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Sintering behavior, microstructures and mechanical properties of porous $CaO-Al_2O_3-SiO_2-Si_3N_4$ glass-ceramics

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ABSTRACT

Novel porous $CaO-Al_2O_3-SiO_2-Si_3N_4$ glass-ceramics with in-situ grown rod-like β-Si_3N_4 crystals were fabricated by sintering under a nitrogen atmosphere. Sintering behavior, microstructures and mechanical properties of various compositions in the $CaO-Al_2O_3-SiO_2-Si_3N_4$ system were investigated, using differential scanning calorimeter (DSC), X-ray diffractometry (XRD) and scanning electron microscopy (SEM) methods, followed by physical and chemical property measurements. Depending on our experiments, the coexistence of $CaO-Al_2O_3-SiO_2$ glass and α-Si_3N_4 can lower the phase transition temperature of α-Si_3N_4 and promote the in-situ formation and growth of β-Si_3N_4 grains during sintering process. The in-situ grown rod-like β-Si_3N_4 grains in the glass-ceramics are useful to the improvement of physical and chemical properties by addition of α-Si_3N_4 to the system. This was attributed to that the in-situ grown β-Si_3N_4 grains formed a spatial inter-locking microstructure. The physical and chemical properties of the porous glass-ceramics are mainly determined by the β-Si_3N_4 content, the porosity and the residual glassy phase. The porous $CaO-Al_2O_3-SiO_2-Si_3N_4$ glass-ceramics with high porosity, high mechanical strength and low dielectric constant were obtained, indicating it is potential high-temperature industrial applications.

1. Introduction

Porous Si_3N_4 ceramics had attracted considerable attention due to their high specific surface area, low density, high bending strength, and low coefficient of thermal expansion, which are expected to be applied to high-temperature gas/liquid filters, radomes for microfiltration, separation membranes, heat insulators and catalyst carriers [1,2]. Compare to other porous ceramics, porous Si_3N_4 ceramics, with a unique interlocking microstructure of elongated β-Si_3N_4 particles, have high flexural strength and thermal shock resistance [3–6]. Properties of porous Si_3N_4 ceramics are closely related to the pore structure (morphology, shape, porosity, orientation, etc.), which affects its practical application [7].

The sintering of glass powders is an efficient way for obtaining glass-ceramic materials [8–10]. $CaO-Al_2O_3-SiO_2$ glass-ceramics have a wide range of applications due to their high strength and high chemical resistance [11–13]. $CaO-Al_2O_3-SiO_2$ glass-ceramics have relatively lower thermal expansion coefficient and lower relative dielectric constant, which is close to silicon and is a potential material for low temperature co-fired ceramic substrates [14]. In addition, Ca–Si–Al–O–N glass had been widely studied for many years. Nitrogen incorporation therein enhances the glass formation and results in increased properties such as elastic modulus, micro-hardness, glass transition and softening temperature, density and so on. In general, the crystallization of Ca–Si–Al–O–N glass results in the precipitation of oxide or nitrogen-containing phases. The first one leads to nitrogen enrichment in the residual glass phase, which may result in an increase in the hardness and mechanical strength of the glass-ceramic. The crystallization of the nitrogen-containing phase may also lead to an improvement in the mechanical properties [15–17].

Porous glass-ceramics are heterogeneous systems that are physically composed of gaseous and solid phases. The solid phases consist of glass-ceramics surrounding single cells of several micrometers thick, and these cells are filled with the gaseous phase. The porous glass-ceramics have unique properties such as low density, good rigidity, resistance to freezing, good non-flammability, thermal and acoustic insulation, and excellent chemical inertness. Porous glass-ceramics have a variety of applications, such as catalyst carriers, films in combustion technology,

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and microbial immobilized carriers [18–20]. Owing to the relatively low mechanical properties of porous CaO-Al_2O_3-SiO_2 glass-ceramics, its practical application has been greatly limited. Porous Si_3N_4 ceramic has excellent properties; however, its densification must rely on sintering additives due to their high covalent bond character. On the other hand, the mechanical properties of porous glass-ceramics remain at a moderate level, and it has yet to be improved. This is related to the phase composition and microstructure of the porous glass-ceramics. Thus, reducing sintering temperature and improving mechanical properties are urgent to be solved.

So far, no work has been reported on the preparation of porous CaO-Al_2O_3-SiO_2-Si_3N_4 glass-ceramics. This study aims to provide a low-cost and efficient method for the fabrication of the porous CaO-Al_2O_3-SiO_2-Si_3N_4 glass-ceramics with excellent comprehensive performances for potential high-temperature industrial applications.

2. Experimental procedure

2.1. Materials and processing

Preparation of porous CaO-Al_2O_3-SiO_2-Si_3N_4 glass-ceramics by pressureless sintering under a nitrogen atmosphere includes the following processes: preparation of CaO-Al_2O_3-SiO_2 glass frits, mixture of α-Si_3N_4 and CaO-Al_2O_3-SiO_2 frits, and sintering at high-temperature. $CaCO_3$ and $CaHPO_4 \cdot 2H_2O$ are chosen as a foaming agent and foaming stabilizer, respectively. The starting materials used for this work were commercial grade α-Si_3N_4 powders (average particle size 0.5 ± 0.05 μm, α-phase ≥95%); Al_2O_3, SiO_2, $CaHPO_4 \cdot 2H_2O$ and $CaCO_3$ (average particle size 1.0 ± 0.1 μm, 99.9% purity). The initial composition of CaO-Al_2O_3-SiO_2 glass is 20 CaO, 45 Al_2O_3, 35 SiO_2 (mol.%).

In the second-step experiment, α-Si_3N_4, $CaHPO_4 \cdot 2H_2O$, $CaCO_3$ and CaO-Al_2O_3-SiO_2 glass frits were mixed in the appropriate proportion of water-free ethanol using an agate ball as the milling medium for 24 h till the average grain size was <50 μm. Table 1 lists the composition of the porous CaO-Al_2O_3-SiO_2-Si_3N_4 glass-ceramics used in this work. The powder mixtures were dried and sifted through a 200 mesh sieves. The mixed powders were uniaxially pressed in a steel mold of 30 mm in diameter at a pressure of 15 MPa. The green pellets were dried at the temperature of 100 °C for 2 h.

Sintering experiments were carried out in a graphite-resistance furnace under a nitrogen atmosphere. The 30 min holding time was adopted at 500 °C in order to remove the residue water and protect the samples from cracking caused by the uneven thermal distribution. Subsequently, two-step sintering process of the porous CaO-Al_2O_3-SiO_2-Si_3N_4 glass-ceramics was carried out (1050 °C/2 h + 1625 °C/4 h) in a graphite-resistance furnace under a nitrogen atmosphere with the pressure of 0.1 MPa, using the heating rate of about 3 °C/min. Excessive heating speed may seriously affect the formation of porous glass-ceramics. The samples were heated from room temperature (about 25 °C) to 100 °C after 30 min, then heated to 500 °C after 2 h, held at 500 °C for 30 min, then heated to 1050 °C after 3 h, sintered at 1050 °C for 2 h, and then the temperature was raised to 1625 °C after 3.5 h and sintered at 1625 °C for 4 h. After the sintering process was completed, the samples were cooled to 800 °C after 4.5 h, held at 800 °C for 1 h, and finally cooled to room temperature after 4.5 h.

Table 1
Composition of the porous CaO-Al_2O_3-SiO_2-Si_3N_4 glass-ceramics investigated in this work.

Samples No.	Compositions (wt%)			
	CaO-Al_2O_3-SiO_2 glass frit	$CaCO_3$	$CaHPO_4 \cdot 2H_2O$	α-Si_3N_4
GS-20	70	7.5	2.5	20
GS-25	65	7.5	2.5	25
GS-30	60	7.5	2.5	30
GS-35	55	7.5	2.5	35
GS-40	50	7.5	2.5	40

2.2. Characterization techniques

The DSC curve of CaO-Al_2O_3-SiO_2 glass was obtained using a differential scanning calorimeter (DSC, Netzsch 404PC, Germany) at a heating rate of 10 °C/min. In high-purity argon, a finely powdered glass sample was subjected to DSC from room temperature to 1400 °C. The standard deviation of the characteristic temperature values obtained by DSC was in the range of ±5 °C.

The phase composition of the CaO-Al_2O_3-SiO_2 glass-ceramics and porous CaO-Al_2O_3-SiO_2-Si_3N_4 glass-ceramics was investigated by X-ray diffractometer (D/max 2500 model) with Cu-Kα radiation ($\lambda = 0.154$ nm). Voltage and current were selected as 40 kV and 50 mA, respectively. The data were collected in the 2θ range of 10–80° with a step size of 0.05° at the temperature of 25 °C.

The microstructural morphology and EDS patterns were examined by a scanning electron microscope (Quanta 200, FEI, Netherlands) which was fitted with a Peltier-cooled stage during SEM operation. Porous CaO-Al_2O_3-SiO_2-Si_3N_4 glass-ceramic samples were covered with a thin layer of gold. SEM tests were used to examine the phase evolution and microstructure of the porous CaO-Al_2O_3-SiO_2-Si_3N_4 glass-ceramic samples.

Both the bulk density and porosity of the porous CaO-Al_2O_3-SiO_2-Si_3N_4 glass-ceramics were measured by the Archimedes method using deionized water as a medium. The result is averaged over 10 measurements for each sample. The measurement error of the porosity and bulk density values is within ±1%.

The three-point bending strength of the sample was measured on the porous CaO-Al_2O_3-SiO_2-Si_3N_4 glass-ceramic bar using a universal testing machine (AGS-10kNG, Shimadzu, Japan). The porous glass-ceramic samples were 3 mm × 1.2 mm × 24 mm with the span length of 18 mm and a crosshead speed of 0.5 mm/min. Compression strength was carried out at a fixed crosshead speed of 0.5 mm/min. The porous glass-ceramic samples with dimensions of Φ 10 mm × 2 mm were machined. For diametral compression, the porous glass-ceramic samples in the form of disks, after grinding and polishing were subject to a compressive stress along their diameter. The average values were obtained from 10 samples. The measurement error of the bending strength and compression strength values is within ±2%.

The thermal diffusivity (λ) for each sintered porous CaO-Al_2O_3-SiO_2-Si_3N_4 glass-ceramic sample was measured, using the laser-flash method (Model Netzsch LFA 427). The thermal conductivity values were calculated by multiplying the thermal diffusivity with the density and specific heat. Dielectric properties for each sintered porous CaO-Al_2O_3-SiO_2-Si_3N_4 glass-ceramic sample were measured by an impedance analyzer (Wayne-Kerr, 6500B, UK) at 1 MHz. For the measurement of dielectric properties, both sides of each polished porous glass-ceramic sample were painted by Ag paste.

3. Results

3.1. DSC analysis of the CaO-Al_2O_3-SiO_2 glass

The DSC curve of the CaO-Al_2O_3-SiO_2 glass powder is shown in Fig. 1(a). The exothermic peak observed at a temperature of 1030 °C is related to the crystallization of Anorthite and Mullite, which has been confirmed by XRD analysis in subsequent experiments