studies by [65Wal], [65Smi], and [70Rex], employing thermal, microscopic, and X-ray methods confirmed the occurrence of the eutectic reaction, but the constituent phases were shown

to be the terminal solutions of Cu with that of B and not with CuB$_{22}$. It was concluded that CuB$_{22}$ does not occur as a separate equilibrium phase.

Liquidus and Solidus. The eutectic temperature and composition values from the foregoing studies, together with those from [74Pit], are all based on thermal analysis and metallography and are presented in Table 1. The results of [54Lih] are based on alloys prepared by the thermit process of reduction of B$_2$O$_3$ or borax by Mg, Ca, graphite, or CaC$_2$ and simultaneous alloying with Cu. Such processes are susceptible to impurity entrapments in the finished alloy, and this can account for the high eutectic temperature reported. Similarly, the amorphous B used for alloy preparation by [65Smi] is also relatively impure (1.9% Mg, 0.65% Al, 0.2% Fe, 0.4% SiO$_3$, and gases), making the reported results inaccurate. On the other

Table 1   Eutectic Temperature-Composition Values

Eutectic temperature, °C	Eutectic composition, at.% B	Reference
1060 ± 2	10.7	[54Lih]
1008 ± 4	≥10.7	[65Wal]
1021 ± 2	10.7	[65Smi]
1013	~13.3	[70Rex]
1010 ± 1	18 to 19	[74Pit]

Fig. 1 Cu-B Equilibrium Diagram
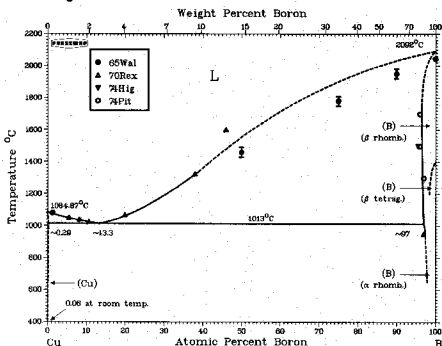
D.J. Chakrabarti and D.E. Laughlin, 1982.

hand, the B used by [70Rex] and [65Wal] are of 99.8 wt.% and of spectrographic purity with 212 ppm total impurities (excluding the nonmetallic impurities), respectively. In the data of [65Wal], use of a still higher purity zone-refined B also was reported, and careful DTA studies enabled the authors to detect a possible allotropic phase transition in the B terminal solid solution at 1022 °C not observed by others. Thus, the material and methods adopted by [65Wal] are of sufficiently high quality to consider the reported eutectic temperature at 1008 ± 4 °C fairly representative. This is evident from the close agreement of the above value with those reported by [70Rex] and [74Pit], the latter using still higher purity material for alloying, namely 99.9995% B and 99.9% Cu.

The eutectic composition, however, is not defined precisely by [65Wal]. The value reported by [74Pit] is considerably higher than other literature values, and the supporting detailed data are not presented. By comparison, [70Rex] presented a complete set of results with supporting data for both the eutectic composition at 13.3 at.% B and the eutectic temperature at 1013 °C that are consistent with other reported measurements and are, therefore, accepted as representative values. It is likely, however, in view of the results of [65Wal] and [74Pit], that the actual eutectic composition may be higher than the extrapolated value given by [70Rex]. The plots of the hypoeutectic liquidus from different works are shown in Fig. 2.

The initial slope of the liquidus at the Cu end appears to be very sensitive to the presence of impurity elements, the magnitude of the slope increasing with purity of the melt. Thus, the liquidus given by [54Lih] for the melt with supposedly highest impurity content has the least initial slope (approximately −4 °C/at.% B) followed closely by that of [65Smi], whereas the liquidus given by

[65Wal] shows the highest initial slope (approximately −11 °C/at.% B). Similar estimation is not possible from the data of [70Rex] for lack of sufficiently dilute alloys. The authors, however, observed a progressive shift of the liquidus from the ideal solution to lower slopes with increasing solute content. The difference in the slope was attributed to the deviation of the solution from ideality and to an increase in the activity coefficient of Cu from 1.00 in the pure state to ~1.06 at 10.7 at.% B. This would imply an increasing tendency toward segregation in the melt with increasing B content. This hypothesis is supported by the existence of miscibility gaps in the liquidus in several binary systems of B, namely with Ag, Au, Ge, Pb, and Sn [65Wal]. Also, theoretical considerations by [50Hil] and [65Mot] support this hypothesis. In fact, as observed by [65Wal] and [70Rex], Cu-B is perhaps the only system of B with Group-B metals that does not display a miscibility gap in the liquidus.

Although the liquidus ordinarily can be determined with greater precision than the solidus, in the present situation the likely strong effect of impurities on the liquidus slope and the lack of data from sufficiently dilute alloys preclude accurate determination of the initial slope of the liquidus. Alternatively, the liquidus could be estimated from a knowledge of the initial slope of the solidus, provided that reliable experimental data of the solidus boundary exist. For infinitely dilute solution, application of van't Hoff's equation produces the following relationship between the limiting slopes of the liquidus and solidus phase boundaries [68Gor]:

$$\frac{\Delta T}{X_B^{\sim s}} = \frac{\Delta T}{X_B^s}\left[1 + \frac{\Delta H_{Cu^\bullet}{}^{\sim t}}{R\left(T_{Cu^\bullet}{}^m\right)^2} \cdot \frac{\Delta T}{X_B^s}\right] \qquad \text{(Eq 1)}$$

In this equation, $\Delta T/X_B^s$ and $\Delta T/X_B^s$ are the initial slopes

Fig. 2 Hypoeutectic Liquidus in Cu-B System
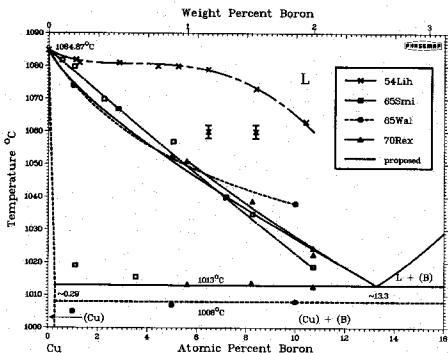
D.J. Chakrabarti and D. E. Laughlin, 1982.

of the liquidus and solidus, respectively; T_{Cu}^{m} is the melting point of Cu (1358.02 K); and $\Delta H_{Cu}^{\circ-\circ-f}$ is the enthalpy of fusion of Cu (13.054 kJ/mol [Hultgren]). For $\Delta T/X_B^{\circ} = -250$ °C/at.% B, based on terminal solid solubility data of B in Cu from [65Smi], the estimated value of $\Delta T/X_B^{\circ}$ calculated from Eq 1 is -11.2 °C/at.% B. This is in close agreement with the initial slope of the liquidus derived from the experimental data of [65Wal]. Accordingly, the liquidus curve from [70Rex] is modified in Fig. 2 at the dilute end to correspond to the above initial slope for thermodynamic compatibility with the initial slope of the solidus line. The suggested initial slope of the liquidus is somewhat higher than that estimated by [71Rao] based on the solubility data of [54Lih].

The hypereutectic portion of the liquidus has been mapped by means of thermal analysis by [70Rex] and [65Wal] in the lower and upper sections of the temperature range, respectively. Where the two measurements overlap, the data points differ by a large offset, precluding the adoption of a smooth liquidus over the entire temperature range. The temperature measurements by [65Wal] at these high ranges were done by pyrometric method and are claimed to be subject to a ±30 °C error. Even allowing for this margin of error, the initial slope of the liquidus at the B end turns out to be higher than the theoretical limiting slope of about 9.3 °C/at.% Cu, corresponding to zero solubility of Cu in B, as calculated from Eq 1. The initial slope in the above was computed from the interpolation of liquidus

data between 90 at.% B (1955 ± 30 °C) [65Wal] and pure B (2092 °C) [81BAP]. Studies indicate that Cu has finite solubility in B even at high temperatures (e.g., ~3.65 at 1700 °C), so that the magnitude of the initial slope of the liquidus should be still lower than 9.3 °C/at.% Cu. Thus, the data of [65Wal] do not appear to be compatible for drawing the liquidus, particularly near the B-rich end. Therefore, the hypereutectic liquidus is tentatively drawn conforming closely with the data of [70Rex], so that the extrapolated limiting slope at pure B is compatible with the thermodynamically acceptable value. Further work is needed to establish the liquidus at high temperatures.

Information on the outline of the B end of the solidus is available from the studies of [74Pit] and [74Hig] involving the equilibration of the B-rich Cu melt at specific high temperatures, followed by cooling to room temperature. The composition of the extracted crystalline forms of the B-rich solid solution is then determined. Using melts made from 99.9995% B and 99.9% Cu in an induction furnace (under argon) and held for 40 minutes at each temperature, [74Pit] obtained the following solubility versus temperature values by the electron probe microanalysis: $CuB_{26.4}$ (96.35 at.% B) at 1700 °C, $CuB_{27.8}$ (~96.53 at.% B) at 1500 °C, and $CuB_{30.5}$ (~96.83 at.% B) at 1300 °C. Likewise, [74Hig, 76Hig] reportedly obtained a single crystal of $CuB_{23.0 \pm 0.1}$ (~95.83 ± 0.02 at.% B) at 1500 °C, using the solution growth technique by holding melt made from 99.5% B and 99.99% Cu for 5 h at 1500 °C (under argon) and subsequently cooling. These results are presented in Fig. 1 and in Table 2. They indicate the formation of a retrograde solubility of Cu in B. The solubility limit (3.5 at.% Cu according to [74And]) is not well defined. It is apparent that the accuracy of the above results depends on the rapidity of cooling of the alloys from high temperatures. Thus, it is possible that the reported solubility figures may be somewhat lower than the equilibrium values.

Terminal Solid Solubility. The solid solubility of B in Cu, according to [65Smi], is ~0.29 at.% B at the eutectic temperature, presumably corresponding to ~1013 °C and 0.06 at.% B at room temperature. Earlier results obtained by [54Lih] were higher, specifically 0.53 and 0.35 at.% B, respectively. This possibly is due to higher impurity contents. It is likely that the actual solubility is even lower

Table 2 Solubility of Cu in B

Temperature, °C	Cu in solution, at.%	Comment	Reference
950	~2.83	(a)	[70Rex]
1300	~3.17	(b)	[74Pit]
1500	~3.47		
1700	~3.65		
?	~3.45	(c)	[74And]
1500	~4.17	(d)	[74Hig]

(a) Suggested maximum solubility based on alloys made from electrolytic Cu and 99.8 wt.% B. (b) EPMA studies on crystals extracted by chemical and electrolytic etching from bulk alloys made from 99.9995% B and 99.9% Cu by induction melting under argon atmosphere. (c) X-ray studies on B-solid solution phase, CuB$_{26}$, in a two-phase alloy of composition CuB$_{21}$, prepared from 99.8% crystalline B and 99.99% Cu by arc melting under pure argon. (d) X-ray studies on single crystal of CuB$_{23.0 \pm 0.1}$ prepared from 99.5% B and 99.99% Cu heated to 1500 °C for 5 h under argon and cooled to room temperature.

Table 3 Cu-B Crystal Structure Data

Phase	Approximate composition, at.% B	Pearson symbol	Prototype	Space group	Lattice parameters, nm a	c	Comment	Reference
Cu	0	cF4	Cu	Fm3m	0.36147	...	(a)	[Landolt-Börnstein]
(Cu)	0.29(max)	cF4	Cu	Fm3m	0.36196	...	(b)	[70Rex]
(B)	≥96	tP192	αAlB$_{12}$	P4$_2$2,2 P4$_1$2$_1$2 (?)	1.126	1.414	(c)	[65Wal]
(B)	≥96	hR105	B	R3m	1.108	2.411	(d, e)	[70Rex]
					1.09605	2.38793	(e, f)	[76Lun]
B(β-rhombohedral)	100	hR105	B	R3m(gl)	1.09302	2.38166	(h, j, k)	[76Lun]
					1.0145		(j, m)	[63Hug]
B(α-rhombohedral)	100	hR12	αB	R3m	0.4908	1.2567	(e, j, n, p)	[59Dec]
B(β-tetragonal)	100	tP192	αAlB$_{12}$	P4$_2$2,2 P4$_1$2$_1$2 (?)	0.5057		(j, n, q)	[59Sal]
					1.0061	1.4210	(j, r, s)	[69Sul]

(a) At 18 °C; for elemental Cu. (b) From two-phase alloy annealed at 950 °C. (c) On two-phase alloy containing 90 at.% B. (d) On 2.8 at.% Cu in B specimen at 950 °C. (e) In terms of hexagonal unit cell. (f) For 2.32 at.% Cu in B. (g) [70Hoa, 70Gei]. (h) Zone-refined boron of 99.9999% purity; in terms of hexagonal unit cell. (j) On elemental boron. (k) Stable down to 1400 °C [70Amb]. (m) $\alpha = 65°$ 17' for rhombohedral unit cell. (n) On single crystal of B. (p) Stable below 1000 °C [71Amb]. (q) For rhombohedral unit cell, $\alpha = 58.06°$. (r) Possibility of being stabilized in presence of impurities such as carbon [71Plo]. (s) Stable down to between 1100 and 1200 °C [70Amb].

than that given by [65Smi]. On the B-side, the maximum solubility of Cu in B obtained by [70Rex] on samples annealed at 950 °C is 2.8 at.% Cu and is consistent with other results at higher temperatures, indicating the retrograde solubility.

Crystal Structures and Lattice Parameters

Boron occurs in nature in both amorphous [60Tal] and crystalline forms of several polymorphic modifications [74Don]. Crystal structures and lattice parameters of the more prevalent forms are shown in Table 3. According to [70Amb], the β-rhombohedral B is stable down to about 1400 °C, followed by β-tetragonal B, which is stable down to between 1100 and 1200 °C. The α-rhombohedral B is found to be stable below 1000 °C [71Amb].

In the Cu-B system, the β-rhombohedral structure is stable at considerably lower temperatures. [70Rex] observed this structure in a 97.2 at.% B sample annealed at 950 °C and [65Wal] in a 90 at.%-B sample annealed at 1000 °C, in the latter situation along with β-tetragonal and α-rhombohedral forms. Impurities are reported to influence the stability of some of the B structures, and the β-tetragonal form is considered by [71Plo, 71Amb] to be stabilized in the presence of carbon. The preponderance of the β-rhombohedral structure in the Cu-B system, even at temperatures considerably below 1400 °C, suggests that Cu stabilizes this structure [73Per]. The Cu atoms occupy the interstitial holes within the icosahedral framework of B atoms, similar to carbon atoms in the tetragonal holes in the β-tetragonal structure. Lattice parameters of the terminal solid solution alloys of B having β-rhombohedral and β-tetragonal structures, according to [70Rex] and [65Wal], respectively, are presented in Table 3. The lattice parameters for the solid solution of Cu by [70Rex] show a finite but very small deviation from the value for pure Cu.

Room temperature lattice parameter values versus composition of the B-rich solid solutions with β-rhombohedral structure, together with those for elemental B, are presented in Table 4. These data indicate that the presence of Cu in the lattice increases the dimensions of the B framework.

Thermodynamics

No thermodynamic data are available for this system. The enthalpy of fusion values for Cu and B, used for the estimation of initial slopes of the two liquidus curves, are 13.054 kJ/mol and 50.208 kJ/mol [Hultgren], respectively.

Cited References

50Hil: Hilderbrand, F.H. and Scott, R.L., *The Solubility of Non-electrolytes*, Reinhold, NY (1950).

54Lih: Lihl, F. and Fleischl, O., *Metall.*, 8, 11-19 (1954) in German.

59Dec: Decker, B.F. and Kasper, J.S., *Acta Cryst.*, 12, 503-506 (1959).

60Tal: Talley, C.P., Line, L.E., and Overman, Q.D., *Boron, Synthesis, Structure and Properties*, Plenum Press, NY, 94 (1960).

Table 4   Lattice Parameters of β-Rhombohedral Boron Solid Solutions

Composition, at.% B	Alternate composition designation	Lattice parameters(a), nm		Comment	Reference
		a	c		
99.9999	(B)........	1.09302	2.38166	(b)	[76Lun]
99.715	CuB$_{342.9}$.......	1.09332	2.38292	(c)	
99.417	CuB$_{170.6}$.......	1.09377	2.38427	(c)	
98.860	CuB$_{86.69}$.......	1.09438	2.38628	(c)	
97.684	CuB$_{42.16}$.......	1.09605	2.38793	(c)	
99.8	(B)........	1.09253	2.38103	(f)	[74And]
~96.5	CuB$_{-28}$........	1.09703	2.38898	(d)	
~96.5	CuB$_{-28}$........	1.09723	2.38894	(e)	
95.9	CuB$_{23.4}$.......	1.0985 ±0.0001	2.3925 ±0.0002	(g)	[76Hig]

(a) In terms of hexagonal unit cell. (b) On elemental boron. (c) Specimens made from 99.998% Cu and 99.9377% boron; zone-refined B by arc melting under purified argon on water-cooled Cu hearth. (d) On single crystal. (e) On powder sample. (f) On arc-melted 99.8% elemental boron. (g) On alloy made from 99.5% B and 99.99% Cu at 1500 °C and cooled to room temperature.

63Hug: Hughes, R.E., Kennard, C.H.L., Sullenger, D.B., Weakliem, H.A., Sands, D.E., and Hoard, J.L., *J. Am. Chem. Soc.*, 85, 361-362 (1963).

65Mot: Mott, R.W., abstract of papers at the "Hauptversammlung der Deut. Ges. Metallk.," Salzburg (1965), cited in [65Wal].

65Smi: Smiryagin, A.P. and Kvurt, O.S., Tr. Gos. Nauchn. Issled. *Proektn. Inst. Splavov Obrabotke Tsvetn. Metal.*, 24, 7-11 (1965) in Russian.

65Wal: Wald, F. and Stormont, R., *J. Less-Common Met.*, 9, 423-433 (1965).

68Gor: Gordon, P., *Principles of Phase Diagrams in Materials Systems*, McGraw-Hill, 141 (1968).

69Sul: Sullenger, D.B., Phipps, K.D., Seabaugh, P.W., Hudgens, C.R., Sands, D.E., and Cantrell, J.S., *Science*, 163, 935 (1969).

70Amb: Amberger, E., Ploog, K., and Druminski, M., and Ploog, K., *Electron Techn.*, 3, 133 (1970), cited in [73Per].

70Gei: Geist, D., Kloss, R., and Follner, H., *Acta Cryst.*, B26, 1800-1802 (1970).

70Hoa: Hoard, J.L., Sullenger, D.B., Kennard, C.H.L., and Hughes, R.E., *J. Solid State Chem.*, 1, 268-277 (1970).

70Rex: Rexer, J. and Petzow, G., *Metall.*, 24, 1083-1086 (1970) in German.

71Amb: Amberger, E. and Ploog, K., *J. Less-Common Met.*, 23, 21-31 (1971) in German.

71Plo: Ploog, K. and Amberger, E., *J. Less-Common Met.*, 23, 33-42 (1971) in German.

71Rao: Rao, M. and Anderson, R., *J. Less-Common Met.*, 25, 427-430 (1971).

73Per: Perry, A., Nicoll, A., Phillips, K., and Sahm, P., *J. Mater. Sci.*, 8, 1340-1348 (1973).

74And: Anderson, S. and Callmer, B., *J. Sol. St. Chem.*, 10, 219-231 (1974).

74Don: Donohue, J., *The Structures of the Elements*, John Wiley, NY, 48-82 (1974).

74Hig: Higashi, I., Takahashi, Y., and Atoda, T., *J. Less-Common Met.*, 37, 199-204 (1974).

74Pit: Piton, J.P., Vuillard, G., and Lundstrom, T., *C.R. Acad. Sci., Ser. C*, 278, 1495-1496 (1974).

76Hig: Higashi, I., Sakurai, T., and Atoda, T., *J. Less-Common Met.*, 45, 283-292 (1976).

76Lun: Lundström, T. and Tergenius, L.E., *J. Less-Common Met.*, 47, 23-28 (1976).

81BAP: *Bulletin of Alloy Phase Diagrams*, 2(1), 145-146 (1981), quoting melting points of elements conforming to the 1968 temperature scale.