Journal of Non-Crystalline Solids 405 (2014) 63–67

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/ locate/ jnoncrysol

Crystallization and microstructure of $CaO–MgO–Al_2O_3–SiO_2$ glass–ceramics containing complex nucleation agents

Xingzhong Guo *, Xiaobo Cai, Jie Song, Guangyue Yang, Hui Yang

Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China

ARTICLE INFO

Article history:
Received 30 May 2014
Received in revised form 22 August 2014
Available online 16 September 2014

Keywords:
Glass–ceramic;
Diopside;
Crystallization kinetics;
Chemical durability

ABSTRACT

The $CaO–MgO–Al_2O_3–SiO_2$ (CMAS) glass–ceramics containing binary complex nucleation agents were prepared by body crystallization process, and the effects of complex nucleation agents on the crystallization and microstructure of CMAS glass–ceramics were investigated by differential thermal analysis (DTA), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The complex nucleation agents consist of constant fluorine (8.0 wt.% CaF_2) and different oxides (3.0 wt.% TiO_2, ZrO_2, or P_2O_5). Compared with the CMAS glass with only CaF_2, the respective addition of oxides promotes the crystallization of CMAS glass, especially TiO_2 or P_2O_5. The addition of TiO_2 or ZrO_2 has no obvious effect on the compositions of main crystalline phases, while P_2O_5 results in the precipitation of pyroxene phase instead of diopside phase, with the existence of more small crystals. The CMAS glass–ceramic containing $CaF_2 + TiO_2$ or $CaF_2 + P_2O_5$ achieves full body crystallization with high crystallization ratio, and has high hardness, good chemical resistance and water absorption.

1. Introduction

$CaO–MgO–Al_2O_3–SiO_2$ (CMAS) glass–ceramic is one of the most promising glass–ceramic systems, and has excellent mechanical properties, high abrasive resistance and good chemical resistance due to the precipitation of crystals like diopside [$CaMgSi_2O_6$], anorthite [$CaAl_2Si_2O_8$] and cordierite [$Mg_2Al_4Si_5O_{18}$] [1–5]. CMAS glass–ceramics have become good candidates for functional applications such as sealant for solid oxide fuel cells, architectural applications such as building materials for interior and exterior walls, and heavy industrial applications such as protective materials for bunker, funnel and chute [1–3]. As well known, the crystallization of CMAS glass–ceramics is very difficult, and also hard to control, which largely restricts the preparation and application of CMAS glass–ceramics [4,5].

Sintering process and body crystallization process are two main preparation methods of CMAS glass–ceramics. Sintering process is derived from the sintering of fine ceramics, consisting of glass melting, water quenching, particle molding and high-temperature sintering, while body crystallization process is similar to the production procedures of plate glass, including glass melting, molding, annealing, nucleation and crystallization. In comparison with body crystallization process, it is relatively easy to control the crystallization of CMAS glass, but it is too difficult to obtain the fully dense glass–ceramics, for sintering process [6].

Recently improving the crystallization of CMAS glass by adding nucleation agent has received considerable attentions. Omara et al. [7] have reported that Cr_2O_3 as a nucleation agent promotes the precipitation of pyroxene crystal phase. Barbieri et al. [8] have found that the increase of Cr_2O_3 heightens the precipitation of diopside crystal phase in CMAS glass. Alexander [9] has studied the effect of Cr_2O_3 on the Fe_2O_3-rich CMAS glass–ceramic, and the main phase precipitated is pyroxene. Wu et al. [10] have compared the effects of Cr_2O_3 and $Cr_2O_3 + TiO_2$ mixture on the crystallization of CMAS glass, and found that the composite nucleation agents are in favor of the precipitation of finer diopside grains. Rezvani et al. [11] have found that the nucleation agents containing Cr_2O_3, Fe_2O_3, and TiO_2 are in favor of the precipitation of diopside crystal. Yekta et al. [12] have studied the crystallization of the CMAS glass containing ZrO_2, and found that diopside and needle zirconia particles are precipitated. Torres et al. [13] have found that the addition of TiO_2 will lead to the precipitation of cordierite phase. Salama [14] has found that $CaF_2 + P_2O_5$ promotes the crystallization of CMAS glass, and affects crystallization temperature and thermal expansion coefficient. Kansal [15] has found that in the CMAS containing La_2O_3, the increase of CaF_2 content decreases the crystallization temperature and reduces the softening temperature, but increases the crystallization activation energy of the glass. However, the present researches mainly focus on the crystallization of CMAS glass–ceramics prepared by sintering process, and there have been no studies on the crystallization of CMAS glass–ceramics prepared by body crystallization process.

In this work, on the basis of constant fluorine nucleation agent (CaF_2), the oxide nucleation agents such as TiO_2, ZrO_2 and P_2O_5 are

* Corresponding author. Tel.: +86 8795 3313; fax: +86 8795 3054.
E-mail address: msewj01@zju.edu.cn (X. Guo).

http://dx.doi.org/10.1016/j.jnoncrysol.2014.08.048
0022-3093/

Table 1
Chemical compositions of the initial CMAS glass batches (wt.%).

No.	CaO (±0.1)	MgO (±0.1)	Al_2O_3 (±0.1)	SiO_2 (±0.1)	Na_2O (±0.1)	K_2O (±0.1)	Sb_2O_3 (±0.1)	CaF_2 (±0.1)	TiO_2 (±0.1)	ZrO_2 (±0.1)	P_2O_5 (±0.1)
F	14.0	10.0	12.0	50.0	3.0	2.0	1.0	8.0	\	\	\
FT	14.0	10.0	12.0	50.0	3.0	2.0	1.0	8.0	3.0	\	\
FZ	14.0	10.0	12.0	50.0	3.0	2.0	1.0	8.0	\	3.0	\
FP	14.0	10.0	12.0	50.0	3.0	2.0	1.0	8.0	\	\	3.0

*Note: F-only CaF_2; FT-CaF_2 + TiO_2; FZ-CaF_2 + ZrO_2; FP-CaF_2 + P_2O_5.

added to construct binary complex nucleation agents respectively. The CMAS glass–ceramics containing complex nucleation agents were prepared by body crystallization process. The effects of complex nucleation agents on the crystallization kinetics, microstructure and properties of CMAS glass–ceramics were investigated in detail.

2. Experimental

All raw materials of reagent grade were purchased from Sinopharm Chemical Reagent Co. and were used as received. SiO_2 (99.0%), Al_2O_3 (99.0%), MgO (99.0%), CaO (99.0%), and CaF_2 (99.0%) and other minor additives were used to produce main glass batches (Table 1), in which CaF_2 was employed as a fluorine nucleation agent. On the basis of fluorine (CaF_2), the additional oxides such as TiO_2 (99.9%, rutile), ZrO_2 (99.9%, monoclinic) or P_2O_5 (99.9%, hexagonal) were introduced into the batches to construct binary complex nucleation agent respectively. Each glass batch was mixed by ball milling for 6 h, melted at 1400 °C for 4 h, and molded in a pre-heated die. Glasses were annealed at 550 °C for 1 h to eliminate the internal stress.

Differential thermal analysis (DTA) of the annealed glass samples was performed by a differential thermal analyzer (NETZSCHSTA 409 PC Luxx, Germany) with alumina as the reference and the sample was heated at 5–20 °C min^{-1} from room temperature to 1100°C. The crystalline phases of the crystallized samples were analyzed by the X-ray diffraction (XRD) method on a XJ10-60 X-ray diffractometer using nickel filtered CuKa radiation in the range of $2\theta = 10–80°$ with a scanning speed of 2°/min. The surface of the glass–ceramic samples was polished and eroded by HF (1 wt.%) for 30 s for the morphology observation on the SEM (scanning electron microscopy, Hitachi S4800, Japan, 5.0 kV acceleration voltage). The chemical resistance was examined by immersing samples in 5% HCl and 5% NaOH solutions at 95 °C for 1 h respectively [16]. Water absorption was measured according to the ISO standard 10545-3: 1995.

3. Results and discussions

3.1. DTA of annealed CMAS glass

Fig. 1 shows the DTA results obtained from annealed glass powders. It is noted that the prominent exothermic peaks of F, FT, FZ and FP samples at 950, 919, 943 and 928 ± 1 °C may be the formation of main crystallization phase (such as diopside) shown below respectively. The temperature corresponding to the prominent exothermic peak is the crystallization maximum temperature (T_p). It is obviously seen that the T_p decreases with the addition of oxide nucleation agent, especially the addition of TiO_2. It indicates that the complex nucleation agent consisting of fluorine and oxide will improve the crystallization of CMAS glass, compared with only a nucleation agent (fluorine).

3.2. Crystallization kinetics of CMAS glass

The effects of complex nucleation agent on the crystallization of CMAS glass were further analyzed by activation energy of crystal growth. The crystallization kinetic of CMAS glass can be described by a non-isothermal DTA method using the Arrhenius [17], Kissinger [18,19] and Augis–Bennett [20] equations as follows:

$$k = \nu \exp\left(-\frac{E}{RT}\right) \tag{1}$$

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

$$n = \frac{2.5}{\Delta T} \times \frac{RT_p^2}{E} \tag{3}$$

wherein, T is the absolute temperature and ν is the frequency factor; E is the activation energy, and low E value indicates high ability of crystallization; R is gas constant; k is the reaction rate constant, which is related to the E and ν; ΔT is the half-height temperature width of the maximum exothermic peak of DTA; T_p is the crystallization maximum temperature in a DTA curve, and a is the heating rate of DTA. E can be calculated by the slope of $\ln(T_p^2/a)$-$1/T_p$. Low E value indicates high crystallization rate and crystallinity. The crystallization index n is related to crystallization manner, $n = 1$ indicates one-dimensional growth (surface crystallization), and $n = 3$ implies three dimensional growth (volumetric crystallization).

Table 2 shows the crystallization maximum temperatures (T_p) from DTA curves at different heating rates. The relationship between $\ln(T_p^2/a)$ and $1/T_p$ is shown in Fig. 2. The activation energy (E) is calculated from the slope of linear fitting of the plots, as listed in Table 3. Compared with the CMAS glass with only CaF_2, the activation energy of CMAS glass obviously decreases with the respective addition of TiO_2, ZrO_2 or P_2O_5. Wherein, the E with FT (CaF_2 + TiO_2) becomes the lowest, and reaches 338.9 kJ·mol^{-1}, which is far lower than the one with only

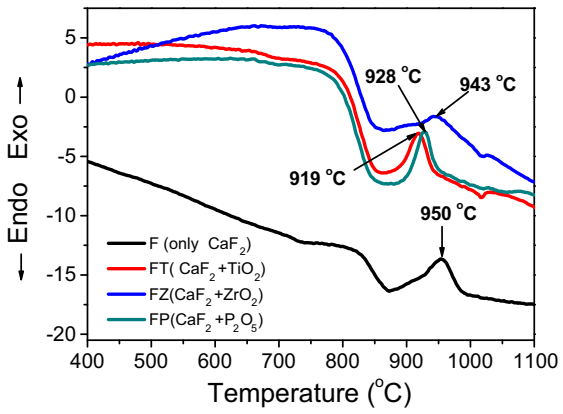

Fig. 1. DTA curves of CMAS glass samples with different nucleation agents. Temperatures inserted indicate crystallization maximum temperature (T_p) with arrows pointing to the corresponding peaks.