

Fabrication of low thermal expansion and low dielectric ceramic substrates by control of microstructure

Sang-Jin Lee* and Waltraud M. Kriven^a

Department of Advanced Materials Science and Engineering, Mokpo National University, Muan 534-729, Korea

^aDepartment of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA

An alumina platelet-filled, cordierite matrix was studied as a ceramic substrate having a low thermal expansion coefficient and low dielectric constant. Alumina platelet powders, 3-5 μm , 5-10 μm , 10-15 μm and 15-25 μm in size, were mixed with amorphous-type cordierite powders, which were fabricated by a soft solution process employing PVA polymer, with various compositions. Slip cast, green bodies were sintered at 1300°C for 2 hours. The microstructures of the sintered bodies were dependant on the mixing content and particle size of the alumina-platelets. In the densified cordierite containing 10 vol% alumina platelets of 5-10 μm in size, a flexural strength of about 90 MPa, a low dielectric constant of 5.0 at 1 MHz and a low thermal expansion coefficient of $3.5 \times 10^{-6} \text{ K}^{-1}$ were obtained. Isolated micropores were formed in the alumina platelet-filled, cordierite matrix, and the micropores reduced the increased dielectric constant which accompanied the alumina platelet filler.

Key words: Alumina platelet, Cordierite, Ceramic substrate, Micropore, Dielectric constant.

Introduction

Cordierite was chosen as a ceramic substrate material because it has an extremely low dielectric constant and a low thermal expansion coefficient [1, 2]. However, its drawbacks are low strength, difficult sintering from conventional powders, and a thermal expansion coefficient somewhat lower than that of silicon. Strength and thermal expansion coefficient can be changed by incorporating a second phase into a cordierite matrix. Anderson *et al.* [3] examined the mechanical, thermal, and dielectric properties of cordierite-mullite composites. In this study, the drawbacks of cordierite were solved to some extent by mixing with mullite. However, they found difficulty in sintering mullite-cordierite composites at temperatures lower than the melting point ($\approx 1470^\circ\text{C}$) of cordierite. In ceramic-filled glass composites, several models have been proposed to predict the effect of a second phase on dielectric properties [1, 4]. In particular, the addition of porosity as a second phase in a ceramic matrix was studied for the purpose of forming a low dielectric substrate. Yarbrough *et al.* [5] fabricated both bulk silica gels as well as thin films, using a colloidal silica. The microstructure of this material showed uniform porosity. Such materials are promising candidates to meet the needs of high-speed, high-performance substrates with very low dielectric permittivity [6-8].

This paper examines cordierite-alumina platelet composites that have been densified at relatively low sintering temperatures. Amorphous-type cordierite powder, which was synthesized by a polyvinyl alcohol (PVA) solution-polymerization route [9] and having a nano-scale powder size, was used to make highly sinterable composites. In the composites, the variation of the thermal, mechanical and electrical properties were examined by the control of microstructure via the addition of alumina platelet. In particular, the effect of pore parameters on the dielectric properties was studied.

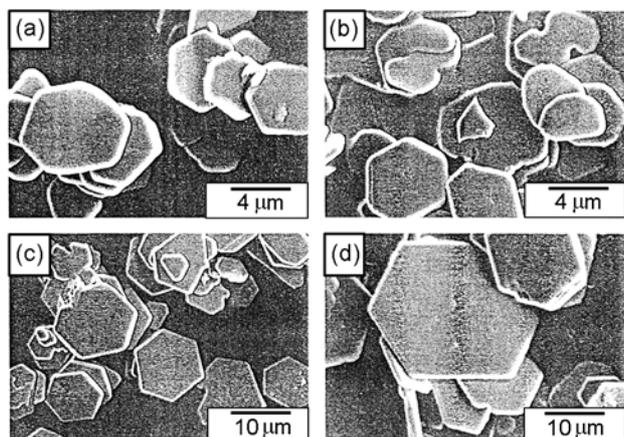
Experimental Procedures

A highly sinterable cordierite powder [9] was prepared in amorphous form, by the PVA solution-polymerization method [10-12]. The powder was attrition-milled for 1 hour after calcination at 800°C for 1 hour. The detailed properties of the amorphous-type cordierite powder and its sintered form are listed in Table 1. The thermal expansion coefficient, flexural strength, and dielectric constant were measured from polycrystalline cordierite samples sintered at 1300°C for 2 hours. The amorphous powder was fully crystallized to α -cordierite after sintering [9]. As the source of the alumina platelet, four types of powders (Atochem, Pierre-Bénité, France) of 3-5 μm , 5-10 μm , 10-15 μm , and 15-25 μm in size were used. The powder morphologies are shown in Fig. 1. The platelets are hexagonal crystals. Aqueous slips consisting of the cordierite powder and alumina platelet powder were made. The alumina platelet content was varied from 0 to 30 vol% for each different particle size

*Corresponding author:
Tel : +82-61-450-2493
Fax: +82-61-450-2490
E-mail: lee@mokpo.ac.kr

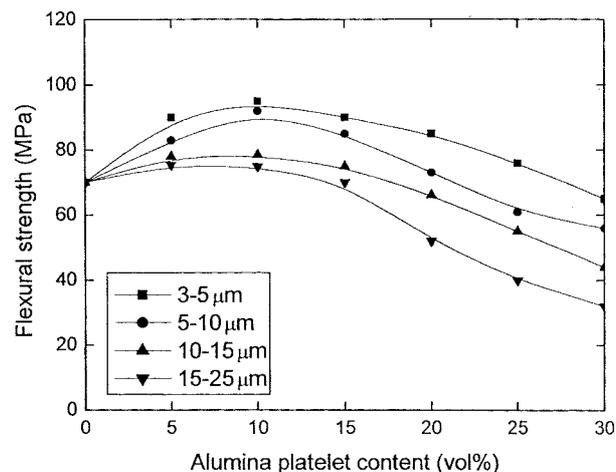
Table 1. Properties of Amorphous-Type Cordierite Powder and Its Sintered Sample Derived from the PVA Solution-Polymerization Method

[†] BET specific surface area (m^2g^{-1})	181
[†] Average particle size (nm)	30
[§] Sintered density (g cm^{-3})	2.50
Thermal expansion coefficient ($\times 10^{-6} \text{K}^{-1}$)	2.1
Flexural strength (MPa)	75
Dielectric constant at 1 MHz	5.3

[†]attritor-milled for 1 h after calcination[§]sintering condition was 1300°C for 2 h**Fig. 1.** SEM micrographs of the alumina platelet powders of (a) 3–5 μm , (b) 5–10 μm , (c) 10–15 μm and (d) 15–25 μm in size.

range. 0.2 wt% (dry weight basis of ceramic powder) ethyl cellulose was mixed to the slips as a deflocculant and binder. The slips were dispersed by ultrasonic process for 10 minutes to break up the agglomerates and to mix homogeneously. After the dispersion process, the slips were stirred to remove bubbles while being placed under vacuum. The samples for characterization were prepared by slip casting in several types of gypsum molds. The green bodies removed from the gypsum molds were dried and sintered at 1300°C for 2 hours in an air atmosphere.

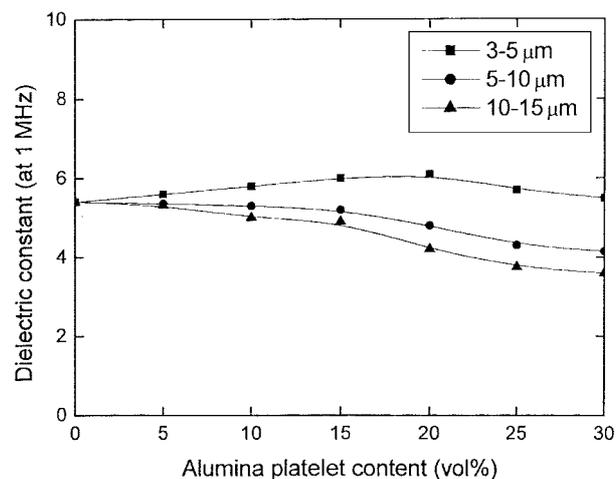
The thermal expansion coefficient of the sintered, cordierite-alumina platelet composites were determined using a dilatometer (Netzsch Dilatometer, 402E, Germany) up to 1100°C at a heating rate of 5 K min^{-1} . Strength was measured by 4-point flexural testing with polished specimens of $30 \text{ mm} \times 2 \text{ mm} \times 3 \text{ mm}$ in size. It was performed using a 10 mm inner span and a 20 mm outer span, at a crosshead speed of 0.1 mm min^{-1} on a universal testing machine (Model 4502, Instron Corp., Canton, MA). A minimum of ten bars were tested for each composition. The average value except for the highest and lowest strength was used as data. Dielectric measurements were made on disk samples coated with silver paint to form electrodes. An HP4275A impedance analyzer was used to make the dielectric measurements. The microstructures of polished and carbon-coated sections

**Fig. 2.** Flexural strength of cordierite-alumina platelet composites at various mixing contents of alumina platelets.

of sintered specimens were examined by scanning electron microscopy, SEM (Hitachi S530, Hitachi, Japan). The porosity of composites was measured by the Archimedes' method, using distilled water as a displacement liquid.

Results and Discussion

The flexural strength, dielectric constant and thermal expansion coefficient of the composites varied according to the alumina platelet size and its content are presented in Figs. 2, 3, and 4. In all cases, flexural strength increased up to the mixing content of 10 vol% platelets as shown in Fig. 2. As the platelet content was increased, however, the strength gradually decreased from the maximum at 10 vol% content. In the larger platelet size range, the flexural strength showed a decrease with larger (–) slope. Because about 70–75 MPa or above is required as a minimum strength for a ceramic substrate, the cordierite-alumina platelet composite containing 15–25 μm platelet size is not suitable as material for a substrate. Therefore, the dielectric

**Fig. 3.** Dielectric constant of cordierite-alumina platelet composites at various mixing contents of alumina platelets.

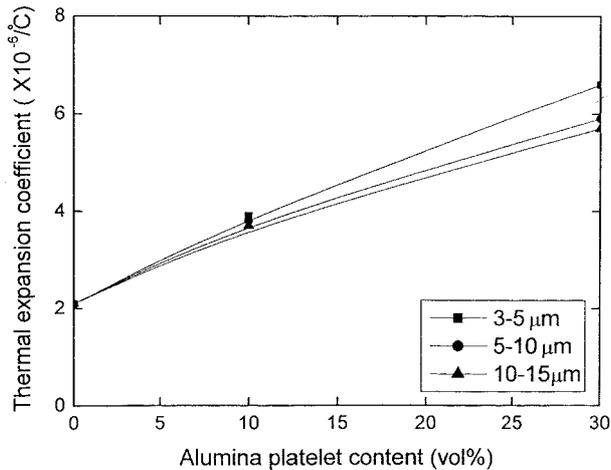


Fig. 4. Thermal expansion coefficient of cordierite-alumina platelet composites at various mixing contents of alumina platelets.

constant and thermal expansion coefficient were examined for the three kinds of platelet powders, excluding the composite made with platelets of 15-25 μm in size. In the composite containing platelet powder of 3-5 μm in size, the dielectric constant increased slightly up to 20 vol% as shown in Fig. 3. However, the composites containing 5-10 μm and 10-15 μm platelets, showed a decrease of dielectric constant, even though the alumina content increased. The decrease of strength and dielectric constant was attributed to the effect of pores in the microstructure. In the thermal expansion behavior, as the platelet content was increased, the thermal expansion coefficient increased (Fig. 4).

Fig. 5 shows the polished surface microstructures of the cordierite-alumina platelet composites and densified cordierite synthesized by the PVA solution-polymerization method. Two representative micrographs at 10 and 30 vol% alumina platelet of 5-10 μm in size are presented, and the pure cordierite microstructure is displayed for comparison with the microstructures varied by platelet mixture. The pore size and pore fraction were almost similar in the 10 vol% alumina platelet content in all composites. Isolated micropores of 5-8 μm in size were formed in the cordierite matrix containing 10 vol% alumina platelets. The isolated micropores took on a role of reducing the dielectric constant which increased by mixing with alumina. In the 30 vol% content, the microstructures were too coarse and resulted in a low substrate strength (Fig. 2). The thermal expansion coefficient for the 10 vol% platelet content was in the range of $3.5\text{-}4.0 \times 10^{-6} \text{ K}^{-1}$ in all cases. The low thermal expansion coefficient of $2.1 \times 10^{-6} \text{ K}^{-1}$ (Table 1) in cordierite was therefore increased, to close to the thermal expansion coefficient of silicon ($3.0 \times 10^{-6} \text{ K}^{-1}$), by the effect of the alumina mixture. Finally, the optimized cordierite-alumina platelet composite for a ceramic substrate, which had a flexural strength of 90 MPa, dielectric constant of 5.0, and thermal expansion coefficient of $3.5 \times 10^{-6} \text{ K}^{-1}$, was made

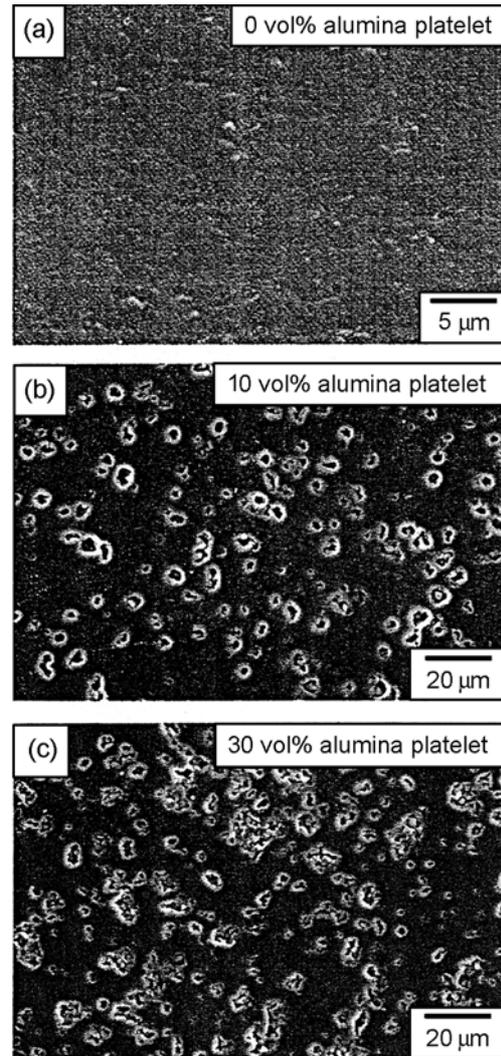


Fig. 5. SEM micrographs of surfaces of (a) densified cordierite prepared by PVA method, and polished surface of cordierite-alumina platelet composites sintered at 1300°C with (b) 10 and (c) 30 vol% alumina platelet of 5-10 μm in size.

from the 10 vol% content, 5-10 μm alumina platelet.

M. Pinero *et al.* [13] examined the mechanical properties of hot-pressed cordierite derived from a sol-gel process. The cordierite contained 15 wt% TiO_2 as a nucleant and was reinforced with alumina fibers. In this study, the composites were hot pressed at 1200°C for 1 h. They obtained a flexural strength of 92.4 MPa for a 90 vol% cordierite/10 vol% alumina composite and 74.6 MPa for a 70 vol% cordierite/30 vol% alumina composite, respectively. In the 10 vol% alumina composite, the cordierite/alumina platelet (5-10 μm) system showed almost the same strength in comparison with the hot-pressed samples. This means the amorphous-type cordierite powder was highly sinterable and alumina platelets were effective for improvement of strength. In the 30 vol% alumina composite, the hot-pressed cordierite showed a much higher strength than the strength of the cordierite/alumina platelet composite because of con-

Table 2. Calculated Dielectric Constant (k) of the Cordierite-Alumina Platelet (10 vol% Platelet of 5-10 μm in Size) Composites Consisted of Pore Free and 10 vol% Pores in the Matrix

[†] Calculated k of pore free composite	5.8
Porosity (pore fraction) of real composite (%)	10
[§] Calculated k of real composite	5.1

[†]by the rule of mixture [3] using measured values of $k_{\text{cord}} = 5.3$, $k_{\text{alum}} = 9.9$

[§]by the Banno equation [5] (in the case of isolated pores in a continuous matrix)

trolling porosity by the hot pressing process.

Dielectric properties depend on porosity, average pore size, and pore size distribution [7, 14]. Table 2 lists the calculated dielectric constant of the cordierite-alumina platelet (10 vol% platelet of 5-10 μm in size) composites which are pore free and which contain 10 vol% pores in the matrix. The measured porosity of the composite comprised of 10 vol% platelet of 5-10 μm size was 10%. The increase in calculated dielectric constant to 5.8 for the pore-free composite decreased to 5.1 for the composite containing 10 vol% pores. The calculated value of 5.1 was close to the measured dielectric constant of 5.0 (Fig. 3). The pores were made during the viscous flow sintering of amorphous cordierite [9]. In the case of the insolubility of the solid phase, the amorphous cordierite underwent incomplete wetting of the alumina platelets. In addition, incomplete rearrangement [15] of alumina platelets during viscous flow sintering was another reason for the formation of micropores.

Conclusions

The properties of cordierite-alumina platelet composites were studied because of the potential of these composites for ceramic substrate applications. The dielectric constant, thermal expansion coefficient and flexural strength of monolithic cordierite were adjusted by control of the microstructure. The mixing with alumina platelets resulted in an increase in mechanical property and thermal expansion coefficient so as to be suitable for applications as a ceramic substrate. The isolated micropores of 5-8 μm in size in the matrix counterbalanced the increase of the dielectric constant

caused by the addition of alumina platelet filler.

Acknowledgements

This work was supported by Korea Research Foundation Grant. (KRF-2001-003-E00376)

References

1. K. Niwa, Y. Imanaka, N. Kamehara and S. Aoki, in *Advanced in Ceramics*, Vol. 26, Ed. by M. F. Yan, K. Niwa, H. M. O'Bryan, Jr. and W. S. Young. The American Ceramic Society, Inc. Westerville, OH, 1989, p. 328-338.
2. R.R. Tummala, *J. Am. Ceram. Soc.* 74[5] (1991) 895-900.
3. R.A. Anderson, R. Gerhardt, J.B. Wachtman, Jr, D. Onn and S. Beecher, in *Advanced in Ceramics*, Vol. 26, Ed by M.F. Yan, K. Niwa, H.M. O'Bryan, Jr., and W.S. Young. The American Ceramic Society, Inc. Westerville, OH, 1987, p. 265-77.
4. Y. Shimada, K. Utsumi, M. Suzuki, H. Takamizowa, M. Nitta and T. Watari, *IEEE Trans. Comp. Hybrids. Manuf. Technol.* 6[4] (1983) 382-386.
5. W.A. Yarbrough, T.R. Gururaja and L.E. Cross, *Am. Ceram. Soc. Bull.* 66[4] (1987) 692-498.
6. Y. Iwata, S. Saito, Y. Satoh and F. Okamura, in *Intermicro-electronic Conference. ISHM*, Reston, VA, 1986, p. 65-70.
7. W. Cao, R. Gerhardt and J.B. Wachtman, Jr, in *Advanced in Ceramics*, Vol. 26, Ed by M.F. Yan, K. Niwa, H.M. O'Bryan, Jr. and W.S. Young, The American Ceramic Society, Inc. Westerville, OH, 1987, p. 409-418.
8. T. Fujiu, G.L. Messing and W. Huebner, *J. Am. Ceram. Soc.* 73[1] (1990) 85-90.
9. S.J. Lee and W.M. Kriven, *J. Am. Ceram. Soc.* 81[10] (1998) 2605-2612.
10. S.J. Lee and W.M. Kriven, *Ceram. Eng. & Sci. Proc.* 19[4] (1998) 469-476.
11. S.J. Lee, E.A. Benson and W.M. Kriven, *J. Am. Ceram. Soc.* 82[8] (1999) 2049-2055.
12. M.H. Nguyen, S.J. Lee and W.M. Kriven, *J. Mater. Res.* 14[8] (1999) 3417-3426.
13. M. Pinero, C.B. Solano, C.J. Solis, L. Esquivias and J. Zarzycki, in *Ceramic Transactions*, Vol. 74, Ed. by N.P. Bansal and J.P. Singh. The American Ceramic Society, Inc. Westerville, OH, 1996, p. 471-482.
14. S.C. Ryu and H.C. Park, *Kor. J. Mater. Res.* 6[2] (1996) 182-187.
15. K.G. Ewsuk, in *Ceramic Transactions*, Vol. 15, Ed. by K. M. Nair, R. Pohanka and R.C. Buchanan. The American Ceramic Society, Inc. Westerville, OH, 1990, p. 279-295.