substance: boron compounds with group IV elements: boron carbide
property: structure, chemical bond, review articles

If the results presented in the following document are not referred to a specific compound, it can be assumed that the chemical composition of the investigated material is close to the carbon-rich limit $B_{4.3}C$ of the homogeneity range. In particular in older publications, however sometimes even in newer publications as well, this limit is incorrectly attributed to the composition B_4C.

Structure, chemical bond

Boron carbide has a large homogeneity range extending from $B_{4.3}C$ to $B_{\sim 11}C$. The composition at the carbon-rich limit was definitely determined to be $B_{4.3}C$ or $B_{13}C_3$ by use of electron probe microanalysis (EPMA) [91S1]. This value agrees with prior results in [74P] and [71A]. The corresponding lattice parameters are almost identical with those reported for nominal B_4C in [71K] and [81B2]. The conclusions in [79B], [81B2], [83B], that the solubility limit of carbon in boron carbide is at the composition B_4C was not confirmed. The reason for the error in the determination of the carbon-rich limit of the homogeneity range is probably the problem to distinguish free and bounded carbon in the chemical analysis because in particular in the vicinity of the carbon-rich limit of the homogeneity range the presence of free carbon in the structure in consequence of an incomplete chemical reaction or excess carbon cannot be excluded. Aside of EPMA mentioned above, a reliable wet-chemical method to distinguish between bounded and free carbon in boron carbide is described in [86S]. The method based on the X-ray diffraction of graphitic free carbon described in [84B] was shown to be incorrect [85W].

In many – in particular older – publications on boron carbide the specific composition is not specified or given as B_4C. Usually, in these cases can be assumed, that the investigations have been performed on technical boron carbide (usually denoted as "B_4C"). This means that the composition of the boron carbide phase of these materials corresponds to $B_{4.3}C$, the composition at the carbon-rich limit of the homogeneity range. However, it cannot be excluded that such samples contain free carbon usually distributed in graphitic form, which is difficult to determine (see e.g. [85W]. It depends on the kind of investigation, in how far the results may be influenced by this free carbon. For example, in the case of optical reflectivity measurements the graphite may essentially lead to a weak unstructured background signal, which does not influence the results significantly, while in the case of electronic transport low-resistivity graphite layers in grain boundaries can lead to quantitatively and qualitatively influenced results.

In the case of boron-rich boron carbides free carbon can essentially be excluded. Even hot-pressing and sintering of powdered ingredients seems to be sufficient to obtain largely homogeneous boron-rich boron-carbide samples.

Phase diagram of the binary system boron-carbon in Fig. 1 [91S1].

general review articles

Boron carbide [66L].

Review on boron carbide (structure, physical properties, chemical properties, production and application in [85S].

Boron carbide – a comprehensive review [90T2].

bonding of boron carbide

Boron and carbon activities at 2300 K in Fig. 2 [91F].

The nature of chemical bonding in $B_{13}C_2$ static deformation densities and pictorial representation [80K1].

The nature of the chemical bonding in boron carbide. Electronic band structure of boron carbide $B_{13}C_2$ and three models of the structure $B_{13}C_2$ [83A].

Atomic interaction in a boron-rich carbon-containing icosahedron (example para-carborane) [87B].

preparation of boron carbide

Preparation of big, high-quality, twin-free single crystals of $B_{4.3}C$ (typical size: 7mm diameter, several cm length, rod axis parallel to the crystallographic [111] axis. Single crystals of other compositions have not yet been obtained. [99L].

Pyrolytic formation of carbon-rich B-C phases [70A].

Growth of boron carbide single crystals by direct RF melting in a cold container [91S2].

Preparation of twinned crystals prepared by slow cooling in molten copper, palladium and platinum solutions in [90A].

Review on laboratory methods for the preparation of boron carbides [90T1].

Laboratory methods for the preparation of boron carbides [90T1].

Review on industrial methods for the production of boron carbide (and metal borides) in [85S].

Effects of the reaction parameters in the carbothermic process [91B].

Kinetics of carbothermal reduction synthesis of boron carbide [92W].

Hot-pressing of boron carbide [84A].

Pressureless sintering of boron carbide phase [86T].

Influence of sintering on the properties of boron carbide [88T].

Preparation of oriented boron carbide films by plasma spraying [91K].

Synchrotron-radiation-induced deposition of boron carbide (and boron) films from boranes and carboranes [91P].

Preparation of crystals from Cu and Pd flux and films by thermal decomposition [87A].

Preparation of low-carbon boron carbides by chemical vapor deposition [87C].

Hot filament chemical vapor deposition of boron carbide [94D].

Composition and structural changes of boron carbides deposited by chemical vapor deposition under various conditions of temperature and supersaturation [81V].

CVD preparation (vapor-liquid-solid process) and investigation of yellow boron carbide whiskers [87M1].

Deposition and characterization of thin boron-carbide coatings [93K].

Chemical vapor deposition of boron-based refractory solids [86M].

Technological processes for production of boron carbide and its associated products [87G].

Area selective chemical vapor deposition of boron carbide achieved by molecular masking [88J].

Formation of B_4C fine powder from boron bromide-methane-hydrogen system. Particle formation by CO_2 laser-induced breakdown [88O, 93O].

analytical investigations

Stoichiometric limits of carbon-rich boron carbide phases [81B3].

Analytical investigation in the B-C system (lattice parameters of boron carbide in the homogeneity range) [81B2].

The properties and structure of the boron carbide phase (lattice parameters, powder IR spectra) [81B1].

Structure and properties of sintered boron carbide [80K2, 79K].

Effect of the preparation method (sintering, hot-pressing) on density, porosity, grain size, hardness, Young's modulus, bending strength, toughness in [87T].

Stoichiometric limits of carbon-rich boron carbide phases [82B].

The influence of carbon on the microstructure of boron carbide [92K2, 92K1, 94K].

Comparison of calculated and experimental high resolution TEM images for twinned boron carbide [87M2].

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Fig. 1.

Boron carbide. Phase diagram of the binary system boron-carbon [91S1].

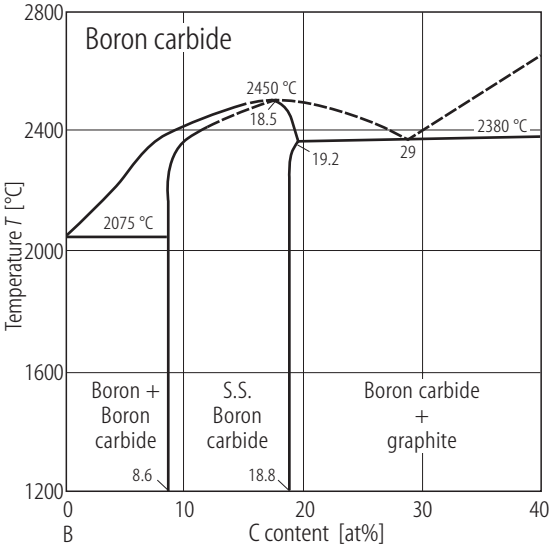

Fig. 2.

Boron carbide. Boron and carbon activity at 2300 K vs. composition. (+) and (+ − +) direct, (Δ) and (Δ–Δ) corrected measurements at compositions chemically determined before and after the experiments, (– • –) measured B activity; (– O –) integration of the Gibbs-Duhem relation from measured B activity; *) discarded data [91F].