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Phase diagrams and synthesis of cubic boron nitride

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Abstract

On the basis of phase equilibria, the lowest temperatures, T_{min} , above which at high pressures cubic boron nitride crystallization from melt solution is allowable in terms of thermodynamics have been found for a number of systems that include boron nitride.

1. Introduction

Due to a low value of molar volume, cubic boron nitride (cBN) is characterized by a wide region of thermodynamic stability at high pressures. Cubic boron nitride is produced at high pressures and temperatures by a direct phase transformation of low-density polymorphous modification (a) and by crystallization from melt solution of BN-containing multicomponent systems (b). In addition, cBN films are prepared by epitaxial growth on substrates at low pressures in the hBN thermodynamic stability region.

The pressure of the direct phase transformation far exceeds the equilibrium pressure (especially at low temperatures) because of the necessity of overcoming a high activation barrier. The emergence of a liquid phase in the system abruptly decreases the activation barrier and lowers the parameters for cubic boron nitride synthesis. Hexagonal boron nitride (hBN) dissolves in the melt of the system, saturates it with respect to the hexagonal modification and supersaturates it with respect to the cubic one, and cBN crystallizes from the supersaturated melt solution. A necessary condition for this crystallization is a stable equilibrium of the cubic modification with the melt. The crystallization, as a result, becomes possible at temperatures exceeding those of eutectic and peritectic reactions with boron nitride participation. Phase diagrams of BN-containing systems show the existence of the above reactions and indicate the lowest parameters for cBN synthesis in particular systems.

Over recent decades the equilibrium phase diagram of boron nitride has been under constant revision. The latest version of the diagram is reported in [1]. The cBN stability under standard conditions has engaged our attention because diamond, to which cBN is identical in crystallographic structure, is metastable over the whole temperature range at atmospheric pressure.

Phase diagrams of multicomponent systems containing boron nitride show that the application of pressure, as a rule, increases the melting temperatures of components and

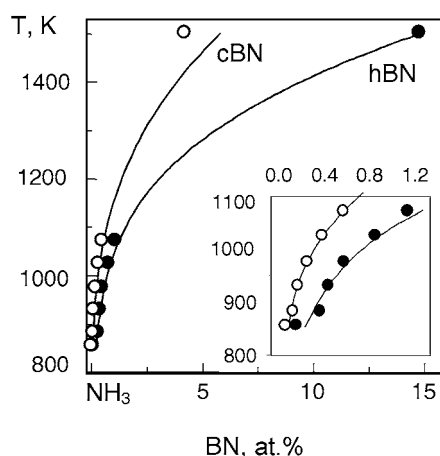


Figure 1. Experimental and calculated values of the hBN and cBN solubility in supercritical ammonia in the 0.065–4.2 GPa region.

chemical compounds (at a rate of $\sim 30\text{--}60\text{ K GPa}^{-1}$) as well as temperatures of eutectic and peritectic reactions (at a rate of $\sim 10\text{--}20\text{ K GPa}^{-1}$). The BN solubility in the melt also increases with pressure.

2. Phase diagrams

The present paper considers phase diagrams of the following systems: $\text{NH}_3\text{--BN}$, Mg--B--N , Ca--B--N , Li--B--N , B--N--O at high pressures.

The $\text{NH}_3\text{--BN}$ system

Supercritical ammonia dissolves boron nitride and in the presence of lithium (magnesium or aluminium) nitride promotes cBN crystallization at 2 GPa [2]. The phase diagram of the $\text{NH}_3\text{--BN}$ system that reflects the equilibrium between condensed phases includes the curves for hBN and cBN limiting solubility in supercritical ammonia. Figure 1 demonstrates the results of experimental determination and thermodynamic calculation of the limiting solubility of BN polymorphous modifications in a fluid of the $\text{NH}_3\text{--BN}$ system. The difference in limiting solubility between graphite-like hexagonal and cubic BN modifications can be well described on the basis of the value of the enthalpy of the transformation: $\Delta H_{\text{hBN--cBN}} = -17\text{ kJ mol}^{-1}$.

The Mg--B--N system

To synthesize cubic boron nitride in the Mg--B--N system, mixtures of hBN with Mg_3N_2 magnesium nitride, pure magnesium and MgB_2 magnesium boride are used. The lowest synthesis parameters (4.7 GPa and 1670 K) were achieved with Mg_3N_2 as a solvent [3]. With Mg present, the pressure and temperature of the cubic boron nitride crystallization are somewhat higher, i.e. 5 GPa and 1770 K [4, 5].

Despite the apparent urgency, the phase diagram of the Mg--B--N ternary system has not been constructed. Data on the equilibria between the phases and boron nitride in this system at atmospheric pressure cannot be found in the literature. Two quasi-binary sections ($\text{Mg--Mg}_3\text{BN}_3$ and $\text{Mg}_3\text{N}_2\text{--BN}$) at high pressures have been constructed [6]. Mg_3BN_3 has two

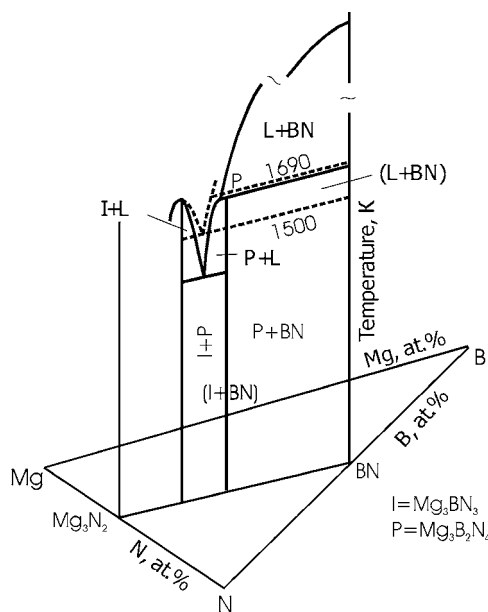


Figure 2. The Mg_3N_2 -BN quasi-binary section of the Mg-B-N ternary system at 5.5 GPa [8].

polymorphous modifications (low- and high-pressure phases). The equilibrium line between them can be described as p (GPa) = $7.2 - 0.0025x(T - 273)$ (K) [7]. The existence of $\text{Mg}_3\text{B}_2\text{N}_4$ magnesium boron nitride has not been taken into account in the earlier paper [6]. The incongruent character of the $\text{Mg}_3\text{B}_2\text{N}_4$ melting by the $\text{L} + \text{BN} \rightleftharpoons \text{Mg}_3\text{B}_2\text{N}_4$ reaction has been reported in [8]. In contrast to the authors of [8], the authors of [9] reason that $\text{Mg}_3\text{B}_2\text{N}_4$ melts congruently and the $\text{L} \rightleftharpoons \text{Mg}_3\text{B}_2\text{N}_4 + \text{BN}$ eutectic equilibrium occurs (figure 2).

The MgB_2 -BN section of the Mg-B-N ternary system is not quasi-binary. On high-pressure-high-temperature treatment of the hBN- MgB_2 initial mixtures, the phase composition of samples was found to change to cBN + MgB_6 + Mg_3BN_3 [10].

The Ca-B-N system

Figure 3 shows two quasi-binary sections ($\text{Ca}_3\text{B}_2\text{N}_4$ and $\text{Ca}_3\text{B}_2\text{N}_4$ -BN) of the Ca-B-N ternary system at 2.5 GPa [11]. The sections are of a simple eutectic type: $\text{L} \rightleftharpoons \text{Ca}_3\text{B}_2\text{N}_4 + \text{hBN}$ (1590 K) and $\text{L} \rightleftharpoons \text{Ca} + \text{Ca}_3\text{B}_2\text{N}_4$ (1305 K). At 2.5 GPa, $\text{Ca}_3\text{B}_2\text{N}_4$ melts at 1685 K.

At pressures below 6.5 GPa, the temperature of cBN synthesis in the Ca-BN and $\text{Ca}_3\text{B}_2\text{N}_4$ -BN systems has been found to be almost the same (1670 K) [11, 12].

The Li-B-N system

The only ternary compound (Li_3BN_2 lithium boron nitride) forms in the Li-B-N system. Li_3BN_2 has three polymorphous modifications, two of which are high-pressure modifications [3]. The Li_3BN_2 section is quasi-binary and characterized by the $\text{L} \rightleftharpoons \text{Li}_3\text{BN}_2 + \text{cBN}$ eutectic equilibrium at 1883 K in the case of 6 at.% BN [3].

According to [3], the lowest temperature of cBN crystallization in the Li-B-N system at 6 GPa is 1823 K. It is lower than that of the $\text{L} \rightleftharpoons \text{Li}_3\text{BN}_2 + \text{cBN}$ eutectics and is appropriate to cBN synthesis in the presence of lithium [13]. In refinement of the data reported in [3],

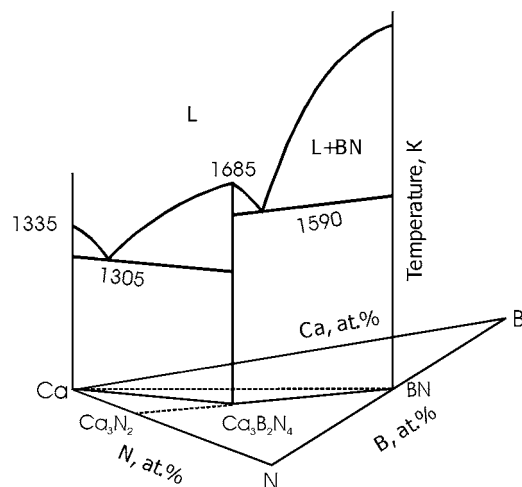


Figure 3. Ca–Ca₃B₂N₄ and Ca₃B₂N₄–BN quasi-binary sections of the Ca–B–N ternary system at 2.5 GPa [11].

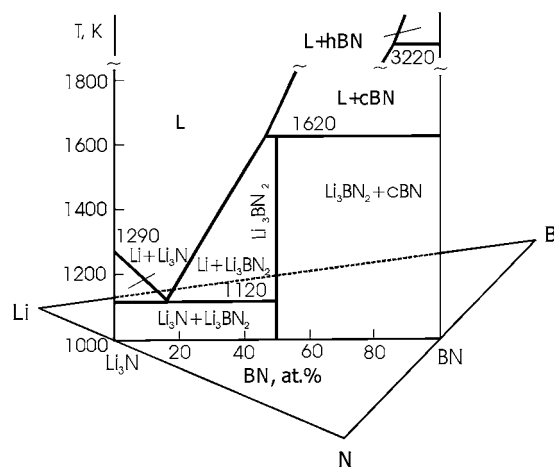


Figure 4. The Li₃N–BN quasi-binary section of the Li–B–N ternary system at 5.3 GPa.

the authors of [14, 15] have found that Li₃BN₂ melts incongruently and the temperature of the L + BN ⇌ Li₃BN₂ peritectic equilibrium (1620 K) is the lowest temperature of cBN synthesis in the Li–B–N system at 5.3 GPa (figure 4).

The B–N–O system

Data on synthesis of cubic boron nitride in the presence of H₃BO₃ boric acid, which is the product of the reaction between the B₂O₃ boron oxide and H₂O, are given in [14]. A very low value of the minimal cBN synthesis temperature (1100–1300 K at 6 GPa) is observed. Using dehydrated B₂O₃, researchers [15] have concluded that the difference in pressure and temperature between the hBN-to-cBN transformations with and without boron oxide is insignificant. The B₂O₃–BN quasi-binary section of the B–N–O ternary system was constructed based on the findings of [15].

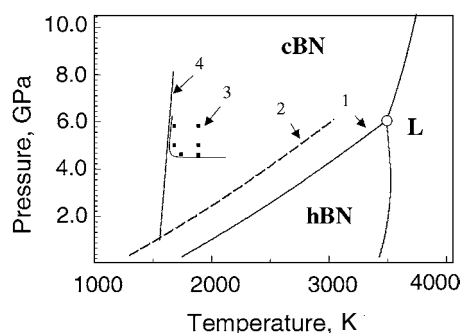


Figure 5. The phase diagram of boron nitride and the region of cBN crystallization from the melt of the Li–B–N system: 1: hBN–cBN equilibrium line; 2: hBN–cBN equilibrium line with 3 at.% oxygen present in BN; 3: parameters p , T of cBN crystallization; 4: pressure dependence of the $\text{Li}_3\text{BN}_2 \rightleftharpoons \text{L} + \text{BN}$ peritectic temperature.

B_2O_3 boron oxide that has a high negative value of the free energy of formation reacts with boron nitride relatively slightly, while the formation of oxygen solid solutions in BN considerably decreases the temperature of the cBN-to-hBN phase transformation causing the transformation to proceed in a certain temperature range [16]. On dissolving in BN, oxygen substitutes for nitrogen atoms and, therefore, all compositions of BN(O) solid solutions are in the BN–BO section.

3. cBN synthesis

All the diagrams in question have a common property. All of them indicate the pressure, temperature and composition at which the compounds that form in these systems melt and the stable liquidus of the cubic phase appears, i.e. the crystallization of the cubic boron nitride from the melt solution becomes a possibility in terms of thermodynamics. This situation does not, however, ensure the obtaining of cBN experimentally. On frequent occasions, to overcome kinetic difficulties characteristic of diffusion transformations, pressures and temperatures far beyond those of equilibrium are required. The rates of cBN crystal nucleation and growth are well below those of diamond crystals. Therefore, to ensure cBN crystal nucleation and growth up to 3–100 μm , experimenters chose the parameters p , T that are deep in the cubic boron nitride stability region (figure 5).

Oxygen impurities in the initial substances shift the position of the hBN–cBN equilibrium line to low temperatures [16]. Because of this, to maintain the chemical potential difference between hexagonal and cubic modifications, which is the thermodynamic impetus to the transformation, a higher pressure is required. The above factors are responsible for the existence of the cBN synthesis threshold pressure, which is defined by kinetics and is not represented in the phase diagrams.

4. Conclusions

Phase diagrams of systems that include boron nitride indicate the pressure, temperature and composition at which crystallization of cubic boron nitride from melt solutions becomes thermodynamically possible. The above condition does not, however, guarantee the obtaining of cubic phases under the experimental conditions. To overcome the kinetic difficulties that are

inherent in diffusion transformations, pressures and temperatures which considerably exceed the equilibrium values should be secured.

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