symmetric shape of the gap is a consequence of the liquid being approximated as a regular solution. Figure 2 also shows the metastable miscibility gap of the fcc phase calculated from Eq 3.

Suggestion for Future Experimental Work

For the sake of completeness of the assessed phase diagram and for comparison with the calculated liquidus, the liquidus in the Cu-Ir system must be determined experimentally.

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

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The Be-N (Beryllium-Nitrogen) System

9.01218 14.0067

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Equilibrium Diagram

The equilibrium phases of the Be-N system are (1) the liquid, L; (2) the terminal solid solution, (Be), which exists at lower temperatures as cph (αBe) and at higher temperatures as bcc (βBe); (3) the nitride, Be_3N_2, which exists at lower temperatures as cubic αBe_3N_2 and at higher temperatures as hexagonal βBe_3N_2; and (4) the gas, g. An azide, $Be(N_3)_2$, has been reported, which may also be an equilibrium phase of the condensed system. Crystal structure and lattice parameter data are listed in Tables 1 and 2.

No published phase diagram for the Be-N system was found. The three-phase equilibria and special points for the phases are listed in Table 3. The locations of the (Be) solvus, solidus, and liquidus are mostly unknown, as are those of the Be_3N_2 liquidus and the speculative miscibility gap. Because pertinent data are lacking not only for the positions of the univariants and invariants but also for the

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Table 1 Be-N Crystal Structure Data

Phase	Composition, at.% N	Pearson symbol	Space group	Strukturbericht designation	Prototype	Reference
αBe	~0	*hP*2	*P*6_3/*mmc*	*A*3	Mg	[King1]
βBe	~0	*cI*2	*Im*3*m*	*A*2	W	[King2]
αBe_3N_2	~40	*cI*80	*Ia*3	*D*5_3	Anti-Mn_2O_3	[Pearson2]
βBe_3N_2	~40	*hP*10	*P*6_3/*mmc*	...	βBe_3N_2	[Pearson2]
$Be(N_3)_2$	~86	...	...	...	...	

Table 2 Be-N Lattice Parameter Data

Phase	Composition, at.% N	Lattice parameters, nm a	c	Comment	Reference
αBe	0	0.22858	0.35843	At 20.5 °C	[63Mac]
βBe	0	0.25515	···	At 1260 °C	[62Sin]
αBe_3N_2	40	0.8150	···	At 25 °C	[Pearson2, Landolt]
βBe_3N_2	40	0.28413	0.9693	At 1400 °C	[60Eck]

Table 3 Special Points of the Assessed Be-N Phase Diagram (Condensed System)

Reaction	Compositions of the respective phases, at.% N			Temperature, °C	Reaction type
$L_2 \rightleftarrows L_1 + \beta Be_3N_2$(a)	···	···	~40	~2200	Monotectic?
L–βBe_3N_2–αBe_3N_2(b)	···	~40	~40	~1400	Unknown
$L \rightleftarrows (\beta Be) + \alpha Be_3N_2$	<0.2?	···	40	~1289	Probably eutectic(c)
$(\beta Be) \rightleftarrows (\alpha Be) + \alpha Be_3N_2$	···	~0.01	40	~1270	Probably eutectoid(c)
$L \rightleftarrows \beta Be$		0		1289 ± 4	Melting point
$\beta Be \rightleftarrows \alpha Be$		0		1270 ± 6	Allotropic
$L \rightleftarrows \beta Be_3N_2$		40		2200	Congruent melting
$\beta Be_3N_2 \rightleftarrows \alpha Be_3N_2$		40		1450 ± 50	Polymorphic

Note: At 0.1 MPa.
(a) Possible, speculative. (b) Required. (c) Another possible pair of reactions is discussed in the sections on "Terminal solid solution, (αBe) and (βBe)" and on "Beryllium nitride, αBe_3N_2 and βBe_3N_2."

types of invariant equilibria, the drawing of even a schematic phase diagram for the condensed system was not attempted.

Terminal Solid Solutions, (αBe) and (βBe). The terminal solid solution is cph (αBe) at lower temperatures and bcc (βBe) at higher temperatures up to the solidus. In the condensed system, (Be) saturated with N coexists stably with αBe_3N_2 [72Ald] or with the liquid. No solid phase between (Be) and Be_3N_2 exists [63Pem].

There is evidence that the solubility of N in (Be) is small but appreciable. [50Gul] interpreted the persistence of colored (tarnish) films of nitride on (αBe) heated at 800 to 970 °C in a vacuum as indicating that the nitride is "not soluble" in the metal. In Be-N alloys containing 0.6 at.% N, which had been added to Be while it was molten, "needles" (or plates) of nitride were observed metallographically [50Kau]. The observation that the "needles" were inclined at an angle of $2\pi/3$ rad to each other suggests that they were precipitated from (αBe). The thermal history of the specimen was unreported; consequently, it can be concluded only that 0.6 at.% N exceeds the solubility in (αBe) at room temperature or somewhat above. [50Kau] stated that, for an unspecified temperature, N appeared to have "negligible" solid solubility in (Be).

The only quantitative measurement of the concentration of N in (αBe) saturated with respect to Be_3N_2 (probably αBe_3N_2) is that of [63Pem]. They reported from metallographic examination of Be-N alloys that (αBe) coexisting with Be_3N_2 contains 0.0039 ± 0.0008 at.% N at 1000 °C. The solubility was within these limits in the observed range from 500 to 1000 °C; [63Pem] suggested that these limits might apply up to 1283 °C. Concentrations of N dissolved in (αBe) near an interface with Be_3N_2 in a diffusion couple annealed at 1025 °C were consistent with the value 0.0039 at.% N for saturation [63Pem]. Reviews [Shunk, 72Ald, 73Gol, 79Ald, 79Sto] subsequent to the [63Pem] publication listed no other solubility data, and none have been found in the current search.

Little is known about the invariants of the condensed Be-N system involving (αBe) and (βBe). The thermal analysis data of [63Pem] are limited and not readily interpretable, but the authors indicated that N depresses the temperatures at which the solid state and melting transformations occur. This, in turn, suggests that the three-phase reactions are probably not peritectoid or peritectic.

(αBe) may participate in only one three-phase equilibrium, a eutectoid reaction with (βBe) and (αBe_3N_2) (Table 3)—or, alternatively, because of the proximity of the αBe/βBe transformation to the βBe melting point, (αBe) might participate in both a eutectic reaction [$L \rightleftarrows (\alpha Be) + \alpha Be_3N_2$] at a lower temperature and a catatectic reaction [$(\beta Be) \rightleftarrows (\alpha Be) + L$] at a higher temperature. The first alternative requires that (βBe) participate not only in the eutectoid reaction already mentioned, but also in a eutectic reaction at higher temperature with the liquid and αBe_3N_2 (Table 3). In the second alternative, (βBe) would participate only in the catatectic reaction already mentioned.

Apart from the thermal analysis data of [63Pem], which are inadequate for determining which of the foregoing situations prevails, there are apparently no data on these transformations. For brevity, only the reactions required in the first alternative are in Table 3.

No data are available for the compositions of coexisting (αBe) and (βBe) or of (βBe) coexisting with αBe_3N_2, if that equilibrium occurs. The (Be) solidus and liquidus are also undetermined.

Beryllium Nitride, αBe_3N_2, and βBe_3N_2. The apparent equilibrium form at lower temperatures is cubic αBe_3N_2 and the equilibrium form at higher temperatures is hexagonal βBe_3N_2. Eckerlin and Rabenau, who established the existence of βBe_3N_2, reported both 1400 [60Eck] and 1500 °C [60Rab] as the temperature above which transformation of αBe_3N_2 to βBe_3N_2 occurs. They indicated that the transformation in heating is very slow, requiring some hours, even at 1650 °C. The instability of αBe_3N_2 relative to another solid phase at high temperatures had been indicated by [52Chi], who noted the disappearance of the X-ray diffraction lines characteristic of αBe_3N_2 after heating to 2000 °C. However, the new phase was not identified, and the [52Chi] specimen evidently was impure [60Eck].

The αBe_3N_2 structure generally is accepted as being stable at lower temperatures. It forms at temperatures up to about 1000 °C when Be metal is reacted with N_2 or NH_3 and is persistent at these temperatures. However, there is some basis for questioning its stability, because αBe_3N_2 was not observed to form when βBe_3N_2 was cooled below 1400 °C [60Eck]. This failure to observe a transformation in cooling does not appear to have been investigated further.

The range of compositions of the Be_3N_2 phases is unknown [72Ald]. The melting point measurement for Be_3N_2 by [15Fic] of 2200 °C apparently is the only determination. The specimen was melted under N_2 gas at 0.1 MPa with fast heating to suppress vaporization; consequently, the value may pertain to αBe_3N_2 which, at least at temperatures lower than 2200 °C, transforms sluggishly to βBe_3N_2.

On its low N_2-fugacity side, αBe_3N_2 coexists stably in the condensed Be-N system with (αBe) (lowest temperatures), probably with (βBe) (intermediate temperatures), or with the liquid (highest temperatures, up to the equilibrium with βBe_3N_2). On this same Be-rich side, βBe_3N_2 coexists stably with the liquid. Thus, as discussed in the section on the terminal solid solutions, (αBe) and (βBe), αBe_3N_2 exists in three-phase equilibria either with (αBe) and L or with (αBe) and (βBe) in one equilibrium and with (βBe) and L in another. In addition, a three-phase equilibrium among αBe_3N_2, βBe_3N_2, and L must exist. Finally, analogous to other systems where a stable high-melting-temperature compound coexists with a much lower-melting-temperature metal, there may be a monotectic equilibrium among βBe_3N_2, L_1, and L_2. Apparently, none of the foregoing three-phase equilibria have been investigated.

As with the solidus, the liquidus compositions on the Be-rich side of Be_3N_2 are unknown. Although [50Kau] introduced 0.6 at.% N into liquid Be, there was no indication of temperature or of whether the mixture before casting was single phase, was N-saturated, or contained undissolved Be_3N_2. [63Pem] reported that his liquid with 0.20 at.% N was "not completely molten" at 1360 °C, but was not explicit on whether excess nitride was present or insufficient time was allowed for completion of the dissolution process.

On its N-rich side, Be_3N_2 has not been observed in coexistence with any other solid nitride. An equilibrium with $Be(N_3)_2$ or with an unreported intermediate nitride may exist.

Beryllium Azide, $Be(N_3)_2$. This compound may have first been prepared by [1898Cur], but water caused its immediate decomposition. This compound was prepared anhydrously by [54Wib] at the melting point of ether (−116 °C) from $Be(CH_3)_2$ and HN_3. It could be warmed to room temperature without decomposition. Its composition range and phase relationships in the Be-N system were not investigated. As the only solid nitride of Be reported other than Be_3N_2, it may be regarded tentatively as a stable phase of the condensed binary system.

Gas. The only vapor species reported for the Be-N system are Be, N_2, and BeN. The only published data for compositions of vapor coexisting with solid Be_3N_2 are those of Greenbaum *et al.* [64Gre, 64Yat] and those of Hoenig and Searcy [64Hoe, 67Hoe]. These reports, for the temperature ranges 1130 to 1430 and 1370 to 1690 °C, respectively, showed that Be_3N_2 vaporizes congruently and decomposes during vaporization to produce Be(g) and N_2(g). Other gaseous species, such as BeN, apparently were not significant in these experiments. Thermodynamic data for BeN(g) [71Stu] indicate that it is very unstable at low temperatures, but increases in relative stability at higher temperatures. The equilibrium total pressure of vapor over Be_3N_2 at 1370 to 1690 °C is given by the following equation [67Hoe]:

$$\log P = +11.946 - 1.952 \times 10^{-4}/T$$

where P and T are in Pa and K, respectively. Agreement between the [64Yat] and [67Hoe] sets of data was termed excellent by the latter investigators.

Crystal Structures and Lattice Parameters

(αBe) and (βBe). The variation of lattice parameters with dissolved N concentration is unknown in either phase. [79Ald] stated that it was undetermined whether N dissolves interstitially or substitutionally in (αBe).

αBe_3N_2 and βBe_3N_2. The structure of αBe_3N_2 was first established and its lattice parameter was measured by [33Sta]. Only the cubic αBe_3N_2 was known until the high-temperature hexagonal modification βBe_3N_2 was reported by [60Eck] and [60Rab]. [60Eck] determined the lattice parameters of βBe_3N_2 and obtained a lattice parameter value for αBe_3N_2 in good agreement with that of [33Sta]. [69Hal] added to understanding the βBe_3N_2 structure by showing the atom positions.

$Be(N_3)_2$. The structure and unit-cell dimensions of $Be(N_3)_2$ apparently are undetermined.

Thermodynamics

(αBe) and (βBe). The thermodynamics of N dissolved in solid (Be) have not been determined [72Ald].

αBe_3N_2 and βBe_3N_2. The variation of the thermodynamic functions with composition has not been determined for Be_3N_2. The thermodynamics of formation of αBe_3N_2 and βBe_3N_2 were reviewed by [71Stu] (αBe_3N_2 only), [72Ald], and [73Spe]; the standard thermodynamic properties were tabulated by these reviewers and by [71Par] and [84Pan]. The compilations were based both on the calorimetric measurements of [66Gro], which are more accurate than those of [32Neu], [34Neu], and [58Api], and the observations of decomposition pressures [64Yat, 67Hoe], in combination with heat capacity data for low temperatures [67Jus, 70Fur] and for high temperatures [69Dou]. The values for the standard enthalpy of formation of αBe_3N_2 obtained by the two experimental methods agree well. The assessed values at 25 °C are −588.3 kJ/mol αBe_3N_2 and −571 kJ/mol βBe_3N_2 for the standard enthalpies of formation [71Par] and 34.4 J/mol αBe_3N_2 for the standard entropy [70Fur].

$Be(N_3)_2$. There are no thermodynamic data for the azide.

Liquid. The thermodynamics of liquid Be-N solutions have not been determined. The thermodynamic properties of liquid Be_3N_2 were compiled by [71Stu].

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