DENSIFICATION KINETICS OF A WURTZITELIKE BORON NITRIDE POWDER IN HOT PRESSING UNDER HIGH PRESSURE

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Polycrystalline superhard materials based on dense forms of carbon and boron nitride, which find increasing application as efficient cutting materials [1], are produced by hot pressing under conditions of high quasistatic pressures generated in high-pressure apparatus [2]. In the development of these materials the attention of investigators has up to now been concentrated mainly on studies of their phase transformations, structure, and physico-mechanical and operating properties [1, 3]. Structure formation in these materials during hot pressing under high pressure and particularly its kinetics have received much less investigation, so that as yet only a limited amount of information on this process is available [4, 5]. According to this information, the presence of porosity, as a result of which in the early stages of sintering of superhard materials under high pressure the uniform stressed state of omnidirectional compression in microvolumes is disturbed, brings about phase transitions in portions of material adjacent to pores. In this manner dense forms of carbon and boron nitride become transformed into the graphite and graphitelike modifications of the same substances but with larger specific volumes. In the course of densification, as the pore volume is reduced and hence the isostatic component of the stress tensor grows, the reverse phase transformation of these structures into the cubic diamondlike modifications is observed in volumes of material adjoining pores [4, 6]. This feature of the sintering of high-pressure phases should be borne in mind in analyses of the process, in particular in assessments of values of theoretical density from results of quantitative structural analyses of specimens, made with a view to determining suitable sintering conditions.

It is also necessary to take into account the influence of gases desorbed during sintering under pressure, which may generate, as will be shown below, a high back pressure. This pressure grows with decreasing porosity and in the final stage of sintering almost completely arrests densification. This is linked both with the specific character of sintering under high static pressure with a pressure-transmitting solid-phase medium (hermetic sealing of the specimen in the chamber, propagation of a thermal front from the periphery to the center, and a relatively high rate of heating, resulting in preferential densification of the periphery of the specimen during the initial stages of sintering) and with the large specific surface of powders, enabling substantial amounts of gases to be adsorbed.

The work described below was undertaken with the aim of carrying out an experimental investigation into the hot pressing of a wurtzite-like boron nitride (BNw) powder and of analyzing its densification during hot pressing under high pressure from the point of view of volume flow of a nonlinearly viscous porous solid [7], with allowance for the effect of gas back pressure. Isothermal hot-pressing experiments were conducted, using a high-pressure chamber, for varying periods of time at fixed pressures and temperatures.

The starting BNw powder had a specific surface of 20 m²/g. X-ray phase analysis showed that it was uncontaminated by graphitelike boron nitride (BNg). To obtain as reliable data as possible, for each experiment five specimens of dimensions d = 9 and h = 6 mm were prepared under identical conditions. All specimens were carefully cleaned of any traces of graphite by grinding away their outer layers (the starting volume of each compact being sintered was ~0.5 cm³). Specimen densities were determined by hydrostatic weighing with an error of not more than ±0.005 g/cm³. Theoretical density (density of the solid phase of the porous material) determinations were made pycnometrically on powders produced by crushing specimens. The same powders were employed for determining, by the method described in [8], the phase compositions of specimens.

The results of our experimental investigation into the densification kinetics of BNw specimens in hot pressing under high pressures are shown in Fig. 1. As can be seen from these data, in spite of the application of high pressures the theoretical density of the specimens was not attained. Moreover, at a temperature of 2070 °K and pressures of 6.6 and 7.7 GPa the relative density after holding under pressure for ~90 sec re-
This preliminary analysis of experimental data suggests that for the case under consideration the hot isostatic pressing equation proposed in [7, p. 81] requires modification. If the flow of the solid phase of such a porous material obeys the nonlinear law

\[ \dot{\varepsilon} = A \sigma^n \]

(\(\dot{\varepsilon}\) is the rate of deformation; \(\sigma\), stress; \(n\), a constant; and \(A\), a temperature-dependent coefficient), which is characteristic of the high-temperature flow of all known types of solids, we can write the following kinetic equation of densification [7, Ch. III, p. 84]:

\[ \frac{\rho^{2n}}{(1 - \rho)^{\frac{n+1}{n}}} \frac{d\rho}{dt} = A(\Delta P)^n, \]

(2)

where \(\rho\) is the relative density; \(t\), time; and \(\Delta P = P - P_g\) (\(P\) is the sum of the applied and Laplacian pressures, and \(P_g\) the gas back pressure). In our case the applied pressure was three orders higher than the Laplacian pressure, and the latter can therefore be ignored.

As the gas pressure in pores depends on their volume and hence on the total porosity, Eq. (2) in a general case cannot be integrated as easily as in the case of a constant applied pressure and absence of back pressure. However, at constant applied pressure, temperature, and weight of gas trapped in pores Eq. (2) may be written

\[ \dot{X}_n(\rho) = \frac{\rho^{2n}}{(1 - \rho)^{\frac{n+1}{n}}} \frac{d\rho}{dt} = A(P - P_g)^n, \]

(3)

from which we have

\[ (\dot{X}_n(\rho))^{\frac{1}{n}} = A^{\frac{1}{n}}(P - P_g), \]

(4)

i.e., the reduced magnitude of the deformation rate of the porous solid \([\dot{X}_n(\rho)]^{\frac{1}{n}}\) decreases linearly with rising gas back pressure in pores. The quantity \(\dot{X}_n(\rho)\) can be determined formally by using tabulated integral functions of the density \(X_n(\rho)\) [7], obtained by integrating Eq. (2) or (3) at \(P = \text{const}\) and \(P_g = 0\). Plots of \(\Delta X_n(\rho)\) or \(X_n(\rho)\) vs \(t\) are constructed, after which values of \(X_n(\rho)\) can readily be obtained by graphic integration. Construction of plots of \(X_n(\rho)\) vs \(t\) with the data of Fig. 1 showed that in the initial stage of densifica-