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STRUCTURE AND SOME PROPERTIES OF FINE-GRAINED GRAPHITE-LIKE BORON NITRIDE*

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Summary

The structure of boron nitride synthesized by carbothermal reduction and simultaneous nitridation in the temperature interval 1000 - 1450 °C was studied by transmission electron microscopy and X-ray powder methods. A starting mixture based on the homogeneously distributed fine-grained amorphous boron oxide and carbon phases was employed for synthesis. It was found that the graphite-like BN produced consisted of a mixture of hexagonal and rhombohedral modifications; the content of the latter amounts to up to 30%. It was concluded that the formation of the polycrystalline particles from BN with various extents of three-dimensional ordering is due to contact reduction of B_2O_3; the prismatic crystals of the rhombohedral phase are formed via gas-phase reactions. The chemical stability in acids of BN produced at 1400 °C is comparable with the stability of coarse hexagonal BN powders.

1. Results and discussion

The problem of the synthesis of graphite-like boron nitride powders is very important both from the point of view of the production of superhard materials at high pressures and the sintering of materials at normal pressures. A number of valuable properties of the BN powders led to the development of effective methods of synthesis enabling one to control the grain size and the structural state of the final product.

This paper is devoted to electron micrography and X-ray powder diffraction studies of the structure and phase composition of graphite-like boron nitride produced by carbothermal reduction of boron oxide with simultaneous nitridation. A homogeneously distributed mixture of fine-grained amorphous boron oxide and carbon phases was used in the BN synthesis.

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It has been found that graphite-like boron nitride, formed under the given synthesis conditions over a range of temperatures (1000 - 1450 °C), is a mixture of the hexagonal BN_h and rhombohedral BN_r modifications. Depending on both the nitridation temperature and the starting composition, the BN_r content reached 10% - 30%.

BN_h synthesized at 1000 - 1200 °C consists of turbostratic and partially three-dimensionally ordered BN; at higher temperatures we obtained three-dimensionally ordered BN_h practically throughout the entire reaction volume.

The BN_h particles formed at 1000 - 1300 °C entirely reflected the geometry of the starting mixture. They characteristically display two types of subgrain structure as revealed by electron microscopy. Type I particles consist of round grains with developed basal planes parallel to the base surface of the particles (Figs. 1(a) and 1(b)). Particles of type II are composed of round grains and platelets; the developed basal planes of the grains of the first kind and prismatic {110} type planes of the second kind are parallel to the base surface of the particles (Figs. 1(c) and 1(d)). Particles of both types are characterized by an unbound texture [0001] defined by the packing of round grains up to the temperature of their synthesis, not above 1300 °C; at higher temperatures the texture of the particles of type I remains the same, but that in the particles of type II is destroyed owing to the process of collective recrystallization accompanied by the formation of polyhedral grains.

The type I particles are formed on the basis of the fine particles of the starting mixture and those of type II from the thickened particles. We thus arrive at the conclusion that the difference in the subgrain structure of the BN_h particles may be attributed to the conditions of their formation and the ordering of the graphite-like phase. In the case of thickened particles the process of grain enlargement and their displacement on grain orientation are hampered, which may cause mechanically stressed particles and, as a consequence, grains of other orientations or twins appear.

The size of the single-crystal grains in the BN_h particles increases with increasing nitridation temperatures (from 100 - 200 Å at 1200 °C to 2000 - 3000 Å at 1450 °C) whereas the size of the particles decreases from 1 - 5 μm at 1200 °C to 1 - 3 μm at 1450 °C. The decrease in the particle-size with increasing temperature of synthesis is determined by the process of their loosening owing to the stresses arising from anisotropic grain growth.

The major part of three-dimensionally ordered BN particles is observed at synthesis temperatures between 1400 °C and 1450 °C, however a small amount of three-dimensionally ordered BN is already produced at 1000 - 1200 °C.

Such low temperatures of "graphitization" (in terms of ref. 1) of the boron nitride can be explained by the unbound texture of the particles and by the presence of boron oxide contributing to the decrease in temperature and increase in the rate of the "graphitization" process [1]. In addition to "graphitization", grain growth in the BN_h particles takes place on isothermic

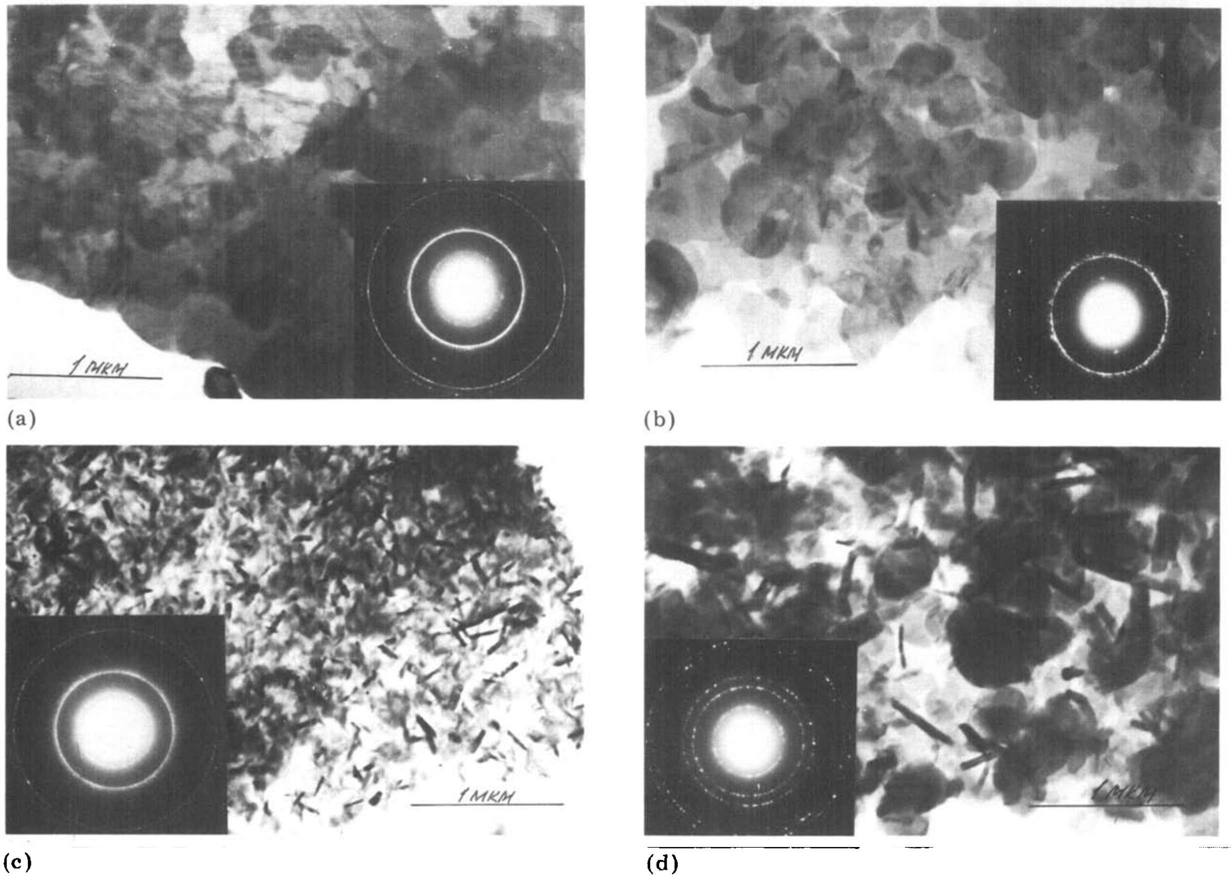

Fig. 1. Electron micrographs and corresponding electron diffraction patterns of particles composed of round shaped grains ((a) and (b)) and grains of round and platelet shape (in the image plane) ((c) and (d)) on BN_h of various degrees of crystal perfection: (a) and (c), partially three-dimensionally ordered BN_h, synthesized at 1350 °C; (b) and (d), three-dimensionally ordered recrystallized BN_h obtained at 1450 °C.

exposure at 1100 - 1200 °C, *i.e.* the process of collective recrystallization occurs.

Such facts as inheritance of the particle morphology of the starting mixture by the BN_h particles formed and the presence of unbound texture [0001] BN of the particles show that carbothermically the synthesis over the temperature range studied takes place via a contact reduction of boron oxide according to the reaction

$$2B_2O_3 + 3C = 4B + 3CO_2$$

followed by the interaction of nitrogen with the high-activity boron produced. The superfine state and homogeneous distribution features of the starting components (the carbon component in the mixture is of honeycomb structure, Fig. 2) ensure a high degree of contact between the components. A marked amount of turbostratic BN was already obtained at a synthesis temperature of 900 °C; under these conditions the vapour pressure of the boron oxides and suboxides is very low (10^{-11} mol kg^{-1} and 10^{-15} - 10^{-13} mol kg^{-1}, respectively), thus the BN produced at 900 °C provides proof of the contact mechanism in the carbothermal reduction of the boron oxide followed by reaction of the elemental boron with nitrogen.

Both the rounding and the appearance of a tendency towards facet formation in grains located on the edges of the BN_h particles (Fig. 1(b)) confirm the involvement of a gas-phase mass transfer at temperatures above 1400 °C.

The presence of a rhombohedral phase in the boron nitride synthesized at temperatures above 1200 °C was clearly observed in the X-ray powder measurements by the presence of characteristic (101) and (012) reflections; the quantitative BN_r content was estimated from the ratio $I_{(100)}/I_{(101)}$. The electron microscopy and microdiffraction investigations established that BN_r is often produced in the form of deformed rectangular prisms elongated along the *c* axis (Fig. 3) or represents inclusions of the same geometry as

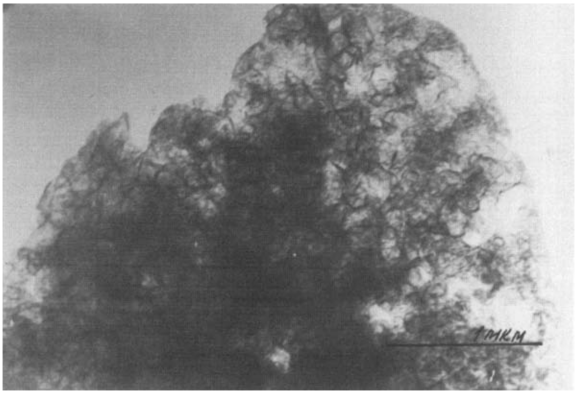

Fig. 2. The particle substructure of the starting mixture based on disperse boron oxide and carbon.

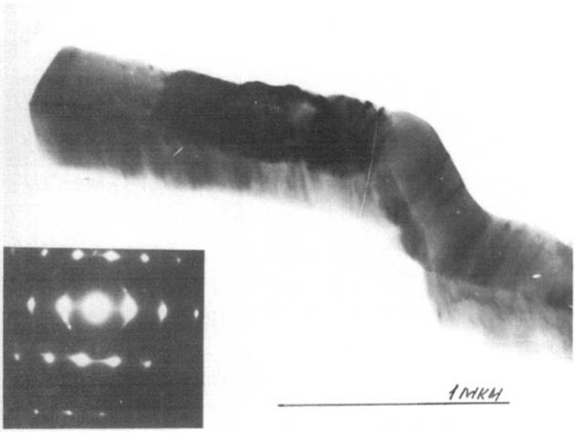

Fig. 3. Crystal morphology of rhombohedral BN and microelectron diffraction pattern of a 3R crystal (inset).

in the BN_h particles. Such a morphology of the BN_r crystals provides some evidence for the gas-phase mechanism in their formation, *i.e.* formation of BN via a gas-phase reaction under carbothermic synthesis conditions. The electron micrographs obtained from prismatic BN_r crystals show strong reflections of the 3R polytype. These reflections are often accompanied by weak reflections of multilayer polytypes of a structure which is undetermined due to the irregular arrangement of reflections. Investigation of individual single-phase 3R crystals revealed that they are characterized by twinning in the (0001) plane.

The BN_r content in the graphite-like BN synthesized at 1300 - 1400 °C amounted to about 30%; annealing the powder at higher temperatures or a long-term isothermic hold at the synthesis temperature led to a decrease in the BN_r content, owing to the phase transformation of the metastable rhombohedral BN modification into the stable hexagonal one. X-ray powder

TABLE 1

The dependence of solubility rates (in grams per hour) of fine-grained boron nitride powder in various environments on the interaction time

Medium	*Temperature* (°C)	*Time* (h)		
		1	2	3
HCl(1:1)	100	0.00243	0.00204	0.00144
HNO_3(1:1)	110	0.00504	0.00493	0.00301
H_2SO_4(1:1)	140	0.02127	0.01289	0.01108
HNO_3(conc)	140	0.01142	0.00703	0.00531
HCl(conc)	110	0.00292	0.00169	0.00144
H_2SO_4(conc)	280	0.05375	0.02711	0.01897
NaOH(40%)	120	0.00074	—	—

analysis established that the phase transformation in BN_h is accompanied by a decrease in the polytype packing defect concentration with the turbostratic packing defect concentrations unchanged.

Taking into account the special features of the phase and structural states of the BN synthesized, it would be of interest to estimate its chemical stability. It was found that in air the oxidation initiation temperature of the product obtained at 1400 - 1450 °C is 900 °C and the rate of its decomposition in inorganic acids is low (see Table 1). A comparison with the existing results on the chemical stability of different types of graphite-like BN shows that despite their fine particle size, the stability of the BN discussed is higher than that for disperse pyrolytic BN [2] and is comparable with the stability of coarse powders of hexagonal BN [3].

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