Effect of Particle Size of Powders Ground by Ball Milling on Densification of Cordierite Ceramics

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コーディエライトセラミックスの緻密化に及ぼすボールミル粉碎原料粉末の粒子径の影響

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Mixtures of calcined kaolin, calcined talc and alumina were ground to submicron particle size by ball milling, and the effect of particle size of the ground mixtures on the densification behavior of a cordierite sintered body was studied. As the particle size of the ground mixtures became smaller, the raw material powders were mixed more uniformly and the formation temperature of α -cordierite became lower. Dense and pore-free sintered bodies were obtained by firing ground mixtures with particle size smaller than $0.39\ \mu\text{m}$ at temperatures as low as 1200°C . Cordierite sintered bodies prepared from mixtures with particle size $0.39\ \mu\text{m}$ or smaller by grinding natural raw materials had bending strengths ranging from 140–160 MPa, and these values were larger than that of cordierite glass-ceramics reported by Hayashi et al.¹⁾ The thermal expansion coefficients of dense, high-strength cordierite bodies increased, because anisotropic thermal expansion could not lower the amount of thermal expansion in the pore-free body.

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1. Introduction

Cordierite ceramics are useful materials with a low thermal expansion coefficient. However, it is difficult to make a dense cordierite body with high strength using natural raw materials, because the difference between the crystallization and decomposition temperatures for cordierite is very small in a sintering process. Although cordierite sintered bodies produced as glass-ceramics^{1)–3)} or prepared from raw materials by the sol-gel method, are predicted to have high strength,^{4)–7)} the preparation processes are complicated and usually require a high cost. Recently, it was reported that dense cordierite ceramics were made from kaolinite and basic magnesium carbonate,⁸⁾ or ultrafine particles of magnesium hydroxide prepared by the precipitation method.^{9),10)}

In order to develop a preparation method for dense cordierite bodies with high strength from natural raw materials, we have been studying the microstructure and the physical properties of cordierite bodies prepared from calcined kaolin, calcined talc and alumina. We have reported the following results elsewhere.^{11)–13)} Talc grains dissolved and gave residual pores of a similar size during the sintering process of a cordierite body.¹¹⁾ As the particle size of ground talc became smaller, the pore size and the porosity of the sintered body decreased and its mechanical strength increased.¹²⁾ Furthermore, the sintered body became denser with decreasing particle size of the ground kaolin in the same manner as the ground talc.¹³⁾ The reaction process that occurred in the mixture composed of several kinds of preground powders was very complicated, and it was difficult to remove pores from the sintered body even if mixtures from the finely ground powders were used.

In the present study, mixtures that are prepared from calcined kaolin, calcined talc and alumina are ground by ball milling for various durations, and the effect of the particle size of ground mixtures on the microstructure and the

physical properties of the sintered bodies is examined.

2. Experiments

Starting raw materials were Georgia kaolin ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, Sumitomo, SSK), talc from Santon Province in China ($3\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$, Sobue Clay, Steatalc) and α -alumina (Al_2O_3 , Showa Denko K.K., AL-160SG). Kaolin and talc were calcined at 1000°C for 5 h. Figure 1 shows the procedure for preparing the ground mixtures. Calcined kaolin was ground to an average particle size of $1\ \mu\text{m}$ by wet ball milling in ethanol with an alumina pot and alumina balls of 3 mm in diameter. Calcined talc was ground also to an average particle size of $1\ \mu\text{m}$ in the same manner. α -alumina with an average particle size of $0.5\ \mu\text{m}$ was mixed with the mixture of ground kaolin slurry and talc slurry to give the following cordierite composition ratio of $\text{MgO} : \text{Al}_2\text{O}_3 : \text{SiO}_2 = 13.2 : 37.8 : 49.0$ mass%, which was reported to give the lowest thermal expansion coefficient by Lachman et al.¹⁴⁾ After grinding these mixtures for 24, 72, 120, 168 and 240 h, their particle size distributions were measured using a particle size analyzer (Shimadzu Corp., SA-CP3L) based on the centrifugal sedimentation method. The chemical compositions of the ground mixtures were determined by the low dilution fusion method using an X-ray fluorescence spectrometer (Rigaku Denki, RIX 2000).

Then each ground mixture was mixed with 2 mass% binder (Chukyo Yushi, Seruna SE604). The mixed slurry was concentrated using a hot plate with a stirrer, dried at 80°C , and then passed through a $175\ \mu\text{m}$ sieve to produce granules. The granules were pressed uniaxially into pellets of 14 mm in diameter and rectangular specimens of $50 \times 25 \times 3\ \text{mm}$ at 30 MPa. The pellets were sintered at 1050, 1100, 1150, 1200, 1250, 1300, 1350 and 1400°C , each for 1 h.

Apparent porosity of the sintered bodies was measured by the Archimedes immersion method in water. Crystalline phases were identified by X-ray diffraction analysis (Philips, PW1729). To estimate the quantitative changes of the crystalline phases in the sintered bodies, X-ray intensities of the following diffraction peaks for several

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Fig. 1. Procedure for preparing ground mixture.

crystalline phases were measured, that is, 121 reflection for mullite, 420 reflection for enstatite, 012 reflection for corundum, 111 reflection for cristobalite, 311 reflection for spinel, 244 reflection for sapphirine and 211 reflection for α -cordierite. The microstructure of the sintered bodies was observed using a scanning electron microscope (JEOL, JSM-840).

The rectangular specimens were sintered at 1300 and 1350°C for 1 h, and then were cut, using a diamond cutting wheel, into bending test pieces (40×4×2 mm). The six bending test pieces for each sintering temperature and each ground mixture were subjected to the three-point bending test. Furthermore, thermal expansions of the specimens were measured by thermomechanical analysis (Shinku Riko, TMA9000) at a heating rate of 10°C/min in the temperature range from 50 to 900°C.

3. Results and discussion

3.1 Chemical composition and average particle size of ground mixtures

Table 1 shows the chemical compositions of the ground mixtures. The mixtures were prepared from natural raw materials such as i.e., kaolin and talc, so it is expected that the mixtures contain impurities such as Fe_2O_3 , TiO_2 , CaO , Na_2O and K_2O . The total amount of these impurities in the ground mixtures is about 1.4–1.6 mass% regardless of grinding time.

Table 1. Chemical Composition of Ground Mixtures

grinding time hour	MgO	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	TiO ₂	CaO	Na ₂ O	K ₂ O
	mass%							
24	12.9	37.3	48.4	0.33	0.78	0.17	0.10	0.06
72	13.2	37.3	48.1	0.34	0.78	0.16	0.13	0.06
120	12.9	37.4	48.3	0.32	0.83	0.15	0.10	0.06
168	12.9	37.9	47.8	0.39	0.77	0.16	0.10	0.06
240	13.1	37.2	48.1	0.34	0.78	0.17	0.28	0.05

Fig. 2. Relationship between milling time and particle size of ground mixtures.

ding time. Since Al_2O_3 content in any of the ground mixtures is predicted to be similar to that of cordierite, the ground mixture seemed not to be contaminated with powder abraded from the grinding media during ball milling.

Figure 2 shows the average particle size of the ground mixtures as a function of milling time. Under the grinding conditions adopted in this experiment, the average particle size of ground mixtures decreased with increasing grinding time. Up to a grinding time of 120 h, the average particle size of the ground mixture shows a marked reduction rate and decreases from 0.51 to 0.39 μm . However, when grinding time exceeds 120 h, the reduction rate of the average particle size becomes very small and the difference in the average particle size between the ground mixtures at grinding times of 120 and 240 h is 0.03 μm . In ball milling of Al_2O_3 powder using an alumina pot and alumina balls of 3 mm in diameter, the reduction rate to an average particle size of 0.5 μm was large, but grinding did not progress much under 0.5 μm . With increasing grinding time, the reduction rate of the average particle size gradually became small because of an increase in the particle number of ground powders.¹⁵⁾ Although calcined kaolin and calcined talc seem to be easy-to-grind materials in comparison to alumina, it is thought that the increase in the particle number of the ground mixture results in the small reduction rate of the average particle size with increasing grinding time.

3.2 X-ray diffraction analysis of sintered bodies

Figure 3 shows the X-ray diffraction intensity of each crystalline phase in the bodies sintered at various temperatures from the mixture ground for 24 h (average particle size of 0.51 μm). The peak intensity of mullite is maximum at 1100°C sintering and disappears at 1150°C. The peak intensities of enstatite and corundum only nominally change from 1050 to 1100°C, but decrease rapidly at 1150°C and disappear at 1200°C. Spinel and sapphirine are generated in the temperature range from 1100 to 1150°C, and the amounts generated show maximum values at 1150°C. Cristobalite, the amount of which is maximum at 1150°C, is thought to be formed by the crystallization of amorphous silica decomposed from kaolin and talc. At 1200°C, α -cordierite is formed instead, while the amounts of spinel, sapphirine and cristobalite decrease. Consequently, cristobalite disappears at 1250°C, the amounts of sapphirine decreases, while the amount of α -cordierite increases rapidly. The amount of α -cordierite is predicted to reach a maximum at 1300°C and then to decrease at 1350°C due to particle decomposition. Finally, the body sintered at 1350°C consists of α -cordierite and a small amount of sapphirine. The

Fig. 3. X-ray diffraction intensity of each crystalline phase in the bodies sintered at various temperatures from the mixture ground for 24 h.

○ Mullite, △ enstatite, ▲ corundum, ◆ spinel, ◇ sapphirine, ○ cristobalite, ● α-cordierite.

Fig. 4. X-ray diffraction intensity of each crystalline phase in the bodies sintered at various temperatures from the mixture ground for 240 h.

○ Mullite, △ enstatite, ▲ corundum, ◆ spinel, ◇ sapphirine, ○ cristobalite, ● α-cordierite.

remaining small amount of sapphirine might have resulted from an alumina-rich composition in comparison with the theoretical cordierite composition in this study.

Figure 4 shows the X-ray diffraction intensity of each crystalline phase in the bodies sintered at various temperatures from the mixture ground for 240 h (average particle size of $0.36 \mu\text{m}$). In the case of $0.36 \mu\text{m}$, the spinel phase is detected at 1050°C , which is 50°C lower than that of in the case of $0.51 \mu\text{m}$. The peak intensities of corundum, enstatite, mullite and spinel decrease rapidly from 1100 to 1150°C , and completely disappear at 1150°C . The body sintered at 1150°C is composed of cristobalite, sapphirine and α-cordierite. α-cordierite is also crystallized at a temperature 50°C lower than that in the case of $0.51 \mu\text{m}$. At sintering temperatures above 1150°C , the quantitative changes of these three crystalline phases indicate a similar tendency regardless of the particle size of the ground mixtures. The ground mixture with fine powders gives a larger

amount of α-cordierite at lower temperatures than that with coarse powders.

Sumi et al.⁹⁾ reported that the mixture of kaolinite and ultrafine particles of magnesium hydroxide gave dense α-cordierite ceramics with a relative density of 97.7% at 1350°C . In the reaction process of material powders during sintering, μ-cordierite, which was crystallized from the homogeneous amorphous state of what with the $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ composition, was transformed into α-cordierite. In this study, α-cordierite ceramics were obtained after 1300°C sintering without the crystallization of μ-cordierite. It can be concluded that this difference in the crystalline phase during the sintering process depends on the difference in the diffusibility of the MgO component in magnesium hydroxide and talc.

3.3 Apparent porosity in sintered bodies

Figure 5 shows the apparent porosity of the sintered bodies from the mixture with several particle sizes as a function of the sintering temperature. The apparent porosity of the sintered bodies for all ground mixtures decreases rapidly in the temperature range from 1050 to 1150°C , and then, at a sintering temperature above 1150°C , the rate of decrease gradually becomes lower. At the same sintering temperature, the apparent porosity decreases with a decrease in the particle size of ground mixtures.

In the sintered bodies obtained from the ground mixture with smaller particle size than $0.39 \mu\text{m}$, the apparent porosity is almost zero at 1200°C . The apparent porosity for the ground mixture with a particle size of $0.44 \mu\text{m}$ also becomes zero at 1250°C . Only the apparent porosity of the sintered body of $0.51 \mu\text{m}$ is 14.8 vol% even after sintering at 1400°C .

Three kinds of raw materials, ground calcined kaolin with an average particle size of $0.51 \mu\text{m}$, ground calcined talc with $0.50 \mu\text{m}$ and alumina powder with $0.50 \mu\text{m}$, were mixed into the cordierite composition by ball milling for 1 h, and after sintering at 1400°C , its apparent porosity was about 10 vol%.¹³⁾ As mentioned above, in this study the sintered body obtained from the mixture with a particle size of $0.51 \mu\text{m}$ showed a high apparent porosity. According to Sumi et al.,⁸⁾ bead milling resulted in a finer mixture of kaolinite and basic magnesium carbonate than ball milling, and dense α-cordierite ceramics with relative densities $\geq 95\%$ were obtained from this fine mixture. If the particle size of the mixture becomes smaller than $0.44 \mu\text{m}$, it would be possible to produce dense, pore-free cordierite ceramics even from natural raw materials.

3.4 Microstructure of cordierite sintered bodies

Figure 6 shows SEM micrographs for the fractured surface of specimens sintered at 1300°C . In the sintered body

Fig. 5. Effect of particle size of ground mixtures on apparent porosity of sintered bodies.

Fig. 6. SEM micrographs for the fractured surface of cordierite bodies sintered at 1300°C.
(a) 0.51 μm , (b) 0.44 μm , (c) 0.39 μm , (d) 0.38 μm , (e) 0.36 μm .

obtained from the ground mixture with an average particle size of 0.51 μm , many continuous pores are observed. As the particle size of ground mixtures decreases from 0.44 to 0.39 μm , the number of pores decreases considerably, and closed pores become smaller and spherical in shape. In particular, in the sintered body obtained from mixtures with average particle size of 0.38 μm , the number of pore is the least. Inversely, in the case of 0.36 μm , both the number and the size of pores increase slightly. These SEM micrographs indicate that dense α -cordierite ceramics are produced from ground mixtures with an average particle size below 0.44 μm , in the same manner in the experimental result for apparent porosity shown in Fig. 5.

Figure 7 shows SEM micrographs for the microstructures of two sintered bodies at 1300°C. In micrograph (a) for the sintered body obtained from a mixture with average particle size of 0.51 μm , the grain size of cordierite is not uniform and is in the range from 0.5 to 3 μm . This seems to be a result of the insufficient mixing and grinding of raw materials due to short grinding time. In particular, the grain size of cordierite close to pores is very large. As most pores are formed by the melting of talc particles,¹¹⁾ it is considered that the large cordierite grain grew in the liquid phase formed by melting of the talc particles. In micrograph (b) of the sintered body obtained from a mixture with average particle size of 0.36 μm , the grain size of cordierite is 0.5 to 1 μm and uniform compared with the body from 0.51 μm . A cordierite body with small uniform grains was obtained using a finer-powder ground mixture.

Although microcracks in cordierite ceramics are sometimes caused by the thermal expansion anisotropy of

Fig. 7. Cordierite grains of bodies sintered at 1300°C.
(a) 0.51 μm , (b) 0.36 μm .

cordierite crystals,¹⁶⁾ there are no microcracks in the sintered bodies, with particle sizes of 0.51 and 0.36 μm , as shown in Fig. 7. This is considered to result in the small grain size of cordierite in the sintered body compared with the critical size which generates microcracks due to the thermal expansion anisotropy of the crystal.

3.5 Bending strength and thermal expansion coefficient of cordierite bodies

Figure 8 shows the bending strengths of cordierite bodies sintered at 1300°C and 1350°C. The bending

Fig. 8. Effect of particles size of ground mixtures on bending strength of cordierite bodies sintered at 1300°C (○) and 1350°C (●).

Fig. 9. Effect of particle size of ground mixtures on thermal expansion coefficient of cordierite bodies sintered at 1300°C (○) and 1350°C (●).

strengths of cordierite bodies at both sintering temperatures increase from 80 to 160 MPa with decreasing particle size of ground mixtures. The low bending strengths in the sintered bodies from the ground mixture with particle sizes of 0.51 and 0.44 μm result in some residual pores. However, in the cases of 0.39, 0.38 and 0.36 μm , the fired bodies have bending strengths of 140–160 MPa at firing temperatures of both 1300 and 1350°C. These bending strength values are larger than that of cordierite glass-ceramic.¹⁾

Figure 9 shows the thermal expansion coefficients of cordierite bodies sintered at 1300 and 1350°C. The thermal expansion coefficients increase from 1.92 to $2.13 \times 10^{-6}/^{\circ}\text{C}$ for bodies sintered at 1300°C, and from 1.80 to $2.10 \times 10^{-6}/^{\circ}\text{C}$ for that sintered at 1350°C, with decreasing particle size of the ground mixtures. The thermal expansion coefficient of the sintered body is a larger value in denser cordierite bodies.

The thermal expansion coefficient, $2.1 \times 10^{-6}/^{\circ}\text{C}$, of densest cordierite body obtained in this experiment is somewhat larger than that of a dense cordierite body with a theoretical cordierite composition, 1.7 – $1.8 \times 10^{-6}/^{\circ}\text{C}$ (25–900°C).^{17),18)} It is thought that the cordierite body in this study contains a small amount of sapphirine with a thermal expansion coefficient as high as $5.4 \times 10^{-6}/^{\circ}\text{C}$.¹⁹⁾

The thermal expansion coefficients show a tendency to increase in dense and pore-free bodies obtained from ground mixtures with fine particles. The small amount of thermal expansion of the cordierite body is caused partly by its thermal expansion anisotropy. On heating, cordierite shows a small amount of thermal expansion in the direction of the *a*-axis but slight contraction in the direction of the *c*-axis.^{20),21)} It is considered that such expansion and contraction of the cordierite crystal easily occur in the sintered bodies with high porosity, and consequently, the thermal expansion coefficient of the body may decrease with increasing particle size of the ground mixture. On the other hand, the thermal expansion coefficient of a dense cordierite body obtained from a ground mixture with fine particles is a large value, because expansion and contraction of the crystal are difficult to occur.

4. Conclusions

Mixtures of calcined kaolin, calcined talc and alumina were ground into a submicron powder by ball milling, and the effect of the particle size of the ground mixture on the

densification behavior of a cordierite sintered body was studied. The results obtained are summarized as follows.

(1) As the particle sizes of the ground mixtures became smaller, mixing of the raw material powders was more uniform and α -cordierite formed at a temperature as low as 1150°C, which was about 50°C lower than that of the usual ground mixture of coarse powders.

(2) The ground mixtures with particle sizes smaller than 0.39 μm gave dense and pore-free bodies sintered at a temperature as low as 1200°C.

(3) The sintered bodies prepared from mixtures with particle size of 0.39 μm or smaller had bending strengths of 140–160 MPa, when they were sintered in the temperature range of 1300 to 1350°C. Those bending strengths were higher than those of cordierite glass-ceramics. Based on these results obtained, it is clear concluded that kaolin and talc can be used as raw materials to produce a dense, high-strength cordierite body, if the mixture is ground to particle sizes smaller than 0.39 μm .

(4) The thermal expansion coefficients of dense, high-strength cordierite bodies increased, because anisotropic thermal expansion does not lower the amount of thermal expansion in pore-free bodies.

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