Pressure Sintering of Beryllium Oxide

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Abstruct

The fabrication of products with theoretical density was achieved by high pressure sintering in a temperature range of 1000 to 1400°C and at 20 kbars. The material produced at optimum condition transmitted light over 60% in the vissible range. The rate of densification was observed to be rapid under the above conditions and the fully dense products were obtained within a few minutes. The densification due to high pressure sintering is explained by the following mechanisms. The fragmentation and rearrangement of particles take place as an operative mechanism in the initial stage of application of pressure. On heating, plastic flow becomes dominant.

1. Introduction

Pressure sintering as a fabrication process of ceramic materials has been finding increasing utility in ceramic industry in recent years with improved properties through composition, microstructure, and density control. The pressure sintering process itself generally consists of applying pressure to powder or cold-pressed powder in a refractory die which is heated to some optimum temperature for densification.

A serious limitation of conventional graphite die pressure sintering is the low strength of the die materials, which is usually less than 700 kg/cm^2. The strength limits of nongraphite die materials, while higher than graphite, are still less than an order of magnitude greater than that of graphite in uniaxial pressure sintering devices.

The extention of pressure sintering into the high pressure regimes involues a greatly increased interest in the consequences of applying very high pressure to different materials. While much deserved attention has been given to high pressure in the synthesis of materials such as diamond[1] and cubic boron nitride[2], it is apparent that high pressure sintering also presents a field of challenge and potential.

In the field of ceramic materials, the effect of high pressure as a fabrication variable on microstructures and properties had been almost entirely overlooked. Recently initiated high pressure sintering studies of ceramics such as Al_2O_3, MgO and HfB_2 have also been reported by Chang et al.[3], Vahldiek[4], Poch[5], and Kalish et al[6]. Most of the experiments have been performed in a temperature range of 800 to 1600°C and at pressures of 10 to 35 kbars. Relative densities in excess of 99% have been achieved for each of these materials. Some specimens with full density showing optical translucency have been obtained by high pressure sintering[7]. Attempts to explain the mechanism of densification have been attempted[3,6].

In this paper, the fabricating method of translucent BeO with theoretical density under high pressure by using piston-cylinder type apparatus is described. The mechanism of densification and grain growth in the process is discussed.

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2. Experimentals

Beryllium sulfate (99.9% in purity) was used to obtain the starting powder. BeO powder with a particle size of 0.1 to 0.5 μ was prepared by calcination of beryllium sulfate at 1100°C for 2 hours in air.

The above-mentioned starting powder was compressed to a form of 7 mm in diameter and 10 mm in length at 1000 kg/cm^2 and prefired at 1100°C for 3 hours in an electric furnace. Then the pellets were enclosed in a platinum capsule and inserted into a piston-cylinder type vessel for high pressure experiments. The cell assemblage capable operation at pressure-temperatures up to 25 kbars and 1600°C is illustrated in Fig. 1. The pressure generated inside the vessel was calibrated

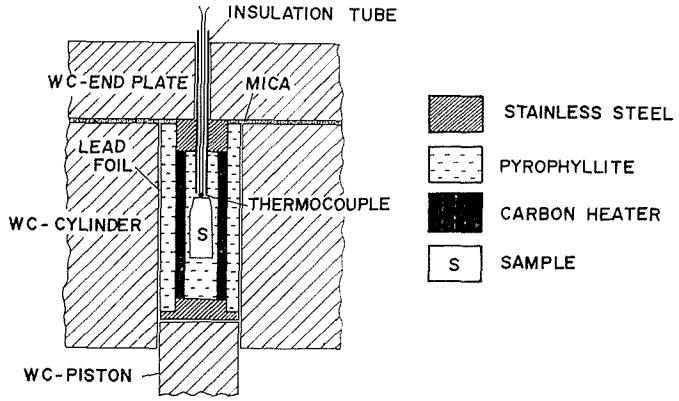

Fig. 1 Piston-cylinder type vessel and cell assemblage for high pressure experiments

by the discontinuous change of volume of NH_4F, $AgNO_3$, KBr at 3.7, 9.8, 17.9 kbars and of electric resistance of Bi metal at 25.2 kbars respectively[8]. The temperature was measured with Pt/Pt–13% Rh thermocouple for all the runs. After maintaning at a required condition, the sample was slowly cooled to room temperature with a simultaneous reduction of pressure. The time duration maintained at a desired temperature-pressure is defined as " pressing time in the present study ". The desired condition of tempeature and pressure was reached within a few minutes.

Cold pressing was also carried out on the starting powder for the measurements of green density at various pressures using a dial gauge. For the measurements of density and grain size, the samples were cleaned by grinding and then the surface was polished to a mirror. Densities of the polished specimens were determined by precise measurements of dimensions and weight or by the water displacement method. A value of 3.01 g/cm^3 was taken as the theoretical density for BeO.

The polished specimens were etched with a hot mixture of 12 N HCl and 36 N H_2SO_4 in equal volumes for a few minutes. The etched specimens were observed for grain size mesurements under a reflective microscope or electron microscpe. The grain size measurements were made by the intercept method for each specimen. The average size was determined on each grain.

The optical translucency was measured using thin section (0.8 mm in thickness) of polished specimens. The measurements were made by the absorptions of visible light and infra-red with wavelengthes ranging from 0.4 to 0.6 μ and 1 to 25 μ respectively.

3. Results

The densities of the samples treated at 1000°C and 1200°C for 2 minutes were 99.0 to 99.6% of the theoretical value. It reached to theoretical density when the experimental duration was prolonged to 5 minutes for all the runs. These results indicated that the densification rate was very rapid compared with the conventional hot pressing or normal sintering. The relation between relative density and pressing time is shown in Fig. 2 with the results of hot pressing of BeO by McCLELLAND[9].

The microstructure of the product sintered at 1200°C and 20 kbars for 150 minutes is shown in Fig. 3, where it may be seen that the grains meet in groups

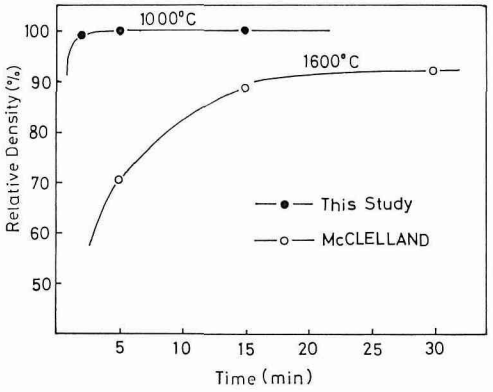

Fig. 2 Curve of relative density vs. sintering time

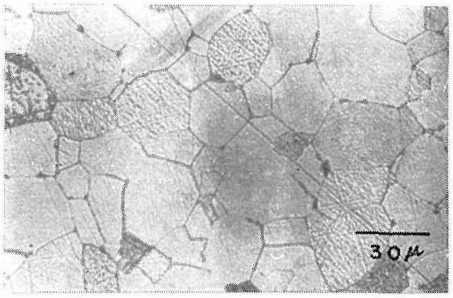

Fig. 3 Microstructure of the sample sintered at 1200°C and 20 kbars for 150 minutes

of three at points. It may also be seen that the grains uniformly distributed and that no closed pores are visible in these grains, and also abnormal grain growth was not recognized. This type of structure is commonly observed in the products treated by normal sintering or conventional hot pressing[10].

The results of cold-pressed BeO are plotted in Fig. 4 for the relative densities at various pressure. Fragmentation was clearly observed on electron micrographs for the starting powders cold-pressed at 20 kbars. In this case, the applied pressure is much higher than the rupture strength in relation to the actual pressure at areas of contact.

Grain growth hardly took place even at 1000 to 1400°C and 20 kbars when the time duration for treatment was short. For the longer sintering time over 5 minutes under the same condition of pressure and temperature, grain growth was observed to proceed.

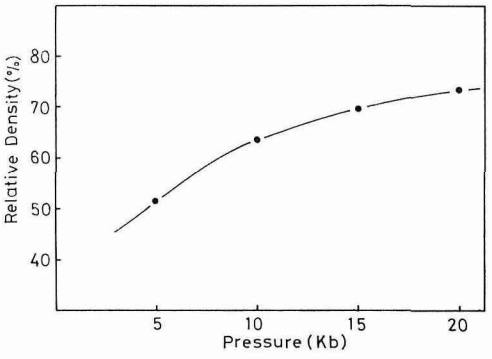

Fig. 4 Relative densities of cold-pressed BeO powders

In a polycrystalline body consisting of grains of uniform size, it was pointed out by Burke[11] that the grain growth rate is inversely proportional to the grain size, and the following relation was given.

$$dD/dt = K/D \tag{1}$$

Where D is instantaneous grain size, t is sintering time and K is temperature-

dependent constant.

Equation (1) can be generally described as equation (2).

$$D=K't^n \tag{2}$$

In Fig. 5 the relation between grain size and time is shown in log-log plots such a way the exponent of time in equation (2) can be computed from the slope of the curves. From the data obtained at 1000°C, 1200°C and 1400°C, the value of n in the equation (2) was determined approximately to be 0.5. Thus the equation (2) is expressed as follows.

$$D=(Kt)^{1/2} \tag{3}$$

Plotting the log K versus the reciprocal of the absolute temperature yield the activation energy for grain growth from equation (4).

$$K=K\exp(-Q/RT) \tag{4}$$

Where K is the activation energy in Arrhenius plots, R is the gas constant and K is the rate constant which is independent of temperature. From the value of K in equation (4), log K versus reciprocal absolute temperature is plotted in Fig. 6.

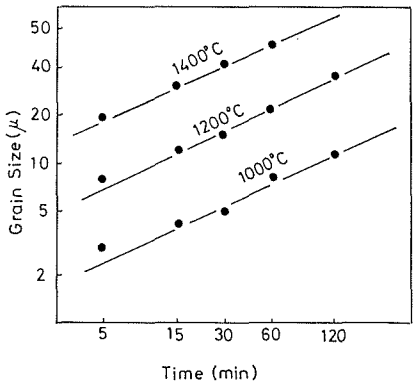

Fig. 5 Grain growth of BeO prepared at 1000 to 1400°C for various durations

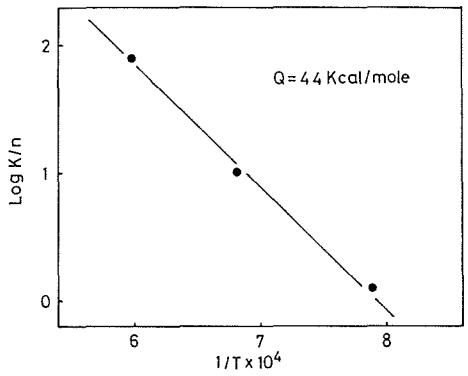

Fig. 6 Temperature dependence of grain growth

The activation energy was calculated to be about 44 kcal/mole. This value is smaller than the activation energies reported for diffusion or grain growth in various oxides[12,13].

Optically translucent products were obtained after the treatment for a sintering time exceeding 5 minutes at each temperature. At the end of the experiments, the temperature and pressure was slowly reduced down to room temperature and atomospheric pressure, and 5 to 10 minutes were required to obtain a crack-free translucent specimen. An example of the products which transmites visible light is shown in Fig. 7. This sample was sintered at 1200°C and 20 kbars for 30 minutes, and was polished to a thickness of 0.8 mm. The transmittance of this sample in the infra-red region is shown in Fig. 8. Similar results were obtained for the sample sintered at 1400°C and 20 kbars for 30 minutes as indicated in Fig. 8.

The relative change of wavelength for these specimens agrees with the result on the pressed plate of BeO reported by During et al[14]. As far as the absolute value is concerned, the transmittance was observed to be higher in the present case if the thickness of these two samples are compared. In the visible region, the translucency of the present sample reached 60% of total light. For various pressing times at a temperature of 1200°C, translucency of these samples did not change remarkably. Accordingly a translucency of about 60% was always observed

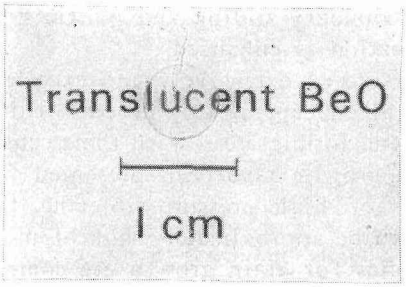

Fig. 7 Demonstrative photograph showing the translucency of sintered BeO

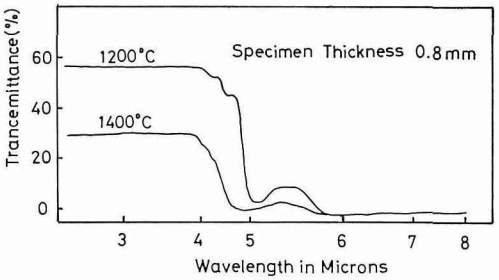

Fig. 8 Transmittance of sintered BeO in the infra-red region

for the products obtained with a sintering time over 15 minutes. Similar transmittance were observed in the case of lower treatment temperature at 1000°C. On the other hand, the samples which were sintered at a high temperature of 1400°C showed a translucency of about 30% less than that value.

4. Discussions

As mentioned before, in the case of high pressure sintering, translucent materials with almost full density are obtained at relatively low temperatures in a short run duration, and densification to full density occurs in a few minutes. These density-time relationship can not be explained with the sintering models proposed by various investigators[15,16,17]. Then by observing the changes in microstructure during the early stages of high pressure sintering and those in particle size of the powders cold-pressed at various pressures, the author has clarified the densification mechanism in high pressure sintering.

The relative density of the cold-pressed specimen at 20 kbars shows a relatively high value of 73.0%. This phenomenon is explained by considering fragmentation and rearrangement of particles under high pressure. Thus, it was considered in these cases that particle size decreases with the increase of magnitude of the applied pressures. Poch also presented the same results in cold-pressed Al_2O_3 and MgO[18].

At heating up at 20 kbars, a reduction of particle size was also observed. The fact indicates that the applied pressure is considerably higher than the yield strength of BeO. Therefore, it is considered that the sintering rapidly proceeds by particle fragmentation and rearrangement at high temperatures and high pressures. Consequently, in high pressure sintering, compaction proceeds by plastic flow without grain growth. Chang and Rhodes[3] also obtained hot pressed uranium carbide at pressures of 10 to 45 kbars and temperatures of 0.29 to 0.64 Tm*. These investigators obtained direct metallographic evidence for grain boundary sliding and fragmentation which led them to conclude that these mechanisms play a dominant role in the densification of uranium carbide. The fragmentation process may well be more important under high pressure. Cold compaction of TiB_2 powder at 7 kbars produced a particle size reduction which can only be attributed to particle fragmentation[19].

From these considerations, the densification due to high pressure sintering is explained by the following mechanisms. The fragmentation and rearrangement of particles take place as an operative mechanism in the initial stage of the application

* Tm: Melting point

of pressure. On heating, particle rearrangement, boundary sliding and plastic flow predominate, and consequently the rate of densification is enhanced.

The grain growth in metal systems has been studied extensively and excellent reviews on the subject are available[20]. The general concept of this process is that the grain boundaries in polycrystalline specimens tend to migrate toward their center of curvature[21]. The activation energies for grain growth have been presented for many refractory materials. In the present study of high pressure sintering, the activation energy for grain growth was calculated to be approximately 44 kcal/mole for BeO. Generally speaking, the activation energies for grain growth are comparable with that of diffusion. Subsequently it is considered that a migration of atoms determines the rate of each process. Although there is no data on activation energies for diffusion under high pressure in literature, the value of the activation enrgy for grain growth obtained here is lower than those for many oxides[13]. Insofar as the activation energies for volume diffusion reported are concernd, the values are 68 to 138 kcal/mole for BeO[22,23], 114 to 152 kcal/mole for Al_2O_3[24,12] and 62.4 to 112 kcal/mole for MgO[25,17] respectively. Compared with these values, the low activation energy for grain growth of BeO under high pressure is explained by considering that the activation energy for grain boundary diffusion is lower than that for bulk diffusion[26], and that the high stress induced in each grains by applying high pressure may enhance the migration of grain boundaries.

Such a small value of activation energy, 22.9 kcal/mole, was given for densification of HfB_2 under high pressure by Kalish et al[6]. They concluded that the rate-controlling process was stress-directed diffusion. In the present experiment, it is considered that, owing to the existence of high stress, the grain boundaries migrate relatively rapid and then the low activation energy is resulted. This explanation will be reasonable to account for the fact that the grain growth constant, K, is larger than other values presented so far. Consequently it is considered that grain growth is largely susceptible to influences from the pressure transmitting materials.

Although the products were optically translucent under conditions of sintering ranging from 1000 to 1400°C and 20 kbars for 5 to 150 minutes, the translucency decreased at higher temperatures. This was supported by the fact that closed pores can be observed at grain boundaries in samples prepared at high temperature of 1400°C for 30 minutes. Consequently the decrease of translucency is attributed to the increase of number of enclose pores at the grain boundaries. The following two cases are considered: (1) Gases generated due to the decomposition of sulfate at high temperatures concentrate at grain boundaries. (2) Pores can not be eliminated on account of the high rate of grain growth at higher temperatures. Then, the following experiment was conducted to examine which of the cases is possible. The translucent specimen of BeO sintered at 1200°C and 20 kbars for 30 minutes was treated again at 1400°C and 20 kbars for 30 minutes. The grade of translucency did not chage. Consequently, it is considered that case (2) is more proable as the reason. Then, translucency of the products is lowered by the closed pores. Furthermore, the grain boundaries which are strongly bonded with each grain are recognized from the results of electron microscopic observations in samples prepared at high temperatures. Therefore, isolated pores on grain boundaries are no longer eliminated.

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