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Kinetics of Deoxidizing of Hexagonal Boron Nitride Preparations

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Kinetic equations were established to describe the removal of oxygen-containing phases from hexagonal boron nitride. The diffusion characteristics of the deoxidizing process are discussed. The refining of turbostratic boron nitride powder by reductive chlorination is selective for boron oxide. Fusion extraction by carbon involves removal of oxinitridically bound oxygen at a rate proportional to the temperature of extraction. Diffusion through the ceramic skeleton is the controlling process of boron oxide evaporation. © 1991 Academic Press, Inc.

1. Introduction

Oxidic compounds of boron serve as the most common raw materials for boron nitride synthesis. Reductive nitridation of these compounds is advantageous from the technology and economy standpoints; however, the purity of the product is rather low.

The turbostratic form of hexagonal boron nitride, which is typically prepared by heating boric compounds in an ammoniacal medium at about 1000°C, is usually contaminated by residual oxide (*1*). This may be washed out with water after thermal stabilization of the product by heating to temperatures above 1250°C (*2*).

Crystalline products of hexagonal boron nitride are most frequently prepared by heating a mixture of boron oxide and carbon in a nitrogen stream at temperatures exceeding 1430°C. These preparations usually contain unreacted carbon and boron carbide occuring as a by-product (*3*).

The content of oxidic admixtures in preparations of turbostratic boron nitride can be considerably decreased by annealing in an inert medium at temperatures exceeding 1500°C (*4*). This process, however, unavoidably involves a considerable growth of boron nitride crystallites, a decrease of specific surface of the powder, and a decrease of sinter activity.

By contrast, reductive halogenation reduces the residual oxygen content to less than 2%. The crystallographic parameters of the powder, and thus also its sinter activity, remain completely unaltered, since the refining temperature coincides with that of primary product synthesis (*5*). A thermodynamic analysis of boron nitride refining by

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gaseous mixture of trichlormethane with ammonia demonstrated that the powder treated in this manner may also contain a secondary pyrolytic product (*6*).

Sintered ceramic materials based on boron nitride usually contain boron oxide, which can be removed by long-term boiling in alcohols or by refining in vacuum above 2000°C (*7*).

In the present paper, the kinetic dependence has been studied for three purification methods: the reductive chlorination of the turbostratic powder, the fusion extraction of oxygen from an ultradispersed mixture of turbostratic boron nitride with carbon, and the evaporation of boron oxide from ceramic boron nitride.

2. Experiments

Turbostratic boron nitride was prepared by thermal decomposition of a mixture of ammonium salts of polyboric acids on an organic carrier, in an ammoniacal atmosphere at 1000°C (*8*); it contained 6.2 wt% of oxygen.

The ultradispersed mixture of turbostratic boron nitride with carbon was prepared similarly, the homogenous distribution of carbon being achieved by pyrolysis of saccharose present in the initial mixture of raw materials used for the boron nitride synthesis, boric acid and urea.

The equipment for the reductive chlorination is essentially identical to that for the preparation of initial boron nitride. It consists of a vertical silica tube heated by an electric tube furnace, in which the reaction zone is defined by foamed carbon partitions, as is detailed in our earlier paper (*5*).

Ceramic boron nitride was prepared by hot pressing on the DSP 100-DAT equipment (Dr. Fritsch KG, FRG) at 1800°C by applying a pressure of 12 MPa.

Boron oxide was removed from the sintered samples by annealing in the argon atmosphere containing 5% hydrogen, at a pressure 103 kPa and a temperature of 1650°C. The specimens were placed in a molybdenum-heated vacuum furnace.

The oxygen content was determined and the kinetics of the fusion extraction of oxygen from the mixture boron nitride–carbon was studied by using the instrument RO 416 (LECO, USA).

The structural characteristics of hexagonal boron nitride are described by the hexagonal indexing scheme J calculated from the formula

$$J = \frac{I_{100} + I_{101}}{I_{102}}, \tag{1}$$

where I_{hkl} are intensities of relevant diffraction lines, determined by the X-ray diffractometer DRON UM-1, USSR, by using CuK_α radiation.

3. Results and Discussion

3.1. Refining of Turbostratic Boron Nitride by Reductive Chlorination

The kinetics of the reductive chlorination was studied at an optimum temperature (1000°C), as determined in earlier work (*6*). For estimating the effectiveness of the trichloromethane–ammonia mixture, the time dependence of the oxygen content was also examined in turbostratic boron nitride preparations exposed to the pure carrier gas, ammonia, at the same temperature.

Oxygen was never completely removed. In the case of the absence of information about the limiting value of oxygen content, the experimental variation was analyzed by using the following equation:

$$-\left(\frac{\partial c_{\mathrm{ox}}}{\partial \tau}\right)_{P,T} = k[c_{\mathrm{ox}} - c_{\mathrm{ox}}(\infty)]. \tag{2}$$

This fitting leads to the values $k = 0.61 \times 10^{-3}$ sec^{-1} or 1.06×10^{-3} sec^{-1} and $c_{\mathrm{ox}}(\infty) = 3.09\%$ or 2.10% for pure ammonia or trichloromethane–ammonia, respec-

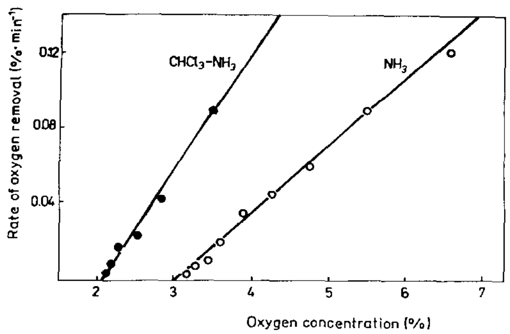

FIG. 1. Rate of removal of oxygen during reductive chlorination vs. the actual oxygen content.

tively, see Fig. 1. The use of the gaseous mixture $CHCl_3$–NH_3 obviously leads to a more rapid and more complete removal of oxygen in comparison to the pure carrier gas.

In our next paper (9) we showed that turbostratic boron nitride prepared by the reductive nitridation of oxidic boron compounds with ammonia at about 1000°C contains approximately 2% of oxinitridically bound oxygen and that the enhanced oxygen content corresponds to boron oxide. The refining of turbostratic boron nitride preparations by reductive chlorination, which occurs at twice the rate as in pure ammonia, attacks the oxidic phase selectively, which can be essentially quantitatively removed in this way.

The slow and imperfect removal of boron oxide by pure ammonia arises from a kinetic barrier of the secondary boron nitride. By the action of compounds containing chlorine, boron oxide is converted to volatile boron chlorides, which are then converted by the pyrolysis to the secondary boron nitride.

On integration of Eq. (2) and substitution of boundary conditions, one obtains

$$\ln = \frac{c_{\mathrm{ox}} - c_{\mathrm{ox}}(\infty)}{c_{\mathrm{ox}}(0) - c_{\mathrm{ox}}(\infty)} = -k\tau. \qquad (3)$$

The value $c_{\mathrm{ox}}(\infty)$ corresponds to oxinitridically bound oxygen content, the numerator on the left represents the time-dependent content of oxidically bound oxygen, while the denominator corresponds to the initial content. Thus, the reductive chlorination is a selective method acting on boron oxide, whose content in refined preparations is given by

$$c_{B_2O_3} = 1.45[c_{\mathrm{ox}} - c_{\mathrm{ox}}(\infty)]. \qquad (4)$$

By combining Eqs. (3) and (4), the following kinetic equation for the removal of boron oxide from turbostratic boron nitride preparations by the reductive chlorination at 1000°C is obtained:

$$c_{B_2O_3} = c_{B_2O_3}(0)\exp[-1.06 \times 10^{-3}\tau]. \qquad (5)$$

At a normal pressure and at the above mentioned temperature, i.e., for turbostratic boron nitride preparations, refining by the reductive chlorination method occurs at a constant rate of boron oxide removal.

3.2. Fusion Extraction of Oxygen from Turbostratic Boron Nitride

Reductive nitridation of oxidic boron compounds with ammonia, accompanied by a simultaneous formation of ultradispersed carbon through the decomposition of saccharose being previously dissolved in the mixture of boric acid and urea by heating at above 80°C, can yield preparations of turbostratic boron nitride containing oxygen at minimal levels. In Fig. 2 it is demonstrated that the oxygen content in the product of nitridation decreases with increasing carbon content. The oxygen content in these products was recalculated after analyses, so that varying carbon content in preparations was excluded. Thus, the oxygen content in this case is comparable with that of carbon-free preparations described earlier. The curve representing the relationship is initially linear; however, for high carbon contents the limit value of oxygen content in boron nitride is of about 2%, which corresponds to

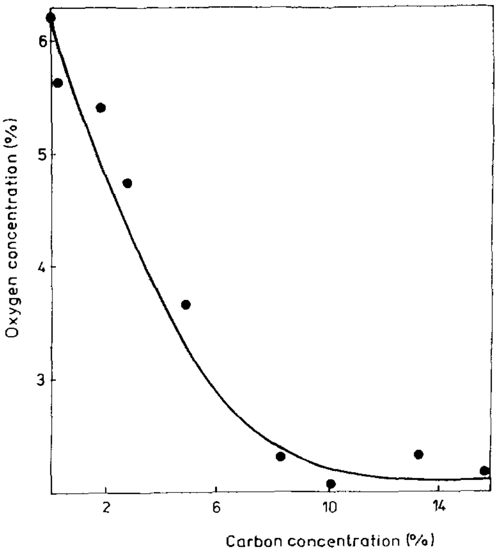

FIG. 2. Dependence of oxygen content in turbostratic boron nitride on carbon content in preparation.

the content of oxinitridically bound oxygen in turbostratic boron nitride, as mentioned earlier.

The presence of ultradispersed carbon simultaneously provides a quantitative course of its reaction with boron oxide due to the thermal exposure of the original turbostratic preparation leading to its crystallization. The size of crystallites is, as a matter of fact, a parameter determining the content of oxinitridically bound oxygen in hexagonal boron nitride, as shown in a paper in preparation (*9*). Thus, the graphite crucible used for the fusion extraction process is not the exclusive source of carbon necessary for the formation of carbon monoxide detected by the analyzer. Thus, the factor of the migration of boron oxide released to the crucible wall is eliminated, which would otherwise distort the form of the kinetic equation.

The curves for the content of oxygen released as carbon monoxide were linearized as shown in Fig. 3 on a log oxygen (extracted with carbon) concentration vs. time scale. Untreated powder contained 10.02% of carbon. The oxygen content related to the carbon-free boron nitride was 2.07%.

Thus, the following equation of the time dependence holds for the residual oxygen content:

$$c_{ox} = c_{ox}(0) \exp[-k\tau]. \tag{6}$$

The proportionality constant k depends on the temperature, as expressed by the equation

$$k = 1.475 \times 10^{-3}(T - 1345). \tag{7}$$

The release of oxinitridically bound oxygen is thus limited by a threshold temperature of T_0 = 1345°C. We have formerly found that close to 1350°C considerable crystallographic changes of the turbostratic boron nitride occur, resulting in the growth of single-crystal zones with a tighter arrangement of layers of this paracrystalline substance (*10*). This demonstrates the interactions between crystallographic characteristics of hexagonal boron nitride and oxinitridically bound oxygen.

3.3. Evaporation of Boron Oxide from Boron Nitride Ceramics

Ceramic materials based on hexagonal boron nitride always contain a certain

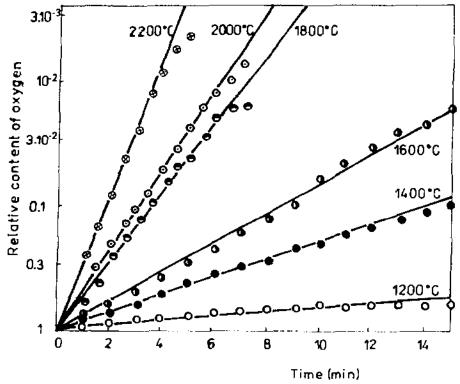

FIG. 3. Oxinitridically bound oxygen content in boron nitride vs. the time and temperature of its fusion extraction.

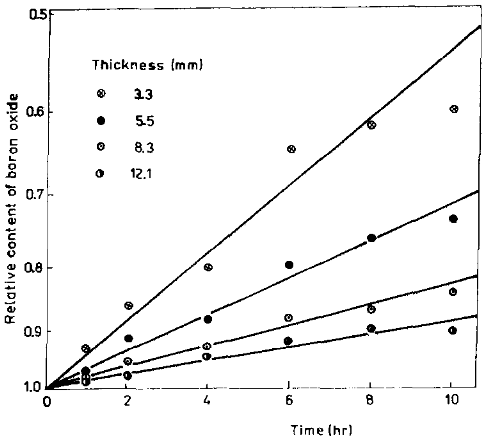

FIG. 4. Relative content of boron oxide in boron nitride ceramics vs. the time of its evaporation and ceramics thickness.

amount of boron oxide which is deleterious, particularly for high-temperature applications. On the other hand, it is present in the sintering process.

The ceramic skeleton is nonhomogeneously impregnated with amorphous boron oxide, this nonhomogeneity being a consequence of the oxide migration and evaporation in the sintering process (*11*). Thus, the boron oxide content should be reduced by a further high-temperature treatment in an inert atmosphere.

If almost all the oxygen is bound as boron oxide in highly crystalline boron nitride ceramics, then for the removal rate of this compound (shown in Fig. 4) the oxygen content in a sample of a constant thickness decreases exponentially. Thus, for this process, relations similar to those considered for the preceding deoxidizing processes are applicable.

In addition, the effect of thickness was further examined, representing a geometric factor for ceramic bodies. Circular plates, 40 mm in diameter, were used, with their thicknesses ranging between 3 and 12 mm. Average pulverized samples obtained by grinding the exposed plates were used for the determination of the residual oxygen content. Thus, it was possible to disregard the inhomogeneity of boron oxide distribution and to consider just the average content in ceramics.

Figure 5 shows that the kinetic factor k and the rate of the boron oxide evaporation is inversely proportional to the thickness:

$$k = 4.44 \times 10^{-5} d^{-1}. \qquad (8)$$

The escaping vapors of boron oxide adversely affect the quality of hexagonal boron nitride crystals, which recover only slowly after the initial shock resulting from the rapid release of boron oxide at the beginning of the process (see Fig. 6). This substantiates the effect of boron oxide on hexagonal boron nitride substructure, as discussed in (*12*). Boron oxide can be partially intercalated between planar macromolecules of boron nitride. As a result of the thermal exposure, a conversion of the oxide along with the subsequent expansion disturbs the regular stratification of the planar nitride network.

4. Conclusions

The kinetic variations of three "dry" processes for deoxidizing boron nitride preparations lead to the following conclusions:

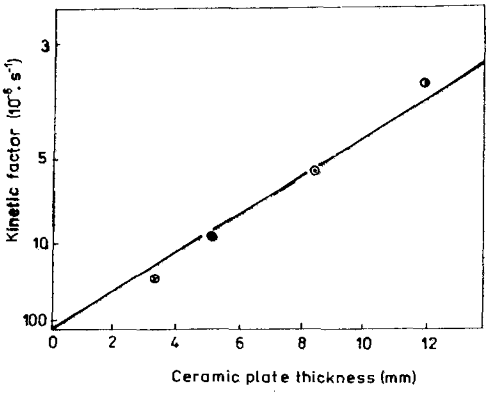

FIG. 5. Kinetic factor of boron oxide evaporation vs. the ceramics body thickness.

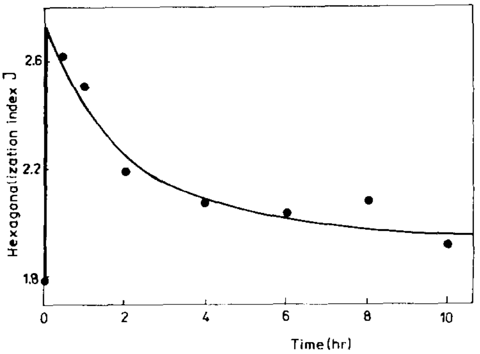

FIG. 6. Boron nitride hexagonalization index vs. the time of annealing ceramics in argon–hydrogen mixture at 1650°C.

A. The effect of the reductive chlorination, which may be used for refining of powder materials, is selectively directed toward boron oxide. A rather low chlorination temperature provides the desired retention of the powder turbostraticity.
   The gaseous agents used, trichlormethane and ammonia, act through intermediate reactive radicals, formed by the pyrolysis of the agents. Their content is strongly dependent on temperature (*5*) so that the temperature dependence of the kinetic factor was examined only at the optimum temperature.
B. In contrast to the above process, the fusion extraction of oxygen from boron nitride preparations does not occur preferentially in the oxygen-containing phase. Due to a maximum suppression of boron oxide as a product of an imperfect nitridation, one can study the thermal decomposition of reactive oxinitride, which is accompanied by the growth of hexagonal boron nitride, occurring at temperatures exceeding 1345°C.
C. The boron oxide evaporation from ceramic boron nitride showed that the ceramic skeleton presents a barrier for the oxide motion, which prevents its transport to the sample surface, from where it is to be evaporated.
D. The fusion extraction of oxygen and evaporation of boron oxide may be comparable in their effects, since boron oxide in the ceramics can also react with carbon.
E. By choosing a suitable refining process, it is possible to obtain boron nitride preparations with characteristics appropriate for their particular applications, as far as chemical and crystallographic parameters are concerned.

Appendix: List of Symbols

c_{ox}	Oxygen content in boron nitride preparations, as a variable in time, [wt%].
$c_{B_2O_3}$	Boron oxide content as a variable in time, [wt%].
$c_{ox}(0)$	Oxygen content in the very beginning of boron nitride preparation treatment
$c_{ox}(\infty)$	Limit value of oxygen content for $\tau \rightarrow \infty$.
d	Thickness of boron nitride ceramic plates, [mm].
J	Hexagonalization index describing regularity in boron nitride macromolecule packing.
k	Coefficient of proportionality in kinetic equations, constant of oxygen removal rate, [sec^{-1}].
P	Pressure of purification atmosphere, [kPa].
T	Temperature, [°C].
τ	Time of purification, [sec].

References

1. T. A. INGLES AND P. POPPER, *in* "Special Ceramics," pp. 144–167. Heywood, London (1960).
2. V. V. VIKULIN, *Poroshk. Metall.* **9**, 64 (1978).

3. Yu. I. Krasnokutskiy, V. D. Parkhomenko, and V. M. Zadorozhniy, *Zh. Prikl. Khim.* **51,** 2019 (1978).
4. J. Economy and R. Anderson, *Inorg. Chem.* **5,** 989 (1966).
5. V. Brožek and M. Hubáček, *Chem. Prum.* **37,** 632 (1987).
6. J. Leitner, P. Voňka, V. Brožek, and M. Hubáček, *J. Mater. Sci.* **58,** 3594 (1988).
7. V. Mandorf Jr., and L. C. Montgomery, U.K. Patent No. 1361024 (1974).
8. T. E. O'Connor, U.S. Patent No. 3,241,919 (1966).
9. V. Brožek and M. Hubáček, to be published.
10. M. Hubáček, Dissertation, Prague Institute of Chemical Technology (1988).
11. M. Hubáček, V. Brožek and B. Řehák, *in* "Proceedings, 2nd International Symposium Solid State Chemistry, Institute of Chemical Technology, Pardubice, 1989," pp. 11–14.
12. A. Gemperle, A. Holý, R. Říman and B. Řehák, *Hutn. Listy* **43,** 285 (1988).