Effect of particle size of tabular talc powders on crystal orientation and sintering of cordierite ceramics

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Cordierite ceramics were prepared from several types of kaolin powders and talc powders having various median particle size with nanometer-sized alumina sol. Powder mixtures were uniaxially pressed, followed by cold isostatic pressing to make thin compacts. Crystal orientation of talc particle and resultant cordierite were evaluated using the X-ray diffraction profile measured on the uniaxially pressed surface of calcined compacts and sintered compacts, respectively. Coarser talc powders above 3 μm aligned their c -axis in vertical to the uniaxially pressed surface of the calcined compact during uniaxially pressing, owing to highly anisotropic tabular shape. The crystal orientation of resultant cordierite increased with an increase in the crystal orientation of talc powders on the pressed surface. This result indicated that the c -axis of cordierite crystal preferably oriented vertically to the c -axis of talc particle oriented. Using the combination of kaolin powders below 5 μm and talc powders having median particle size between 3 and 5 μm , densely sintered cordierite, having a relative density of 95% and high crystal orientation of approximately 85% [$I_{110}/(I_{110}+I_{002})$], could be obtained.

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1. Introduction

Cordierite ($2\text{Al}_2\text{O}_3 \cdot 2\text{MgO} \cdot 5\text{SiO}_2$) is in the hexagonal crystal structure and has large anisotropic coefficients of thermal expansions (CTEs) of 2.5×10^{-6} and $-0.9 \times 10^{-6} \text{K}^{-1}$ along the a and b axes, and c axis, respectively. Sintered cordierite ceramics have low CTE of approximately $1.7 \times 10^{-6} \text{K}^{-1}$ in the range from room temperature to 900°C. Hence, they have superior thermal shock resistance. It has been considered to be difficult to produce dense cordierite ceramics from natural raw materials such as kaolin ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) and talc ($3\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$), since they incongruently melt near the sintering temperature. For these reasons, porous cordierite ceramics have been prepared by extruding the powder mixtures composed mainly of kaolin and talc, and have been utilized for a honeycomb structured catalyst carrier in car exhaust systems and a diesel particulate filter (DPF). It is well known that the porous cordierite prepared from kaolin and talc exhibits extremely low CTE less than $1.0 \times 10^{-6} \text{K}^{-1}$ along the direction parallel to extruding direction since the c -axis of cordierite crystal having negative CTE aligns parallel to the extruding direction during a sintering reaction and thermal reaction.^{1),2)} When cordierite ceramics are prepared from mixtures of kaolinite, talc and alumina, preferable orientation of cordierite crystals occurs, because tabular kaolinite particles preferably orient in the green bodies and the resultant fired body has inherited property from the green body.³⁾ Many researchers^{4),5)} also reported that structure of tabular kaolinite mainly contribute to the preferable orientation of cordierite crystals. Moreover, several researchers⁶⁾⁻⁹⁾ reported that talc powders react with Al_2O_3 component in the other raw materials to form eutectic melt during thermal reaction, and as a result, tabular frame work

of talc particle was destructed during firing. From these reports, exclusively the crystalline structure or the anisotropic tabular shape of tabular kaolinite particles has long been believed to affect the crystal orientation of cordierite.

On the other hand, talc powders also have tabular particle shape and layered structure similar to kaolinite. In this study, cordierite ceramics were prepared from several types of kaolin powders and tabular talc powders having various particle size distributions with nanometer-sized alumina sol. Crystal orientation of talc particles and crystal orientation of resultant cordierite were evaluated using the X-ray diffraction measured on the surface of calcined and sintered compact, respectively. From the relation between two evaluated crystal orientations, effect of crystal orientation of talc powders on the preferable orientation of cordierite crystals were clarified. Using the optimum combination of kaolin and talc powders, we could prepare the dense cordierite ceramics having as high crystal orientation as a cordierite honeycomb structured catalyst carrier.

2. Experimental procedure

2.1 Materials

Seven types of kaolin powders designated as BR, J, UK, GB, KG, NK and NZ, and talc powder (KCM Corp, Haicheng, China) were individually wet-milled with alumina balls ($\phi = 20 \text{ mm}$) in water, and then classified via elutriation into prescribed median particle sizes.

Table 1 shows the crystalline phase, median particle size, and the chemical composition of 7 types of kaolin powders. Each kaolin powders have only a small amount of alkali and alkali earth metal oxide. Their median particle size determined by a laser diffractometry are also shown in Table 1. Five types of talc powders having median particle size between 1.8 and 16.1 μm were obtained via elutriation as shown in Table 2.

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Table 1. Crystalline phase, median particle size and chemical component of seven types of kaolin powders

	BR	J	UK	GB	KG	NK	NZ
Crystalline phase	Kaolinite	Kaolinite	Kaolinite	Kaolinite	Dickite	Dickite	Halloysite
Median size/ μm	0.5	2.7	0.5	1.5	5.7	5.6	0.4
SiO ₂	45.54	44.9	47.19	46.46	46.99	45.67	45.66
Al ₂ O ₃	39.54	38.6	37.66	38.39	37.71	39.82	38.86
Fe ₂ O ₃	0.18	0.57	0.47	0.52	0.49	0.04	0.18
TiO ₂	<0.01	1.6	0.02	0.01	0.24	0.2	0.08
CaO	0.01	0.11	0.03	0.01	0.01	0.13	<0.01
MgO	0.03	0.11	0.27	0.23	0.07	0.05	0.02
K ₂ O	0.1	0.07	0.47	0.01	0.15	0.03	<0.01
Na ₂ O	0.01	0.01	0.02	0.01	0.05	0.1	<0.01
P ₂ O ₅	0.03	—	0.11	—	—	—	0.07
Ig.Loss	14.55	13.7	13.52	14.33	13.73	13.96	15.1
Total	99.99	99.67	99.76	99.97	99.44	100	99.97

Table 2. Median particle size and chemical component of elutriated talc powders

Sample name	T2	T3	T5	T9	T16
Median size/ μm	1.8	2.7	5.2	9.2	16.1
SiO ₂	62.45	62.45	62.81	62.91	62.54
Al ₂ O ₃	0.27	0.18	0.17	0.13	0.02
Fe ₂ O ₃	0.06	0.06	0.06	0.06	0.05
TiO ₂	<0.01	<0.01	<0.01	<0.01	<0.01
CaO	0.03	0.08	0.05	0.05	0.33
MgO	29.49	30.79	30.94	31.29	31.91
K ₂ O	<0.01	<0.01	<0.01	<0.01	<0.01
Na ₂ O	<0.01	0.01	0.01	<0.01	0.02
P ₂ O ₅	<0.01	<0.01	<0.01	<0.01	0.05
Ig.Loss	7.42	6.32	5.86	5.47	5.04
Total	99.72	99.89	99.9	99.91	99.96

2.2 Preparation

Each kaolin powders, talc powders having various particle size distributions and nanometer-sized alumina sol (Nissan Chemical Industries Co. Ltd.) were ultrasonically dispersed in the stoichiometric composition of cordierite (2MgO·2Al₂O₃·5SiO₂), and then the mixtures were stirred and dried under an infrared lamp. Forty mass % of kaolin powders necessary for preparation of the mixtures were replaced with calcined NZ kaolin at 700°C in order to suppress a crack occurrence in the sintered body during heating. The powder mixtures were uniaxially pressed into a 25 mm-diameter die at the pressure of 98.0 MPa followed by a cold isostatic pressing at the pressure of 196 MPa. The resultant green compacts were heated to 1000°C in an electric furnace at the rate of 5°C/min and then heated at the rate of 2.5°C/min from 1000 to 1350°C. The furnace was maintained at 1350°C for one hour and then it was left to cool.

2.3 Characterization

Particle size distributions of kaolin powder and talc powder were measured with laser diffraction particle sizer (SALD-2200, Shimadzu Corp., Japan). Morphology of various talc powders were individually observed by scanning electron microscope (JSM-6335FM, JEOL Corp., Japan) at an acceleration voltage of 2.0 kV. The X-ray diffraction (XRD) measurement was carried out with RINT2500 (Rigaku Corp., Japan) utilizing Cu K α X-ray and a graphite monochromator. Crystal orientations of talc particle and resultant cordierite were individually semi-quantified with XRD profile measured on the surface of calcined and sintered compacts, and represented as the orientation indices

I_T and I_C . In this study, the orientation index of talc I_T was defined by the next equation.

$$I_T = \frac{I_{004}}{I_{004} + I_{020}} \times 100$$

where I_{004} and I_{020} are the XRD intensity of 004 and 020 planes, respectively, based on the diffraction date (JCPDS 19-0770). Increasing in the I_T indicates that the c -axis of talc particle is oriented vertical to the uniaxially pressed surface of compacts. Pressed compacts were calcined at 700°C to decompose the crystalline structure of kaolinite before XRD measurement, since the diffraction peaks 004 and 020 of talc overlap with those of kaolin. The orientation index of cordierite I_C was calculated by next equation as shown by Lachman et al.¹⁾

$$I_C = \frac{I_{110}}{I_{110} + I_{002}} \times 100$$

where I_{110} and I_{002} are the XRD intensities of 110 and 002 planes respectively, based on hexagonal crystal structure (JCPDS 13-0249). Increasing in the I_C indicates that the c -axis of cordierite crystal is oriented parallel to the pressed surface of the sintered specimens. The relative density of the sintered specimens were calculated from the ratio of the bulk density determined by Archimedes' immersion method to the density of 2.507 g/cm⁻³ calculated from lattice parameters of hexagonal cordierite. The coefficient of thermal expansion (CTE) anisotropy of the sintered cordierite compacts were measured with thermo dilatometer (TMA8310, Rigaku Corp., Japan) at a heating and cooling rate of 10°C/min between room temperature and 900°C.

3. Results and discussions

3.1 Crystal orientation of talc powders

Figure 1 shows the SEM images of various talc powders. When ball-milled talc powder has the smallest median particle size of 1.8 μm (T2), its tabular shape was almost broken down. Above 2.7 μm in a median particle size (T3–T16), talc powders exhibited anisotropic tabular shape. Their anisotropic tabular shape was clearly observed for talc powders having a large median particle size.

According to the works by Hampel et al.¹⁰⁾ and Chen et al.,¹¹⁾ compacts mainly composed of kaolinite powders anisotropically shrank during the firing process, since kaolinite powders having layered crystal structure aligned well in compacts by pressing. Talc also has a layered crystal structure similar to kaolinite: The crystal structure of talc is constructed by a unit layer, consisting of two SiO₄-tetrahedral layer and one MgO₄ (OH)₂-octahedral

Fig. 1. SEM images of five types of talc powders.

Fig. 2. Relationship between shrinkage anisotropy and median particle size of talc powders.

layer stacked as sandwich, and these unit layers are combined with each other along the *a*-*b* plane by weak Van der Waals force. Additionally, Mg^{2+} , Si^{4+} and O^{2-} are bonded by ionic force in the directions of *a*- and *b*- axes of talc crystal. Therefore, talc powders have an anisotropic tabular shape also similar to kaolinite, as shown in Fig. 1. For these reasons, an anisotropic shape of talc powder was thought to be very influential in the sintering anisotropy of compacts. Figure 2 shows the effect of particle size of talc powders on the shrinkage anisotropy of the compacts sintered at 1350°C. The shrinkage anisotropy was defined as the ratio of the vertical shrinkage to horizontal one in this study. In case for using all types of kaolin powders, the shrinkage anisotropy increased with an increase in the median particle size of talc powders. Especially, increase in the shrinkage anisotropy

Fig. 3. Effect of median particle size of talc powders on orientation index of talc.

was almost proportional to the median particle size of talc powders up to 2.7 μm. Probably, shrinkage anisotropy depended on the degree of shape anisotropy of tabular talc. Above 2.7 μm in median particle size of talc powders, on the other hand, kaolin also affected the shrinkage anisotropy, since the shrinkage anisotropy increase with a decrease in mean particle size of kaolin powders.

In order to estimate the effect of packing orientation of talc powders, crystal orientation index of talc particle I_T was plotted as a function of the median particle size of talc powders. M. J. Murtagh¹²⁾ reported the method estimating quantitatively the degree of anisotropic tabular shape of talc particle from the orientation property of talc particle quantified with the aid of XRD profile measured on glass slides coated with a slurry of talc powders. R. R. Wusirika¹³⁾ adopted Murtagh's method¹²⁾ utilizing a sample holder packed with talc powders to evaluate a morphological property of talc powder for cordierite ceramics and prepared the cordierite ceramics having extremely low CTE from the mixtures using talc powders having an optimum morphological property (orientation property). In this study, on the other hand, the crystal orientation index I_T was directly measured on the pressed surface of the compact of the mixture. Figure 3 shows the orientation index of talc I_T as a function of particle size of talc powders. The I_T rapidly increased with an increase in median particle size of talc powders 1.8 to 2.7 μm. Above 2.7 μm, the I_T increased gradually with a further increase in the median particle size independently on the type of kaolin powders. This suggested the difference of the shrinkage anisotropy with a particle size of kaolin powders in Fig. 2 to be the effect of packing anisotropy of kaolin powders. Talc particles above 2.7 μm exhibited a large anisotropic tabular shape as shown in Fig. 1, so that *c*-axes of these particles aligned well in vertical to the pressed surface of compacts in proportional in the particle size.

Figure 4 shows the relationship between the shrinkage anisotropy of the sintered compacts and the orientation index of talc I_T . The good linear correlation was obtained between the shrinkage anisotropy of the sintered compacts and the orientation index I_T . The difference in the slope of the straight line was thought to be an effect of the particle size and morphology of kaolin powders.

3.2 Effect of the particle orientation of talc powders on crystal orientation of cordierite

Figure 5 indicates the orientation index of cordierite I_C as a function of the orientation index of talc I_T . The I_C increased with

Fig. 4. Relationship between shrinkage anisotropy and crystal orientation index of talc I_T of sintered specimens.

Fig. 5. Relationship between orientation index I_T of talc powders and orientation index I_C of cordierite crystals.

an increase in I_T , and varied depending on the type of kaolin powders for the mixtures. In case for using the kaolin powders J, KG, NK and NZ together with talc powders showing high orientation index I_T about 95%, high crystal orientation indexes I_C about 90% were attained. From these results, crystal orientation of talc powders also contributed to crystal orientation of cordierite, and the c -axis of cordierite crystals was found to align well in vertical to the c -axis of talc particle using talc powders above $2.7\mu\text{m}$. When cordierite ceramics was prepared from the mixtures containing GB kaolin, the I_C showed the lowest value in this experiment, and the reason could not be clarified.

In order to eliminate the effect of crystal orientation of kaolin particles on crystal orientation of cordierite, only calcined NZ kaolin powders was used as a kaolin material for starting mixture and orientation index of talc powder I_T was evaluated using large talc powder having median particle size of $16.1\mu\text{m}$. **Figure 6** shows XRD patterns measured on the pressed surface of as-pressed compacts with that of talc powder dispersing in resin. Only diffraction peaks of talc were observed on the pressed surface of the as-pressed compact, because crystalline structure of NZ kaolin powder completely decomposed. XRD pattern of talc observed on the surface of as-pressed compact was different from that of talc powder dispersing in resin. The diffraction peak 004 vertical to c -axis of talc was clearly observed on the pressed

Fig. 6. XRD patterns of the pressed surface of as-pressed compact from calcined kaolin powder and coarse talc powder (a) and talc powder dispersed in resin (b).

Fig. 7. XRD patterns of the pressed surface of sintered cordierite compact (a) and cordierite powder (b).

surface, while the diffraction peak 020 parallel to c -axis of talc was hardly observed. In this case, the orientation index I_T showed 95.6%, corresponding to the samples using talc powders $16.1\mu\text{m}$ as shown in Fig. 3. XRD patterns of this compact sintered at 1350°C is shown in **Fig. 7** along with a pattern of cordierite powder. On the pressed surface of the compacts, high orientation index of cordierite I_C of 89.2% was obtained and was in good agreement with specimens using J, KG, NK and NZ with the talc powder as shown in Fig. 5. This result clearly indicates that the preferable crystal orientation of tabular talc particles lead to the preferable orientation of cordierite crystals.

3.3 Effect of particle size of talc powders on densification of cordierite ceramics

As well known, sinterabilities of ceramic powder compacts depend on particle size of starting powders. In this section, the

Fig. 8. Relative density of sintered specimens.

Fig. 9. Relative density of specimens with various orientation index I_C of cordierite.

effect of particle size of talc powders on the densification of cordierite ceramics were examined by combinations of many kaolin powders and talc powders. **Figure 8** shows the relative density of the compacts sintered at 1350°C prepared from several types of kaolin powders and talc powders having various particle size distributions with alumina sol. Relative densities of the sintered compacts decreased with an increase in a median particle size of talc powders. When talc powders below 10 μm were used for the mixtures, the relative density of the sintered compacts depended largely on particle size of kaolin powders. The larger kaolin powders for the mixtures became the lower relative density of the sintered compacts. Higher relative density than 95% was accomplished using fine kaolin powders and fine talc powders for the mixtures.

Figure 9 shows the relationship between the relative density and the orientation index of cordierite I_C of the sintered compacts. The dense cordierite ceramics having a higher relative density than 95% with higher crystal orientation index I_C than 85% were prepared, when talc powder in the median particle size between 3 and 5 μm and UK or KG kaolin (both are dickite) were used for the mixtures.

4. Anisotropic CTE of sintered cordierite ceramics

When the anisotropic crystal grains were preferably orientated in polycrystalline body, it should have different CTEs in the vertical direction and the parallel direction. **Figure 10** shows the relationship between the orientation index of cordierite I_C and CTE difference between the directions vertical and parallel to uniaxially pressed surface of specimens heat-treated at 1350°C.

Fig. 10. Relationship between orientation index of cordierite I_C and CTE difference.

The increase in the I_C means that the c -axis of cordierite crystal having negative CTE aligned more favorably in parallel to the pressed surface. Therefore, the CTE difference increased proportionally with an increase in the I_C . When cordierite grains distribute randomly in a polycrystalline ceramics, CTE should be equal in all directions and CTE difference is zero. When cordierite grains of c -axis perfectly aligned in one plane, CTE in this plane is an average value of α_a and α_c . From the thermal expansion measurement of lattice parameter of cordierite crystal by authors,¹⁴⁾ $0.88 \times 10^{-6} \text{ K}^{-1}$ could be obtained. On the other hand, CTE in vertical direction corresponds to that of a -axis $3.36 \times 10^{-6} \text{ K}^{-1}$. In this case, the maximum difference in CTE was calculated to be $2.4 \times 10^{-6} \text{ K}^{-1}$ and was too large to explain the experimental results in Fig. 10.

We already reported that a thermal expansion coefficient of cordierite was lowered by the occurrence of microcracks between domains larger than 40 μm induced by the thermal expansion anisotropy of cordierite crystal axes. In this study, an average thermal expansion coefficient in two directions of many specimens heat-treated at 1350°C was lower than $1.7 \times 10^{-6} / ^\circ\text{C}$ corresponding to the average value of the crystal axes, so that the absolute difference of thermal expansion coefficient was thought to be suppressed by the occurrence of microcracks.

5. Conclusions

In this study, preferable crystal orientation and sintering characteristics of cordierite ceramics were investigated using several types of kaolin powders and talc powders with various median particle size with alumina sol, and the following conclusions were obtained:

The c -axis of talc powders in median grain size of above 3 μm was preferably oriented vertical to the pressed surface of the green compact during uniaxially pressing, since the talc powders having median particle size above 3 μm showed a large anisotropic tabular shape.

The crystal orientation of cordierite increased proportionally with an increase in the crystal orientation of talc powders. Moreover, high crystal orientation was also attained in the case of cordierite ceramics prepared using the combination of calcined kaolin and coarse talc powders. Even if isotropic calcined kaolin was used, resultant cordierite crystals preferably orientated depending on the crystal orientation of talc powders.

By the combination of fine kaolin powders about 5 μm and talc powders with median particle size between 3 and 5 μm, dense cordierite ceramics having a higher relative density than 95%

were attained with high crystal orientation index I_C of about 85%, corresponding to the orientation property of a honeycomb structured catalyst carrier of porous cordierite.

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