Effect of calcium fluoride on sintering behaviour of SiO$_2$-CaO-Na$_2$O-MgO glass-ceramic system

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Abstract

The crystallization characteristics of glasses based on the SiO$_2$-CaO-Na$_2$O-MgO (SCNM) system containing calcium fluoride (CaF$_2$) have been investigated by differential thermal analysis (DTA), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The partial replacement of CaO by CaF$_2$ in the studied glass-ceramics led to the development of different crystalline phase assemblages, including wollastonite and diopside using various heat-treatment processes. With the increase of CaF$_2$ content, the crystallization temperature of the glass and the strength of the crystallization peak temperature decreases. Addition of CaF$_2$ up to 6.0 mol%, as expected, improved the sinterability. This sample reached to maximum density by sintering at 950 °C.

Keywords: glass ceramic, SiO$_2$-CaO-Na$_2$O-MgO, calcium fluoride, characterization, sintering

I. Introduction

Glass-ceramics are polycrystalline solids produced by the controlled crystallization of glasses [1]. The bulk chemical composition, final phase assemblage and microstructure are the most important factors affecting their properties. Crystallization of glass from the surface of a small number of sites in the interior usually results in low strength materials with coarse-grained microstructures [2]. The microstructure of such materials can be obtained by a sintering process as well, where crystallization and densification of the glass particles occur during firing [3]. The role of nucleating agents in initiating glass crystallization from a multitude of centres was the major factor allowing the introduction of glass-ceramics into industrial applications [4,5]. Sintering of these materials is a major disadvantage and would make it relatively expensive and difficult to produce complex shapes. The classic glass-ceramic production route of converting a monolithic glass to a monolithic glass-ceramic is a more convenient method to fabricate these materials [6]. The mechanism of the process is greatly influenced by the type of catalysts and chemical systems of the base glass-composition. The properties of glass-ceramics are determined both by the inherent characteristics of the constituent phases and by the microstructure resulting from the nucleation and growth sequence [7]. The use of efficient nucleating agents has allowed the development of highly crystalline materials of wide industrial applications [8]. In the CaO-MgO-SiO$_2$ system, glass-ceramics of diopside, wollastonite, and melilite have been thoroughly investigated [9–12]. Good mechanical and chemical properties of glass-ceramic materials from the CaO-MgO-SiO$_2$ system are suitable for use in wear resistant, thermo-mechanical, biomedical [13–15] and ceramic-coating applications [16,17]. Nevertheless, the relatively high processing temperatures (e.g. for glass melting or devitrification) characterize this family of materials. Obviously, high energy consumption opposes the current global trends related to environmental and economic issues [18]. Different varieties of nucleating agents greatly promote the crystallization process of the glass and enhance the formation of fine-grained microstructure [1]. CaF$_2$ is often used as a nucleating agent for crystallization of glass ceramics [19–23]. Has and Stelian [19] realized that when glasses are crystallized, the crystals of fluorite first come out of the base glasses and become the sites of heterogeneous nucleation of other crystals. Gan [20] and Wilson et al. [21] also realized that fluoride improved the nucleation and growth of glass ceramics.

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through F$^-$ ions entering the glass network to replace non-
bridge oxygen ions and decrease the aggregation extent of the
glass network [22]. The crystallization treatment
commences in homogenous glass and therefore a glass-
ceramic may be produced with essentially zero porosi-
ty [24]. Glass-ceramics from the SiO$_2$-CaO-Na$_2$O-MgO
system are important materials, due to their special dur-
bility and mechanical properties for using as glaze on ce-
ramic and tiles.

This paper investigates the effect of compositional
changes on the crystallization behaviour of glasses from the
SiO$_2$-CaO-Na$_2$O-MgO (SCNM) system, the growth
morphologies and the change of mechanical properties of glasses using CaF$_2$ as nucleating agent.

II. Experimental

The compositions of the glasses studied are listed in Table 1. The glass batches were prepared from reagent
grade powders: calcium carbonate (CaCO$_3$, 98.9%), magnesium oxide (MgO, 98%), quartz (SiO$_2$, 99.9%),
calcium fluoride (CaF$_2$, 99%) and sodium carbonate
(Na$_2$CO$_3$, 99%). The components of the batch, after being accurately weighed, were thoroughly mixed in an
agate mortar for about 15 min to ensure complete homogeneity. The weighed batches were melted in an
electrically heated furnace within an alumina crucible,
followed by cooling cycle: from 20 to 500 °C at 5 °C/min, from 500 to 1500 °C at 10 °C/min and finally
30 min at the maximum temperature of 1500 °C. Glasses in frit form were obtained by quenching the melts in cold water. The frits were dried and then
dry milled in a high-speed porcelain ball mill for 0.5 h. The glass powders were granulated (by stirring in a mortar) in a 5 vol.% polyvinyl alcohol solution (PVA,
Merck; the solution of PVA was made by dissolving in warm water) in a proportion of 98.5 wt.% of frit and 1.5 wt.% of PVA solution. Rectangular bars with di-

Table 1. Chemical compositions of glass-ceramics (in mol%)

<table>
<thead>
<tr>
<th>Samples</th>
<th>SiO$_2$</th>
<th>CaO</th>
<th>Na$_2$O</th>
<th>MgO</th>
<th>CaF$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>60</td>
<td>28</td>
<td>5</td>
<td>7</td>
<td>0</td>
</tr>
<tr>
<td>G2</td>
<td>60</td>
<td>27</td>
<td>5</td>
<td>7</td>
<td>1</td>
</tr>
<tr>
<td>G3</td>
<td>60</td>
<td>25</td>
<td>5</td>
<td>7</td>
<td>3</td>
</tr>
<tr>
<td>G4</td>
<td>60</td>
<td>22</td>
<td>5</td>
<td>7</td>
<td>6</td>
</tr>
</tbody>
</table>

Figure 1. DTA curves of samples containing different amount of CaF$_2$.
duce the crystallization at lower temperatures. The comparison of glass transition temperatures (T_g) (Table 2) again confirms the process of viscosity reduction due to the addition of CaF_2 additive.

Figure 2 depicts the sintering behaviour of various glasses. Addition of CaF_2 up to 6.0 mol% improves sinterability, possibly due to the increase of viscous flow of the glass. It can also be noted that the increase of the sintering temperature from 950 °C to 1000 °C reduces the linear shrinkage of the investigated samples, which is probably related to the volatility of this glass-ceramics at high temperatures. By comparing the crystallisation peak temperature of glass powders (Table 2) and their sintering behaviour (Figs. 2 and 3) it can be concluded that the sinterability depends on the temperature at which the crystallization starts, i.e. CaF_2 addition. It means that with increasing the crystallization temperature, the glassy phase would have enough time for viscous flow which leads to complete densification [25]. As discussed beforehand, the highest density was observed in samples containing 6.0% mol CaF_2 (Fig. 3). It is also observed that the maximum density of the samples was obtained at about 950 °C. The comparison of relative density of glasses shows that the sample G4 reaches an acceptable densification at the temperature ~140 °C higher than its crystallization peak temperature.

XRD analyses of the samples G3 and G4 are shown in Fig. 4. After sintering at 850 °C the appearance of very weak wollastonite (β-CaSiO_3) and diopside (Ca,Mg(SiO_3)_2) peaks can be seen in the XRD patterns of the glass-ceramics G3 and G4. It seems that those peaks are more pronounced in the sample with higher fluoride content (G4). Compared with wollastonite, diopside belongs to monoclinic system and has better mechanical properties and chemical stability. Thus, Toya et al. [14] have proposed that diopside is a preferable crystalline phase since it results in stronger materials than glass-ceramics based on wollastonite [14]. SEM images, presented in Fig. 5, confirmed the crystalline nature of the samples G3 and G4. It is believed that during the sintering process fluoride precipitated from the glass and formed

<table>
<thead>
<tr>
<th>Glass</th>
<th>T_g [°C]</th>
<th>T_c [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>950</td>
<td>1000</td>
</tr>
<tr>
<td>G2</td>
<td>910</td>
<td>920</td>
</tr>
<tr>
<td>G3</td>
<td>820</td>
<td>880</td>
</tr>
<tr>
<td>G4</td>
<td>810</td>
<td>810</td>
</tr>
</tbody>
</table>

Figure 2. Linear shrinkage of glasses versus firing temperature

Figure 3. Relative density of glasses versus firing temperature

Figure 4. XRD patterns of glass-ceramics G3, G4, after heat treatment at 950 °C for 2 h
nucleation points for the crystallization of wollastonite and diopside, and consequently induced the crystallization of the glasses. According to the investigation of Cheng et al. [26] CaF₂ is helpful for the formation of diopside. Thus, the addition of CaF₂ in the samples increased diopside and decreased wollastonite phase content (it can also be seen in Fig. 5). Since the ionic radius of fluorine (1.36 Å) is close to that of oxygen (1.40 Å), two Si–F bands can replace one Si–O–Si band, which contributes to the breakage of the silica network and the reduction of the stability of the glass structure.

Figure 6 shows the SEM micrograph of the surfaces of the G4 sample sintered at 900 and 950 °C for 2 h. As far as sintering is concerned, the experimental results showed that densification of glass-powder compacts starts at low temperatures (850 °C), advances at higher temperatures, likely by viscous flow sintering, and is almost complete at 950 °C. On the other hand, crystallization starts at temperatures below <850 °C and the crystallinity increases at higher temperatures, resulting in fully dense glass-ceramic materials. Karamanov et al. [27] have proposed that the crystallization of diopside may cause formation of additional porosity since there is a significant difference between the density of diopside in glassy (2.75 g/cm³) and crystal state (3.27 g/cm³). Note that the difference of density is negligible in the case of wollastonite (2.87 g/cm³ and 2.92 g/cm³ for the glass and the crystals, respectively) [28]. Figure 6b
shows that the sample G4 sintered at 950 °C is without surface porosity. This means that the increase of the viscous flow at higher temperatures (950 °C) is enough to eliminate the porosity that formed due to the crystallization of diopside.

Figure 7 shows the variation of bending strength of the investigated glass-ceramics with firing temperature. The bending strength of the specimens increases continuously up to the optimum sintering temperature, i.e. 950 °C. It seems that low densities of the samples G1, G2 and G3 are responsible for lower bending strength.

IV. Conclusions

The glass-ceramics were prepared by controlled crystallization from the SiO_{2}-CaO-Na_{2}O-MgO system containing up to 6.0 mol% of CaF_{2} and the relationship between processing schedules and properties was investigated. The addition of CaF_{2} results in a decrease of the transformation and crystallization temperature of the glasses, and increases the trend of crystallization. The main phases of the glass-ceramics are wollastonite (β-CaSiO_{3}) and diopside (CaMg(SiO_{3})_{2}). The relative density and bending strength of the SCNM glass-ceramics with 6.0 mol% content of CaF_{2} increase continuously up to the optimum sintering temperature, i.e. 950 °C.

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References


