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High-temperature behaviour of hexagonal boron nitride[1]

Milan Hubáček [a,*], Masanori Ueki [a], Tadao Sato [b], Vlastimil Brožek [c]

[a] *Advanced Technology Research Laboratories, Nippon Steel Corp., 1618 Ida, Nakahara-ku, Kawasaki 211, Japan*
[b] *National Institute for Research in Inorganic Materials, 1-1 Namiki, Tsukuba 305, Japan*
[c] *Prague Institute of Chemical Technology, Technická 5, 167 18 Praha 6, Czech Republic*

Abstract

Three boron nitride processes have been studied—synthesis of turbostratic powder, sintering of hexagonal ceramics and transformation into diamond-like phases. It is shown that the crystallization of boron nitride proceeds in three distinctive steps. The first step is the recombination of boron and nitrogen forming semi-organic oligomers; this is followed by a double coalescence on the basis of this mechanism, three fundamental sub-polytypes of layered boron nitride (turbostratic, mesographitic and graphitic) have been defined. Compared with most other inorganic materials, the chemical properties and the character of the interaction with the environment are strongly dependent on the crystallographic direction. The crystal structure of boron nitride is thus a result of a competition between the combination of boron nitride monolayers and their chemical interaction with the environment.

Keywords: BN; Crystallization; Crystallographic direction; Graphitic boron nitride; Hexagonal boron nitride; High-temperature behaviour; Layered boron nitride; Mesographitic boron nitride

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1. Introduction

Hexagonal boron nitride powders are prepared in various grades depending on the intended application. Basically two grades are being supplied— a microcrystalline type with rather low purity but with good sinterability, and a pure crystalline grade, mostly used as a lubricant or filler for composites with improved thermal conductivity

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* Corresponding author.

[1] Dedicated to Takeo Ozawa on the Occasion of his 65th Birthday.

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[1,2]. The process of boron nitride synthesis can be subdivided into three consecutive steps.

Initially, boron nitride precursors are prepared from components containing boron and nitrogen, respectively. Typical carriers of boron are boric oxide, boric acid and boron trichloride while nitrogen is mostly supplied as ammonia gas or nitrogen-containing organic compounds such as urea, thiourea and biuret, among others [3,4]. When mixed in the appropriate ratio, the ingredients are heated to a relatively low temperature (ca. 500 °C) to form a precursor. The precursor is usually an oligomeric material with abundant concentrations of leaving monovalent groups such as the hydroxy group, hydrogen, chlorine, and amine [5–7]. For example, when a precursor originating from boric acid and urea is studied, a comparable molar ratio between B–N and B–O bonds can be found. Despite of the high concentration of the additional elements, such a precursor often bears the layered character of the boron nitride [8].

Especially in the next step, when the microcrystalline (turbostratic) boron nitride is being prepared, the temperature is the major factor controlling the yield of the product. For example, when the oxide-based precursor are further nitrided in ammonia, an optimum temperature range, when the yield is the highest, can be found between 900° and 1100 °C [9].

The aim of the final process, requiring temperatures above 1500 °C, is to thermally stabilize the material, making it chemically independent of oxide-based phases which are later removed by washing in water [10].

The temperature of the synthesis and the purity of the product are the parameters primarily determining the particle size and the crystallinity of the powders. In general, with increased temperature, the boron nitride grains grow and improve the arrangement of the hexagonal networks within them, especially in low-purity materials [11].

2. Synthesis of boron nitride

It was shown in a previous paper [12] that actual composition of hexagonal boron nitride can be expressed by a formula $(NH)(BN)_x(BOH)$. The NH and BOH groups are located on the periphery of hexagonal networks and the parameter x is proportional to their size measured in XRD patterns as the L_a parameter. In this work it was further shown that the L_a size identical to the width of the single-crystal zone (the crystallite) is the primary parameter determining the interlayer distance d_{002} and the thickness of the crystallite, L_c. The formula, then, mathematically expresses the circumference-to-width ratio since the fraction of the groups decreases with increasing size of the networks. The formula $(NH)(BN)_{26}(BOH)$ was assigned to a typical BN powder for which the parameter L_a was found to equal 11 nm.

For further analysis, an experimental curve shown in the work mentioned in the previous paragraph is here transferred to a graph depicting the dependence of L_a on the grain size of the initial turbostratic powder (Fig. 1). It can be seen that the growth of BN grains proceeds in three consecutive steps.

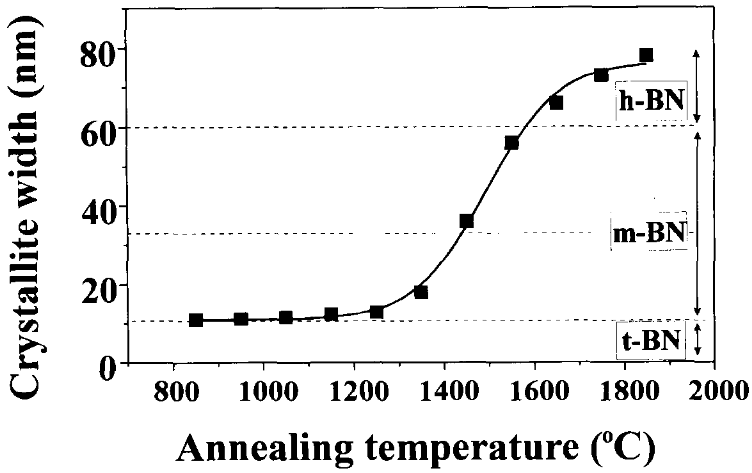

Fig. 1. Dependence of the crystallite width of boron nitride on annealing temperature: t-BN, turbostratic boron nitride; m-BN, mesographitic boron nitride; h-BN, crystalline hexagonal boron nitride.

(1) In the first stage, the growth proceeds at a moderate rate; most probably supplementary decomposition of the precursor oligomers is the rate-controlling process of the growth (Fig. 2a).

(2) At around 1350°C, rapid growth can be seen. If measured by the graph in Fig. 1., this stage can be characterized as a spontaneous coalescence, when nine turbostratic units join together to form a network with a triple value of the L_a parameter (Fig. 2b). This type of structure with its L_a strongly dependent on the temperature but still not possessing layers large enough to form perfectly crystalline material may be assigned as the mesographitic form of hexagonal boron nitride.

(3) In the final stage, nine (again) mesographitic units combine to form a perfectly crystalline product with a width three times that of the mesographitic material (Fig. 2c). In this stage, however, the growth is not as spontaneous as it was in the previous stage. This can be explained by a lowering of the mobility of the planer BN macromolecules due to their growth; this is accompanied by a reduction in the relative concentration of chemically active peripheral sites of the networks.

The width of the BN macromolecules is nothing but an average parameter measured in a polydisperse powder consisting of a continuous spectrum of sub-polytypes with infinitesimal differences in the L_a parameter. Existence of singular structural types with distinctive structural parameters is thus beyond consideration. Moreover, the two coalescence processes overlap with each other and the actual crystallographic parameters cannot, therefore, be ascertained on the basis of on these considerations, the structural sub-polytype of hexagonal boron nitride cannot be understood as a unique and singular object but rather as a set of sub-polytypes having structural parameters statistically scattered around the average. From the dependence shown in Fig. 1, however, the three crystallographic forms of layered boron nitride can be defined.

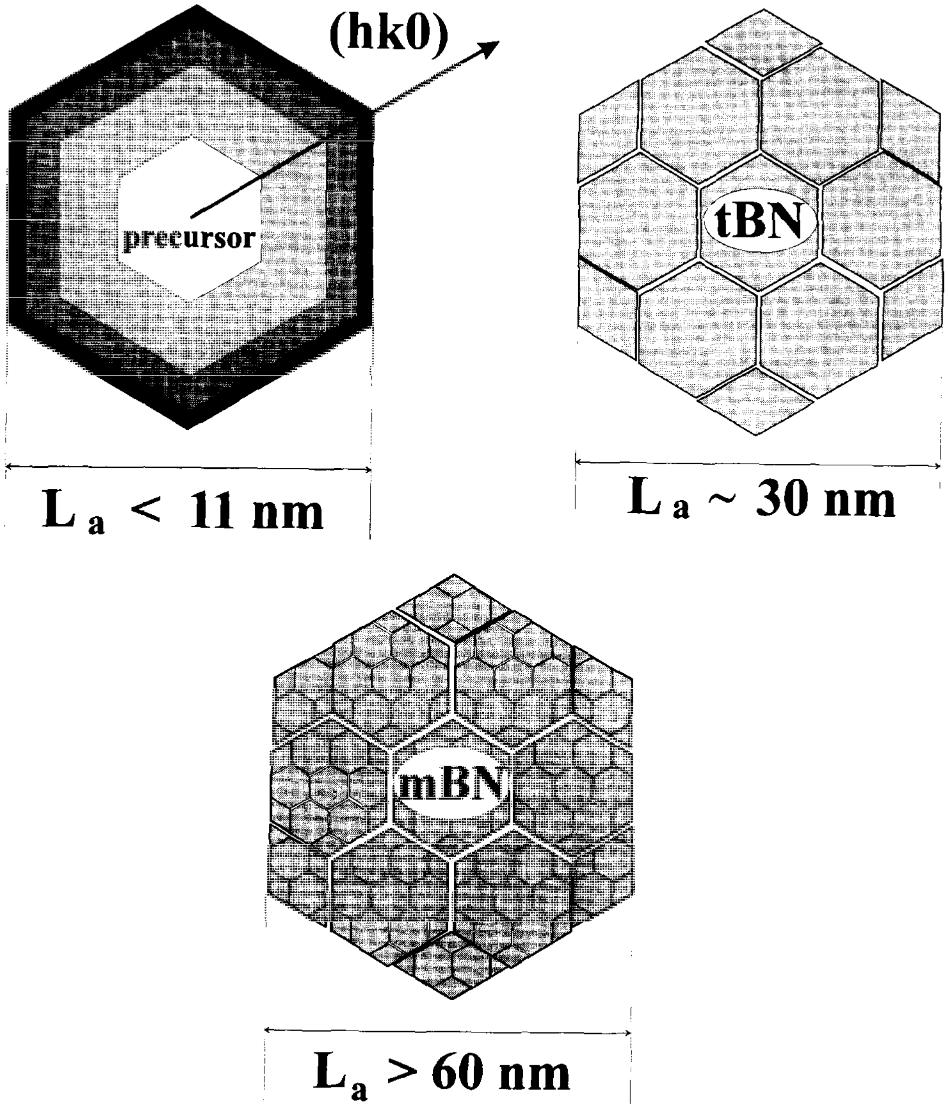

Fig. 2. Formation of a monolayer of (a) turbostratic boron nitride, (b) mesographitic boron nitride, and (c) crystalline hexagonal boron nitride.

(1) Turbostratic boron nitride: a set of sub-polytypes with the mean crystalline width not exceeding 12 nm which occurs at temperatures up to 1300°C during the heat treatment.

(2) Mesographitic boron nitride: a set of polytypes with the mean crystallite width ranging between 12 and 60 nm which is formed at temperatures typically ranging from 1300°C to 1600°C.

(3) Crystalline boron nitride: a set of polytypes with the mean crystallite size above 60 nm which is typically formed by annealing of turbostratic or mesographitic sub-polytypes above 1600°C.

It is a matter of fact that it is quite difficult to define the range of the occurrence of a particular sub-polytype and the boundary of occurrence determined is fully dependent on the approach of a particular investigator.

3. Directionalism in the chemical properties of hexagonal boron nitride

Microcrystalline boron nitride was hot-pressed in the presence of two types of elemental material—boron [13] and copper [14]. The crystallinity of the so obtained ceramics was compared with that of ceramics produced by the same technique from boron nitride powder of the same grade but free from any additives. The three types of ceramic differed substantially in the size and orientation of boron nitride grains. The aim of this section is to compare controlling mechanisms in particular processes.

The ceramics obtained from the mixtures of boron nitride with elemental boron consisted of two phases— boron nitride with a grain size not substantially exceeding that of the starting powder, and boron suboxide as B_6O as a product of extraction of oxygen-containing phases from the powder during hot pressing. The extraction inhibited the catalytic effect of the oxide-based phase on crystal growth. Being smaller, the BN grains in the ceramics were oriented with their facets perpendicular to the pressure axis as is typical for boron nitride hot-pressed without any additives [15].

In the experiments when boron nitride was exposed to copper vapour, the boron nitride grains reached the size found solely hot-pressed powder, although two differences were noticed—the grains were about three times thicker and were prevailingly aligned with their facets parallel to the pressure axis. In this case, the interaction between localized p electronic couples and vacant orbitals of the atomized transition metal was suggested as being the controlling mechanism of the growth. A similar interaction between transition metals and polymers possessing π electronic couples has been recently described [16].

It can be deduced from the difference between the two chemical interactions that the anisotropy of boron nitride crystals, which is mostly characterized by physical parameters [3, 17], has its immediate origin in the character of chemical bonds between boron and nitrogen atoms in hexagonal boron nitride crystallites based on the hybridization of the electronic orbitals of both boron and nitrogen. This directionalism, then, determines the character of the reactions of hexagonal boron nitride with surrounding substances.

Boron, because of its grain size and chemical character, reacts preferably with peripheral sites of the networks, approaching them in a direction parallel to the planes of the networks—the (hk0) direction. The cause of this directionally selective approach is that the elemental boron has to share the kind of hybridization of its electronic orbitals with the boron and nitrogen atom bonds in the networks to undergo Lewis-type reactions with the peripheral ligands, especially with the OH groups (Fig. 3). The growth of the BN networks and subsequently of the crystallites is hindered by

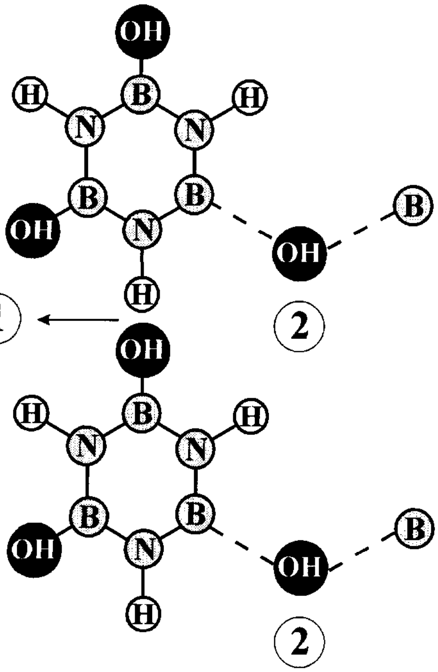

Fig. 3. Coalescence by water elimination (1), and boron-assisted growth passivation in hexagonal boron nitride (2).

the extraction of the oxygen. In this sense, formation of pyrolytic layers is a reverse process where the BN networks are forced to grow excessively owing to the ready availability of the precursor material. This may explain why two-dimensional objects (layers) are preferably formed from the gaseous phase.

Compared with boron, atomized copper can offer orbitals from more remote electron shells for interaction with boron nitride electronic orbitals occupied with the π electrons, forming thus a bond with donor–acceptor character. The B_3N_3 rings in the planar networks have an aromatic structure and the copper atoms can bind to their π faces through a non-covalent force. The direction of the force between atomized copper and boron nitride is then perpendicular to the fecets of BN crystallites—the $< 001 >$ direction (Fig. 4). It was found that the occurrence of this phenomenon is significant in the system where both the components—BN and copper—are treated under an external pressure, compared with the system annealed at the atmospheric pressure [18]. This finding supports the explanation based on the metal–π interaction, since this is substantially weaker than the covalent interaction. The efficiency of the overlapping of the electronic orbitals can be thus increased by the external pressure.

The applicability of this mechanism can even be extended to the process of catalytic transformation of layered boron nitride into the superhard modification if pressure several orders of magnitude larger are considered: under high pressures, overlapping of the electronic orbitals reaches a level comparable with that in the covalent interaction.

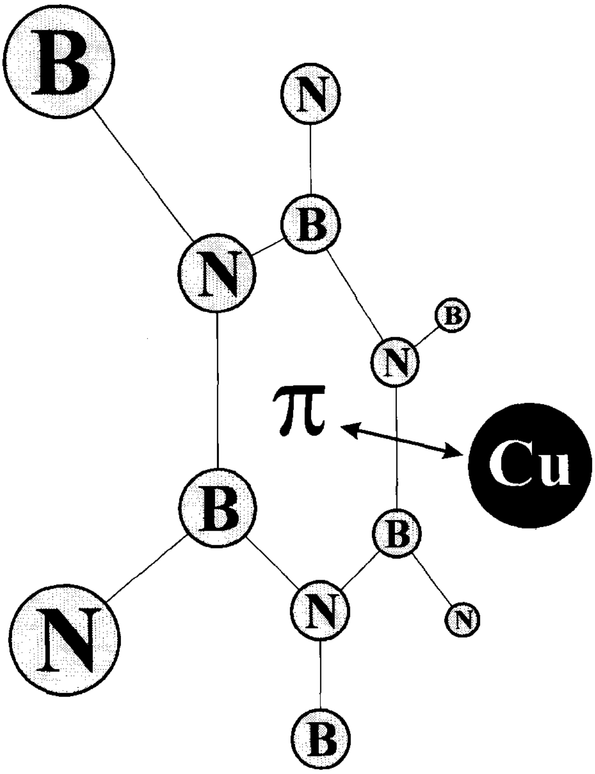

Fig. 4. Metal–π interaction in hot-pressed boron nitride–copper system.

As a result of this approach, the remaining sp^2 bonds originally lying within a triangle are deformed—elongated and tilted out from the original hexagonal network—and then (meta) stabilized to form a diamond-like phase. This mechanism might be even used to explain the process of re-conversion of the superhard phases back to the layered systems by heat treatment: the re-conversion represents thermal recovery of the system which is no longer exposed to the deformative action of a π-active catalyst under a high pressure.

It can be summarized here that the crystal of layered boron nitride are secondary objects formed from planar hexagonal networks (the primary objects) during their formation form precursor phases. The process of network formation and subsequent crystallization can be controlled by the chemical character of the environment; the following typical cases may be distinguished (Fig. 5):

(1) free crystallization of hexagonal boron nitride from turbostratic precursors by thermal recombination of peripheral ligand groups;

(2) preparation of fine-grained boron nitride free from boric oxide by extraction and conversion of the ligands;

(3) preparation of two-dimensional BN objects (pyrolytic layers) as a result of the ready availability of the precursor phases; and

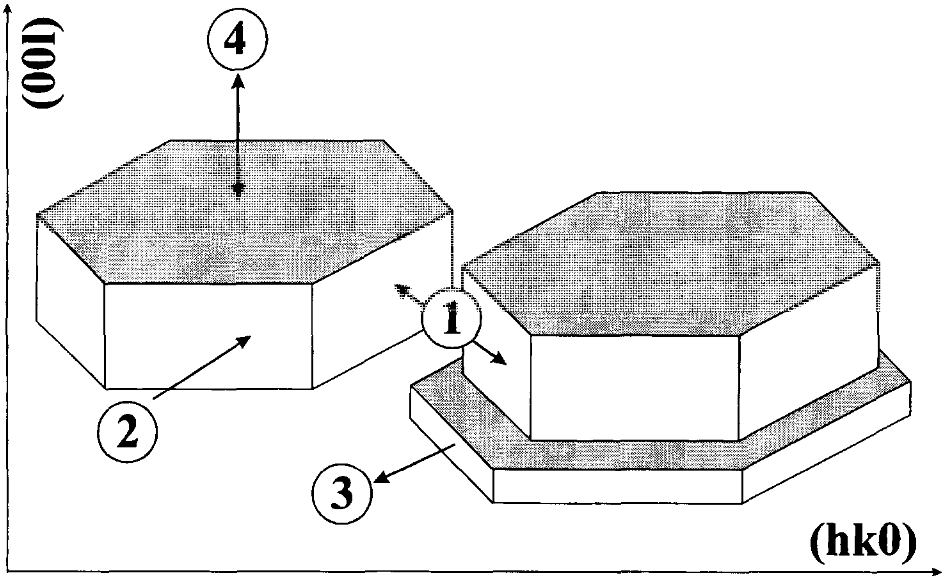

Fig. 5. Formation of typical boron nitride materials: (1) crystalline hexagonal boron nitride; (2) fine-grained boron nitride; (3) pyrolytic boron nitride; (4) diamond-like boron nitride.

(4) transformation of layered boron nitride into diamond-like phases by a high-pressure metal–π interaction.

(5) It can be concluded that the crystal structure of boron nitride is a result of a competition between the arrangement of boron nitride monolayers and their chemical interaction with the environment.

4. Conclusion

Layered boron nitride is characterized as a substance composed of planar hexagonal networks, the size of which primarily determines the crystallinity. Three fundamental sub-polytypes—turbostratic, mesographitic, and fully crystalline—are defined with respect to the size of the monolayers within them, and from the viewpoint of their mobility. It is, however, difficult to define unambiguously the structure of the sub-polytypes because instead of singular objects they can be characterized solely by values of the crystallographic parameters of representatives with mean values in the analysed set of the sub-polytypes.

The crystallinity of boron nitride is shown to be a consequence of two competitive processes—one is based on chemical interactions of the monolayers with their environment and the other consists in the arrangement of the layers to form a three-dimensional solid object.

This approach enables characterization and explanation of the primary mechanisms in formation of all fundamental types of boron nitride—materials with a high crystallinity, layers synthesized by the pyrolytic method and diamond-like modifications prepared by catalytic transformation at very high pressures.

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