Glass-ceramics one-step crystallization accomplished by building Ca\textsuperscript{2+} and Mg\textsuperscript{2+} fast diffusion layer around diopside crystal

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Abstract

CaO–MgO–Si\textsubscript{2}O\textsubscript{3} (CMS) glass-ceramics preparation normally needs two-step heat treatment (nucleation and crystal growth). In this work, CMS glass-ceramics are successfully produced by one-step heat treatment by building Ca\textsuperscript{2+} and Mg\textsuperscript{2+} fast diffusion layer between the residual glass and diopside crystal. High-temperature X-ray diffraction (HTXRD) shows that diopside crystals formed during the crystallization of CMS glass. At the glass layer between diopside crystal and residual glass, an enrichment of Na\textsuperscript{+} is observed by energy dispersive spectroscopy line scanning (EDSLS), which increases the Si–O–Na bonds that promote Ca\textsuperscript{2+} and Mg\textsuperscript{2+} ions diffusion. This layer eventually promotes further growth or ripening of the diopside crystals. Thus, nucleation and crystal growth of the CMS glass proceed continuously at the crystallization peak temperature (T\textsubscript{nc}), detected by differential scanning calorimetry. Thereby, one-step crystallization of the CMS glass-ceramics becomes possible and practical.

1. Introduction

Glass-ceramics are polycrystalline materials produced by melting and subsequent heat treatment [1,2]. Glass-ceramics is one of the most promising systems due to its excellent mechanical properties, high abrasive resistance and adequate chemical resistance. In recent years, glass-ceramics have been used as a sealant for solid oxide fuel cells [2,3], biomedical materials [4], optical [5,6] and building materials [7].

Usually, glass-ceramics is produced by either sintering or two-step crystallization due to its poor crystallization ability [3,8,9]. However, both of them have nonnegligible drawbacks: in the sintering process, the quenching step wastes a lot of heat and generates a large amount of wastewater, resulting in environmental pollution; meanwhile, the two-step crystallization contains two heat treatment steps (nucleation and crystal growth) [10–12], which is highly energy-consuming and carbon-emitting. Thus, high costs of economic and environmental protection issues involving in glass-ceramics production largely restrict their industrialized preparation and large-scale applications [13].

For many years, researchers have been working on new methods to reduce the manufacturing cost and carbon emissions in glass-ceramics preparation. One very promising way is the one-step heat treatment that conducts the nucleation and crystal growth at the same temperature (T\textsubscript{nc}) [14]. Small temperature difference (\Delta T) between the optimal nucleation (T\textsubscript{n}) and crystal growth temperature (T\textsubscript{c}) is the necessary condition for one-step crystallization of glass-ceramics. Generally, the T\textsubscript{n} and T\textsubscript{c} of an oxide glass are sensitive to the chemical composition of parent glass [15,16]. Hence, optimizing composition of the parent glass is considered as a feasible way to reduce \Delta T, with the improvement of nucleation capacity or crystal growth capacity of parent glass [17–20].

Recently, improving the nucleation capacity of the glass is believed to be significant to decrease \Delta T [18,19]. However, to the best of our knowledge, just a few papers reported success [14]. During the crystallization of glass, glass network modifiers and nucleation agent ions are concentrated in the crystals. Then, the glass layer between the crystals and residual glass is rich in glass network formers such as Al and Si. Thus, the glass layer becomes a diffusion barrier layer for ions of the crystal phase such as Ca\textsuperscript{2+} and Mg\textsuperscript{2+} [11,21–23], as shown in Fig. 1. The diffusion barrier layer would suppress crystal growth [24–26]. Thereby, higher temperature (T\textsubscript{c}) for crystal growth is necessary to overcome the diffusion barrier [27]. Therefore, avoiding the formation of diffusion barrier...
layer is necessary to improve the crystal growth capacity, decrease ΔT and achieve one-step crystallization of glass-ceramics. Generally, alkali metal ions are considered as glass network modifiers. Some researchers agree that some alkali metal ion will bond with the MO4 tetrahedron (M is a trivalent cations, such as Cr and Fe) to balance the local charge in the crystal lattice [28]. And, the remaining alkali-metal ion will escape the crystal phase and get into the glass layer between the crystal particle and residual glass [7,29]. Then, alkali metal ions help to increase the Si–O–Na bond content in the glass layer by transferring the Si–O–Si bonds to Si–O–Na bonds [7]. Consequently, the diffusion rate of Ca2+ and Mg2+ in this glass layer increases, manifested as enhanced crystal growth ability of the glass [7,30]. Thus, alkali metal ions changes the Ca2+ and Mg2+ diffusion barrier layer to a Ca2+ and Mg2+ fast diffusion layer, as shown in Fig. 1. Further, the Ca2+ and Mg2+ fast diffusion layer will promote the one-step crystallization of glass-ceramics.

To prove the feasibility of the above hypothesis, we tried to prepare CMS glass-ceramics by one-step crystallization. Na2O was considered as the glass network modifier to build the Ca2+ and Mg2+ fast diffusion layer. For comparison, CaF2 was used as the nucleation agent to improve the nucleation capacity of CMS glass. The crystallization kinetics index of the CMS glass was calculated using the Kissinger and Augis-Bennett equations. Experimental evidence of the Ca2+ and Mg2+ fast diffusion layer are also presented in this manuscript.

2. Experimental procedure

The raw materials were reagent grade CaO, MgO, SiO2, Al2O3, Fe2O3, Cr2O3, Na2CO3 and CaF2. The compositions of 4 samples are listed in Table 1. Homogeneous mixtures of the batches were obtained by dry mixing for 1 h in a ball mill. The mixtures were pre-heated at 900 °C for 2 h for Na2CO3 decomposition, then melted in alumina crucible at 1460 °C for 2 h in air. To obtain parent glass, the melts were cast into preheated steel molds and annealed at 600 °C for 30 min, close to the glass transition temperature, Tg. After annealing, the parent glass was cooled to room temperature in the furnace.

Differential scanning calorimetry (DSC) scans were obtained with a NETZSCH STA 409 C/CD thermal analyzer in air. The reference material was α-Al2O3 powder, and the parent glass powder samples were heated from room temperature to 1000 °C at different heating rates of 10 °C min⁻¹, 15 °C min⁻¹, 20 °C min⁻¹ and 30 °C min⁻¹. The crystalline phases in the glass-ceramics samples were identified from X-ray diffraction (XRD) patterns, which were obtained using an X-ray diffractometer (Philips APD-10, monochromatic Cu Kα radiation), at a scan rate of 9° min⁻¹. The dynamic crystallization process of the glasses was examined by in-situ high-temperature X-ray diffraction (HTXRD) using a 21 kW power diffractometer (model M21XVHF22, Mac Science, Yokohama, Japan). For the high-temperature measurements, the scan rate of the 2θ angle was 9° min⁻¹, and the heating rate was 10 °C min⁻¹. The microstructure of the glass-ceramics bulk samples was investigated on fresh fracture surfaces using Carl Zeiss EVO 18 scanning electron microscope (SEM), working in the secondary electron detector mode at 10 kV acceleration voltage. The composition of the crystalline and glassy phases was estimated using energy dispersive X-ray spectroscopy (EDXS) on a fracture surface.

3. Results and discussion

3.1. Crystallization kinetics parameters of CMS glasses

As seen in Fig. 2(a), no crystalline phases were detected by XRD analysis. This indicated that the nucleation and crystal growth didn’t occur during casting and annealing processes. The parent glass is completely amorphous. Hence, investigating one-step crystallization behavior of the parent glass is reasonable and reliable.

Excellent crystallization capacity and three-dimensional
crystallization mechanism are the two basic conditions of the glass-ceramics one-step crystallization. The crystallization activation energy ($E$) is an important index for evaluating the crystallization capacity of parent glass [32]. The Avrami index ($n$) is directly related to the crystallization mechanism of parent glass [20]. Thus, DSC experiments were used to investigate the crystallization kinetics indexes ($E$ and $n$) of the parent glasses. Fig. 2(b) shows the DSC results obtained from the parent glass powders. There is just one exothermic peak located in the DSC curves. It is noted that the unique exothermic peak may be associated with the formation of the main crystallization phase. The effects of Na$_2$O and CaF$_2$ on the crystallization kinetics of the CMS glass were further analyzed by the non-isothermal DSC method. $E$ and $n$ were calculated using the Arrhenius, Kissinger and Augis-Bennett equations as follows [33–36]:

$$k = \nu \exp\left(\frac{-E}{RT}\right)$$

$$\ln\left(\frac{T_p^2}{\alpha}\right) = \frac{E}{RT_p} + \ln\frac{E}{\nu} - \ln \nu$$

$$n = \frac{2.5 \times RT_1^2}{E}$$

Here, $k$ is the reaction rate constant, $\nu$ is the frequency factor, $E$ is the crystallization activation energy, $R$ is the gas constant, $T$ is the absolute temperature; $T_p$ is the crystallization peak temperature in the DSC curve and $\alpha$ is the heating rate of DSC; $n$ is the Avrami index; $\Delta T_1$ is the width at half maximum of the DSC exothermic peak. $E$ can be calculated from the slope of $\ln(T_p^2/\alpha)$–1000/T$_p$. Low $E$ value indicates high crystallization ability [20]. The value of $n$ is related to the crystallization mechanism of the glass, and $n = 1$ indicates surface crystallization, while $n = 3$ implies three-dimensional crystallization [36,37].

Fig. 2(c) shows the relationship between $\ln(T_p^2/\alpha)$ and 1000/T$_p$. The activation energy was calculated from the slope of the oblique lines, as listed in Table 2. Compared with the sample GC-1, the $E$ value of GC-2 increases slightly with the CaF$_2$ addition. However, the $E$ values of the samples GC-3 (195.4 kJ/mol) and GC-4 (216.6 kJ/mol) obviously decrease with Na$_2$O addition, compared with the samples GC-1 (301.2 kJ/mol) and GC-2 (337.3 kJ/mol). This implies that Na$_2$O improves the crystallization ability of the CMS glass.

The $n$ value of the sample GC-1 is 1.2, indicating surface crystallization. Compared with GC-1, the $n$ value increases with the respective addition of Na$_2$O or CaF$_2$. The $n$ values of the GC-2, GC-3 and GC-4 samples are 3.4, 2.8 and 2.9, respectively, close to 3, indicating three-dimensional crystallization. This means that both Na$_2$O and CaF$_2$ promote three-dimensional crystallization.

### 3.2. Crystalline phases and microstructure of the CMS glass-ceramics

The above crystallization kinetics analysis implied the one-step crystallization potential of the CMS glasses. However, the Arrhenius, Kissinger and Augis-Bennett equations are based on a series of fundamental assumptions. Hence, it is necessary to verify the one-step crystallization capacity of the CMS glass using experimental results.

Fig. 3(a) shows XRD patterns of the glass samples crystallized at $T_p$ for 1 h. The $T_p$ is considered as $T_{cr}$ for one-step crystallization of CMS glass. The XRD pattern of GC-1 was obtained from the surface crystallized parts of the sample, since internal part of GC-1 was still glass. The four crystallized glasses have the same main crystalline phase (diopside, CaMgSi$_2$O$_6$). This indicates that the addition of Na$_2$O or CaF$_2$ has no effect on the main crystalline phase.

The SEM micrographs of the one-step crystallized glasses are presented in Fig. 3. For the GC-1 sample, the diopside crystals grew from the surface to the interior of the parent glass, resulting in a typical surface crystallization microstructure, as seen in Fig. 3(b). In the GC-2 sample, just a few crystal nuclei grew up during the one-step heat treatment, forming mixed microstructure of the bulk diopside phase and the massive glass phase, as seen in Fig. 3(c). This may be the result of high crystallization activation energy of the GC-2 sample, as discussed above.

In Fig. 3(d) and (e), a large number of granular diopside crystals were uniformly located in the CMS glass-ceramics and formed typical three-dimensional crystallization microstructure. This suggests that the majority of crystalline nuclei grew uniformly with the addition of Na$_2$O. The crystal particles in Fig. 3(e) are smaller and more homogeneous than in Fig. 3(d). Thus, it is reasonable to say that the addition of CaF$_2$ contributes to grain refinement and improves the microstructure of Na-containing CMS glass-ceramics by increasing the crystal nucleus density.

In summary, the one-step crystallization of CMS glass was successfully achieved by adding Na$_2$O into the parent glass. Although

<table>
<thead>
<tr>
<th>Sample</th>
<th>GC-1</th>
<th>GC-2</th>
<th>GC-3</th>
<th>GC-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$ (kJ/mol)</td>
<td>301.2</td>
<td>337.3</td>
<td>195.4</td>
<td>216.6</td>
</tr>
<tr>
<td>$n$</td>
<td>1.2</td>
<td>3.4</td>
<td>2.8</td>
<td>2.9</td>
</tr>
</tbody>
</table>

Fig. 2. (a) XRD patterns of the parent glasses; (b) DSC curves at 10 K/min of the glasses, (c) Variation of $\ln(T_p^2/\alpha)$ vs. 1000/T$_p$ for different CMAS glasses.
CaF$_2$ does not have the ability to promote one-step crystallization, CaF$_2$ contributes to refine grain and improve microstructure of Na$_2$O-containing CMS glass-ceramics.

### 3.3. The effects of Na$_2$O and CaF$_2$ on one-step crystallization of CMS glass

The parent glasses are metastable [38]. During the one-step heat treatment, amorphous phase separation, nucleation and crystal growth proceed continuously in the CMS glass at $T_{nc}$. Generally, the amorphous glass will separate into phase-separated regions and residual glass phase during the phase separation stage. The phase separated regions are rich in certain elements, bringing the composition closer to that of the resulting crystal nucleus [23,39]. Therefore, it is easier for the formation of crystal nucleus, since the atomic species required for the crystal nucleus growth are sufficient. Besides, the interface between the two regions can act as heterogeneous nucleation sites, which further reduces the nucleation barrier [9,39]. As a result, the nucleation activation energy will be decreased.

Usually, CaF$_2$ is considered as the nucleation agent, which contributes to promoting phase separation and nucleation [18,19]. It is a surprising result that the $E_a$ value of the GC-2 glass with CaF$_2$ is higher than GC-1 with no addition, as mentioned above. The authors hoped that the $E_a$ value would decrease with adding CaF$_2$. This concurs with the findings of other authors, where $E_a$ increased with the addition of CaF$_2$.

A possible explanation for this phenomenon is, with the addition of CaF$_2$, that there is a large crystal nucleation density during the isothermal hold [39]. The crystal nucleus grows to a small extent because of the open glass network. This could lead to a situation where there is less F present in the residual glass surrounding the nuclei. When the nucleation ends, a fluorine-deficient layer forms around the nuclei. Then the crystal nuclei growth is suppressed because of the closed network and lower ions diffusion mobility, which is manifested by the increase of $E_a$. After all, $E_a$ measures mainly the easiness of glass crystallization rather than that of glass nucleation [40]. The mixed microstructure and corresponding explanation of crystallized glass GC-3 (as shown in Fig. 3(c)) also prove the speculation above.

The GC-3 sample with Na$_2$O has $E_a$ values as low as 195.4 kJ/mol. The low $E_a$ value indicates that the parent glass easily nucleates and crystallizes [41]. The $n$ value of GC-3 is close to 3, implying that there are enough nuclei that grew up during the crystal growth stage [42]. All these results are confirmed by the high degree of crystallization (as seen in Fig. 3(a)) and the uniform crystal particles in Fig. 3(d). In brief, it can be concluded that there are enough nuclei formed and grew up in the GC-3 sample during the one-step heat treatment.

The sample GC-3 completed nucleation and crystal growth continuously at $T_{nc}$. According to the above hypothesis, the one-step crystallization of CMS glass is accomplished by the forming of Ca$^{2+}$ and Mg$^{2+}$ fast diffusion layer. Thus, two experimental phenomena should be observed in the sample GC-3: 1) Na$^+$ will prefer to diffuse into the glass layer around the crystals; 2) the residual glass will eventually transform into Na-containing crystal phase in midst of crystallization, with the existence of Ca$^{2+}$ and Mg$^{2+}$ fast diffusion layer.

Fig. 4(a) shows the SEM image of the GC-3 glass heat treated at 700 °C for 25 min and EDXS line scan along the trace of the straight line indicated in the SEM image. The Na$^+$ content in the crystal particle is obviously lower than in glass layer around the crystals, as seen in Fig. 4(a). This result indicated that Na$^+$ diffused into the glass layer around the crystal. Thus, it is the direct evidence of the first predicted experimental phenomena. The reason for this phenomenon maybe that the chemical potential of Na$^+$ in the glass phase is lower than in the crystal phase. As a result, the Na$^+$ changes the Si–O–Si bond to Si–O–Na bond and increases the Si–O–Na bond content in the glass layer. Thus, the silica network of the glass layer will be more “open”. Because the Si–O–Na bonds contribute to Ca$^{2+}$ and Mg$^{2+}$ diffusion, the glass layer turns into a Ca$^{2+}$ and Mg$^{2+}$ fast diffusion layer. This layer will help the crystals to grow, which is proved by the low $E_a$ value and three-dimension crystallization mechanism (n = 2.8) of the GC-3 glass.

To prove the second experimental speculated phenomenon, the isothermal phase formation sequence of the GC-3 glass was collected using HTXRD. To obtain more phase evolution details, 700 °C was chosen, at which the phase evolution rate is relatively slow and convenient for detection. Fig. 4(b) displays the HTXRD patterns recorded at 700 °C with elapsed time of 40 min. As seen in Fig. 4(b), the Na-containing phases (sodium aluminum silicate and sodium silicate) appeared when the diopside crystallization process was finished. This indicates that some Na$^+$ escaped from the diopside crystals and entered in the glass phase. At the late stage of crystallization, the residual glass is rich in Na$^+$. In the end, these Na$^+$ ions were bound with silicon and aluminum ions to form the sodium silicate and sodium aluminum silicate phases. This further confirmed the existence of the Ca$^{2+}$ and Mg$^{2+}$ fast diffusion layer.
The sample GC-4 contains both Na$_2$O and CaF$_2$. The two typical experimental phenomena of the Ca$^{2+}$ and Mg$^{2+}$ fast diffusion layer were also observed during the GC-4 glass one-step crystallization, as shown in Fig. 4(c) and (d). Unlike the Na$^+$ distribution trend, there is no distinct F content fluctuation between the crystal phase and glass phases, as shown in Fig. 4(c). Besides, the F-containing phase (cuspidine) and Na-containing phase (sodium aluminum silicate, SAS) were detected near the end of crystallization stage of the GC-4 glass, as seen in Fig. 4(d). These experimental phenomena can be explained by the following reasons (or conjecture). First, CaF$_2$ induced the formation of large density crystal nucleus. However, the F content fluctuation between the crystal nucleus and the glass layer is too small to be detected. Because the glass layer around these crystal nucleus was Na-rich, the growth ability of these crystal nucleus was increased. With the development of crystallization, the F content fluctuation disappeared gradually. Finally, the residual glass crystallized into the SAS and cuspidine phases. Due to the high nucleation density and excellent crystal growth ability, the GC-4 glass-ceramics has uniform compact microstructure, as seen in Fig. 3(e).

All these results along with the above discussion confirm that the one-step crystallization of CMS glass-ceramics can be achieved by building Ca$^{2+}$ and Mg$^{2+}$ fast diffusion layer surrounding the crystals. The aim of building Ca$^{2+}$ and Mg$^{2+}$ fast diffusion layer is to improve the “open degree” of the glass network around the crystals and then increase the Ca$^{2+}$ and Mg$^{2+}$ ions diffusion ability within the glass layer around crystals. Besides, based on the results and discussion above, it is suggested that building a fast diffusion layer around the crystals to achieve one-step crystallization may be also effective in other glass-ceramics systems.

4. Conclusions

The one-step crystallization of CMS glass-ceramics was achieved by building Ca$^{2+}$ and Mg$^{2+}$ fast diffusion layer between the diopside crystal and the residual glass, as evidenced by SEM-EDXS and HTXRD. The probable explanation for this phenomenon is proposed as follows. During the crystallization, diopside crystals phase out from the homogeneous parent glass, concomitantly forming a glass layer between diopside crystal and residual glass. As experimentally observed, Na$^+$ ions are rich in this layer, which promotes the formation of Si–O–Na bond. The Si–O–Na bonds further promote Ca$^{2+}$ and Mg$^{2+}$ ions diffusion in the glass layer. This layer eventually promotes further growth or ripening of the diopside crystals, leading to the nucleation and crystal growth of the CMS glass proceed continuously at $T_{nc}$. Thus, one-step crystallization of the CMS glass-ceramics becomes possible and practical.

Author contributions

S. G. Zhang, J. Yang and B. Liu conceived and performed the research. J. Yang wrote the manuscript. Alex A. Volinsky polished the manuscript.
Competing financial interests

The authors declare no competing financial interests.

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