Dependence of Crystallization Behavior and Microstructural Change in Cordierite-Based Glass-Ceramics upon Acid-Etching on Glass Frit

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Abstract

The crystallization behavior and microstructural change in glass-ceramics with a cordierite composition were analyzed as a function of concentration and etching time of the HF solution in order to enhance the degree of crystallinity of the glass. Compared to a specimen without etching, the glass frit specimens etched with HF solution showed increased crystalline peak intensities of the μ-cordierite phase in the XRD pattern. The crystal size in the glass matrix also increased with an increasing concentration of the HF solution for the etched glass frit. The crystal peak intensity of the α-cordierite phase in the glass-ceramics made with glass frit etched with 0.5-1.5 wt% HF solution had a slightly higher value than that of pure glass frit regardless of the etching time. The intensity of the specimen with etched glass frit with 3.0 wt% HF solution, however, was lower than that of the specimen of the pure glass frit. Obviously, for the glass-ceramics etched with HF solution of various conditions, the μ-cordierite phase is more favorable for crystallization than the α-cordierite phase. This study revealed that the microstructure and ratio of the crystallinity of the μ-cordierite phase over the α-cordierite phase in the obtained glass-ceramics could be controlled by changing the HF-etching conditions followed by a heat treatment process.

Keywords: HF-etching, Glass-ceramic, Cordierite, Crystallization

1. Introduction

Cordierite ($2MgO-2Al_2O_3-5SiO_2$) has a high thermal shock resistance, a low thermal expansion coefficient and high thermal conductivity, so it has been used in many fields, such as low temperature co-fired ceramic (LTCC) materials and porous catalyst carriers for purifying harmful exhaust emissions discharged from vehicles [1-5]. Fabricating the ceramics by a glass-ceramic process is possible at a relatively low temperature, usually lower than 1,000 ℃, while fabricating the ceramics by sintering a green body requires high temperature. Thus, glass-ceramic processing to obtain ceramics has many advantages, including processes that require low energy consumption and those for multi-layered devices in which LTCC material is essential. The surfaces of materials are unstable due to broken bonds toward the atmosphere, and that surface instability plays an important role in creating nucleation sites. When the glass is heat-treated, surface crystallization generally occurs rather than internal crystallization due to heterogeneous nucleation mechanism [6].

Surface crystallization, however, results in poor properties such as lower mechanical strength and chemical durability due to a lower degree of crystallinity in the final product. Adding a nucleating agent to the glass is a popular way to induce an internal crystallization and to increase the degree of crystallinity in the glass [7-9]. Another

method that increases the degree of crystallinity of glass is the 2-stage heat-treatment method in which the nucleation is induced first at a lower temperature followed by development of crystallization at a higher temperature [10]. To use the 2-stage heat-treatment method to fabricate a glass-ceramic, the optimum nucleating temperature (T_N) and crystallizing temperature (T_P) should be measured in advance using DTA analysis. Furthermore, the potential number of nucleating sites can be increased when the glass frit is scratched or corroded by physical or chemical methods, which makes the surface topology of the glass frit rough and the specific surface area of the glass frit increases [6, 11].

In this study, glass frit was HF-treated and formed to a pellet-shaped green body by cold isostatic pressing. The green body was sintered in air to produce glass-ceramics with a cordierite composition. The purpose of this study was to control the crystallization behavior of glass-ceramics with a cordierite composition by HF-treating the glass frit. The cordierite phase had two polymorphic forms, α- and μ-forms, with different physical and chemical properties, so the ratio of crystallinity of the α- and μ-forms could be controlled. We also measured the physical properties, such as the density and thermal conductivity of the fabricated glass-ceramics, to determine how the ratio of the two forms of cordierite would affect the physical properties of the glass-ceramics. In particular, we chose the concentration of the HF solution and the treatment time as experimental factors to increase the potential number of nucleating sites during the HF-treatment of the glass frit.

2. Experimental Procedure

The starting reagents used to prepare the cordierite glass in this study were MgO (High Purity Chemicals, 99.9%, Japan), SiO_2 (High purity Chemicals, 99.9%, Japan), TiO_2 (High Purity Chemicals, 99.9%) and Al_2O_3 (Samchun Chemicals, 99.0%, Korea). A batch powder of cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$) composition containing 1.5 wt% TiO_2 was prepared. The batch powders were dry-milled using zirconia balls for 24 hours. The uniformly milled powders were fused at 1600 ℃ for 3 hours using a platinum crucible and then poured rapidly into cold water to obtain a homogeneous parent glass. The glass frit was then pulverized and sieved to obtain a specimen of less than 45 μm. The glass frit was etched with HF of various concentrations for 1 s, 10 s or 60 s, filtered using filter paper with a pore size of 1 μm and then washed in water and and dried at 100 ℃ for 24 hours.

The green pellet with a diameter of 9 mm and a height of 3 mm was formed using the glass frit etched with HF solution by cold isostatic pressing at a pressure of 42,000 kgf/cm^2. The green pellets were sintered at 980 ℃ for 3 hours in air with a heating speed of 10 ℃/min and cooled in the furnace. Thermal analysis of the glass frit with 45 μm was performed using Differential Thermal Analysis (DTA) (STA 409C/CD, Netzsch Co., Germany) with a heating speed of 10 ℃/min. The bulk density of the sintered specimen was measured using Archimedes's method and analysis of the crystalline phase was performed using X-ray diffraction analysis (XRD) (Pan'alytical, X'pert Pro, Netherlands). The cross section and fractured surface were observed with the Field Emission Scanning Electron Microscope (FESEM) (JSM-6500F, JEOL, Japan) after the sintered body was etched in of 1 vol% HF for 15 s. In addition, the Laser Flash Apparatus (LFA) (NETZSCH, Germany) was used for the thermal conductivity and thermal diffusion coefficient of the glass-ceramics fabricated in this study.

3. Result and Discussion

The DTA curve for the TiO_2-added cordierite glass system measured at a heating rate of 10 ℃/min is shown in Figure 1.
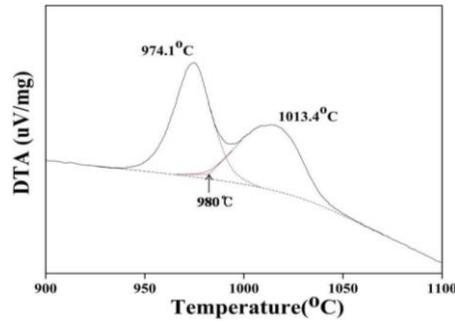
Figure 1. DTA Curve for a Tio₂-Added Cordierite Glass System Measured At a Heating Rate of 10 ℃/min

Two exothermic peaks appeared on the DTA. The first peak at 974.1 ℃ and the second peak at 1013.4 ℃ corresponded to crystallization of the α- and μ-cordierite phases, respectively. In this study, we chose a crystallization temperature of 980 ℃ because both α- and μ-cordierite could be formed at that temperature, and that temperature is lower than 1000 ℃, which is essential for the LTCC process.

Figure 2 shows the XRD patterns of glass-ceramic cordierite sintered at 980 ℃ for 3 hours as a function of various HF etching conditions for glass frit. The graphs shown on the right, excerpted from the XRD graphs on the left, indicate the main peak intensities for α-cordierite and for μ-cordierite phase crystals according to concentration of the HF solution.

(a)

(b)

(c)
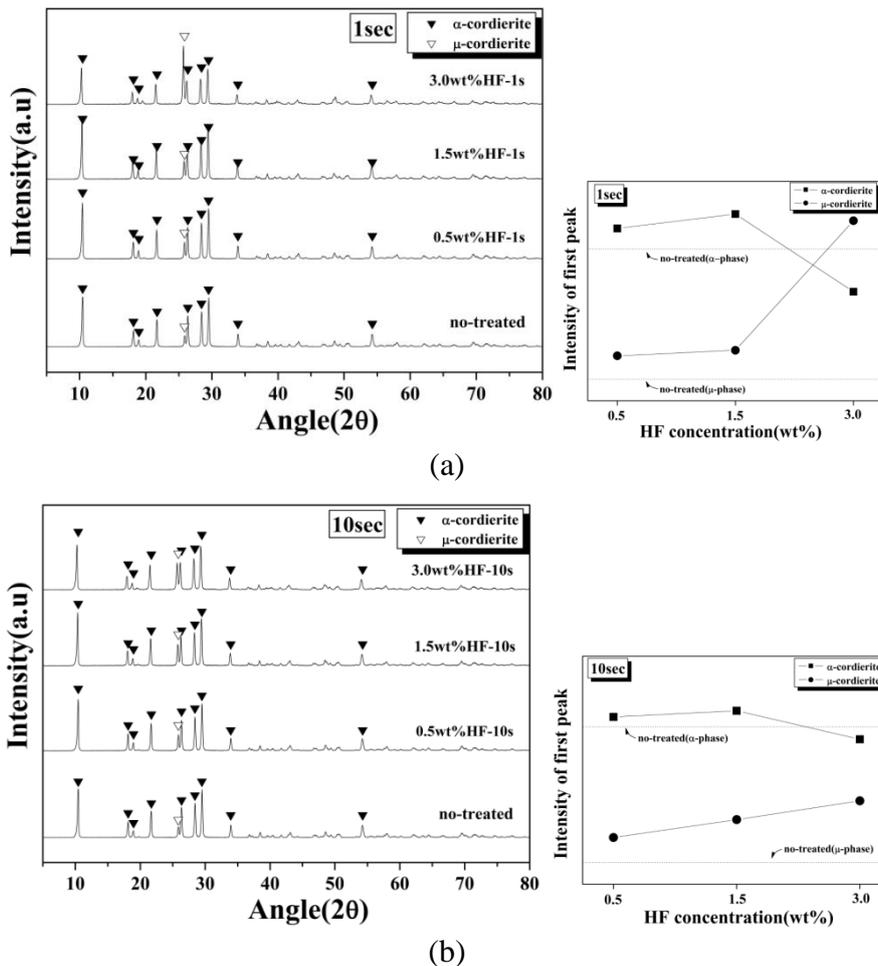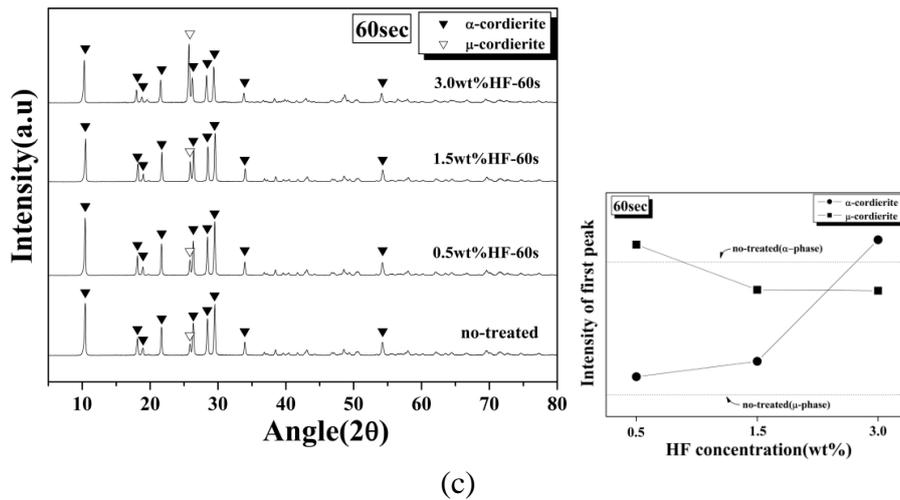
Figure 2. XRD Patterns of Glass-Ceramic Cordierite Sintered At 980 ℃ For 3 Hours As A Function of Various HF Etching Conditions For Glass Frit. HF-Treating Time Is (A) 1 S, (B) 10 S, and (C) 60 S. The Graphs Shown On the Right, Excerpted From the XRD Graphs on the Left, Indicate the Main Peak Intensities for α-Cordierite and For μ-Cordierite Phase Crystals

When glass with a cordierite composition is heated, both α- and μ-cordierite phases compete with each other to crystallize. When the concentration of the HF solution used to treat the glass frit increased, the crystal peak intensity of the α-cordierite phase decreased, while the crystal peak intensity of the μ-cordierite phase increased. This means that treating glass frit with an HF solution is favorable for generating sites for nucleation for the crystal phase of μ-cordierite rather than for the α-cordierite phase. Jo *et al.* researched the crystallization behavior and microstructural change of the glass-ceramics of bottom ash containing 15 wt% Li_2O and found that nucleation sites seemed to be generated where the Si ions were eluted [11]. They also found that a precise conclusion as to why the HF treatment on glass frit induced crystallization of the μ-cordierite phase but not the α-cordierite phase could be drawn only if more experiments were performed.

The shrinkage and density of glass-ceramic cordierite as a function of the concentration of the HF solution and the etching time are shown in Figure 3. The difference in shrinkage among the specimens made with HF-treated glass frit at various times was not significant. Increasing the concentration of the HF solution, however, decreased the shrinkage of the specimen. The density of specimen made with glass frit HF-treated for 1 s was higher than that of the specimen with glass frit HF-treated for over 10 s. Furthermore, the density of the specimen decreased with an increasing concentration of the HF solution.

The density of glass-ceramics using pure glass frit was always higher than that of the specimens made with HF-treated glass frit. This is because the frit had a relatively wide size distribution, which enhanced the efficiency of packing. The better packing in the green specimen created a higher density in the glass-ceramics. The shrinkage and density of the specimen with HF-treated glass frit were lower than with pure glass frit because a small size frit of below 1 μm passed through the filter paper during the filtering process. We used a filter paper with a small hole with a diameter of 1 μm. Thus, the glass frit smaller than 1 μm could pass through the hole, which narrowed the size distribution of all the filtered glass frit, which decreased the packing efficiency.
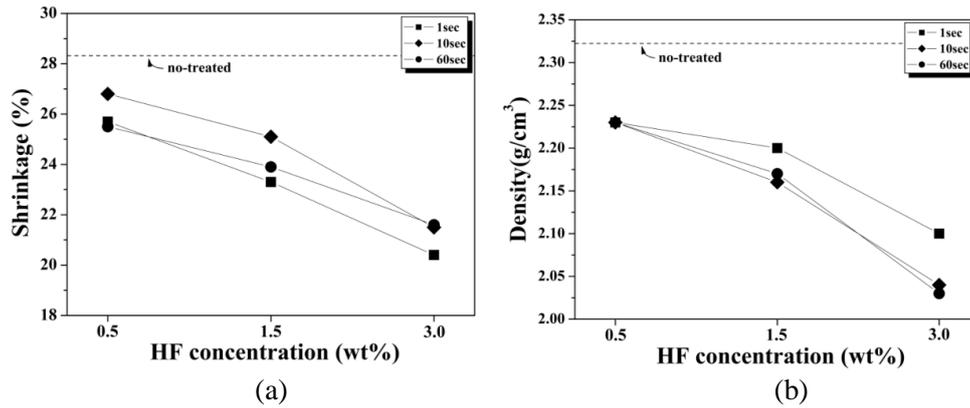
Figure 3. (a) Shrinkage and (b) Density of Glass-Ceramic Cordierite as Function of the Concentration of the HF Solution and the Time for HF Etching

Figure 4 gives the thermal conductivity and the thermal diffusivity of cordierite glass-ceramics. The thermal conductivity of the pure glass frit was always higher than that made with HF-treated glass frit.
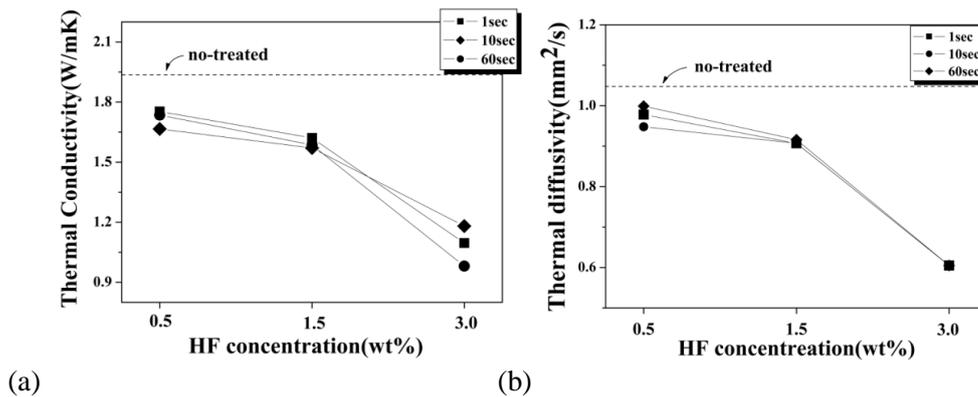
Figure 4. (A) Thermal Conductivity and (B) Thermal Diffusivity of Cordierite Glass-Ceramics Made With HF-Treated Glass Frit under Various Conditions

As shown in the XRD patterns in Figure 2, HF-treatment on glass-frit induced crystallization of the μ-cordierite phase but not of the α-cordierite phase. The thermal conductivity of the μ-cordierite phase is known to be lower than that of the α-cordierite phase, so the decreased thermal conductivity of glass-ceramics was due to the increased crystallinity of the μ-cordierite phase.

The thermal conductivity, (κ), is determined using Equation (1):

$$\kappa = D \cdot \rho \cdot C_p \tag{1}$$

where D, ρ, and C_p indicate the thermal diffusivity [mm^2/s], density [g/cm^3], and heat capacity [J/gK], respectively [9,10]. Figure 3 and 4 reveal that both the density and the thermal diffusivity had a linear relationship to the thermal conductivity of the glass-ceramics of the cordierite composite fabricated in this study.

The microstructures pictured at low-magnification (x 500) for the glass-ceramics made of different types of frit observed by using SEM is shown in Figure 5. The specimen made with pure frit showed a dense microstructure without pores, while the specimen made with HF-treated frit had a non-uniform microstructure with many pores and voids. The porous structures might be due to insufficient packing of the frit during the forming

process due to the narrow size distribution of the glass frit. Thus, the reason that the specimen containing more μ-coriderite phase than α-cordierite phase had lower thermal conductivity is that the specimen had a porous structure in addition to higher occupation of the μ-cordierite phase, which has a lower thermal conductivity than the α-cordierite phase.

(a) (b)
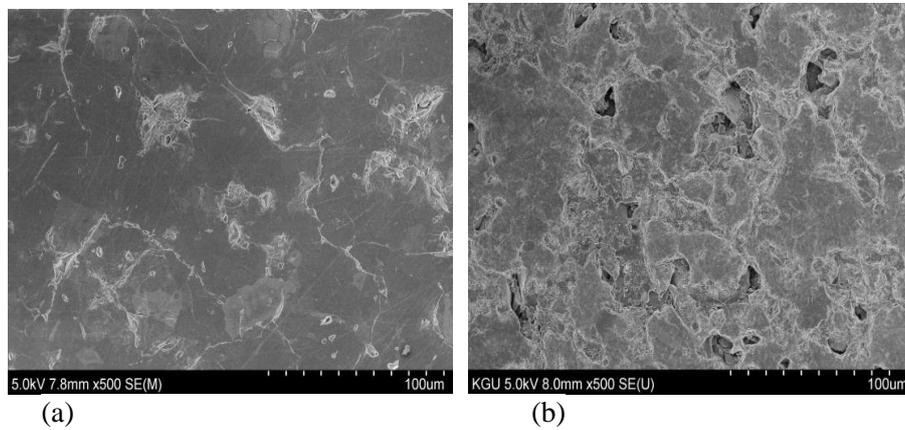
Figure 5. The Microstructures Pictured at Low-Magnification (X 500) for the Glass-Ceramics Made of Various Types of Frit Observed Using SEM. The Specimens Were Made With (A) Untreated Glass Frit and (B) HF-Treated Glass Frit

Figure 6 shows the microstructures pictured at high-magnification (x 20,000) of cordierite glass-ceramics observed using SEM. The specimen made with pure frit had a very uniform microstructure with grains with diameters of 0.2-0.4 μm, while the specimen made with HF-treated frit had relatively large rectangular crystals with a thickness of about 0.5 μm. The thickness of the rectangular crystals decreased with a decreasing concentration of the HF solution used to treat the glass frit.

(a) (b)
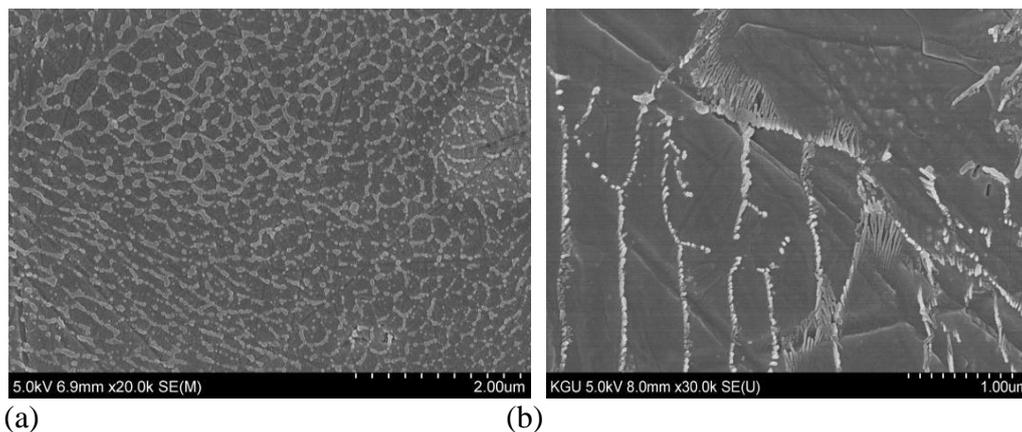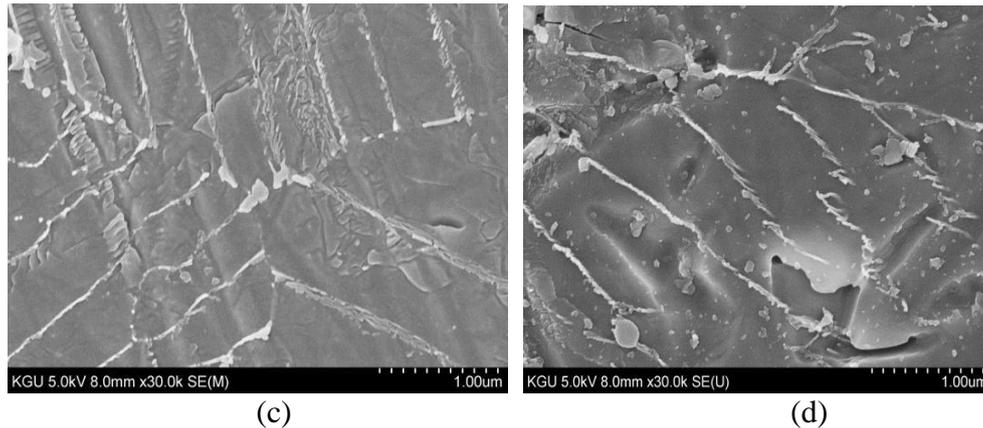
Figure 6. Microstructures of Cordierite Glass-Ceramics Pictured at High-Magnification (x 20,000) observed using by SEM. The Specimens Were Made With Various Types Of Glass Frit: (a) Untreated, and Treated with (b) 0.5 wt%, (c) 1.0 wt% and (d) 3.0 wt% HF Solutions

4. Conclusion

In this study, we fabricated a glass-ceramic composite with a cordierite composition with HF-treated glass frit and investigated the crystallization behavior of the specimen.

When heating the glass with a cordierite composition, the α- and μ-cordierite phases competed with each other in the crystallization process. Treating glass frit with an HF solution was favorable for generating sites for nucleation of the crystal phase of μ-cordierite but not the α-cordierite phase. In addition, the crystal size in the glass matrix observed by SEM increased with an increasing concentration of the HF solution used to etch the glass frit.

The density of glass-ceramics with pure glass frit was always higher than that of the specimens made with HF-treated glass frit because the pure frit had a relatively wide size distribution, which enhanced the efficiency of packing. Better packing in the green specimen created higher density in the glass-ceramics.

Both the density and thermal diffusivity had a linear relationship with the thermal conductivity of the glass-ceramics with the cordierite composition fabricated in this study.

The specimen made with pure frit had a dense microstructure without pores, while the specimen made with HF-treated frit had a non-uniform microstructure with many pores and voids. Porous structures might have been caused by insufficient packing of frit during the forming process due to the narrow size distribution of the glass frit.

This study revealed that the ratio of crystallinity of the μ-cordierite phase over the α-cordierite phase in the obtained glass-ceramics was able to be controlled by changing the HF-etching conditions and then performing a heat treatment process.

Acknowledgment

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