

Microstructure control of sintered glass-ceramics in silicate system

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Glass sintering process has more advantages when compared to casting process in glass-ceramic fabrication. However, there is a disadvantage in the process-one must complete the glass sintering before crystallization starts to reduce the porosity of glass-ceramic. The crystallization of glass occurs through either internal or surface crystallization mechanisms, depending on the glass composition and other factors which are not easily controlled artificially. In either case, nucleation and crystal growth are involved during the glass sintering with internal factors (composition, nucleating agents, glass powder (size, surface)) and external factors (temperature, time, atmosphere, heating source, etc.), which affect the crystallization process. This paper answers, "How do the factors affect glass sintering in silicate glass systems?" in order to control microstructures in glass-ceramics. Following a review of earlier work, as a case study, glass powder sintering was discussed on a heating sources, microwave heating in sinter glass-ceramics.

Key words: Crystallization, Glass-ceramic, Nucleation, Crystal growth.

Introduction

Application for electronic device (substrate), bio-materials as a dense or a porous glass-ceramic for mechanical, electrical, thermal and optical properties have been prepared by sintering and crystallization of the glass powder compacts [1]. There are two ways to produce glass-ceramics: 1) casting (by melting composition, melt molding and crystallization) for a monolithic glass-ceramic, and 2) sintering (by preparing glass powder, forming (dry pressing, slip/tape casting, extrusion, and injection molding) and sintering) for a sintered glass-ceramic. Compared to the well known conventional process, casting, sintering processes have the possibility of making complex shapes as well as glass-ceramic composites in the field of application. Sintering of glass-ceramic is carried out in two processes: one is two stages as densification of glass (sintering) and crystallization consequently and separately; the other occurs simultaneously as one stage. In any case, the important factors in the glass sintering (earlier stage) are the viscosity, surface tension and glass powder size [2]. The factors of glass powder size and size distribution are the same as the conventional ceramic sintering except hot pressing. In glass sintering, densification occurs just above T_g (glass transformation temperature) and at that time applying load on the glass powder will achieve higher compactness during the heating. The condition of surface glass powder,

however, has different effect on the densification and crystallization compared to normal oxide sintering.

In this paper, we briefly review these results and discuss new results on the effect of heating sources on the microstructure of sintered glass. This paper reviews the reasons for particle rearrangement in glass sintering, as well as recent progress in the understanding of this crystallization mechanism in sintered glass-ceramics. Finally, the effect of microwave heating source on sintered glass-ceramics, instead of the heating sources of electric furnaces, is discussed in the ZrO_2 - CaO - SiO_2 glass system where the sintering result is compared with conventional sintering process.

Sintered Glass-Ceramics

If glass is finely ground and sintered, each particle will crystallize separately from the original surfaces. As a result, bulk glass-ceramics are usually free from porosity. Sintered material can be expected to have 1~5% porosity, depending on how far the sintering process can proceed before it is halted by crystallization. As the first step in the process, glass sintering should be controlled and then crystallization should follow to form a pore-free sintered microstructure.

Concept of glass sintering

The sintering of glass particles is based on the mechanism of viscous flow. In the overall process of glass sintering, all three stages involve the physical movement of glass particles within and on the surfaces of the green compact. The stage are: 1) growth of weld necks, 2) closure of the channels connecting pores, and 3) densification.

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Table 1. Comparison of glass sintering models

Stage	Factors	Relations	Models	References
Initial stage	γ, η, r	$\Delta L/L_0 = 3\gamma t/4\eta r$	Frenkel	3
Intermediate stage	γ, η	$T(\text{reduced time}) = \gamma n^{1/3}(t-t_0)/\eta$	Scherer	4
Final stage	γ, η, r	$Dp/dt = k\gamma n^{1/3}(1-p)^{2/3}p^{1/3}/\eta$	Mackenzie and Shuttleworth	5

Key to Table 1: L, the length at isothermal sintering time t; L_0 , the original length; γ , the surface tension; η , the viscosity; r, the radius of the glass particle; p, the relative density, which is equal to the bulk density divided by the true density of porous glass containing n pores per unit volume of glass, and k is a constant that depends on geometry.

Hence, the most important factors to the rate of glass densification are the surface tension, viscosity and particle size of glass as observed in Table 1. For silicate materials, the surface tension is not changed much by glass composition, but the viscosity, however, is. Thus, changing the glass composition to lower the viscosity of the glassy material increases the rate of densification.

The theory of viscous sintering is explained by two models developed by Frenkel and Scherer [3-5]. The former model explains the sintering behaviour of glass containing closed spherical pores, while the latter explains open pores and nonspherical glass powder, which appears in the intermediate stage of sintering. Frenkel model analyzes the surface tension, the viscosity and the powder size of glass in the process. Scherer model is related to the strong effect of viscosity and specific surface area on the sintering rate. In fact, the glass-sintering rate depends on the packing structures, shapes of powder, green density coordination number as well as particle size, viscosity, and surface tension.

Crystallization of glass

For sintered glass-ceramic using glass powder, the sintering mechanism is different from powder size: in the case of coarse powders, sintering is completed before surface crystallization occurs, while crystallization causes viscous sintering to cease before it has time to reach completion for the finer powders. Sintered glass-ceramics are commonly produced by the following procedure: (i) Melting of glass composition, (ii) Quenching of molten glass, (iii) Preparation of glass powders, (iv) Forming at room temperature, (v) Firing for densification and crystallization, (vi) Hot pressing, instead of steps (iv) and (v). (vii) Sol-gel process at low temperature [6].

As shown in Table 1 the viscosity of glass at high temperature should be low enough to permit the glass to flow in order to get a pore-free and well sintered structure. The dynamics of the viscosity changes during the crystallization of glass-ceramics can be explained in terms of two completing processes during hot press sintering: the rate of heating (which decreases the viscosity) and that of crystallization (which increases the viscosity) of the residual glass. In glass-ceramics produced by sintering, crystallization must be delayed until sintering is completed or it must take place simultaneously with sintering, otherwise a coarse, non-

uniform structure will be formed together with residual porosity. By careful choice of the glass composition, heat treatment etc., this surface crystallization phenomenon has been applied technologically in the production of sintered ceramic bodies by a number of workers [7-18]. In terms of the macroscopic sintering mechanism, however, the classical theories of glass sintering are not considered for the following:

Factors in sintered glass-ceramics

Internal factors

Shape of glass powders: It has been shown that non-equilibrium particle shapes of glass sinter more rapidly, about five times, than equilibrium or spherical particle shapes of glass of the same size [7]. Researchers explained that the faster sintering rates of crushed glass is due to the sharper radii at the points of contact between the glass powders as shown in Table 1.

Surface condition: Devitrification of glasses by surface-induced nucleation would be useful for production of glass-ceramics, in some cases, depending glass-composition, for example, Neoparies product [8]. In general, it is dust particles, contaminations on the glass surface, and surface quality (mechanically polished, fractured and fire polished) that promote surface crystallization of glasses. Recently, for dense and porous cordierite sintered glass-ceramic, it was suggested to use surface induced method [9]; surface nucleation density can be altered by different surface preparation using various milling techniques.

Distribution of glass powder size and packing conditions: In general, glass particle size has a strong effect on the sintering rate; in changing from 10 μm to 1 μm , the rate of sintering is increased by a factor of 10 [10]. Liniger and Raj reported on the spatial variations in the sintering rate of ordered and disordered glass particle structures [11]. In ordered structures made from mono-sized spheres, the local sintering rates varied from 1/2 to 2 times the average sintering rate. In contrast, disordered arrays made from bimodal particle sizes, sintered more homogeneously, with the local sintering rate deviating less than 15 % from the average. The total average densification strain was also greater for the disordered structures. As a result, for the same time and temperature cycle, the disordered structures sintered to near full density while the ordered structures did not.

The powder size has a positive effect on the densifi-

cation of glass/glass-ceramic sintering. Recently the effective size in sintering has been suggested [12]. For the $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-ZnO}$ system, there is a threshold mean particle size ($\sim 7 \mu\text{m}$) for the glass powders investigated, after which the sinterability decreased rapidly. However it is not clear whether the upper limit of glass powder is available for other glass systems.

Viscosity of glass: This factor is very important for densification of glass before conversion to the glass-ceramic stage. The temperature interval between T_g (transformation temperature) and T_o (onset of crystallization temperature in DTA curve) is a criterion for the sinterability of glasses: if $\Delta T = T_o - T_g$ is small, then the glass is not able to be fully densified by sintering below T_o . To lower glass viscosity for improving densification rate, it has been shown that cordierite ($2\text{MgO Al}_2\text{O}_3 5\text{SiO}_2$) and spodumene ($\text{Li}_2\text{O Al}_2\text{O}_3 4\text{SiO}_2$) glasses do not sinter well, while adding small amount of B_2O_3 and/or P_2O_5 was found to improve densification due to the lowest crystallization tendency of the glass-ceramics [13].

Formation of Micro pores: Micro pores are found in microstructure of glass-ceramic due to shrinkage resulting high crystallinity and surface crystallization after internal crystallization happened [14]. In general, the shape of pores shows irregular type rather than regular shape as spherical ones, which are less than sub-micron size. Such pores could be advantage to mechanical properties, specially improving fracture toughness in $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ glass-ceramic [15]. On the other hand, intentionally a porous glass-ceramic can be produced as appeared in cordierite ($2\text{MgO } 2\text{Al}_2\text{O}_3 5\text{SiO}_2$) glass-ceramic suggested by Muller *et al.* [9]: sintered cordierite glass-ceramic was obtained by tuning nucleation density at the glass powder surface for glass-ceramic containing up to 40 % of porosity.

External factors

Gravity force: Gravity-induced flow causes the viscosity of glass at high temperature to decrease: e.g., the softening point of $10^{6.6} \text{ Nsm}^{-2}$ corresponds to an apparent viscosity of about 10^8 Nsm^{-2} [16]. The above sintering theories are restricted to the assumption of a homogenous glass matrix. If a mixture of two different powders (glass powders and other powders) is sintered and devitrification involves during the glass sintering, it is difficult to give any quantitative theory of the sintering.

Atmosphere: Exner and Petzow found that the atmosphere has a strong effect for the neck growth: e.g., the inside angle change of the three particles was larger in wet than in dry air, and even larger in argon [17, 18]. As a result, they proposed that the atmosphere influences a thin surface layer and the spheres, therefore, can no longer be treated as a material of constant viscosity. Thus, water vapour may reduce the viscosity and therefore increase the apparent densification rate.

Heating source: Microwaves are introduced in sintered glass-ceramic process, but, an explanation for the

process is not clear, specially on the microwave effect on sintering and crystallization during microwave processing of glass powder: $\text{CaO-ZrO}_2\text{-SiO}_2$, $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ systems [19, 20].

In the $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ systems, Clark reported that the decrease in loss factor observed during crystallization could offer additional advantages for microwave processing over conventional techniques [20]. The detailed results, however, are not found in literatures. The following section is concerned on the comparison of different microwave sintering and conventional sintering on glass powder sintering.

A Case Study: Using Microwave Heating Source on $\text{CaO-SiO}_2\text{-ZrO}_2$ Glass System

Experimental

Mixtures of raw materials (57 % SiO_2 , 28 % CaO and 15 % ZrO_2) were melted in Pt crucibles at 1500°C . The melts were quenched in water to obtain glass powder and were wet-milled for a powder. After the glass powders were dried, they were separated fine ($< 38 \mu\text{m}$) and coarse ($45\sim 150 \mu\text{m}$) powder using sieves. Pellets were then pressed with a pressure of 300 kg/cm^2 and were heated at 500°C for 2 h to evaporate binder (7 wt% stearic acid). The sintering was carried out by microwave (2.45 GHz, Max. power, 1.5 KW; Ceramic Engineering, Warragamba, Australia) heating at 900, 1000, 1100 and 1200°C for 0~20 min soaking time. The glass transition and the crystallization temperatures were determined with a differential thermal analyzer (DTA) on samples ground to a grain size of less than $40 \mu\text{m}$. Polished and etched (4 % buffered HF) glass-ceramic samples were coated by sputtering Au for scanning electron microscopy (SEM) to obtain the microstructure. The density of sintered samples was measured by Archimedes method.

Results

Sintering of Glass Powder

Densification of fine powder ($< 38 \mu\text{m}$) showed a little higher shrinkage than coarse powder ($45\sim 150 \mu\text{m}$): the sintering of fine glass powder proved to have a good sinterability in the microwave sintering, rather than using coarse glass powder (Fig. 1). For both of powders, the rate of densification slows as temperature and time increase, above the onset of crystallization peak temperature resulted from the crystallization of glass. Crystallization hinders the viscous flow of glass in sintering and the process is summarized as a function of temperature: $770 < T < 940^\circ\text{C}$: glass sintering for fine powder; $800 < T < 970^\circ\text{C}$: glass sintering for coarse powder; $900/970 < T < 1000/1040^\circ\text{C}$: internal crystallization process (fine/coarse powder); $T > 1100, 1200^\circ\text{C}$: 2nd crystallization/transformation [21]. With increasing temperature and soaking time, the decrease of density and densification rate resulted from the formation of a number of large pores, which have non-

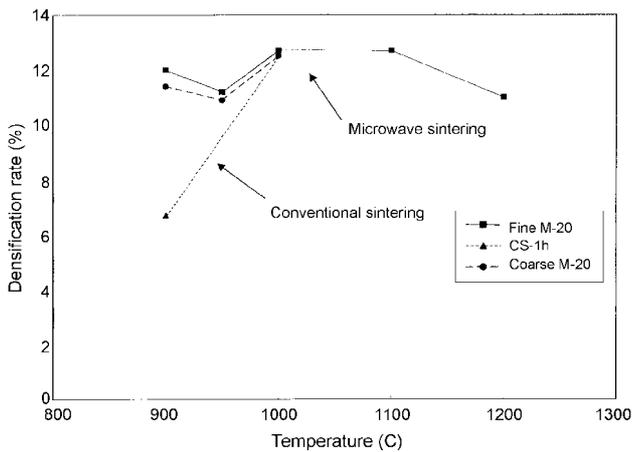


Fig. 1. Densification rate of sintered samples prepared by MS and CS (Fine M-20 and Coarse M-20 mean sintered samples with fine and coarse powder by microwave heating for 20 min, respectively., and CS-1h, samples produced by conventional sintering with fine powder for 1h).

spherical shapes as shown in Fig. 2. It is thought that the residual glass which plays a buffer role in glass-ceramic totally disappears in the microstructure of the later sintering stage due to high crystallinity and solid transformation.

Crystallization of Glass

The conventional sintering (CS) result showed the surface crystallization, whereas microwave sintering (MS) result internal crystallization (Fig. 2). In the process of the crystallization by MS, the crystal growth may be attributed to nucleation in the glass. The surface crystallization rate was measured to be $5\sim 8 \times 10^{-2} \mu\text{m}/\text{min}$ at 1000°C by CS and the crystal growth rate was 1/20 times of $1 \mu\text{m}/\text{min}$ by MS at the same temper-

ature. Based on the Tamman theory [1], the result was supposed that the nucleation rate and the crystal growth rate were overlapped, so that the crystallization occurred by a single stage process during the MS. Thus, it is suggested that the crystal growth rate of internal crystals may be related to increasing diffusion coefficient of ions under the microwave heating process in spite of not supporting the result in this study. After sintering and crystallization using CS and MS, the property and crystal phases are compared as given in Table 2.

Implication of sintered glass-ceramic using MS

Based on the thermal analysis of glass powders and the loss tangent of glass during the heating, the result of crystallization suggests surface crystallization because of the different exothermal peak temperature between fine and coarse powders [21]. The result of sintered microstructure after MS, however, showed internal crystallization rather than surface crystallization. The phenomena could be explained as follows: the $\text{CaO}/\text{SiO}_2/\text{ZrO}_2$ glass shows a constant $\tan\delta$ up to T_g , because of the existence of a rigid bulk (relatively high viscosity), but in the range of the glass transition $T_g(=770\sim 800^\circ\text{C})$ and the crystallization peak temperature (900°C), the thermal effect contributes to decrease the glass viscosity and enhance the effective conductivity (σ) of the glass, so that $\tan\delta(=\sigma/2\pi f\epsilon_0\epsilon')$ of glass is increased. Considering that the power absorbed per unit volume by microwave (P_v) is represented to be $P_v=kE^2f\epsilon \tan \delta$, assumed nearly constant dielectric constant (ϵ) in glass/glass-ceramic ($\epsilon=6.0, 4.3$ and 6.0 for soda lime glass, borosilicate glass and glass-ceramic, respectively [20]), the MS in the $\text{CaO}-\text{SiO}_2-\text{ZrO}_2$ glass is very effective sintering process compared to CS when only the $\tan\delta$ determined is considered in this

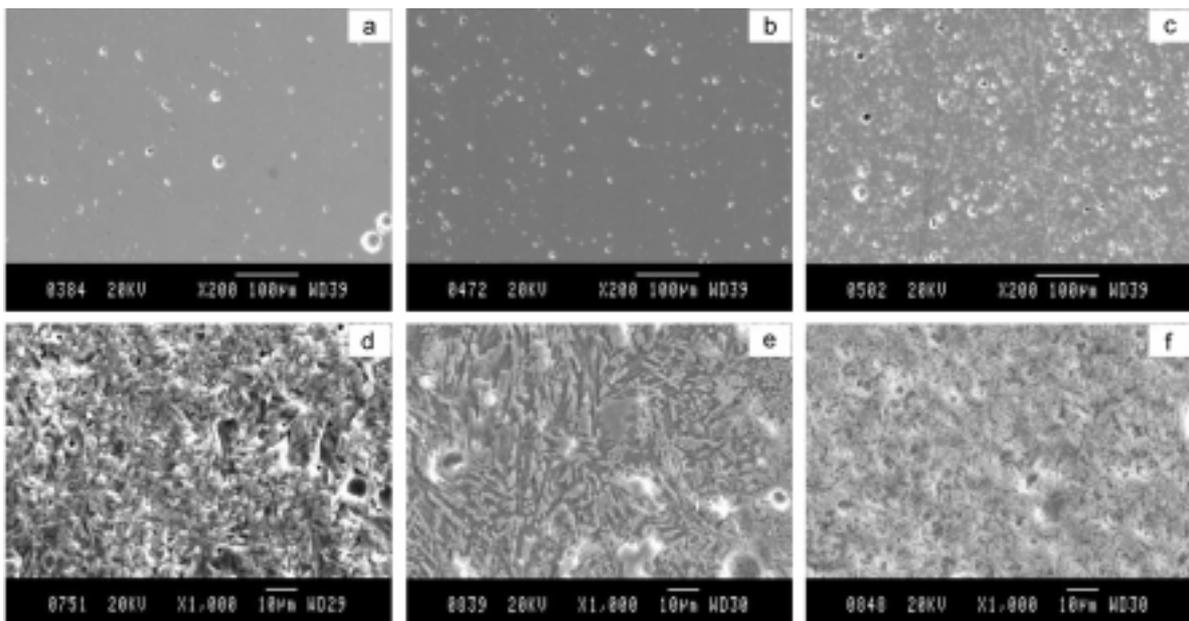
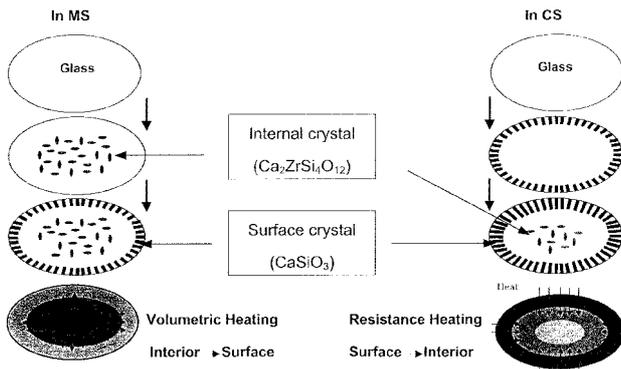


Fig. 2. Microstructure of sintered glass-ceramic (coarse powder) (a, b and c) before etching (d, e and f) after etching

Table 2. The comparison of properties of sintered glass ceramic produced by different processes

Process	Compositions (mol%) CaO/SiO ₂ /ZrO ₂	Crystallization	Crystal phases	Reference
CS	35/53/12	Internal	CaSiO ₃ (I) Ca ₂ ZrSi ₄ O ₁₂	Current work
CS	37/57/6	Surface	CaSiO ₃ (I) Ca ₂ ZrSi ₄ O ₁₂	Current work
MS	37/57/6	Internal	CaSiO ₃ (I)	[19]

Crystallization Mechanism

**Fig. 3.** Crystallization mechanism of CaO-SiO₂-ZrO₂ glass powder by MS and CS sintering.

system.

The process of microwave heating is different from that of resistance heating in terms of thermal gradients on glass powder. Since microwave absorption involves volumetric heating within the sample itself, heat loss by radiation from the surface would be expected to lead to from interior to surface, which is contrary to resistance heating, from surface to interior [22]. Thus, the different heating process induced different crystallization mechanism (Fig. 3). As presented in Table 2, internal crystallization, having uniform and fine crystals, occurred in only MS which makes effectively the nucleation and crystal growth during heating for a short time, since T_{crit} of ZrO₂ and the glass are about 600°C and 800°C, respectively.

Summary

Research has shown that there are several factors to control sintered glass-ceramics from glass powder. In this study, the system is fixed in silicate glass systems and the factors for sintering of glass-ceramic are classified into two groups and discussed: the internal factors such as composition, nucleating agents, glass powder size and surface, and the external factors with temperature, time, atmosphere, and the heating source, which affect the crystallization process. As a case study, on the effect of a heating sources in glass-ceramic sintering, microwave and conventional sintering were compared and discussed on the CaO-SiO₂-ZrO₂ sinter glass-ceramic. It was revealed that microwave absorption involves volumetric heating within the sample

itself, and that heat loss by radiation from the surface would be expected to lead to from interior to surface, contrary to resistance heating, from surface to interior. Thus, the different heating processes induced different crystallization mechanisms.

Acknowledgements

This paper was supported in part by NON DIRECTED RESEARCH FUND (HSK), Sunchon National University

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