Low-temperature sintering of mullite with alumina and solution derived yttria

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Abstract

Mullite exhibits low dielectric constant, high strength and relatively low thermal expansion coefficient, and therefore, is useful as a substrate for high-speed computer. Mullite is also a candidate material for high-performance low-temperature co-fired ceramic (LTCC) substrate because of the same reasons mentioned above. To apply the mullite substrate to LTCC, the reactivity of the mullite with elements that are contained in the glasses for low-temperature sintering should be investigated to choose the sintering aid for LTCC. In this paper, effect of the small amount of solution-derived yttoria addition on the sinterability of the mullite was investigated for the low-temperature sintering as well as the optimum amount of the alumina addition. The amount of the alumina addition was restricted within the solubility limit in mullite. As a result, faint amount of solution-derived yttria addition greatly enhanced the sinterability of the mullite because of the promotion of the liquid pahse sintering by the uniformly dispersed yttria phase. In this paper, the relation between microstructures and the mechanical properties of the resultant mullite ceramics was discussed.

1. INTRODUCTION

Most of the research on mullite have related to the improvement of the mechanical properties of the resulting mullite ceramics, including the powder preparation and their morphology control [1, 2, 3]. Recent trend of the research on mullite focuses on the low-temperature sintering with suitable additives and their thermal and electrical properties such as low thermal expansion coefficient and low dielectric constant [4, 5, 6]. This trend has been attracting much attention because of the increasing demand for the hybrid integration of the electronic devices using LTCC. So far, Hashimoto et al. have investigated the effect of the MgO addition on the reaction sintering of mullite ceramics with Al_2O_3 and SiO_2 as sintering aids [6]. Ushifusa et al. and Mitamura et al. also reported the effect of Y_2O_3 and other rare earth oxides addition on the sintering and properties of the mullite ceramics [4, 5]. These additives react with residual SiO_2 in mullite powders to form rare earths silicate with low melting points, resulting in the low-temperature sintering. Among them, Y_2O_3 addition results in the eutectic reaction to accelerate the liquid phase sintering of mullite because of the eutectic point for SiO_2-Al_2O_3-Y_2O_3 system is 1345 °C [7].

In this study, effect of the solution-derived yttria and alumina addition on the sintering behavior of the mullite ceramics have been investigated to achieve the low-temperature sintering of mullite ceramics for LTCC. In addition mechanical properties of the resultant mullite ceramics have been reported in relation to the microstructure.

2. Experimental procedure

2.1 Preparation of raw mixtures of yttria doped mullite powders and alumina

The chemical composition of mullite powder used in this study was 71.80 wt.% of Al_2O_3 and 28.05 wt.% of SiO_2. Main impurities of this mullite powder were 0.10 wt.% of TiO_2 and 0.01 wt.% of Na_2O. Mullite powder was mixed with yttrium nitrate aqueous solution by ball milling to form mullite powders with 0.05, 0.14, 0.2 and 1.0 wt.% yttria dopant (hereafter abbreviated as 0.05Y, 0.14Y, 0.2Y, and 1.0Y), respectively, (Fig.1). After ball milling, the mixtures were calcined at 600 °C for 24 h to form yttria doped mullite powders with different yttria content. In some cases, yttria doped mullite powders were mixed with alumina powder by ball milling for 2 h.

2.2 Sintering and characterization

The mixture powders of yttria doped mullite and alumina were uniaxially pressed at 30 MPa, followed by the cold-isostatic pressing at 100 MPa to form green body. The green body was calcined at 600 °C for 6h to burn out the residual organics and binders, followed by the sintering in the temperature range from 1400 °C to 1600 °C for 3 h in a electric furnace.

The density of the sintered body was measured by Archimedes method. The microstructure and the crystalline phases of the resulting mullite ceramics were observed by a scanning electron microscope (SEM) and the X-ray diffraction (XRD) using Cu-Kα radiation. Fracture toughness and bending strength were measured using samples prepared by the JIS B0601.

Fracture toughness was measured by the indentation fracture method [8]. Three point bending strength was measured according to the JIS R1601.
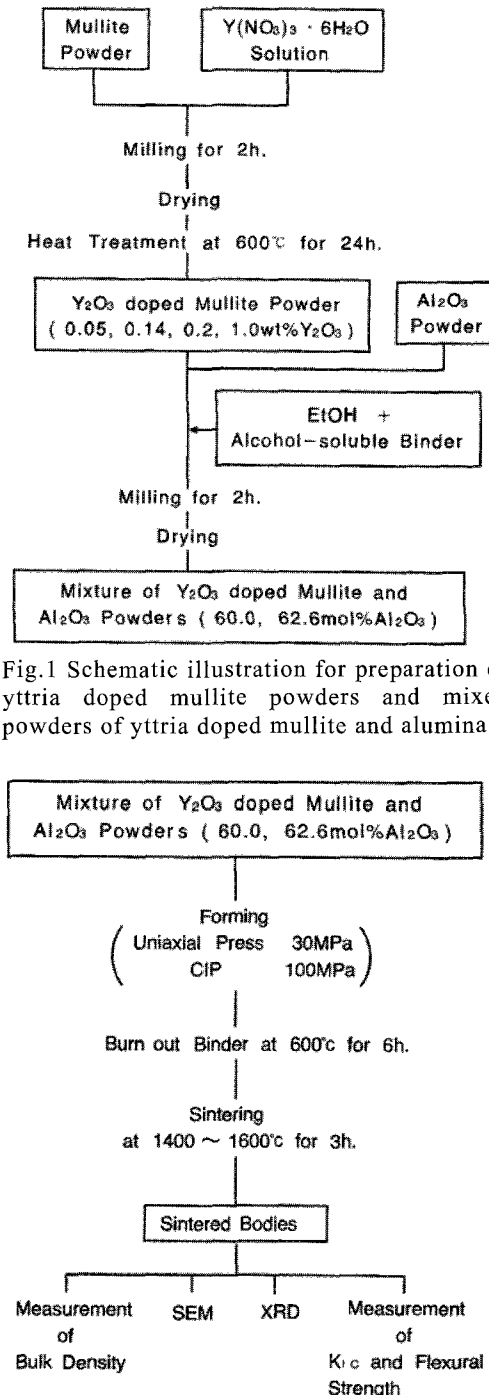

Fig.1 Schematic illustration for preparation of yttria doped mullite powders and mixed powders of yttria doped mullite and alumina.

Fig.2 Schematic illustration of forming, sintering and evaluations of sintered body.

3. Results and Discussion

3.1 Sintering behavior of yttria doped mullite

Mitamura et al. reported that $Y_2Si_2O_7$ was identified as a secondary phase in the mullite ceramics with 5 wt.% of yttria as a sintering aid,

sintered at 1500 °C [5]. However, in this study, secondary phase of $Y_2Si_2O_7$ was not identified by XRD in a sintered body except for the case of ceramics with 1.0 wt.% yttria, sintered at 1400 °C and 1450 °C. This could be ascribed to the amount and the homogeneity of the sintering aid in the mullite ceramics.

Figure 3 showed the sintering behavior of yttria doped mullite ceramics, together with that of the non-doped mullite. The green density for these samples were almost same and ranged from 50 to 51 % of theoretical. This figure indicated that small amount addition of yttria greatly enhanced the sinterability of mullite ceramics even at lower temperature. For the case of 1.0Y sample, relative density reached more than 90 % at 1500 °C. Therefore, combined effect of yttria and alumina addition was investigated for 1Y sample and shown in Fig.4.
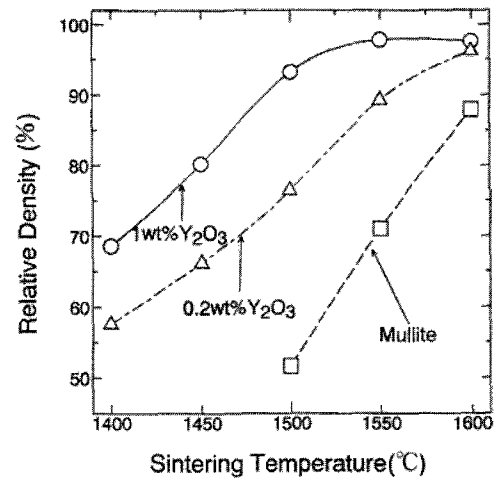

Fig.3 Sinterign behavior of yttrria doped mullite ceramics
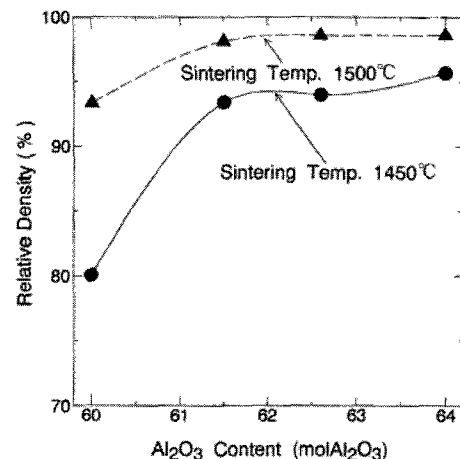

Fig.4 Change in relative density of 1 wt.% yttria doped mullite with amount of alumina addition.

As shown in figure 4, effect of alumina addition to yttria doped mullite was significant and the relative density for the mullite ceramics

with 61.5 mol.% Al_2O_3 composition reached about 95 % of theoretical at low temperature of 1450 °C. In addition, $Y_2Si_2O_7$ phase did not identified in this sample, showing the formation of liquid phase to enhance the sintering by the reaction between the uniformly dispersed solution derived yttria and alumina.

Next, we investigated the sintering behavior for the yttria doped mullite with solubility limit of 62.6 mol.% Al_2O_3, and shown in Fig.5 [9, 10, 11].
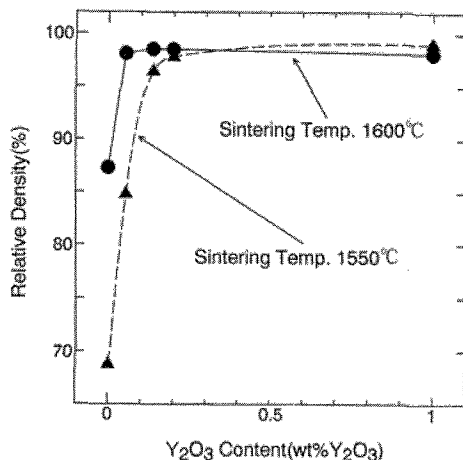

Fig.5 Change in relative density of 62.6 mol.% mullite ceramics with yttria content.

For the case of liquid-source yttria doped mullite with additional amount of Al_2O_3, liquid phase sintering is remarkably accelerated to increase the density by the combined effect of yttria and alumina addition. Therefore, the relative density for the 0.05Y sample increased to about 98 % of theoretical at 1600 °C, higher more than 10% compared with non-doped mullite. Even at 1550 °C, 0.14Y sample attained the relative density of 97 % of theoretical, showing the significant effect of co-doping.

3.2 Characterization of sintered mullite ceramics

Sintered mullite ceramics with (62.6 mol.% Al_2O_3; YA series) and without additional alumina addition were characterized by SEM, 3-point bending test and fracture toughness measurement using indentation fracture method. Figure 6 shows the SEM images for the surface of the sintered mullite ceramics. It is clear that the grain size and aspect ratio for the yttria doped mullite became larger with increasing amount of yttria addition and the microstructure of the sintered body consisted of large elongated grains and relatively small round shape grains. This result was ascribed to the formation of the liquid phase during sintering. On the other hand, grain size of the yttria doped mullite with 62.6 mol.% Al_2O_3 was larger than that of yttria doped stoichiometric mullite, showing the enhanced self diffusion

coefficient of mullite at high temperature by the doping of additional alumina. In addition, there was no big difference in microstructure between 0.05YA and 1.0YA samples (Fig.6 (d) and (f)). This suggested that the suppression of the secondary recrystallization or unusual grain growth during sintering by the doping of additionl alumina.
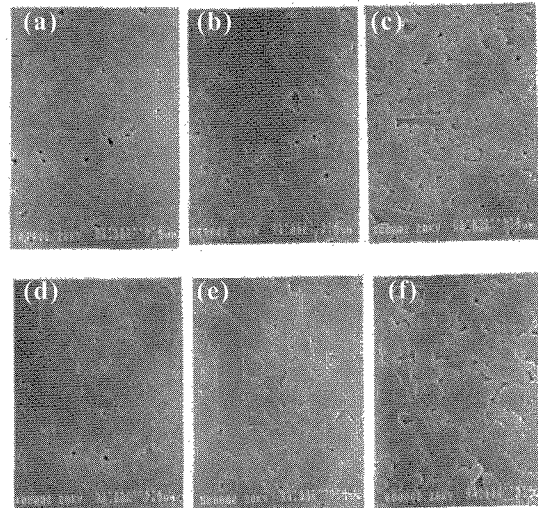

Fig. 6 SEM photographs for polished and thermally etched surfaces of yttria doped mullite ceramics sintered at 1600 °C for 3 h.
(a) 0.05Y, (b) 0.2Y, (c) 1.0Y, (d) 0.05YA, (e) 0.2YA and (f) 1.0YA, respectively.

Figures 7 and 8 show the mechanical properties of the resultant mullite ceramics. The mechanical properties of the ceramics strongly depend on the microstructure including the boundary phases. In these figures, only the mullite ceramics with stoichiometric composition was sintered at 1650 °C to obtain the dense ceramic. However, stoichiometric mullite without additives exhibited relatively low bending strength of about 220MPa and fracture toughness of about 2.5 (MPa · $m^{1/2}$). The bending strength of the yttria doped mullite increased almost linearly with increasing amount of yttria. On the other hand, fracture toughness exhibited at 0.05 wt.% yttria addition. This may be ascribed to the microcracks developed during cooling by the difference of the glassy boundary phase (usually more than 10 x 10^{-6} / °C) and the mullite matrix (ca 5 x 10^{-6} / °C) [12, 13]. For the case of yttria doped mullite with 62.6 mol.% Al_2O_3 composition, small amount of yttria addition dramatically increased the bending strength of the resultant mullite ceramics (ca 340 MPa), whereas the excess amount of yttria addition more than 1 wt.% degraded the bending strength because of the microcracks developed by the same reason mentioned above. These results indicate that the addition of the suitable amount of the sintering additives is very important to obtain the good mechanical properties and to attain the low temperature sintering.
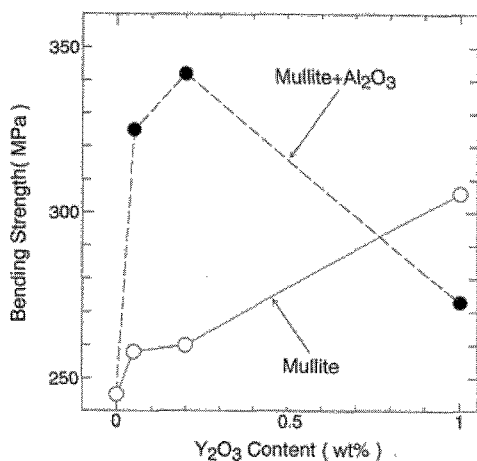
Fig.7 Change in fracture strength of mullite ceramics of 60 mol.% and 62.6 mol.% Al_2O_3 with yttria content sintered at 1600 °C.
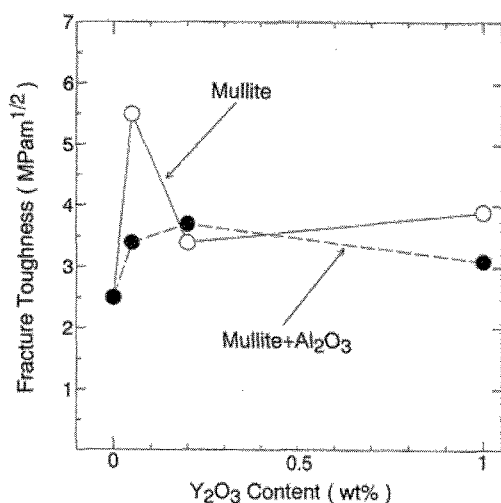

Fig.8 Change in fracture toughness of mullite ceramics of 60 mol.% and 62.6 mol.% Al_2O_3 with yttria content sintered at 1600 °C.

4. Conclusions

In this study, effect of additives of solution derived yttria and alumina on the sintering behavior of the mullite ceramics were investigated. As a result, followings were concluded.

(1) Only a faint amount of solution derived yttria additive remarkably increased the sinterability of mullite ceramics.

(2) Additional alumina additive enhanced the self diffusion coefficient of mullite during sintering to increase the sintered density.

(3) Highest bending strength was obtained by the 0.2 wt.% yttria addition and 2.6 mol.% alumina to the stoichiometric mullite. The bending strength of this sample was more

than 340 MPa and the fracture toughness was about 3.8 (MPa · $m^{1/2}$).

(4) Excess amount of yttria addition and alumina degraded both bending strength and fracture toughness.

(5) Yttria addition to the stoichiometric mullite linearly increased the bending strength, whereas the highest fracture toughness was attained at 0.05 wt.% yttria addition, probably due to the microcracks developed during sintering originated in the difference in the thermal expansion coefficient between grain-boundary glassy phase and mullite matrix.

References
1) H. Suzuki and H. Saito, Yogyo-Kyokai-Shi, 95, 697 (1987)
2) H. Suzuki, Y. Tomokiyo, Y. Suyama, H. Saito, J. Ceram. Soc. Jpn, 96, 67 (1988)
3) Y. Hirata, K. Sakeda, Y. Matsushita, K. Shimada and Y. Ishihara, J.Am.Ceram.Soc., 72, 995 (1989)
4) Ushifusa and T. Ogihara, J. Ceram. Soc. Jpn, 97, 690 (1989)
5) T. Mitamura, H. Kobayashi, Ishibashi and Akiba, J. Ceram. Soc. Jpn, 99, 351 (1991)
6) Hashimoto and Tanba, Yogyo-Kyokai-Shi, 95, 1037 (1987)
7) I. A. Bonder and F. Ya. Galakhov, Izv., Akad. Nauk SSSR, Ser. Khim., 7, 1325 (1963)
8) K. Niihara, R. Morena and D. P. H. Hasselman, J. Mater. Sci. Letters, 1, 13 (1982)
9) I. A. Aksay and J. A. Pask, J. Am. Ceram. Soc., 58, 507 (1975)
10) I. A. Aksay, D. M. Dabbs and M. Sarikaya, J. Am. Ceram. Soc., 74, 2324 (1991)
11) S. Aramaki and R. Roy, J. Am. Ceram. Soc., 45, 229 (1962)
12) M.G.M.U. Ismail, Z. Nakai, Shin-Sozai Series Mullite 2, Uchida-Roukakuho, 69 (1987)
13) S. Somiya, M. Yoshimura, Suzuki, and Yamaguchi, Shin-Sozai Series Mullite, Uchida-Roukakuho, 63 (1985)