Sintering of BeO under Hydrostatic Pressure of 20 Kbars

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Abstract

An attempt to examine the effect of hydrostaticity of pressure at 20 kbars on sintering of BeO was made using glass cell. The activation energy for grain growth was found to be about 71 kcal/mole. The values of activation energy and rate constant of grain growth are in good agreement with those for hot isostatic pressing at 2 kbars. The effect of applied pressures on grain growth was not depend on the magnitude of pressure in a range of 2 to 20 kbars.

1. Introduction

Recently, studies on pressure sintering and hot isostatic pressing have been reported by Vahldiek[1], Poch[2] and others[3,4]. Most of the experiments were performed in a range of 800 to 1600°C and at pressures from 1 to 30 kbars. The authors attempted high pressure sintering of BeO using piston cylinder type vessel at 20 kbars[5]. BeO with full density showing optical translucency was obtained by this method. The mechanism of densification and grain growth have been already described in details.

On the other hand, although the applied pressure is lower than that in high pressure sintering, hot isostatic pressing has been utilized at a useful way for bonding and densifying wide varieties of metal and ceramic powders. The hot issostatic pressing of BeO make possible the application of equal pressure to all sides of an object have been performed in a high pressure gas autoclave at 2 kbars[6]. Properties of the products, densification and grain growth mechanisms were also discussed.

In order to discuss the results described above, the effect of hydrostaticity of pressure on grain growth at 20 kbars was investigated on the interrelation of the results from high pressure sintering and hot isostatic pressing experiments.

In this paper, the authors describe the result of sintering at 20 kbars under hydrostatic pressure generated by using glass instead of pyrohyllite as the pressure transmitting material for piston cylinder type vessel. The activation energy for grain growth in this process was also discussed in comparison to that of high pressure sintering with hot isostatic pressing.

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2. Experimental

BeO powders with particle sizes of 0.2 to 0.5 μ were prepared by calcination of beryllium sulfate at 1100°C for 2 hours in air. The starting material obtained in this manner was compressed to pellet 3 mm in diameter and 5 mm in length and fired once more at 1100°C for 3 hours in air. The pellet was enclosed in a platimum capsule and inserted into a piston cylinder type vessel for high pressure experiments which was carried out by the same procedures as described already[5]. The only one difference here is the use of glass in stead of pyrophyllite as the pressure transmitting medium for the cell assembly as shown in Fig. 1. The glass cell consists of a pyrex glass cylinder containing a graphite heater. A schematic diagram of this cell assembly as designed by Kennedy[7]. Since the pyrex glass begins to soften at about 600°C, it behaves as a fluid above the temperature. It has pressure transmitter qualities which are superior to talc, pyrophyllite and other solid materials. Using the above assembly, an ideal hydrostatic pressure can be applied to specimens as in the case of hot isostatic pressing.

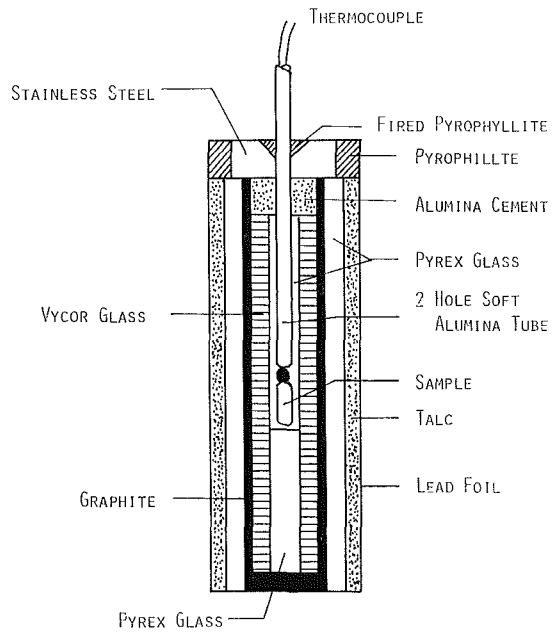

Fig. 1. Schematic diagram of glass cell assembly.

The experiment was conducted at 1000 to 1300°C and 20 kbars for 30 minutes. The grain size was measured in both thin sections and surface of fractured specimens. Electron microscopic observations were also performed on the surface of fractured specimens.

3. Results

Pressures applied to the specimen placed in the high pressure cell made of pyrophyllite is not perfectly hydrostatic. On the other hand, the use of glass as the pressure transmitting medium makes it possible to generate hydrostatic pressure in the cell at high temperatures. An attempt to examine the effect of hydrostaticity of pressure at 20 kbars on sintering of BeO was made by the use of a glass cell as described already.

The products sintered at 1000 and 1100°C were white in color. Slight translucency was observed in the specimens prepared at 1200 and 1300°C. Grains of the product which were sintered at 1000°C for 30 minutes were uniformly

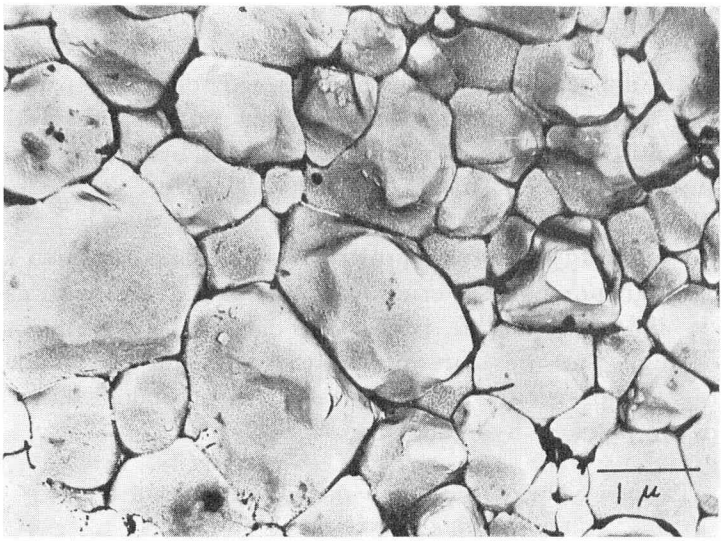

Fig. 2. Fracture characteristics of the product sintered at 100°C and 20 kbars for 30 minutes.

distributed, and abnormal grain growth was not recognized. The electron micrograph of the fractured surface of this specimen is shown in Fig. 2. This picture indicates predominant intergranular fracture characteristics, but the grain boundaries are not so sharp as that in specimens obtained by hot isostatic pressing.

The grain size was 1, 7, 3.5, 7 and 15 μ for the products prepared at 1000, 1100, 1200 and 1300°C for 30 minutes. These values are very close to those for the specimens by hot isostatic pressing. In the calculation of activation energy for grain growth, the value of 2/5, which was obtained in the case of hot isostatic pressing, was used as the time exponent n, since, regarding grain size, the results obtained under hydrostatic pressure at 20 kbars are identical with those for hot isostatic pressing. And then, rate constants of grain growth for each temperature were calculated, and plotted against reciprocal absolute temperatures as indicated in Fig. 3. From the slope of the line, activation energy for grain growth was calculated to be about 71 kcal/mole. These values for activation energy and rate constant of grain growth were in good agreement with those for hot isostatic pressing at 2 kbars.

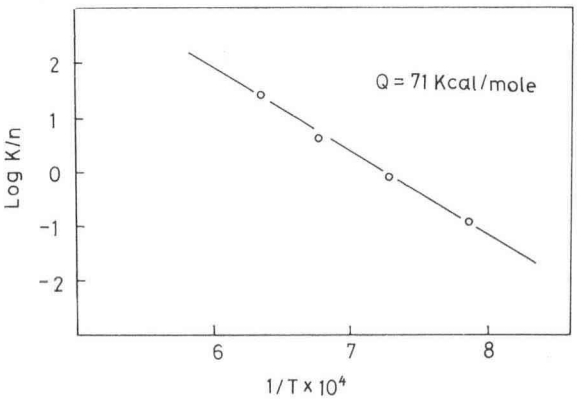

Fig. 3. Temperature dependence of grain growth at 20 kbars under hydrostatic pressure.

4. Discussion

The effects of applied pressure on grain growth do not depend on the magnitude of pressure in the range of 2 to 20 kbars under hydrostatic conditions. In other words, it is considered that grain growth at hydrostatic pressure occurs by the same mechanism which has no connection with pressure magnitude. The details are as follows.

The activation energy for grain growth was calculated for two types of pressing conditions (high pressure sintering and hot isostatic pressing) as indicated in Table 1. It is difficult to decide from these data alone whether the difference between Q for high pressure sintering with pyrophyllite cell (44 kcal/mole) and that for hot isostatic pressing (75 kcal/mole) can be attributed either to the pressure magnitude or pressure hydrostaticity.

TABLE 1 The activation energy for grain growth under the pressing conditions of two types.

Pressing method	Pressing conditions	Q, kcal/mole
High pressure sintering with pyropyllite cell	Quasi-hydrostatic at 20 kbasr	44
Hot isostatic pressing	Hydrostatic at 2 kbars	75

At pressures greater than 10 kbars, the pressure is transmitted through a solid. One of the transmitters most frequently used for this purpose is pyrophyllite. It is said, however, that the pressure transmitted by solid is not hydrostatic, but quasi-hydrostatic[8]. Thus, an attempt was made to use the pyrophyllite hardened by firing at 1300°C instead of the pyrex glass placed inside the graphite heater of the cell assemblage illustrated in Fig. 1. Using the new assembly, a run was made at 1200°C and 20 kbars for 30 minutes to examine the uniaxial property. The intensity ratio of I (100) to I (002) in X-ray diffraction pattern of the product was observed to be 2.30, and, in contrast, that of ASTM card[9]was 0.63. From these result, it was concluded that a large amount of preferred orientation exists in the specimen. Therefore, uni-axial characteristics in parallel with the direction of the applied pressure in the high pressure cell are inevitable when a solid is used as the pressure transmitting material.

As mentioned above, the pressure generated inside the piston cylinder type high pressure cell made of pyrophyllite is not perfectly hydrostatic, and the pressure generated by the use of hot isostatic pressing technic is considered perfectly hydrostatic.

Thus, in order to determine which factor, pressure magnitude or hydrostaticity, causes the difference of Q value, the experiments of sintering at 20 kbars under perfectly hydrostatic pressure were carried out by using a glass cell. The following value as indicated in Table 2 was obtained as the activation energy for grain growth. This value is comparable with that in hot isostatic pressing namely

TABLE 2 The activation energy for grain growth at 20 kbars under hydrostatic condition.

Pressing method	Pressing condition	Q, kcal/mole
High pressure Sintering with glass cell	Hydrostatic at 20 kbars	71

75 kcal/mole. Consequently, it was concluded that the same mechanism can be applied to grain growth of particles at hydrostatic pressures. As reported in detail[10], volume diffusion may well be the rate determining step for grain growth under hydrostatic pressures.

On the other hand, in the experiments of high pressure sintering of BeO, the values of activation energy for grain growth were given as 44 kcal/mole for pyrophyllite cell and as 71 kcal/mole for glass cell as mentioned before. Thus it is concluded that the difference in these values results in pressure hydrostaticity, since the applied pressure in both experiments is the same pressure of magnitude of 20 kbars, and is perfectly hydrostatic for the experiment of glass cell, and quasi-hydrostatic for that of pyrophyllite cell. Thus the low activation energy is due to the quasi-hydrostatic conditions which produces high stress in the samples. For instance, as an effect of high stress, rate constants of grain growth, K, in high pressure sintering is about four figures greater than that in hot isostatic pressing. Under this condition, it may be concluded that grain boundaries migrate rapidly, and thus, the values of low activation energy may be obtained.

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