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Glass-frit size dependence of densification behavior and mechanical properties of zinc aluminum calcium borosilicate glass-ceramics

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ABSTRACT

Glass-ceramic frits of various sizes composed of zinc aluminum calcium borosilicate ($CaO-B_2O_3-SiO_2-ZnO-Al_2O_3$) were prepared by mechanical milling and subsequent size selection of the glass melt. Glass frits with mean particle sizes of 1.2 ± 0.9 μm, 2.9 ± 2.1 μm, and 4.8 ± 2.3 μm were successfully obtained using a two-step size selection process combined with gravity sedimentation and centrifugation methods. Dilatometry, DTA, XRD, SEM, and high-resolution TEM were utilized to examine densification/crystallization behaviors of the produced materials, while mechanical properties of sintered samples were evaluated using a three-point bending test and micro-indentation method. The obtained results show that densification temperatures of the produced glasses were notably lowered, while bending strength and indentation hardness of the sintered samples increased as the initial frit size decreased to ~1 μm. The observed enhancement of mechanical properties is attributed to pore reduction, small grain sizes, and formation of nano-sized crystalline phases in the glass matrix.

1. Introduction

Glass-ceramics (also known as *pyroceramics* and *vitroceramics*) are polycrystalline materials formed by controlled crystallization of parent glasses, which are characterized by a number of remarkable properties including high chemical durability, high mechanical strength, good thermal shock resistance, low tunable thermal expansion coefficients, and good biocompatibility. They are widely used in various applications such as cookware, low-temperature co-fired ceramics (LTCCs), hermetic sealing, and bone replacement materials [1–7].

The LTCC technology, which utilizes metallic circuits combined with reliable ceramic dielectric layers, has been extensively studied because of its various advantages that include using low-melting electrodes (such as Ag with a melting point $T_m = 961$ °C) and increments of integration density [3,8]. For LTCCs, dielectric constants (k) of substrate materials should be lower than that of alumina ($k = 9$) to reduce signal propagation delays [9]. In addition, substrate flexural strengths must be high, while the corresponding densification temperatures have to be less than 950 °C for successful co-firing with silver electrodes [10,11]. In this regard, glass-ceramics, obtained through the control of the crystalline phase of a glass matrix, are one of the best candidates because they have high densification at low temperatures, good shape stability, high mechanical strengths, and low thermal expansion coefficients [11–13]. Among various glass-ceramics, calcium borosilicate glass ($CaO-B_2O_3-SiO_2$, CBS) and its modified derivatives have been studied as important materials that can be used to manufacture LTCC substrates for mass production and are demonstrated low thermal expansion coefficients, small dielectric constants, and low production costs [14–16].

In addition, glass-ceramic-based bioactive and biodegradable materials have recently been studied as potential bone replacement materials. For example, bioactive and biodegradable properties of CBS glass systems were reported by C. Ohtsuki et al. [17]; however, they exhibited poor mechanical properties. Ryu et al. reported that CBS glass can be crystallized (leading to glass-ceramic formation) by heat treatment and controlling its chemical composition, thus demonstrating improved mechanical properties (such as bending strength and fracture toughness) of the material [18]. However, the number of reported studies on this topic is limited, and the related mechanical properties of glass-ceramics should be further enhanced in order to become suitable for more advanced applications [7].

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Microstructures and densification behavior of glass-ceramics are significantly affected by various ceramic processing parameters, such as size and morphology of the initial powder, presence of glass-forming additives, compositions, and sintering conditions [4,19]. Regarding the mechanical properties of glass-ceramics, produced glasses must possess controllable crystallinity, low porosity, and high relative densities of sintered samples because glass pores often act as crack-initiation points [5].

In this study, ZnO–Al_2O_3-modified calcium borosilicate glass (ZnO–Al_2O_3–CaO–B_2O_3–SiO_2) was prepared, followed by an investigation of its related frit-size dependent densification behavior and mechanical properties (including flexural strength and indentation hardness). Basic techniques such as mechanical milling, gravity sedimentation, and centrifugation methods were employed for the size selection process, while the related conditions were optimized to prepare three different glass frits with mean particle sizes of 1.2 μm, 2.9 μm, and 4.8 μm. Densification behavior and microstructural changes during sintering were investigated using dilatometry and scanning electron microscopy (SEM). Finally, indentation hardness, crystallization behavior, and initial glass-frit size dependent flexural strength were evaluated for the obtained materials.

1.1. Experimental procedure

1.1.1. Preparation of glass melts and frits

A quenching method was used to prepare ZnO–Al_2O_3-modified calcium borosilicate glass (ZA-CBS) composed of $CaCO_3$ (9 mol. %), B_2O_3 (21 mol. %), SiO_2 (67 mol. %), ZnO (1 mol. %), and Al_2O_3 (2 mol. %). According to a typical procedure, a stoichiometric combination of the starting materials ($CaCO_3$, B_2O_3, SiO_2, ZnO, Al_2O_3: 99.9%, High Purity Chemicals, Japan) was mixed in a polyethylene bottle with zirconia media for 6 h and then melted in a platinum crucible at 1500 °C for 2 h followed by quenching in ice water. The obtained glass frits were roughly milled using jet-milling and ball milling methods (zirconia media, 6 h). During the first size selection step, both fine (<1 μm) and large (>25 μm) glass frits were removed by using a sedimentation method (12 h). During the second size selection step, a centrifugation method was utilized to obtain three different glass frit sizes of 1.2 μm, 2.9 μm, and 4.8 μm (this procedure was repeated several times to narrow down size distributions). The obtained glass frits were first granulated with a polyvinyl alcohol aqueous solution (10 v/v %), then uniaxially pressed into disk-type pellets at a pressure of 1000 kg/cm^2, and finally sintered between 875 °C and 925 °C with a heating rate of 10 °C/min inside a box furnace.

1.1.2. Characterization and measurements

Morphologies and size distributions of the obtained glass frits were evaluated and measured using field-emission SEM (FE-SEM) and a particle size analyzer (PSA: Model S3500, Microtrac, U.S.A.), while the Archimedes method and a pycnometer were utilized to determine bulk and true densities, respectively. Sample shrinkage that occurred during the annealing was measured using a uniaxial horizontal dilatometer with alumina rams and boats (model DIL402C, Netzsch Instruments, Germany). Crystallization behavior was examined by using an X-ray diffractometer (XRD) and differential thermal (DTA) analysis. SEM (model JSM-6330F, Jeol) and transmission electron microscopy (TEM, JEOL JEM-3000F, Jeol) were used to examine microstructures and crystal phases of the sintered samples. A 200 g load was applied to evaluate Vickers hardness (micro-indentation apparatus MVK–H2) by performing five measurements for each sample surface. Flexural strengths of the sintered samples (30 samples total) were measured using a three-point bending method with a crosshead speed of 5 mm/min and span length of 25 mm. The sample dimensions were approximately 3 mm × 4 mm × 37 mm.

2. Results and discussion

2.1. Preparation of glass frits with different particle sizes

The obtained ZA–CBS glass melt was first crushed using a jet-milling method followed by the application of ball-milling and gravity sedimentation techniques to obtain glass frits with sizes ranging between 100 nm and 25 μm Fig. 1, a–d shows the schematic of the two-step size selection process and the SEM images of the resultant glass frits. After the second size selection step, in which centrifugation (at 200–600 rpm for 20 min) was used, three different glass-frits with angular shapes and relatively narrow size distributions were obtained (Fig. 1, b–d). To determine the centrifugation speed and time for the given size range of glass-frits, the following equation derived from the Stokes law was used [20]:

$$t_c = t_2 - t_1 = \frac{(18 \times 10^8 \times \eta_o)}{(\rho - \rho_o)\omega^2 d^2} \times log_c\left(\frac{r_2}{r_1}\right) \quad (1)$$

where t_c is the time required for centrifuging particles with size d from distance r_1 to distance r_2, η_o is the absolute viscosity of the media (water), ρ_o is the density of the media, ρ is the true density of the particles (g/cm^3), ω is the angular velocity, and d is the particle diameter. The obtained PSA results (Fig. 1, e–f) clearly indicate that the initial glass-frits with wide size distributions (from 100 nm to 25 μm) were successfully separated into three different groups with relatively narrow size distributions (±2 μm) and mean volume particle diameters of 1.2 ± 0.9 μm (denoted as ZA–CBS–1.2), 2.9 ± 2.1 μm (ZA–CBS–2.9), and 4.8 ± 2.3 μm (ZA–CBS–4.8), which is in good agreement with the SEM results.

2.2. Densification behavior

In the next step, a DTA and dilatometer were used to investigate the crystallization and densification behaviors of the three previously obtained ZA-CBS glass-frits. First, as shown in Fig. 2a, the glass transition temperature (T_g) and crystallization peak temperature (T_p) of the ZA-CBS-1.2 sample slightly lowered compared to that of the ZA-CBS-4.8 sample. Second, the shrinkage and related shrinkage rate curves of the ZA–CBS glass-frits are plotted in Fig. 2b–c as functions of temperature. As shown in Fig. 2b, the shrinkage onset-temperatures of the ZA–CBS glass-frits decreased with a reduction in glass-frit sizes (ZA–CBS–4.8: 680 °C, ZA–CBS–2.9: 675 °C, ZA–CBS–1.2: 665 °C). In general, shrinkage onset-temperatures (or softening points) are related to glass transition temperatures (T_g) of glass [21]; therefore, as shown in Fig. 2a, it is considered that the decrease of the shrinkage onset-temperature of the ZA-CBS-1.2 sample was due to the reduced T_g. Second, the three ZA–CBS samples differ in temperatures corresponding to the maximum shrinkage rates (from 930 °C to 900 °C) as the glass-frit size is reduced; thus, different shrinkage rates of the samples are certainly related to their corresponding particle sizes. In addition, the maximum sample shrinkages at 900 °C are 17.8% (ZA–CBS–1.2), 13.9% (ZA–CBS–2.9), and 13.0% (ZA–CBS–4.8); therefore, the crystallization and densification temperatures of the ZA–CBS samples are affected by the initial glass frit sizes and decrease when the latter are reduced.

Fig. 3 depicts the measured (d_{mea}) and relative theoretical (d_{th}) densities of the ZA–CBS samples as functions of sintering temperature. The d_{mea} of the ZA–CBS–2.9 and ZA–CBS–4.8 samples rapidly increases from 1.6 g/cm^3 to 2.2 g/cm^3 as the sintering