Preparation and Sinterability of Forsterite Powders Derived from Heterogeneous Alkoxide Solution Containing Fine MgO Powders

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Forsterite (Mg_2SiO_4) precursors were synthesized from heterogeneous alkoxide (tetraethyl orthosilicate : TEOS) solution including very fine MgO powders and homogeneous alkoxide solution with $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The precursors from MgO were crystallized to forsterite with drastically exothermic reaction at about 840 °C. The precursors from $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ consisted of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and little amorphous SiO_2 . The precursors began to crystallize to forsterite at a lower calcining temperature than those from MgO. However, MgO and enstatite (MgSiO_3) existed as a second phase in forsterite powders even at a calcining temperature more than 1000 °C. The forsterite powders obtained from heterogeneous alkoxide solution with fine MgO had excellent sinterability. Sintering temperature of 1400 °C was found to be enough to make forsterite ceramics with theoretical density.

1 Introduction

Synthesis of ceramic precursors by sol-gel process from alkoxide solution has been extensively studied because of high-purity, homogeneity, low temperature processing and fabrication¹⁻³. These advantages are suitable for synthesizing high-purity submicroscopic powders as a starting material. In alkoxide method, first, homogeneous alkoxide solution should be usually prepared. Then the solution is hydrolyzed and polymerized to ceramic precursors. For mixed-oxide ceramics, however, it is very difficult to synthesize homogeneous precursor from mixed alkoxide solution because of difference in chemical reactivity of each alkoxide, such as hydrolysis and polymerization rate⁴. In present study, forsterite ceramic precursor was tried to be synthesized from heterogeneous alkoxide solution including fine MgO powders, not from homogeneous alkoxide solution.

2.1 Preparation of forsterite precursors

Forsterite precursors were synthesized from tetraethyl orthosilicate, TEOS (98% : Aldrich Chem. Co Inc.) and ultra-fine MgO powder (99.98% : Ube Industries Ltd.). The mean particle size of MgO was 10nm. Preparation of the precursors is schematically shown in Fig.1. MgO powders were added to

Fig.1 Schematic of preparing forsterite precursor.

2 Experimental procedure

partially hydrolyzed TEOS solution and subsequent addition of distilled water promoted gelation of the solution. The obtained gels were dried at 100°C and calcined to forsterite at a temperature from 500°C to 1300°C. In order to examine effects of a starting material on properties of precursors and calcined powders, magnesium nitrate solution was added to the alkoxide solution instead of MgO powders (Fig.1(B)).

2.2 Characterization of precursors and calcined powders

Thermal behaviors of precursors were examined with DTA and TGA. Crystalline phases of calcined powders and sintered bodies were identified by XRD analysis. The obtained forsterite powders were compacted to disk (20 x 5mm) at a pressure of 20 MPa and isostatically pressed to 300 MPa. The disk was fired at a temperature from 1250 °C to 1550 °C. The microstructures of forsterite were observed with scanning electron microscopy (SEM). In order to estimate sinterability of each powder, density of sintered bodies were measured as a function of sintering temperature.

3 Results and discussion

Heterogeneous alkoxide solution with MgO powders was creamy white and stable. Subsequent addition of H₂O promoted gelation of the solution. The gelation with a small amount of H₂O ($H_2O/Si(OC_2H_5)_4 = 4$) was finished in about 20 min and the gelation time decreased with increasing a ratio of $H_2O/Si(OC_2H_5)_4$. For $H_2O/Si(OC_2H_5)_4 \geq 7$, for example, the gelation was finished in 10 min during addition of H₂O. The dried precursors with a small amount of H₂O were identified as a mixture of amorphous SiO₂ and MgO. On the other hand, alkoxide solution prepared with $Mg(NO_3)_2 \cdot 6H_2O$ was homogeneous and uniformly transparent. During drying process, however, the solution became translucent to gel because of precipitation of $Mg(NO_3)_2$.

Fig.2 DTA curves of forsterite precursor prepared from MgO and magnesium nitrate.

6H₂O. The nitrate in precursors was identified by XRD analysis.

Fig.2 shows thermal behaviors of forsterite precursors prepared with MgO powders and magnesium nitrate. For the precursor prepared with MgO powders, drastically exothermic reaction occurred around 840 °C. Weight of the precursor was gradually decreased with temperature and no remarkable change was recognized at 840 °C. For the precursor with $Mg(NO_3)_2 \cdot 6H_2O$, on the other hand, only endothermic reaction occurred gently at about 380 °C and weight of the precursor decreased, accompanied with the endothermic reaction. This change at 380 °C was found to be due to the decomposition of nitric group because of the odor and color of the decomposed gas. In order to examine the formation of forsterite phase, XRD analysis was carried out. The patterns of each precursor calcined at various temperatures are given in Fig. 3 and 4. In case of the precursor prepared with MgO powders by using a small amount of H₂O ($H_2O/Si(OC_2H_5)_4 = 4$), no forsterite phase was observed below the exothermic reaction temperature shown in Fig.2, but the precursor all crystallized to forsterite beyond the temperature. Consequently, the exothermic peak was judged to be caused by

Fig.3 XRD patterns for forsterite powders prepared from TEOS and MgO after calcining at various temperatures.

Fig.4 XRD patterns for forsterite powders prepared from TEOS and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ after calcining at various temperatures.

crystallization to forsterite from a mixture of MgO and amorphous SiO_2 . The formation of forsterite was remarkably promoted like self-combustion reaction by heat of the reaction. And the heat was so large to enhance the crystallinity of forsterite powders. As for the precursor prepared with $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, forsterite phase began to form at a lower temperature than that of the precursor with MgO powders. Forsterite phase was recognized to form even at a calcining temperature of 700 °C.

In case of utilizing magnesium nitrate for preparation of forsterite precursors, however, monolithic forsterite powders could not be obtained regardless of a calcining temperature. For example, MgO existed as a second phase at low calcining temperatures, and MgO and enstatite (MgSiO_3) at high temperatures. As mentioned above, the precursors from $\text{Mg}(\text{NO}_3)_2$ consisted of $\text{Mg}(\text{NO}_3)_2$ and a little amorphous SiO_2 macroscopically, according to XRD analysis. Takeuchi⁵⁾ investigated glass-forming region of SiO_2 -MgO system from TEOS and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ by sol-gel method. For a low content of $\text{Mg}(\text{NO}_3)_2$ (0–15 mol% as MgO concentration), no $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was detected in dried gels by XRD analysis and the gels formed as amorphous. For a content more than 20 mol% of MgO, however, more $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ appeared in the dried gels with increasing the content. Concentration of MgO in forsterite is 66 mol% and only $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was detected in this concentration. It is inferred that the gels have a wide distribution in size of precipitated $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and that $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with small size contributes to formation of forsterite at lower temperatures and that some of large $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ are left as MgO powders at higher temperatures.

Powders calcined at 900 °C were pressed to a disk with 20 mm in diameter and 5 mm in thickness and isostatically pressed at a pressure of 300 MPa. The obtained compacts were sintered at various temperatures to examine their sinterability. Fig. 5 shows relative density of sintered forsterite body as a function of sintering temperature. For powders from MgO, sintering at 1400 °C was enough to obtain fully dense forsterite. Higher sintering temperatures made the density only a little lower. Such degradation is inferred to result from remarkable grain growth. Photo. 1 (A) and (B) show typical microstructures of forsterite ceramics sintered at 1400 °C and 1550 °C, respectively. The mean grain size of forsterite sintered at 1400 °C is 2.7 μm and grains

Fig.5 Effect of sintering temperature on relative density of polycrystalline forsterite.

Photo 1 Typical microstructures of forsterite sintered at 1400°C (A) and 1550°C (B).

were relatively uniform. Large cracks are observed on the ceramics sintered at higher temperatures. These cracks are guessed to be caused by remarkable grain growth. For

powders from $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, denser forsterite ceramics were produced at lower sintering temperatures but higher sintering temperatures did not enhance the density. MgO existed in sintered bodies and was inferred to result from MgO in calcined forsterite powders. In order to improve forsterite powders from $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, particle size of precipitated nitrate was expected to be much smaller and uniform. The microstructures of forsterite from $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were almost resemble to those from MgO powders.

4 Summary

Forsterite (Mg_2SiO_4) precursors were synthesized from heterogeneous alkoxide solution including very fine MgO powders and homogeneous alkoxide solution with $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The precursors from MgO were crystallized to forsterite with drastically exothermic reaction at about 840 °C. The precursors from $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ consisted of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and a little amorphous SiO_2 . The precursors began to crystallized to forsterite at a lower calcining temperature than those from MgO . However, MgO and enstatite (MgSiO_3) as second phase existed in forsterite powders even at a calcining temperature more than 1000 °C. The forsterite powders obtained heterogeneous alkoxide solution with MgO showed excellent sinterability.

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