Comparison between Pulse Electric Current Sintering and Hot Pressing of Silicon Nitride Ceramics

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窒化ケイ素セラミックスのパルス通電焼結とホットプレス焼結の比較

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Samples of a Si_3N_4 mixed powder with oxide sintering additives, Y_2O_3 5 mass% and Al_2O_3 3 mass%, were sintered separately by pulse electric current sintering (PECS) and by hot pressing to discuss the characteristic features of these two processing techniques. The low-temperature consolidation and the plasma effect, which have been reported to be features of the PECS process, could not be confirmed in this study. In the sintering of Si_3N_4 ceramics as a material for electrical insulators, the rapid consolidation, which enables the nanometer-scale grain size to be maintained in the dense material, was shown to be the only advantage of the PECS process.

[Received February 15, 1999; Accepted July 21, 1999]

Key-words: Pulse electric current sintering (PECS), SPS, PAS, Hot pressing, Si_3N_4

1. Introduction

Pulse electric current sintering (PECS) has been applied to consolidate various materials such as metals, plastics, ceramics, composites and functionally gradient materials.¹⁾ PECS is performed using a spark plasma sintering (SPS) or plasma activated (or assisted) sintering (PAS) system. Though there is a little difference between the SPS and PAS systems, a dc pulse current of several tens of milliseconds is applied directly to an electrically conductive die set, which is usually made of graphite and is similar in construction to that used for hot pressing (HP) in principle. The following features of the SPS and PAS have been reported: (1) The dc pulse generates plasma in the powder to be consolidated and the plasma (or spark discharge) efficiently removes impurities and/or oxide layers on the powder.^{2),3)} (2) The powder is heated by a spark discharge between the particles of the powder.⁴⁾ (3) The powder consolidates at a lower temperature than in the case of conventional HP.⁵⁾ (4) Rapid consolidation retards grain growth and the nanostructure is realized.⁵⁾⁻⁷⁾

Several ceramics such as Si_3N_4 ,^{4),5),7),8)} AlN ,^{2),3)} Al_2O_3 ,^{6),8),9)} and SiC ¹⁰⁾ have successfully been sintered by this method. However, some of the features mentioned above are doubtful, because the sintering was performed only by the PECS method and no comparison with other sintering methods such as HP and conventional sintering, except in the case Ref. 5). Moreover, few experimental details, such as the temperature measurement method, were reported.

The objective of this experiment is to determine the features of PECS in comparison with those of HP using silicon nitride mixed powder from the same batch.

2. Experimental

Silicon nitride powder (Ube, E-10) was mixed with 5 mass% Y_2O_3 (Mitsubishi Chemicals Co., Ltd.) and 3 mass% Al_2O_3 (Taimicron Chemicals Co., Ltd., Taimicron TM-D) using ethanol as a solvent in a ball mill for 24 h. The average particle size and the specific surface area of

the mixed powder, measured using a laser scattering particle size distribution analyzer (Horiba, LA-910), were 0.68 μm and 9.4 m^2/g , respectively.

SPS-1020 equipment (Sumitomo Coal Mining Co., Ltd.) was used for PECS. In SPS equipment, a pulsed voltage is always applied. HP was performed using carbon-heater-type equipment (Fuji Dempa Kogyo Co., Ltd., FRET-45).

The die set used for PECS is shown in Fig. 1. The diameter of the specimen was 20 mm. To ensure electrical contact, a graphite foil was inserted between the punches and the die. The die set was covered with a ring of ceramic wool. The die set used for HP was almost the same except

Fig. 1. Schematic diagram of the die set used for PECS.

Fig. 2. Typical heat patterns of PECS and HP.

for the dimensions. In HP, the diameter of the punch was 40 mm.

In PECS, the temperature of the external wall of the graphite die (the portion A shown in Fig. 1) was measured and controlled by a monochromic optical pyrometer. In HP, the temperature at the bottom of the graphite tube, which was set near the graphite heater, was measured and controlled by a two-color optical pyrometer. Typical heating-patterns of PECS and HP are shown in Fig. 2. Mechanical pressure was applied from the start of the heating to the end of the holding time. The pressure was 30 MPa for PECS and 20 MPa for HP.

The bulk density was measured by the Archimedes method using water. The surfaces of specimens were ground by about 0.5 mm to avoid the surface effect⁽¹¹⁾ and the ground surfaces were analyzed by X-ray diffraction to measure the α -phase content. The α -phase content was calculated using Gazzara and Messier's equation.⁽¹²⁾ The microstructure was observed using scanning electron microscopy (JEOL, FE-SEM JSM-890).

3. Results and discussion

Bulk densities of HP specimens are shown in Fig. 3. The true density of the composition was not measured experimentally, but the maximum bulk density measured was 3.243 g/cm³. The time, at which the bulk densities reached almost full density (3.24 g/cm³) at each holding temperature, was 60 min at 1650°C, 30 min at 1700°C and 15 min at 1800°C. Figure 4 shows the relation between the temperature and time at which the bulk densities of HP

Fig. 3. Bulk density of the HP specimen as a function of sintering temperature and holding time.

Fig. 4. Relationship between temperature and holding time at which bulk densities reached to 3.24 g/cm³ in HP.

specimens reached the full density. In this figure, the temperature at which the bulk density will reach 3.24 g/cm³ at 0 min is extrapolated as being above 1850°C. The bulk density of the PECS specimen was 3.242 g/cm³ at 0 min. Although there is no theoretical basis for substantiation, the temperature of the PECS specimen was estimated to be above 1850°C from the data mentioned above.

Bowen et al. reported that the α - to β -transformation rate of Si₃N₄ is defined by the following equation⁽¹³⁾

$$d\alpha/dt = -K\alpha \quad (1)$$

where K is the rate constant. The α -phase contents of HP and PECS specimens are shown in Figs. 5 and 6, respectively.

K values signify the gradients of lines in Figs. 5 and 6. K is also related to the sintering temperature (T) as shown in Eq. (2),⁽¹³⁾ where R is the gas constant and E is the activation energy.

$$K = K_0 \exp(E/RT) \quad (2)$$

The Arrhenius plot of values of K for HP specimens, derived from the data in Fig. 5, is shown in Fig. 7 (mark $\blacktriangle$). The activation energy was -230 kJ/mol, which was about one half of that for Si₃N₄ with 5 mass% MgO.⁽¹³⁾ When the K value for PECS specimens (mark $\star$), derived from the data in Fig. 6, was plotted on the Arrhenius line of K for HP

Fig. 5. Alpha-phase content of HP specimens as functions of sintering temperature and holding time (Circle at 0 min denotes α -phase content in raw powder).

Fig. 6. Alpha-phase content of PECS specimens as a function of holding time.

Fig. 7. Estimated PECS temperature from Arrhenius plot of K , derived from the data in Figs. 5 and 6 using Eq. (1).

specimens, the temperature of PECS specimens was estimated to be 1870°C.

The microstructures of the HP specimen (A) and PECS specimen (B) are shown in Fig. 8. Although the grain sizes of both specimens were not quantitatively measured, the average grain size and the size of grains grown abnormally are similar in both SEM photographs. Consequently, it was suggested that the temperature of the PECS specimen was not 1700°C, but about 1850°C.

As seen in Fig. 8(B), most of the Si_3N_4 grains in the PECS specimen heated at 1700°C for 8 min were less than 1 μm in diameter. The bulk density of the PECS specimen reached full density at 1700°C for 0 min as previously mentioned. Although a SEM image of the specimen is not shown here, the grain diameters of the specimen were less than 0.5 μm . Therefore, PECS is verified as being a process which enables maintaining nanometer-scale grain size in

Fig. 8. SEM microstructure of HP specimen (A) at 1850°C for 15 min and PECS specimen (B) at 1700°C for 8 min.

the dense material.

Direct measurement of the temperature of the specimen was attempted using a platinum/13% rhodium-platinum thermocouple and the results were compared with those using an optical pyrometer. The thermocouple was set at the center of the specimen through a hole made in the wall of the carbon die in Fig. 1. The temperature was controlled by an optical pyrometer and measured between 800–1400°C. The temperature of the thermocouple (T_t) was always higher than that of the optical pyrometer (T_o). T_t is related to T_o by the following equation in the temperature range of 800–1400°C.

$$T_t = 1.12(T_o - 800) + 820 \quad (3)$$

From Eq. (3), T_t at $T_o = 1700^\circ\text{C}$ can be calculated as 1828°C, if the relation holds above 1400°C. Further details of the experiments performed for measuring the temperature of the specimen directly will be reported elsewhere.

It is obvious that the temperature of the specimen in the case of PECS was higher than that measured by the optical pyrometer by about 150°C. Therefore, PECS is not recognized as a sintering method enabling low-temperature sintering.

On observing the glow of the die set surface with the naked eye, the glow of portion B appeared brighter than that of portion A. If the electric current passes through the punch-die-punch in Fig. 1, most of the joule heat will be generated in the punches because the cross section of the die is 3 times

than that of the punch and the length of the punch, 20 mm, is longer than the effective current pass in the die, which corresponds to the thickness of the specimen of 5 mm. Consequently, we presume that the heat was mainly generated in the punches and was conducted to the specimen via the spacers. From the viewpoint of the above discussion, it is reasonable to consider that the temperature of the specimen was higher than that of portion A, at which the temperature was controlled using the optical pyrometer.

Silicon nitride is an electrically insulating material. Therefore, it is thought that substantial electrical current does not pass through the specimen. However, several papers have discussed the effect of a plasma spark as mentioned in the introduction. In all the experiments to date, the material of the spacer in Fig. 1 was carbon (Toyo Tanso Inc., SG-11). Some experiments were performed using a hexagonal boron nitride spacer. The material was KD-3S (pure BN, Shin-Etsu Chemical Co., Ltd.) and the dimensions were the same as in the case of carbon, 20 mm in diameter and 1 mm in thickness. The electrical resistance and the thermal conductivity of the BN material and the carbon were estimated to be about 100^{14} and $0.9 \Omega \cdot \text{cm}^{15}$ and $50\text{--}60^{14}$ and $40 \text{ W/m} \cdot \text{K}^{15}$ at $1700\text{--}1800^\circ\text{C}$, respectively. PECS was performed using the BN spacer or the carbon spacer at 1650°C (optical pyrometer temperature) for 4 min. The shrinkage vs. time curves were almost the same for both the spacers. The bulk densities and α -phase contents in the sintered specimens were 3.241 g/cm^3 and 67% for the carbon spacer and 3.242 g/cm^3 and 60% for the BN spacer, respectively. Although Kinemuchi et al.¹⁶ found that the PECS promoted the reaction between the coated-carbon and oxidation layer on Si_3N_4 powder, the sintering was not affected by the spacer material in this experiment. It is concluded that substantial electrical power did not pass through the specimen.

As discussed above, we believe that the electric power or current which passes through the specimen has no effect. There still remains the question as to whether a plasma forced by an electric discharge between powders affects the sintering or not because the electric discharge will occur when the gap between the powder particles is very small, even if the total voltage is only a few volts. Logically, it is impossible to prove <no effect>. In this sense, we conclude that, in this experiment, we could not observe any valid effect of the plasma in the sintering of an electrically insulating material such as silicon nitride.

4. Conclusions

Samples of a mixed powder of Si_3N_4 with sintering ad-

ditives, Y_2O_3 5 mass% and Al_2O_3 3 mass%, were sintered both by PECS and HP.

(1) The temperature of the specimen in the case of PECS was estimated, from the data on the bulk density, α -phase content, microstructure and direct temperature measurement using a thermocouple, to be about 150°C higher than that of the die as measured by the optical pyrometer. From the facts, PECS is not recognized to be a low-temperature sintering process.

(2) As the spacer set on both sides of a specimen, BN was used as well as carbon. The shrinkage curve, the bulk density and α -phase content were not affected by the type of spacer material. Therefore, we concluded that we could not observe any valid effect of the plasma in the sintering of an electrically insulating material such as silicon nitride.

(3) The rapid consolidation to maintain nanometer-scale grain size was thought to be one of the advantage of PECS.

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