INFLUENCE OF NONSTOICHIOMETRY ON THE THERMAL CONDUCTIVITY OF BORON CARBIDE

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It is shown that the deviation of the boron carbide composition from stoichiometry results in a change in its thermal conductivity.

Boron carbide at present is an extensively utilized absorption material in operational nuclear reactors, in those being constructed, and in those still being designed [1, 2].

Numerous investigations of the properties of boron carbide have shown that this material, obtained by different methods (pressing and sintering, hot pressing, etc.), possesses different mechanical, chemical, and thermophysical properties. Thus, the thermal conductivity of hot-pressed and cold-pressed polycrystalline boron carbide at 100°C is 28 and 17 W/(m•deg), respectively [3]. Boron carbide obtained by precipitation [4] possesses a still lower thermal conductivity value [8.5 W/(m•deg)]. It has been established by experiment that such large discrepancies are explained by a number of reasons: the difference in purity of the initial ores, the nonhomogeneous density of the material, the differences in the magnitude of the pores and their distribution in the volume of material, etc.

However, still another reason exists which can exert considerable influence of the thermal conductivity of B_4C: the deviation of its composition from stoichiometry. It is known that there is a broad range of homogeneity of the compound B_4C [5]. A change in the technological parameters (for instance, the sintering temperature) can alter the boron—carbon ratio to either side of the stoichiometric composition. It is expedient to determine the influence of a change in the B/C ratio on the magnitude of the thermal conductivity of boron carbide. This problem is of great practical and scientific interest, since spoilage of the stoichiometry is characteristic for industrial boron carbide as well as for many other ceramic materials [6].

In this paper we investigate boron carbide fabricated by the following technology. Powders are obtained by synthesizing amorphous boron and soot (99.8% initial purity). A different relationship between boron and carbon is achieved by appropriate dosages of the components during the synthesis. Compact specimens were obtained by hot pressing of synthesized powders in a vacuum ($5 \cdot 10^{-3}$ mm Hg, 1950 ± 50°C, 40 kg/cm^2). The composition of the sintered specimens was checked.

The boron content was determined by decomposition of the B_4C charge by sintering it with calcium oxide and subsequent lixiviation and titration of the solution by an alkali in the presence of manite (the coefficient of variation of the method is 0.5% for an ∿80% boron content). The carbon content is determined by combustion of the charge in an oxygen current (coefficient of variation 1% for 20% C), and the quantity of Si, Fe, Al, C, and Mg impurities in the specimens is determined by a spectral method. Their total content did not exceed 0.1 wt. %. The specimen density was determined by hydrostatic weighing (∿1% accuracy).

The main characteristics of the specimens are presented in Table 1.

The thermal conductivity of boron carbide was measured by the method of two plates [7] in an air atmosphere. The specimens were in the form of 20-mm-diameter tablets 6-8 mm thick,

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TABLE 1. Density and Chemical Composition of Boron Carbide Specimens

Specimen No.	1	2	3	4	5	6
Density, g/cm³	1,90	2,10	2,10	2,10	2,18	2,17
Boron content B, wt.%	78,5	70,0	71,5	74,2	77,3	82,7
Carbon content, wt. %	21,3	29,0	28,3	25,9	23,0	16,8

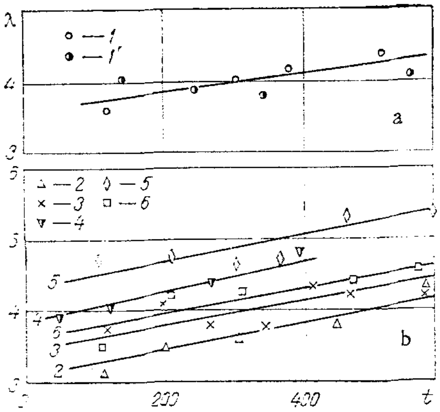

Fig. 1

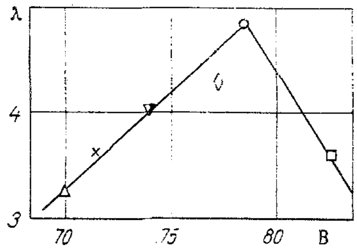

Fig. 2

Fig. 1. Temperature (°C) dependence of thermal conductivity of boron carbide: a) specimen No. 1 of stoichiometric composition; b) specimens Nos. 2-6 of nonstoichiometric composition; 1) specimen No. 1; 1') the same, comparative method; 2) No. 2; 3) No. 3; 4) No. 4 (comparative method); 5) No. 5; 6) No. 6. λ, W/(m•deg); t, °C.

Fig. 2. Dependence of the thermal conductivity of boron carbide on the content of boron B (wt. %) at 100°C, γ = 2.10 g/cm³. The notation is the same as in Fig. 1.

where each pair of tablets was cut from one 20-mm-thick initial specimen. Chromel—Alumel thermocouples were used. The accuracy of measuring the thermal conductivity was estimated at 6-8%. Part of the measurements (specimens Nos. 1 and 4) was performed by the comparative method of longitudinal heat flux.

The measurement results are shown in Fig. 1. The coefficients of thermal conductivity of the boron carbide specimens investigated at 100-600°C temperatures lie within 3.3-5.4 W/(m•deg) limits and increase insignificantly with the temperature. Therefore, the technology used results in still lower values of the thermal conductivity than in the above-mentioned examples. But in this case, the difference between the thermal conductivity of the specimens rather than the absolute value is of interest. As is seen from Fig. 1, this difference reaches 35% and cannot be explained by measurement errors.

This difference is not even explained by the difference in specimen density. Indeed, the thermal conductivity of specimen No. 1 with the minimum density is higher than that of the denser specimens Nos. 2 and 3. The influence of density can be eliminated by reducing the data in Fig. 1 to one value of the density by using the dependence $\lambda = f(\gamma)$. For boron carbide the dependence mentioned has the form $\lambda/\lambda_0 = 1.8$, $\gamma/\gamma_0 = 0.8$ (according to the data in [1, 2] for t = 100°C and in the range of densities 1.8-2.5 g/cm³), where λ_0 is the value of the thermal conductivity at a theoretical density γ_0, which is taken equal to 2.5 g/cm³.

Values of the thermal conductivity of the six boron carbide specimens investigated at 100°C, and reduced to a common density (2.1 g/cm³), are shown in Fig. 2 as a function of the boron content in the specimens. The curve in Fig. 2 has a quite definite maximum at the stoichiometric composition (78.3 wt. % boron), to which specimen No. 1 is close. Specimens Nos. 2-5, with the excess carbon, and specimen No. 6, with the excess boron, have a lower thermal conductivity, the difference reaching 75%.

Therefore, the deviation from the stoichiometric composition to either side results in a reduction in the thermal conductivity of boron carbide. Two mechanisms can be proposed for the change in thermal conductivity. First, part of the excess boron or carbon atoms form a defect in the crystalline boron carbide structure which results in additional phonon scattering. The steeper slope of the right-hand branch in Fig. 2 is possibly associated with the fact that the large-scale boron atoms produce greater distortions in the structure than do the carbon atoms. Secondly, the excess boron or carbon atoms can exert an influence on the formation of the boron carbide microstructure and, particularly, on the degree of thermal contact between its grains, on which the magnitude of the thermal conductivity depends.

LITERATURE CITED

1. B. G. Arobeya and V. V. Chekunov (editors), Absorbing Materials for Nuclear Reactor Regulation [in Russian], Atomizdat, Moscow (1965).
2. Specialists' Meeting on Development and Application of Absorber Materials. Summary Report, Scientific-Research Institute of Atomic Reactors [in Russian], Dmitrovgrad (1973).
3. H. W. Deem and C. F. Lucks, Batelle Memorial Inst., US Atom. Energy. Comm., BMJ-713 (1951), p. 10.
4. V. S. Neshpor et al., Refractory Carbides [in Russian], Naukova Dumka (1970), p. 41.
5. G. V. Samsonov, L. Ya. Markovskii, A. F. Zhigach, and M. G. Valyashko, Boron, Its Compounds and Alloys [in Russian], Izd. Akad. Nauk UkrSSR (1960).
6. W. D. Kingery, Introduction to Ceramics, Wiley (1960).
7. V. Ya. Chekhovskoi, R. A. Belyaev, and Yu. F. Vavilov, Inzh.-Fiz. Zh., 22, No. 6 (1972).

DETERMINATION OF THE THERMAL DIFFUSIVITY OF MATERIALS BY MEASURING TEMPERATURES AT THE STAGE OF IRREGULAR OPERATION

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Explicit relations are obtained for the thermal diffusivity of materials on the basis of measurements of the temperatures at the stage of irregular operation in specimens of different geometrical shape (a plate, a cylinder, and a sphere).

The main aspect of existing methods of determining the thermal diffusivity of materials by measuring the temperatures at the stage of irregular operation is the solution of the direct problem of thermal conduction with boundary conditions obtained by experiment, and on the basis of this solution to obtain information on the required parameters. Since, as a rule, the solution of the problem is given in the form of an infinite series of transcendental functions, the thermal diffusivity cannot be expressed explicitly in terms of experimentally measured values of the temperature. However, it turns out to be possible to express the thermal diffusivity explicitly in terms of the measured values of temperature without solving the direct problem by using the integral Laplace transform. The use of the integral Laplace transform enables one to write the general solution of the one-dimensional thermal conduction equation

$$r^{1-k}\frac{\partial}{\partial r}\left(r^{k-1}\frac{\partial T}{\partial r}\right)=\frac{1}{a}\frac{\partial T}{\partial \tau} \tag{1}$$

in transform space in the following form:

$$T(r, s)=A\varphi_1(r, s)+B\varphi_2(r, s), \tag{2}$$

where k = 1, 2, 3 for a plane, cylindrical, and spherical field, respectively, while $\varphi_1(r, s)$ and $\varphi_2(r, s)$ are expressed in terms of hyperbolic Bessel functions [1]. The constants A and

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