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Ceramics International 36 (2010) 1033–1039

CERAMICS INTERNATIONAL

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# Effect of the processing on the production of cordierite–mullite composite

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Received 3 September 2009; received in revised form 27 October 2009; accepted 8 November 2009
Available online 29 November 2009

**Abstract**

In this study, effect of process on the production of cordierite–mullite composite was studied. For this reason two different processing methods were used in the production of cordierite–mullite composites. In first process, *in situ* cordierite–mullite composites were produced from cordierite and mullite layers which were formed by using aqueous tape casting method. In second one, composite was produced by addition of pre-produced mullite powders (in different weight percents, 0–30) into cordierite starting powders. The results show that the addition of pre-sintered mullite powders to the cordierite slip has more effect on densification behavior and mechanical properties of composites than layered production method.

*Keywords:* A. Pressing; A. Tape casting; B. Composite; D. Cordierite; D. Mullite

## 1. Introduction

Aluminosilicate-based ceramics such as cordierite ($2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$) and mullite ($3Al_2O_3{\cdot}2SiO_2$) have attracted much attention as refractory and substrate materials due to their good high-temperature and excellent electrical insulating properties [1].

Cordierite materials are difficult to sinter by solid state process. Liquid phase sintering by addition of sintering aids is not used for dense cordierite ceramics because electrical and thermal properties of cordierite are degraded by sintering aids [2]. The relatively poor mechanical properties of cordierite ceramics can be improved by adding a reinforcing phase such as mullite and fabricating a ceramic composite [1]. For mullite–corierite composites, interrelations between processing, microstructure and electrical and mechanical properties were studied [3].

Compared with conventional dry pressing technologies, aqueous tape casting has great advantages in producing homogeneous and flat tapes [4]. In recent years, slip casting and tape casting methods were used for shaping of cordierite in order to improve the steps of powder processing before sintering to reach higher green density [4,5].

In our previous study, aqueous tape casting of raw materials (Kaolin, $Al_2O_3$ and Talc) to form cordierite was investigated and the microstructures of the green and sintered tapes have been studied [6]. The results show that there is a possibility of the production of dense cordierite ceramics by tape casting method. In this study, the production of cordierite–mullite composite was investigated by using three two different types of processes. The results were discussed by comparing of mechanical and physical properties of samples.

## 2. Experimental procedures

### 2.1. Preparation of suspensions and layered cordierite–mullite composite

The starting raw materials used in this study are given in Table 1. Kaolin, alumina and talc were used as starting materials for cordierite production whereas kaolin and alumina were used for mullite. The aqueous suspensions were prepared by mixing starting materials in stoichiometric proportions for both of them. A typical batch of cordierite and mullite are given in Table 2.

To produce tape casting slips, stoichiometric cordierite and mullite mixtures were mechanically ground in the planetary ball milling (Pulverisette 5 Fritsh, Germany) by using water as grinding mediums for 1.5 h.

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0272-8842/$36.00
doi:10.1016/j.ceramint.2009.11.013

Table 1
Chemical composition of starting materials (wt.%).

| Materials | $SiO_2$ | MgO | $TiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $Na_2O$ | $K_2O$ | A.K. |
|---|---|---|---|---|---|---|---|---|
| Talc | 63.49 | 31.64 | 0.2 | – | 0.2 | – | – | 4.47 |
| Kaolin | 49.75 | – | 0.11 | 34.52 | 0.81 | 0.2 | 2.84 | 11.78 |
| Alumina | – | – | – | 100 | – | – | – | – |

L.O.I., loss of ignition.

Table 2
Staring compositions of cordierite and mullite samples.

| Sample | Amount of starting materials (wt.%) | | |
|---|---|---|---|
| | Kaolin | $Al_2O_3$ | Talc |
| Cordierite | 44.0 | 17.0 | 39.0 |
| Mullite | 52.0 | 48.0 | – |

The sedimentation test of cordierite suspensions were done in the previous work [6]. In this study PVA and PEG were used as binder and plasticizer, respectively. The PVA/PEG weight ratio was used as 1 for 10 wt.% (PVA + PEG).

Sedimentation method for mullite suspension was done for the determination of adequate dispersant in order to get good dispersion. This test was carried out at different dispersant levels (0–3.3 wt.%). Sodium tripolyphosphate (STPP, $Na_5P_3O_{10}$, Esan, Turkey) was used as a dispersant and optimum dispersant level was determined for dispersing the powders. The sedimentation test of mullite suspension was carried out by same method with the earlier study of tape casting of cordierite [6]. Then suspensions were transferred into sealed cylindrical glass tubes and the interfaces (sediment height) were observed periodically during 1000 h. After that, mullite tape casting slips containing optimum amount of dispersant were prepared at 55 wt.% solid content with 10 wt.% (PVA + PEG).

The cordierite and mullite slurries were deagglomerated in polyethylene bottles by milling process for 24 h. Subsequently, slurries were de-aired under a mechanical vacuum for several minutes to remove entrapped air bubbles. After that, slurries were cast on a flat glass carrier using the doctor blade method. The casting speed was constant at 1 cm/s and the gap between the blade and carrier was adjusted to 0.5 mm. For the production of layered cordierite–mullite composites, pure cordierite and mullite tapes were obtained from tape casting slips. After casting process, tapes were cut as 1 cm × 1 cm dimension and these sheets were placed in order of layers such as one cordierite layer and one mullite layer similar to sandwich and pressed with uniaxial pressing (about 25 MPa) in a die. The processing route for layered cordierite–mullite composites is illustrated in Fig. 1.

The elimination of the solvent and the burning out of organic additives in the green bodies were carried out by slow heating (1 °C/min) up to 500 °C with the plateau at 150, 300 and 500 °C. Sintering was carried out in electric furnace with 5 °C/min heating rate up to 1300 °C for 3 h.

### 2.2. Preparation of cordierite–mullite composites with adding pre-produced mullite powder

For the production of cordierite–mullite composites with adding pre-produced mullite powder, firstly mullite powder was synthesized from kaolin and alumina powders. Starting powders were mixed in water by using $ZrO_2$ ball for 1 h and then calcined at 1450 °C for 4 h.

To produce cordierite–mullite composites of different amount of pre-produced mullite powders (0, 10, 20 and

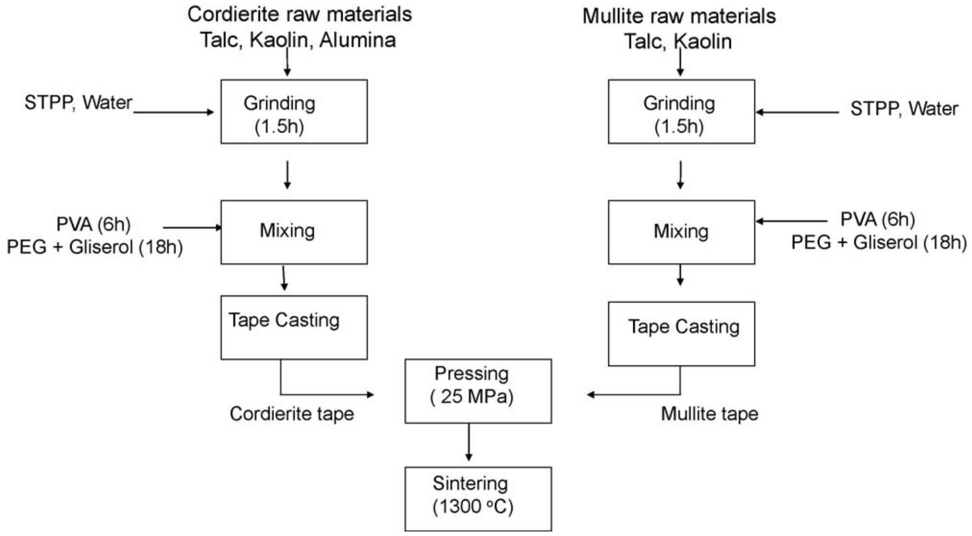

Fig. 1. Production of layered cordierite–mullite composite.

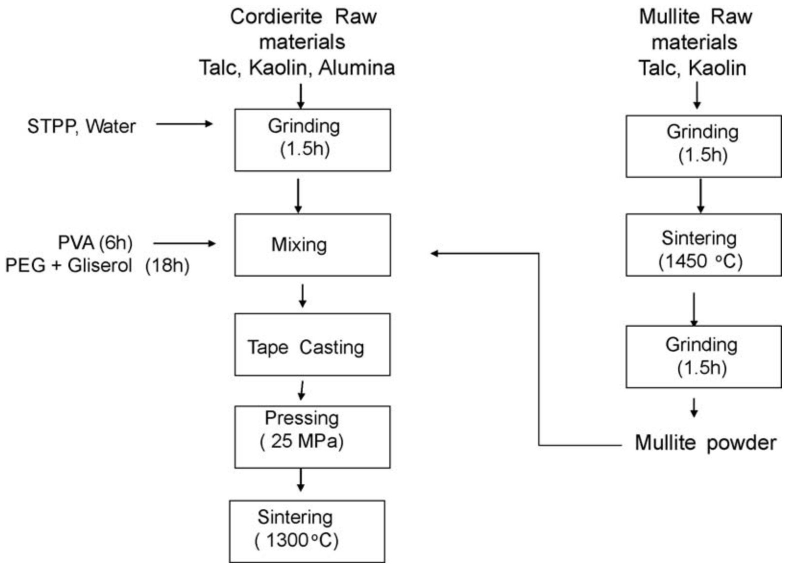

Fig. 2. Production of cordierite–mullite composite with tape casting by adding pre-produced mullite powders.

30 wt.%) were added to slurry. The tape casting slurry was prepared by same tape casting preparation route as with the earlier process. These slurries were coded as TCX, X shows amount (as weight percent) of mullite addition to slurry and it changes between 0 and 30 wt.%. After the casting process, tapes were cut at 1 cm × 1 cm dimensions and these sheets were pressed with uniaxial pressing (about 20 MPa) in a die. The processing route for cordierite–mullite composite by adding pre-produced mullite powders is illustrated in Fig. 2.

In order to determine the effect of the process routes on the physical and mechanical properties of cordierite–mullite composite, additional samples were produced with conventional dry pressing method. In this method, cordierite–mullite composites with different proportions of mullite (0, 10, 20 and 30 wt.%) were prepared. Pre-produced mullite powder and cordierite starting powder were mixed in a ball mill in water for 1.5 h. Dried powders were uniaxially pressed at 20 MPa in a die. According to mullite addition these samples were coded as DPX.

### *2.3. Characterization techniques*

Viscosities of cordierite and mullite slurries were measured by rheometer (Bohlin Gemini Rheometer) before the casting of the slurries .The sintered samples were characterized to determine open porosity, bulk density and flexural strength. The microstructural evolution of green bodies and sintered samples was observed by using scanning electron microscope, SEM (Zeiss, Supra 50 VP) on polished sections. The crystalline phases of sintered samples were determined by using X-ray difractometer, XRD (Rigaku).

The flexural strength test was performed at a cross head speed of 0.5 mm/min using an Instron (with a 2 kN loadcell) for mechanical testing. For every sintering condition, five sintered specimens from each composition were used to carry out the flexural strength test. The modulus of elasticity values were also measured simultaneously.

Thermal expansion coefficients ($\alpha$) of samples were determined using dilatometer (Netzsch DIL 402 PC) at temperature range of 25–650 °C with heating rate of 10 °C/min. The analyzed specimens were bars of 2.5 cm × 0.5 cm × 0.3 cm prepared by uniaxial pressing at 20 MPa and sintered at 1300 °C for 3 h. The average values were calculated from the expansion length up to 650 °C.

## 3. Results and discussion

### *3.1. Layered cordierite–mullite composites*

For cordierite tape casting, slurry stability of cordierite powder has been evaluated in previous work [6]. The results showed that well-dispersed slips obtained with 2.1 wt.% dispersant by sedimentation method.

For mullite tape casting slip, slurry stability was evaluated by measuring the settling of mullite starting powder (sedimentation height) for the different amount of the dispersant at 20 wt.% solid content. To see the effect of the dispersant concentration on the sedimentation height of slurry, the sedimentation heights measured as a function of time and amount of dispersant for slurry, containing 20 wt.% solid, are

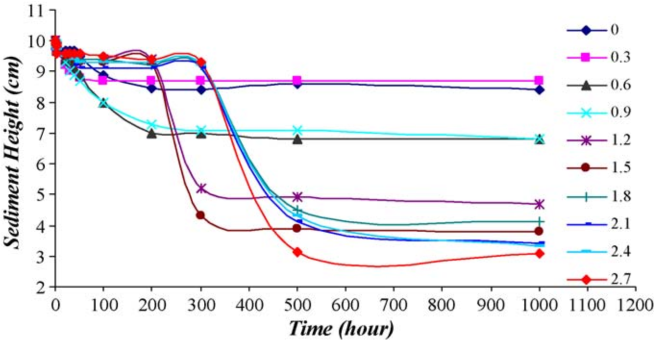

Fig. 3. Sedimentation heights of mullite slurry for 20 wt.% solid content as a function of time.

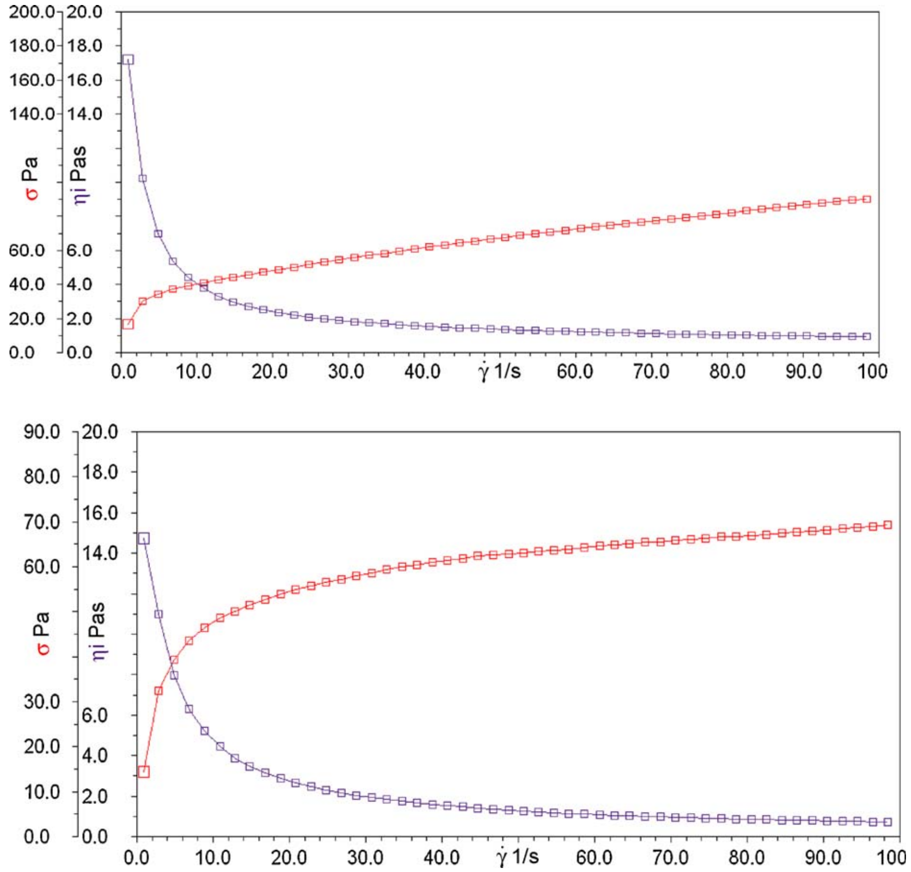

Fig. 4. The viscosity changing verses to shear rate of (a) cordierite and (b) mullite slurry.

given in Fig. 3. Sedimentation height decreased quickly during the early stages at low dispersant levels (0.3–0.9 wt.%). In this case, poorly dispersed slurry was rapidly settled and the sedimentation density was low. On the other side well-dispersed slips settling with high density, were observed at higher dispersant levels after 200 h or more.

The result showed that, the sedimentation height gradually decreased up to the minimum value of dispersant level, obtained with 2.4 wt.% dispersant addition, by increasing the amount of dispersant. Thus the optimum amount of dispersant was selected as 2.4 wt.% corresponding to the lowest sedimentation height and consequently the highest sediment density. Consequently further amount of dispersant addition was not studied.

The rheological properties of the slurry of cordierite and mullite, containing 55 wt.% solid content and 10 wt.% (PVA + PEG) (S55-10 sample), are given in Fig. 4. The viscosity of slurries decreases sharply as the shear rate increases. Both slurries also display shear thinning behaviors with increasing shear rate.

X-ray diffraction pattern of layered cordierite–mullite composites, sintered at 1400 °C, is shown in Fig. 5. This result indicates that starting materials have completely reacted to form cordierite (JCPDS card no. 13-0294) and mullite (JCPDS card no.15-776) phases. Except these both phases additionally small amount of amorphous phase formation was also observed.

Fig. 6a shows polished cross-section microstructures of sintered layered composite. It was observed that there were significantly differences between density of cordierite and mullite layers. As it is shown from Fig. 6a, there are larger pores in cordierite layer of composites and they are indicating that poor densification of cordierite. On the other side, mullite layers showed better densification than cordierite. SEM images of layered cordierite–mullite composite, etched with HF acid solution for 0.5 min, shows interconnection of layers with mullite crystals (Fig. 6b). It was clearly seen that well-formed needle like mullite crystals between cordierite and mullite layers. Additionally, these needle shape mullite crystals have

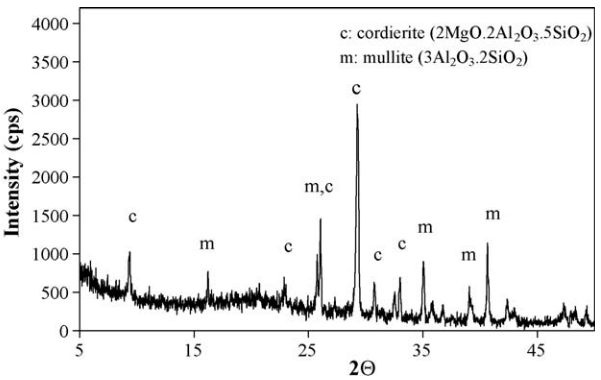

Fig. 5. XRD patters of cordierite–mullite layered composites sintered at 1400 °C.

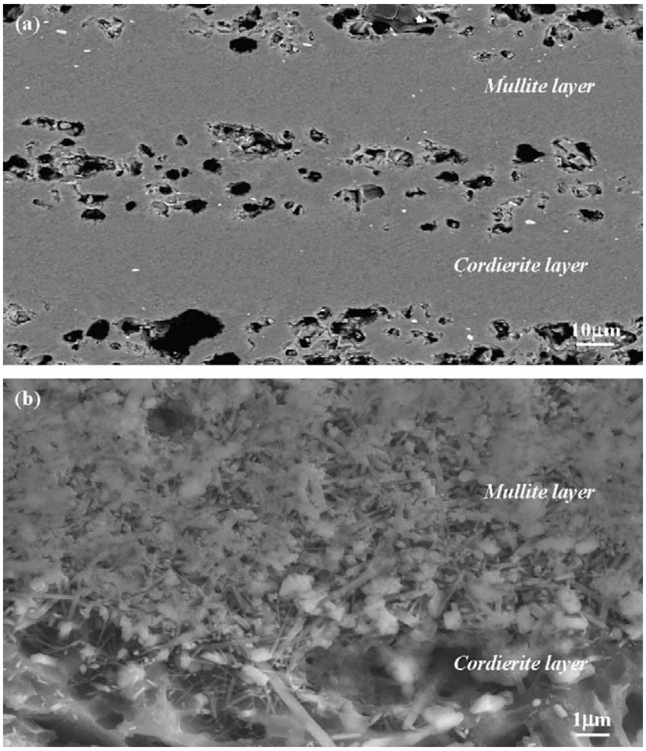

Fig. 6. (a) SEM image of layered cordierite–mullite composite sintered at 1300 °C and (b) SEM image of layered cordierite–mullite composite etched with HF acid solution for 0.5 min.

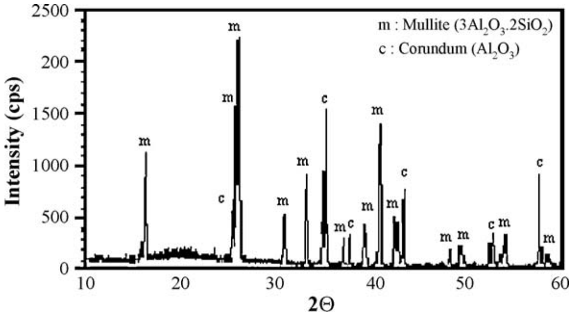

Fig. 7. XRD pattern of mullite powders formed at 1450 °C.

grown in cordierite layer. That mullite grains have finer and higher aspect ratio than that of mullite layer. The average bulk density of layered composite was determined as 2.67 g/cm$^3$ and relatively sintered density was 92% (Table 3).

### 3.2. Cordierite–mullite composite produced by adding pre-produced mullite powders

Fig. 7 shows the XRD pattern of pre-produced mullite powder. At 1450 °C, kaolin and quartz powders reacted completely and mainly converted to mullite phase. Corundum (JCPDS card no.10-173) phase was observed as secondary phase in structure. This can be explained by the non-reacted $Al_2O_3$ powder in composition.

Table 3 shows the bulk density of samples. Sample TC0 has the lowest bulk density. However, addition of mullite powder into composition showed positive effect on densification behavior of samples. As it was seen from Fig. 8, microstructural analyze also support this result. The pore structure, size and distribution significantly decreased by addition of mullite powder into composition. Sample TC0 do not present a compact microstructure, having pores with a larger size and more irregular shape, and show incomplete densification (Fig. 8a). Similar porous microstructure was obtained in TC10 sample but pore size is smaller than that of TC0 (Fig. 8b). The increase in mullite powder addition caused a larger development of microstructure and decreased the porosity (Fig. 8c). Therefore mullite powder addition proves to be denser microstructure to prepared cordierite base ceramics.

Fig. 9a reports the flexural strength and modulus of elasticity analyze results of the fired bodies as a function of mullite powder additions. The flexural strength is ranging from 52 to 93 MPa. The flexural strength of sample TC0 is 52 MPa. Generally, mullite addition affected the flexural strength positively (>52 MPa) compared with sample TC0. This result can be explained by two reasons. Firstly, the lower strength can be attributed to the much greater pores observed in SEM images of sample TC0. Secondly, additional mullite powders were resulted with needle shape mullite grains. This mullite grains has a positive effect on flextural strength of samples due to their high aspect ratio. Additionally, the modulus of elasticity of bodies fired at 1300 °C increased with mullite powder addition into cordierite composition. These results indicate that mullite phase accelerate the densification during the firing process, yield lower porosity and modify the mechanical and microstructural properties.

Additionally samples were prepared by dry pressing method to compare the processing effect on cordierite–mullite composite

Table 3
Effects of mullite addition on density of sintered cordierite–mullite composites.

| Codes | Mullite content (wt.%) | Sintering temperature (°C) | Bulk density (g/cm$^3$) | Relative sintered density (%) |
|---|---|---|---|---|
| TC0 | 0 | 1300 | 2.00 | 77 |
| TC10 | 10 | 1300 | 2.31 | 93 |
| TC20 | 20 | 1300 | 2.41 | 94 |
| TC30 | 30 | 1300 | 2.53 | 96 |
| DP0 | 0 | 1300 | 2.45 | 95 |
| DP10 | 10 | 1300 | 2.50 | 97 |
| DP20 | 20 | 1300 | 2.54 | 96 |
| DP30 | 30 | 1300 | 2.57 | 97 |
| Layered | – | 1300 | 2.67 | 92 |
| Composite |  | 1350 | 2.76 | 95 |

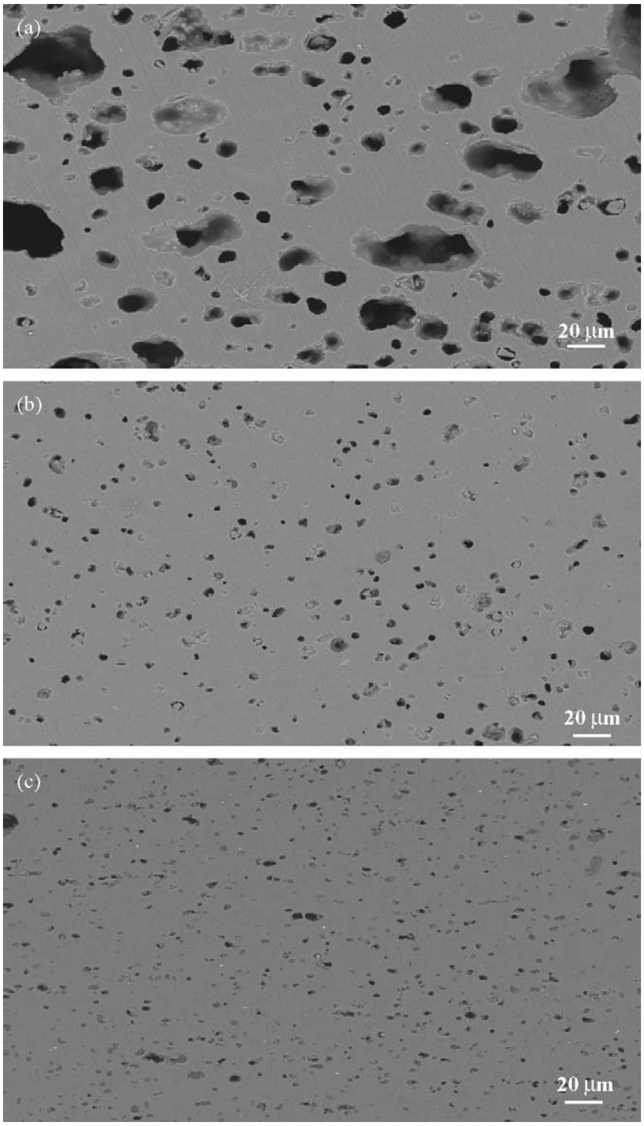

Fig. 8. SEM images of sample (a) TC0, (b) TC10 and (c) TC20 sintered at 1300 °C.

produced by adding pre-produced mullite powder. Physical properties of samples, prepared with dry pressing, are also given in Table 3 in order to see the effect of the producing method on the physical properties of cordierite–mullite composites. The higher densifications were obtained by a dry pressing method rather than the tape casting method with independent of mullite powder addition. Additionally flexural strengths of samples, prepared with dry pressing, are higher than samples prepared with tape casting (Fig. 9b). It can be concluded that, tape casting method is suitable for pure cordierite ceramic whereas dry pressing is the most convenient method for cordierite–mullite composites due to the higher compaction density.

In order to investigate the effect of mullite powder addition on thermal expansion coefficient thermal analyzes were done. The thermal analyzes results showed that thermal expansion of cordierite–mullite composites increases with increasing mullite content (Fig. 10). This can be explained by pure cordierete ($\alpha$cordierite = $2.2 \times 10^{-6}\,°C^{-1}$) has lower thermal expansion coefficient than and mullite ($\alpha$mullite = $6 \times 10^{-6}\,°C^{-1}$).

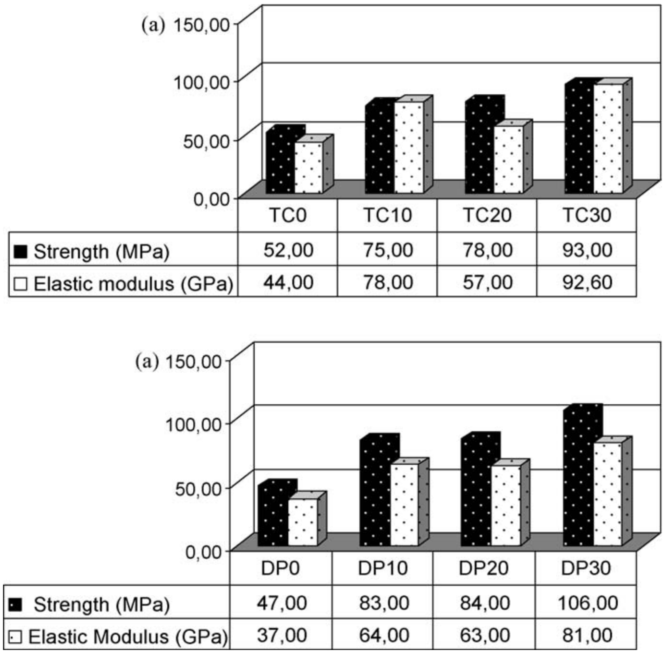

Fig. 9. The average flexural strength and elastic modules of (a) tape cast samples and (b) dry pressed samples (sintered at 1300 °C for 2 h) as a function of mullite additions (standard deviations for strength ±12.0 and elastic modules ±10.0).

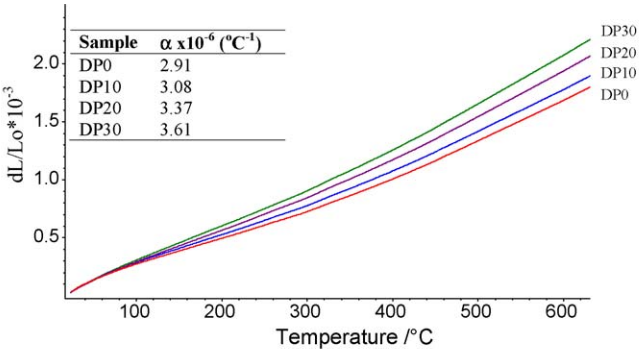

Fig. 10. Thermal expansion coefficient of cordierite–mullite composites sintered at 1300 °C.

Thermal expansion coefficient of the sample DP30 is $3.61 \times 10^{-6}\,°C^{-1}$. There is a close correlation between the experimental values and the Cammeruchi et al.'s study [2].

## 4. Conclusion

Tape slurry stability was evaluated by measuring the settling of powder (sedimentation height) for the different amount of the dispersant (STPP). Optimum amount of dispersant was selected as 2.4 wt.% for mullite slurry due to sedimentation height was low whereas the density was high at this dispersant level. Tape casting slurry containing dispersant was prepared at 55 wt.% solid content and addition of 10–12 wt.% (PEG + PVA) showed the shear thinning behavior.

In both processes, addition of mullite to the cordierite systems has positively affected the sintering behavior of samples. In layered cordierite–mullite composites, mullite crystals were observed between mullite and cordierite layers finer and higher aspect ratio then mullite side. In tape casting method, densification, strength of the cordierite–mullite composite and thermal expansion coefficient increased with increasing the amount of the mullite phase.

The physical and mechanical properties of cordierite–mullite composite were effected the processing methods and better properties were obtained with the dry pressing method than the tape casting method with an independence of the mullite powder addition.

## Acknowledgements

We would like to thank Mr Can Özer, Miss Melek Koparan and Miss Seray Demirci for the help they provided during the course of this work.

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