

Phase Evolution, Thermal Expansion, and Microwave Dielectric Properties of Cordierite- Al_2O_3 Composite

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Abstract: Phase evolution, thermal and microwave dielectric properties of cordierite- Al_2O_3 composite were investigated. As the content of Al_2O_3 increased, mullite, sapphirine, and spinel were formed as secondary phases, implying that cordierite may be decomposed by the reaction with Al_2O_3 . All sintered specimens exhibited dense microstructures. The densification occurred through liquid phase sintering. As the content of Al_2O_3 increased, the thermal expansion coefficient and the dielectric constant increased, whereas the quality factor decreased. The thermal expansion coefficient, the dielectric constant, and the quality factor of the 90 wt% cordierite 10 wt% Al_2O_3 composite sintered at 1,425°C were $2.9 \times 10^{-6} \text{ K}^{-1}$, 5.1, and 34,844 GHz, respectively.

Keywords: Cordierite, Liquid phase sintering, Thermal expansion, Microwave dielectric properties

1. INTRODUCTION

Cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$), which was studied by the French mining engineer and geologist Cordier, has many applications in various fields because of its unique thermal and electrical properties [1]. Cordierite typically has a very low thermal expansion coefficient ($0.9 \sim 2.5 \times 10^{-6} \text{ K}^{-1}$) [2] and can withstand repeated heating and cooling cycles. Therefore, cordierite is used as an electrical heater supports a heat exchanger for gas turbine engines, and a catalyst carrier to purify the exhaust gas of automobiles [3-5]. Cordierite also possesses superior microwave dielectric properties, as the range of the dielectric constant (ϵ_r) is low (5.3~6.2), and that of the quality factor ($Q \times f_0$) is high (39,900~59,682 GHz) [6-8], which is expected of a good candidate for microwave dielectrics. The primary

characteristics required for microwave dielectric materials are the low dielectric constant and the high quality factor, i.e., the inverse of the dielectric loss tangent [9].

However, cordierite shows a relatively poor mechanical strength [2]. Thus, studies on cordierite-based composites, such as cordierite-mullite and cordierite- ZrO_2 composites, have been performed to improve the mechanical properties of cordierite [10,11]. Lee et al. reported that the mechanical strength of cordierite was improved by the addition of alumina platelet [6]. However, they discussed the improvement of the properties from the viewpoint of the microstructure. The aims of this study were to prepare a cordierite- Al_2O_3 composite and to investigate the phase evolution, microstructure, and thermal expansion and microwave dielectric properties of the composite.

2. EXPERIMENTAL PROCEDURE

MgO (purity 2N, High Purity Chemicals Co., Ltd., Japan), Al_2O_3 (purity 2N, Sumitomo Co., Ltd., Japan), and SiO_2

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(purity 2N, Tokyo Electronic Materials Co., Ltd., Japan) raw powders were mixed to synthesize cordierite powder. The calcination was carried out at 1,300°C or 1,325°C for 2 or 5 h. The synthesized cordierite powder and Al₂O₃ were mixed to prepare a series of different (100-x) cordierite-x Al₂O₃ composites, where x corresponds to 10 (hereafter referred to as A10), 30 (A30), 50 (A50), or 70 (A70) wt%. Each composite was mixed by adding the mixture to a polyethylene-based container with zirconia balls and an ethanol medium and allowing it to set for 12 h. The sintering was carried out at temperatures ranging between 1,400°C and 1,500°C for 2 h in ambient air after uniaxial pressing at 100 MPa. The crystalline phases of the sintered specimen were identified by using a powder X-ray diffractometer (D/MAX-2500V/PC, Rigaku, Japan). The microstructure of the sintered specimens was characterized by performing a field-emission scanning electron microscope (FE-SEM, S-4200, Hitachi, Japan) after thermal etching. The thermal expansion coefficient of the sintered specimens was measured using a dilatometer (DIL 402C, NETZSCH, German) between room temperature and 400°C with the heating rate of was 5°C/min. in N₂ gas. The microwave dielectric properties of the sintered specimens were measured by employing a network analyzer (HP8720ES, Agilent, USA) with the Hakki-Coleman fixture configuration [12].

3. RESULTS AND DISCUSSION

The powder diffraction patterns of the cordierite-Al₂O₃ composites sintered at 1,450°C are shown in Fig. 1. As the content of Al₂O₃ increased, mullite (Al₆Si₂O₁₃, ICDD #15-0776), sapphirine ((Mg_{3.5}Al_{4.5})(Al_{4.5}Si_{1.5})O₂₀, #71-2398), and spinel (MgAl₂O₄, #21-1152) were observed as the secondary phases. Mullite and sapphirine formed in the A10 composite, implying that cordierite may have been decomposed by the reaction with Al₂O₃. Cordierite remained the major phase until the content increased beyond 30 wt% (i.e., the A30 composite). Although Al₂O₃ started to appear at this point, it is not considered to have been in an equilibrium state. It has been reported that the tie line exists in the cordierite-Al₂O₃ binary system below 1,386°C in the MgO-Al₂O₃-SiO₂ ternary system; however, there is another tie line in the mullite-sapphirine binary system at higher temperatures [13]. Further increasing the content to 50 wt% (i.e., A50) significantly reduced the

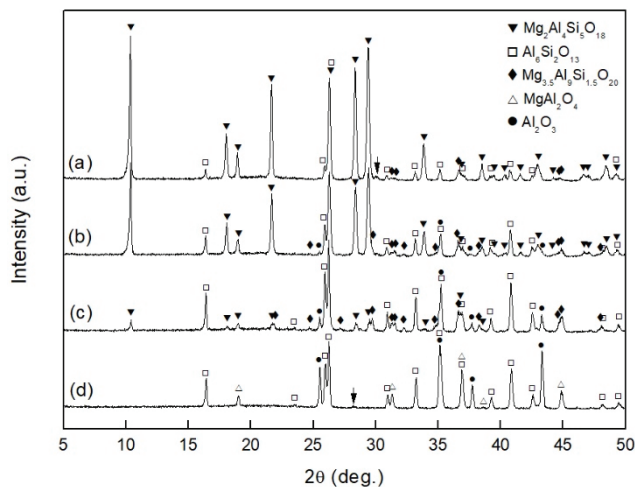


Fig. 1. Powder X-ray diffraction patterns of cordierite-Al₂O₃ composite; (a) A10, (b) A30, (c) A50, and (d) A70.

intensity of the diffraction peaks corresponding to cordierite, and resulted in mullite becoming the major phase. Cordierite and sapphirine were not present in the A70 composite and spinel was observed, implying that a tie line existed in the mullite-spinel binary system. The unidentified peaks of 2θ~30.0° [Fig. 1(a)] and 2θ~28.2° [Fig. 1(d)] indicated by arrow do not match the peaks of the MgO-Al₂O₃-SiO₂ ternary compounds. The further study on unidentified compounds is necessary.

The microstructures of the cordierite-Al₂O₃ composites observed using FE-SEM are shown in Fig. 2. Sintering was carried out at 1,425°C for the composites ranging from A10 to

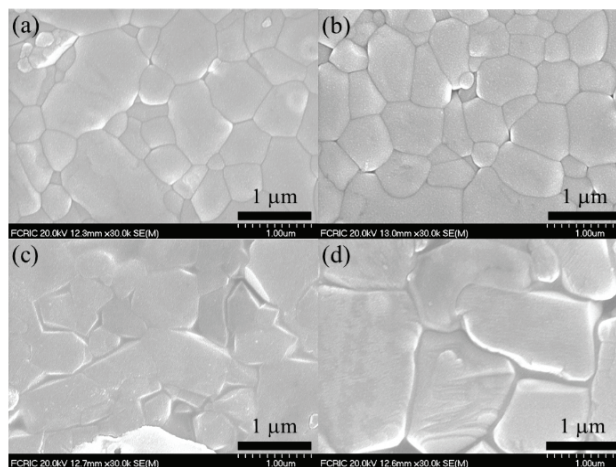


Fig. 2. FE-SEM photographs of cordierite-Al₂O₃ composite; (a) A10, (b)

A30, (c) A50, and (d) A70.

A50, and at 1,500°C for the A70 composite. All composites possessed dense microstructures. Moreover, flat-faced grains were observed, implying that the grain growth was determined by a solution-precipitation process that occurred during liquid phase sintering. According to the theory of liquid phase sintering, the dissolved solid diffuses through the liquid and precipitates onto solid surfaces with lower energies during the solution-precipitation process [14]. Furthermore, the formation of large and irregularly shaped grains is consistent with the occurrence of liquid phase sintering.

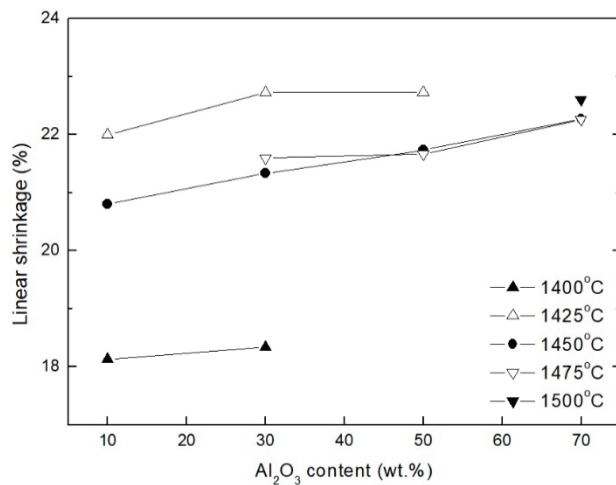


Fig. 3. Linear shrinkage of cordierite- Al_2O_3 composite as a function of Al_2O_3 content.

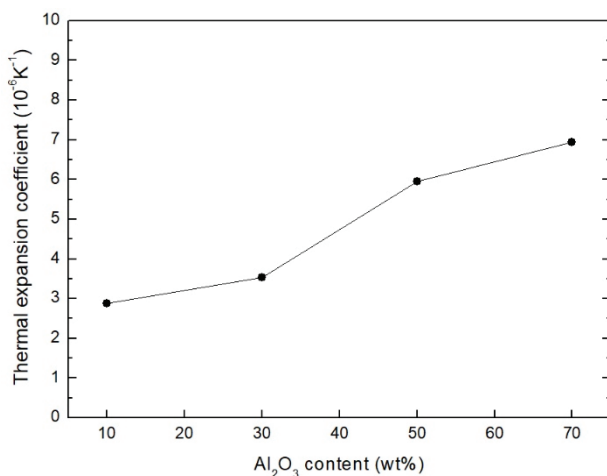


Fig. 4. Thermal expansion coefficient of cordierite- Al_2O_3 composite as a function of Al_2O_3 content.

The linear shrinkage of cordierite- Al_2O_3 composites sintered between 1,400°C and 1,500°C is shown in Fig. 3. The linear shrinkage of the specimens sintered at 1,400°C was approximately 18%, whereas that of the specimens sintered above 1,425°C exceeded 20%. As the Al_2O_3 content increased, the linear shrinkage increased, which is considered to be due to the formation of liquid phase as mentioned above. The thermal expansion coefficient results for cordierite- Al_2O_3 composites sintered between room temperature and 400°C are shown in Fig. 4. As the content of Al_2O_3 increased, the value of the thermal expansion coefficient increased. The increase in the thermal expansion coefficient is considered to be due to the formation of mullite and spinel, and/or the presence of Al_2O_3 , as each of these compounds has a higher thermal expansion coefficient value than cordierite. The thermal expansion coefficient values for cordierite, mullite, spinel, and Al_2O_3 are reported to be $0.9\text{--}2.5 \times 10^{-6} \text{ K}^{-1}$ (20~1,000°C) [2], $4.4\text{--}5.3 \times 10^{-6} \text{ K}^{-1}$ (20~1,000°C) [2,15], $5.6\text{--}7.9 \times 10^{-6} \text{ K}^{-1}$ (25~200°C and 25~1,000°C) [16], and $7.1\text{--}8.3 \times 10^{-6} \text{ K}^{-1}$ [17], respectively.

The dielectric constant (ϵ_r) results for cordierite- Al_2O_3 composites sintered between 1,425°C and 1,500°C are shown in Fig. 5. As the content of Al_2O_3 increased, the value of the dielectric constant increased. The increase of the dielectric constant is also considered to be due to the formation of mullite and spinel, and/or the presence of Al_2O_3 , as each of these compounds has a higher dielectric constant value than cordierite. The dielectric constant values for cordierite, mullite, spinel, and Al_2O_3 are reported to be 5.3~6.2 [6-8], 6.7~7.5 [18], ~8.3 [16,19], and 9.3~11.5 [17], respectively. Furthermore, the dielectric constant of all specimens exhibited minimal change, regardless of the sintering temperature. The quality factor ($Q \times f_0$) results for cordierite- Al_2O_3 composites sintered between 1,425°C and 1,475°C are shown in Fig. 6. The value of the quality factor for the A10 specimen with mullite and sapphirine as the secondary phases was measured to be 34,844 GHz; this value is reasonable because, as previously mentioned, the quality factor of cordierite was reported to range between 39,900 and 59,682 GHz [6-8]. As the content of Al_2O_3 and sintering temperature were further increased, the value of the quality factor decreased. As shown in Figs. 1 and 2, the formation of the secondary phases and the presence of the liquid phase may have reduced the quality factor of the cordierite- Al_2O_3 composite. The quality factor, i.e., the inverse of the dielectric loss tangent, is associated with imperfections

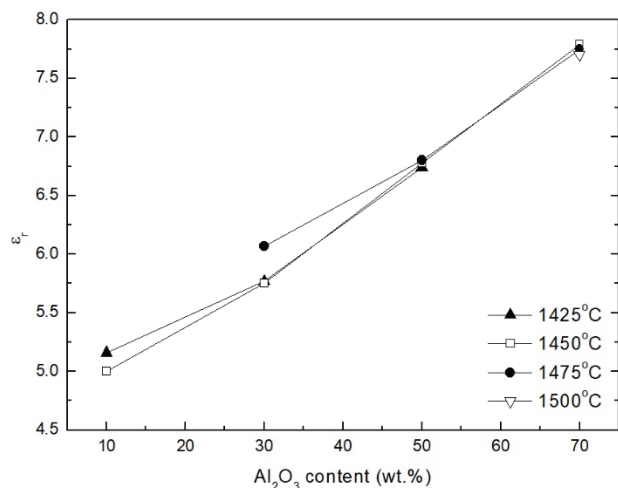


Fig. 5. Dielectric constant of cordierite-Al₂O₃ composite as a function of Al₂O₃ content.

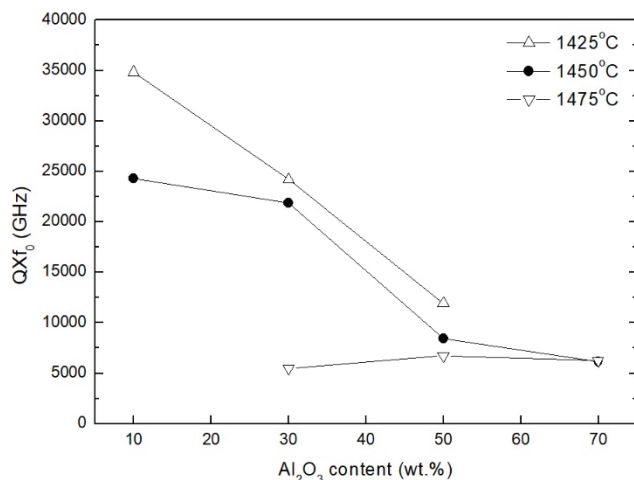


Fig. 6. Quality factor of cordierite-Al₂O₃ composite as a function of Al₂O₃ content.

in the crystal structure, e.g., impurities, microstructural defects, grain boundaries, pores, microcracks, and random crystallite orientation [20,21]. As the Al₂O₃ content increased, the linear shrinkage, thermal expansion coefficient, and dielectric constant increased but the quality factor decreased. The A10 composite (i.e., the 90 wt% cordierite and 10 wt% Al₂O₃ composite) sintered at 1,425°C showed a dense and pore-free microstructure, superior thermal expansion coefficient of $2.9 \times 10^{-6} \text{ K}^{-1}$, and the following microwave dielectric properties: $\epsilon_r=5.1$ and $Q \times f_0=34,844 \text{ GHz}$. It is expected that the A10 composite, which exhibits a low thermal expansion coefficient, can be applied as a ceramic heater.

4. CONCLUSIONS

The phase evolution, microstructure, microwave dielectric properties, and thermal expansion of cordierite-alumina composites were investigated. Increasing the Al₂O₃ content caused mullite, sapphire, and spinel to occur as the secondary phases, implying that cordierite may have been decomposed by the reaction with Al₂O₃. Cordierite and sapphire were not observed in the 30 wt% cordierite and 70 wt% Al₂O₃ composite, and all specimens possessed dense microstructures. Additionally, flat-faced grains were observed, implying that the grain growth was determined by a solution-precipitation process that occurred during liquid phase sintering. Furthermore, the thermal expansion coefficient and dielectric constant increased as the Al₂O₃ content increased, whereas the quality factor decreased. The thermal expansion coefficient, dielectric constant, and quality factor of the 90 wt%

Table 1. Phase evolution, thermal expansion coefficient, dielectric constant and quality factor of cordierite-Al₂O₃ composite.

Notation	Major phase (s)	Minor phase (s)	Thermal expansion coefficient (10^{-6} K^{-1})	Dielectric constant	Quality factor (GHz)
A10	Cordierite	Mullite sapphire	2.9	5.1	34,844
A30	Cordierite mullite	Sapphire Al ₂ O ₃	3.5	5.6	24,214
A50	Mullite	Cordierite sapphire Al ₂ O ₃	6.0	6.8	11,914
A70	Mullite Al ₂ O ₃	Spinel	7.0	7.7	6,120

cordierite and 10 wt% Al₂O₃ composite sintered at 1,425°C were 2.9×10^{-6} K⁻¹, 5.1, and 34,844 GHz, respectively. It is expected that the A10 composite, which exhibits a low thermal expansion coefficient, can be applied as a ceramic heater.

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