Preparation of Cordierite Ceramics from Metal Alkoxides (Part 1)

Preparation and Characterization of the Powder

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A new method for preparing homogeneous cordierite ceramics by a sol-gel process is described. Reactive and fine cordierite-type amorphous powder with high homogeneity was prepared by the sol-gel method. The hydrolysis of metal alkoxides used as starting materials was controlled. Namely, Si(OC₂H₅)₄, with a hydrolysis rate lower than that of Mg(OC₂H₅)₂ or Al(OC₃H₇i)₃, was partially hydrolyzed and then mixed or reacted with Mg and Al alkoxides which had been reacted in butyl-alcohol. The cordierite powders prepared by the sol-gel method were characterized by infrared spectroscopy, X-ray diffraction study, differential thermal analysis (DTA) and transmission electron microscopy (TEM) with an energy dispersion X-ray microprobe analyzer (EDX). Homogeneous cordierite powders were obtained from Mg(OC₂H₅)₂, Al(OC₃H₇i)₃ and Si(OC₂H₅)₄. The homogeneity of resultant oxides depended upon the hydrolysis method of alkoxides. [Received July 14, 1986]

Key-words: Cordierite, Reactive powder, Metal alkoxide, Hydrolysis rate, Partial hydrolysis

1. Introduction

Cordierite ceramics have intrinsic low thermal expansion coefficient and are practically used as a carrier of catalyst for exhaust gas control in automobiles. Cordierite ceramics are also expected to be used as heat exchangers for gas turbine engines, industrial furnaces and integrated circuit substrate. But it has been impossible to sinter pure cordierite without any sintering aid. Adding the sintering aid resulted in a large thermal expansion and an increase of dielectric constant8). Therefore, the preparation of homogeneous and fine cordierite powder has been considered to be indispensable. In Part 1, preparation and characterization of such a fine and homogeneous cordierite powder is described and the sintering of the powder is carried out in Part 2.

It is well known that alkoxy-derived gel powders are very fine and reactive because desiccated gel has a higher free energy than that of glass or crystal9). However, in the multi-component systems, the difference in hydrolysis rates of each alkoxide caused inhomogeneity in the resultant oxides10-14). For example, the hydrolysis rate of tetraethylorthosilicate (TEOS) is too low to prepare homogeneous amorphous solids. Therefore, partial hydrolysis of TEOS prior to being mixed with other alkoxides should be necessary to prepare the silicates.

Yoldas demonstrated that the degree of hydrolysis of alkoxides could be controlled by the hydrolysis temperature, types of catalyst and concentration of alkoxides and water7,8). Slow addition of a small amount of water is also effective to avoid inhomogeneity in the resultant gels3-5). However, it has been difficult to determine the optimum condition of hydrolysis. In this paper, the preparation of a fine and homogeneous cordierite powder by a partial hydrolysis method to bring about homogeneous hydrolysis and subsequent dehydration condensation is discussed and the prepared powders are characterized.

2. Experimental procedure

2.1 Preparation of gel powders

Three series of gel powders having the cordierite composition were prepared from Mg(OC₂H₅)₂, Al(OC₃H₇i)₃ and TEOS. A schematic diagram of the sol-gel process is shown in Fig. 1. The A-series of powder was prepared by mixing TEOS, Al(O-C₃H₇i)₃ and Mg(OC₂H₅)₂ at 90°C and by adding sufficient amount of water
(H₂O/Si(OC₂H₅)₄=20 mol/mol) to completely hydrolyze the alkoxides by vigorous stirring at room temperature. The B- and C-series of powders were prepared by using the partial hydrolysis method. TEOS was partially hydrolyzed for 50 and 100 h at 70°C in the B- and C-series, respectively. The catalyst used was hydrochloric acid (HCl/Si(OC₂H₅)₄=0.1 mol/mol). Concentration of TEOS was 1 (mol/1) and the ratio of water to TEOS was 4 and 2 (mol water/mol TEOS) in the B- and C-series, respectively. The partially hydrolyzed TEOS solutions were reacted with magnesium-aluminum double alkoxide and transparent solutions with cordierite composition were prepared. These solutions were completely hydrolyzed by adding enough amount of water (H₂O/Si(OC₂H₅)₄=20 mol/mol). All the gel powders obtained were dried at 100°C and calcined up to 1400°C.

2.2 Analyses of the powders
The gel powders dried at 100°C and calcined at each temperatures for 2 h were analyzed. A differential thermal analysis (DTA) was carried out in the air up to 1350°C. Crystalline phases precipitated were identified by X-ray diffraction using Cu Kα radiation and the lattice constants of μ- and α-cordierite were calculated by using the sets of (112) and (211) reflections, and (224) and (413) reflections, respectively. An infrared analysis was applied to examine the chemical bonds in the powders. The homogeneous and fine powders prepared by the partial hydrolysis method were observed by TEM and its composition was determined by EDX.

3. Results and discussion
3.1 Control of the hydrolysis rates of alkoxides and preparation of gel powders
In this study, high degree of homogeneity was achieved by the hydrolysis and subsequent polymerization of partially hydrolyzed TEOS and magnesium-aluminum double alkoxide. The hydrolysis process of silicon alkoxides has been reported by many workers⁹⁻¹¹. Sakka and Kamiya investigated the sol-gel transition in the hydrolysis of TEOS by measuring the density, the viscosity, the intrinsic viscosity etc., of the solution¹². But it was still difficult to make a general forecasting with respect to the resulting species. Consequently, the optimum condition of its partial hydrolysis of TEOS should be determined case by case.

The change in the viscosity of the TEOS-ethanol solutions with time is shown in Fig. 2. The catalyst used was hydrochloric acid because hydrolysis in an acidic solution might well near completion before any significant condensation.
even though the water concentration for hydrolysis was high (curves a and e). The hydrolysis reaction was undertaken at 70°C to accelerate the reaction. As shown in Fig. 2, the viscosity of the TEOS solution abruptly increased in a shorter time when a larger amount of water for hydrolysis was added (curve a) and the concentration of TEOS was higher (curve d). The increase in the viscosity with time suggested the increase of polymerization. It has been known that spherical colloidal particles are formed when the hydrolysis-polycondensation of TEOS is carried out with NH₄OH as a catalyst₁³,₁₄ and they are aggregated to form large particles as the reaction progresses₁₅. On the other hand, the acid catalyzed hydrolysis-polycondensation of TEOS results in the formation of chain-like polysiloxane polymers when the water concentration is low₁₂,₁₆ (curves b and c). Therefore, a short chain-like polymer (Si₅O₇)₂₋(OH)ₓ₋₄ (where n was 2 or 3 when the amount of water for hydrolysis was 2 mol/mol TEOS¹⁷) (curve c)) would form and HCl was considered to be superior to NH₄OH as a catalyst because cordierite (Mg₂Al₃(Si₅O₁₈)₆) has a similar structure to beryl and has a cyclic (Si₅O₁₈)₁₃⁻ ion in its structure.

Three series of alkoxy-derived powders (A-C series of powders) were prepared from partially hydrolyzed TEOS solutions, of which the extent of hydrolysis was different, and magnesium-aluminum double alkoxide mixture solution. It was considered that the polymerization of TEOS before being mixed with double alkoxide had fairly progressed in the B-series, which was confirmed by measuring the viscosity of the TEOS solution. On the contrary, there was scarcely in progress in the polymerization of TEOS in the C-series. Accordingly, the highest homogeneity in the resultant powder was expected in the C-series. The reactions in the C-series are considered as follows;

\[
\begin{align*}
\text{Si(OR)}_4 + x\text{H}_2\text{O} & \rightarrow \text{Si(OR)}_{4-x} \text{(OR)}_x + x\text{ROH} \quad (x \geq 2) \\
\text{Mg(OR)}_2 + 2\text{Al(OR)}_3 & \rightarrow \text{RO-Mg} + \text{RO-Al} \\
\text{SiSi-OH} + \text{RO} & \rightarrow \text{SiSi-O-RO}
\end{align*}
\]  

where R is C₅H₅, CH(CH₃)₂, or (CH₃)₂CHCH₂. In the reaction, alkyl groups R could be (CH₃)₂CHCH₂ because (CH₃)₂CHCH₂OH was used as a solvent in this study and if the alkyl group should be exchanged to (CH₃)₂CHCH₂, the hydrolysis reaction of alkoxide would be restrained by steric hindrance. The possibility of the alkyl group in magnesium-aluminum double alkoxide to be (CH₃)₂CHCH₂ was higher, which made a uniform dehydration-condensation of alkoxides possible. Infrared (IR) spectrum of the mixture solution in C-series was different from that of partially hydrolyzed TEOS solution or magnesium-aluminum double alkoxide solution, indicating that the reaction (3) would be proper.

A sufficient of water (H₂O/TEOS=20 mol/mol) was added to hydrolyze the mixed alkoxides or the intermediate compound shown in reaction (3) perfectly after uniform mixing and reaction. Then the solvent was removed at 100°C. The homogeneity was examined later by X-ray diffraction, IR spectra, DTA and TEM.

3.2 Heat-treatment of gel powders and the formation mechanisms of cordierite

DTA and analysis by X-ray diffraction were taken on the three series of powders, which were shown in Fig. 3 and Table 1. No crystalline phase was seen below 900°C (Table 1). Therefore, all the exo- and endothermic peaks (peak Nos. 1-5) in the DTA curves below 900°C correspond to the decarbonizing and desorption of water and alcohol, respectively (Fig. 3). Above 1000°C, β-quartz solid solution, spinel and unknown phase were precipitated in the powders of A- and

![Fig. 3. DTA curves of the powders. A-100; A-series of powder dried at 100°C, B-100; B-series of powder dried at 100°C, C-100; C-series of powder dried at 100°C.](image-url)
B-series. On the other hand, $\mu$-cordierite was the only crystalline phase in the C-series (Table 1). Therefore, the exothermic peaks in the DTA curves around 1000°C (peak Nos. 6, 7 and 8) could be identified as crystallization of spinel (No. 6), $\beta$-quartz solid solution (No. 7) and $\mu$-cordierite (No. 8”), respectively. $\alpha$-cordierite was detected at the temperatures of above 1200°C in all the series and the crystallization temperatures of $\alpha$-cordierite determined from the DTA curves were about 1226°C (No. 9) and about 1298°C (No. 9’) in the A- and B-series, respectively. On the other hand, crystallization temperature of $\alpha$-cordierite in the C-series was about 1140°C (No. 9”) which was lower than that in the A- or B-series. Furthermore, the additional phase of spinel was detected up to 1400°C in the A- and B-series. These results would be due to the higher homogeneity in the C-series than that in the A- or B-series. It was concluded that in the A- and B-series, $\alpha$-cordierite was formed by the solid state reactions among spinel, $\beta$-quartz solid solution and the unknown phase, while in the C-series, $\mu$-cordierite directly transformed into $\alpha$-cordierite.

3.3 Infrared spectroscopy studies and lattice constants of cordierite calculated by X-ray diffraction

As shown in Fig. 4, the infrared spectra of the C-series of powders calcined above 1200°C gave that of $\alpha$-cordierite. The C-series of powder calcined at 1400°C was identified as $\alpha$-cordierite by X-ray diffraction, but its infrared spectrum was similar to that of $\mu$-cordierite. This showed that the C-series of powder calcined at 1400°C for 2 h would be an intermediate state cordierite which transformed into $\beta$-cordierite by a prolonged (more than 2 h) heating at 1400°C. The infrared spectra of the A- and B-series (Fig. 4) did not correspond to that of cordierite and the characteristic bands corresponding to Si-O stretching vibrations were appeared around 1100 cm⁻¹, indicating the formation of $\beta$-quartz solid solution. The characteristic bands of magnesium-aluminum spinel (700 and 526 cm⁻¹) were also observed in the A- and B-series. These results coincided with the X-ray diffraction studies.

In the C-series, the characteristic band corresponding to the Si-O stretching vibrations was observed at lower wavenumbers of about 1050 cm⁻¹ and the absorption peak belonging to the ring structure of SiO₄ tetrahedra of about 800 cm⁻¹ could not be found (Fig. 5). These results suggests that no serious polymerization of TEOS would occur. An infrared spectrum of the C-series powder calcined at 1000°C ($\mu$-cordierite) resembled that of the Mg-cordierite glass (broad bands at 440, 935 and 1100 cm⁻¹) except for the absorption peak at about 700 cm⁻¹ which would be given by M-O stretches (M=Mg, Al) indicating that Si-O-M (M=Mg, Al) bonding would have formed in the case of the C-series powder.
calcined at 1000°C. Lattice constants of the powders (Table 2) were calculated on the assumption that the crystal form of the C-series powders calcined above 1000°C was hexagonal. In practice, μ- and α-cordierite were identified at the same time in the powder calcined at 1100°C, which resulted in the fluctuation of the lattice constant. Lattice constants of the C-series powders calcined above 1200°C were in good agreement with the value reported in ASTM 13-293.

3.4 Transmission electron microscopy

The C-series powders calcined at 800°C, 1200°C, 1300°C and 1400°C for 2h were characterized by TEM with EDX. The results are shown in Fig. 6, Fig. 7 and Table 3. The powder calcined below 800°C was amorphous (Fig. 7(a)) and very fine powders, of which primary particle size was about 100 Å (Fig. 6(a)). And the composition estimated by EDX (beam diameter of approximately 200 Å) coincident with that of stoichiometric cordierite (Table 3). Fluctuation of the composition in each particle analyzed was very small. Fluctuation of the powder composition calcined at 1200°C (Table 3) would probably ascribed to the difference in the respective absorption coefficient of Si, Al and Mg. These results show that the cordierite-type powder prepared from the controlled hydrolysis-polymerization process of metal alkoxides in this study is very homogeneous. The fine particles were gradually incorporated into the large particles with increasing temperature. The electron diffraction patterns of cordierites at 1200°C and 1400°C (Figs. 7(b) and (d)) were superimposed, indicating that a lot of particles had been incorporated and crystallized. This was confirmed by the moire patterns in Fig. 6(b). Amorphous particles were frequently observed in the powder calcined at 1200°C. Considering the fact that the composition of each particle determined by EDX was in good agreement with that of stoichiometric cordierite, it was concluded that the amorphous particles in the powder calcined at 1200°C were due to its small particle size. Therefore, a prolonged heating at 1200°C would result in the crystallization of amorphous particles. At the temperatures above 1300°C, almost all particles were crystallized and their habits were observed (Figs. 6(c) and (d)). The crystallite, approximately 100 Å in diameter, was observed at elevated temperatures. Thus, it was concluded that the C-series of powder was very homogeneous.

4. Conclusions

Homogeneous cordierite powder was prepared by the hydrolysis and subsequent dehydration-

Table 2. Lattice constants of C-series of powders calcined at different temperatures for 2h.

<table>
<thead>
<tr>
<th>Calcination Temp. (°C)</th>
<th>μ-cordierite a₀ (nm)</th>
<th>μ-cordierite c₀ (nm)</th>
<th>α-cordierite a₀ (nm)</th>
<th>α-cordierite c₀ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM 14-269</td>
<td>0.5200</td>
<td>0.5345</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>0.5192</td>
<td>0.5355</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1100</td>
<td>0.5189</td>
<td>0.5364</td>
<td>0.9737</td>
<td>0.9357</td>
</tr>
<tr>
<td>1200</td>
<td>0.9761</td>
<td>0.9354</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1300</td>
<td>0.9761</td>
<td>0.9354</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1400</td>
<td>0.9760</td>
<td>0.9354</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ASTM 13-293</td>
<td>0.9770</td>
<td>0.9352</td>
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</table>

Table 3. Results of the EDX analysis of powders calcined at 800°C and 1200°C for 2h.

<table>
<thead>
<tr>
<th>Calcination Temp. (°C)</th>
<th>MgO (wt.% )</th>
<th>Al₂O₃ (wt.% )</th>
<th>SiO₂ (wt.% )</th>
</tr>
</thead>
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<tr>
<td>800</td>
<td>13.73</td>
<td>34.37</td>
<td>51.90</td>
</tr>
<tr>
<td>1200</td>
<td>13.65</td>
<td>32.89</td>
<td>53.46</td>
</tr>
<tr>
<td>stoichiometry</td>
<td>13.78</td>
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condensation of metal alkoxides. TEOS, of which hydrolysis rate was considerably low compared with that of magnesium or aluminum alkoxides, was hydrolyzed prior to being mixed with magnesium-aluminum double alkoxide and then sufficient amount of water was added for the purpose of perfect hydrolysis and subsequent polymerization. In the course of the dehydration-condensation process, it was deduced that an intermediate compound would form which was shown in reaction (3). The C-series powder prepared in this way was directly crystallized at 1000°C to μ-cordierite and then transformed into α-cordierite at 1100°C. At temperatures above 1200°C, no crystalline phase was detected except for the α- or β-cordierite in the C-series. In the present study, homogeneous cordierite powder was prepared from metal alkoxides, which having been verified by the infrared spectroscopy, X-ray diffraction studies and TEM with EDX.
Fig. 7. Electron diffraction patterns of the C-series powders calcined at different temperatures. (a) 800°C-2 h, (b) 1200°C-2 h, (c) 1300°C-2 h, (d) 1400°C-2 h

References