Effect of TiO$_2$ on Crystallization of the Glass Ceramics Prepared from Granite Tailings

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Abstract: The effect of TiO$_2$ on the crystallization behaviors of the glass ceramics prepared from granite tailings was investigated by differential scanning calorimetry (DSC), X-ray diffraction (XRD), and field emission scanning electron microscopy (FESEM). The results showed that the crystallization peak temperature decreased firstly, and then increased with the increase of TiO$_2$ content. The optimum addition amount of TiO$_2$ was 8 wt%. With a single-step heat treatment at 924 ℃ for 1 h, augite precipitated as the only crystalline phase both on the surface and in the interior. The avrami parameter of the sample was 3.25, suggesting a two-dimensional crystallization mechanism. The activation energies for phase separation and crystallization of augite were 321.75 and 698.83 kJ/mol, respectively.

Key words: glass ceramics; crystallization kinetics; granite tailings; nucleating agent

1　Introduction

Utilizing inexpensive waste materials to produce glass ceramics has been an important advance in glass technology in recent years. The industrial wastes such as fly ash, incinerator slag, steel slag, red mud, basalt and cement kiln dust are used as the starting materials to fabricate glass ceramics[1-6]. The compositions of the above-mentioned glass ceramics can mainly be located in the CaO-MgO-Al$_2$O$_3$-SiO$_2$ system. Many investigators have studied the crystallization process in this glass system and indicated that one of the main difficulties is to induce internal nucleation and bulk crystallization in the parent glass[7-9]. According to some researchers, TiO$_2$ is one of the most recommended oxides to induce effective bulk crystallization in the glasses of CaO-MgO-Al$_2$O$_3$-SiO$_2$ system and related glass systems[10-12]. The conventional method for producing glass ceramics in CaO-MgO-Al$_2$O$_3$-SiO$_2$ system is a two-step heat treatment, namely, a nucleation and a crystallization stage. Considering the complication of the two-step heat treatment in the manufacturing process and the higher energy consumption, a single-step heat treatment to prepare glass ceramics is tried in this study.

In this study, glass ceramics using granite tailings as main starting materials and TiO$_2$ as nucleating agent were prepared by a single-step heat treatment. The effect of TiO$_2$ on the crystallization behaviors was evaluated by DSC, XRD, and FESEM, which provided a theoretical basis for using granite tailings to prepare glass ceramics.

2　Experimental

2.1　Sample preparation

The main chemical compositions of the granite tailings detected by X-ray fluorescence spectrometer (XRF, Axios MAX, PANalytical) are given in Table 1. Granite tailings were used as the main raw material to prepare glass ceramics with other supplement constituents, namely MgO, Al$_2$O$_3$, CaCO$_3$, Na$_2$CO$_3$ and TiO$_2$, which were all analytical grades except granite tailings. The glass compositions with varying TiO$_2$

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Table 1 Main chemical compositions of granite tailings (GT)/wt%

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Compound	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	Fe_2O_3	Ignition loss
GT	3.699	0.141	11.211	75.903	4.783	0.185	1.021	2.941

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Table 2 Main chemical compositions of the prepared glasses/wt%

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Sample No.	GT	MgO	Al_2O_3	$CaCO_3$	Na_2CO_3	TiO_2
CT0	62.604	5.02	22.448	12.228	5.044	0
CT4	62.604	5.02	22.448	12.228	5.044	4
CT8	62.604	5.02	22.448	12.228	5.044	8
CT12	62.604	5.02	22.448	12.228	5.044	12

content in the $CaO-MgO-Al_2O_3-SiO_2$ system have been studied in the present work and the detail compositions are shown in Table 2. Glass batches were mixed thoroughly in a ball mill and thereafter, melted in an alumina crucible at 1 530 ℃ for 2 h using electrical furnace. The melted glasses were then cast in the preheated brass mold to form glass samples, and then annealed at 650 ℃ for 2 h.

2.2 Characterization techniques

2.2.1. Differential scanning calorimetry (DSC)

Glass powders with different particle sizes (coarse particle size range, 0.6-0.7 mm; fine particle size range, <65 μm) were characterized by differential scanning calorimetry (DSC, Netzch STA 404) apparatus. Alumina was used as the reference material. DSC measurements were performed at heating rates of 5, 10, 15 and 20 ℃/min from ambient temperature to 1 200 ℃ in air to evaluate the activation energy of crystallization (E_c) and avrami parameter (n).

2.2.2 X-ray diffraction (XRD)

The crystalline phases of these glass ceramics were detected by X-ray diffraction (XRD, D/MAX-UItimaIV, Rigaku). The Cukα radiation (λ= 0.154 05 μm) was used at 40 kV and 40 mA. The diffraction patterns were recorded with 2θ=10-70°.

2.2.3. Field emission scanning electron microscopy (FESEM)

The microstructures of the fracture section of these glasses were evaluated by the field emission scanning electron microscope (FESEM, Ultra plus-43-13, Zeiss). The fracture surface was etched chemically by 4 % HF (volume percentage) for 30 s.

3 Results and discussion

3.1 Effect of TiO₂ on crystallization kinetics

The DSC curves of CT0, CT4, CT8 and CT12 with different particle sizes at a heating rate of 10 ℃/min are shown in Fig.1. The results confirm that the crystallization peak temperature, T_p decreases firstly, and then increases with the increase of TiO_2 content. According to some investigators[7,10,12], Ti^{4+} ions remain 4-fold coordination in super cooled process. But this network is in the metastable state, a heat treatment may lead it to depolymerize, and Ti^{4+} will get off from the network to reach a 6-fold coordination structure [TiO_6]. When TiO_2 content increases, the amounts of Ti^{4+} ions changing from the network formers to network modifiers increase, at the same time the aggregation extent of glass network and viscosity decreases. Therefore the T_p shifts to the lower temperature. The abnormal behavior of T_p increasing significantly with the addition of 12 wt% TiO_2 is due to the appearance of a new crystalline phase.
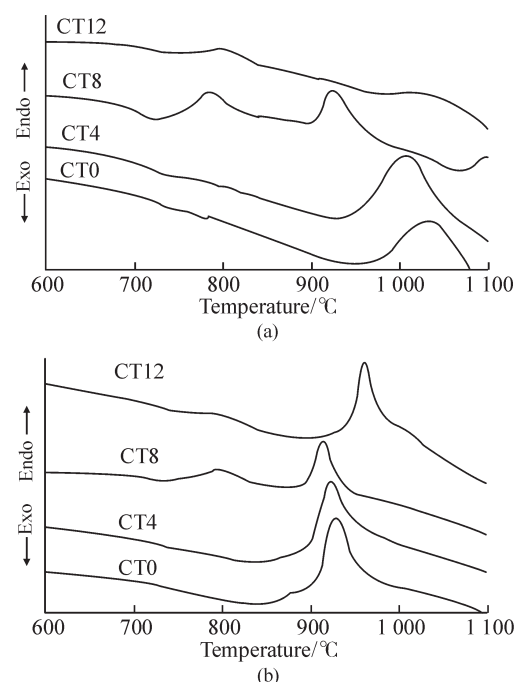

Fig.1 DSC curves of the glass specimens CT0, CT4, CT8 and CT12 at a heating rate 10 ℃/min: (a) coarse particle sizes, 0.6-0.7 mm; (b) fine particle sizes, <65 μm)

The degree of exothermic peak shift (ΔT) upon the variation of sample particle sizes is an indication of

the existence or absence of an effective bulk nucleation mechanism. The high ΔT value indicates the marked effect of glass surface area upon the nucleation rate and consequently the higher contribution of surface nucleation and crystallization to the process[13]. Table 3 shows the ΔT values of these glass samples. The ΔT values of CT0, CT4 and CT12 are 107, 83 and 72 ℃ respectively, indicating the relatively significant role played by surface crystallization in the crystallization process. The addition of 8 wt% TiO₂ to the base composition gives rise to a relatively sharp peak above 900 ℃ and low ΔT value, indicating the occurrence of a considerable degree of bulk crystallization in the glass specimen. The appearance of crystallization peak at about 790 ℃ in CT8 suggests that the liquid phase separation occurs (because there is no significant crystalline phases detected by XRD, shown in Fig.3(c)), which plays an important role in both nucleation and crystallization processes. Compared with CT8, the intensity of the exothermal peak at low temperature decreases when the TiO₂ content increases to 12 wt%.

Table 3 Summary of DSC results for glass samples with two different particle sizes

Sample No.	Particle Size	T_p/℃	ΔT
CT0	a b	1 036 929	+107
CT4	a b	1 008 925	+83
CT8-T_{p1}	a b	785 794	−9
CT8-T_{p2}	a b	924 913	+11
CT12-T_{p1}	a b	800 791	+9
CT12-T_{p2}	a b	1 032 960	+72

a:coarse particle sizes: 0.6-0.7 mm; b: fine particle sizes: <65 μm

Table 4 Crystallization peak temperature (T_p) with different heating rates

Sample no.	Heating rates/(℃/min)			
	5	10	15	20
CT0	1 017	1 036	1 049	1 058
CT4	990	1 008	1 021	1 030
CT8(T_{p1})	769	785	798	807
CT8(T_{p2})	913	924	931	936
CT12(T_{p1})	783	800	811	820
CT12(T_{p2})	1 015	1 032	1 044	1 053

Table 4 shows the crystallization peak temperature (T_p) with different heating rates of these samples. The non-isothermal crystallization kinetics of glass batches can be described by the modified Kissinger equation[14] expressed as (1):

$$\ln \frac{T_p^{\,2}}{\alpha} = \frac{E_c}{RT_p} + C \qquad (1)$$

where, E_c is the activation energy, T_p is the crystallization peak temperature of the DSC trace, α is the heating rate, R is the gas constant, C is the constant number. Fig.2 shows the variation of $\ln(T_p^2 / \alpha)$ *vs* $1\,000/(R \times T_p)$ of the specimens CT0, CT4, CT8 and CT12.

Avrami parameter, n could be evaluated by a single DSC experiment using the Augis and Bennett equation[15] shown as (2):

$$n = \frac{2.5}{\Delta T} \times \frac{RT_p^2}{E_c} \qquad (2)$$

where, ΔT is the width of the crystallization peak at half height, the other parameters have the same meaning mentioned above.
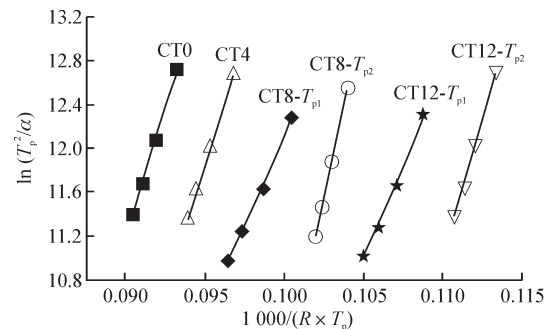

Fig.2 Variation of $\ln(T_p^2/\alpha)$ *vs* $1\,000/(R \times T_p)$ of the specimens CT0, CT4, CT8 and CT12

Different n values correspond to different crystal growth mechanisms. The higher of n, the more crystal dimensions, as shown in Table 5.

Table 5 Avrami parameters (n) for different crystallization mechanisms[16]

Crystallization mechanisms	Avrami parameters n
Surface crystallization	1
One-dimensional crystal growth	2
Two-dimensional crystal growth	3
Three-dimensional crystal growth	4

Table 6 shows the values of E_c and n. For CT0, CT4 and CT12, the exponent n values are all close to 1,

Table 6 Values of activation energy E_c and Avrami parameter n

Item	CT0	CT4	CT8(T_{p1})	CT8(T_{p2})	CT12(T_{p1})	CT12(T_{p2})
E_c/(kJ/mol)	459.97	451.61	321.75	698.83	343.83	496.89
n	0.98	1.05	2.76	3.25	1.36	0.89

corresponding to a surface crystallization process. For CT8, the *n* values of the two peaks are 2.76 and 3.25 respectively, which are close to 3, indicating a two-dimensional crystal growth in the bulk.

3.2 Effect of TiO₂ on crystallization behaviors
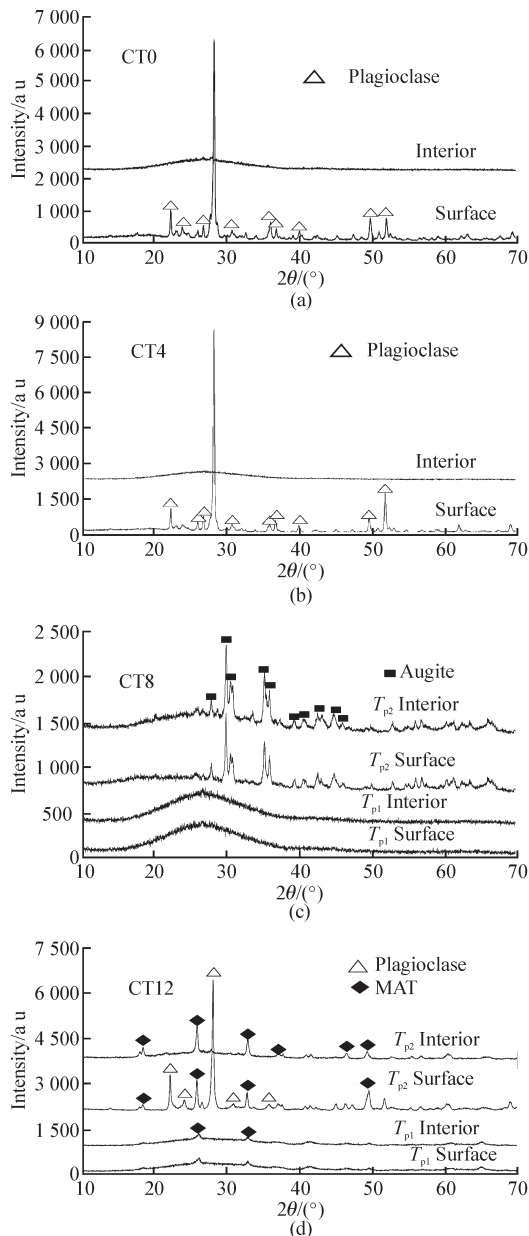

Fig.3 XRD patterns of CT0, CT4, CT8 and CT12 obtained by a single-step heat treatment

CT0, CT4, CT8 and CT12 are all crystallized by a single-step heat treatment at their T_p for 1 h. Block samples are scanned on the surface by XRD. Glass powders derived from the interior of the samples are also investigated by XRD. XRD patterns of the surface and interior of CT0, CT4, CT8 and CT12 are shown in Fig.3. The XRD patterns of CT0 and CT4 show that plagioclase is the main crystalline phase on the surface, and the interior of both samples remains amorphous.

CT8 after heat treated at T_{p1} shows a broad scattering spectrum and the main phase is amorphous glass. When heated at T_{p2}, augite precipitates as the main crystalline phase both on the surface and in the interior. At 800 ℃, CT12 is nearly amorphous and only a small amount of $Mg_4Al_2Ti_9O_{25}$ (MAT) precipitates. When sample is heated at T_{p2}, MAT precipitates in the interior of CT12, and plagioclase along with a few MAT is observed on the surface.
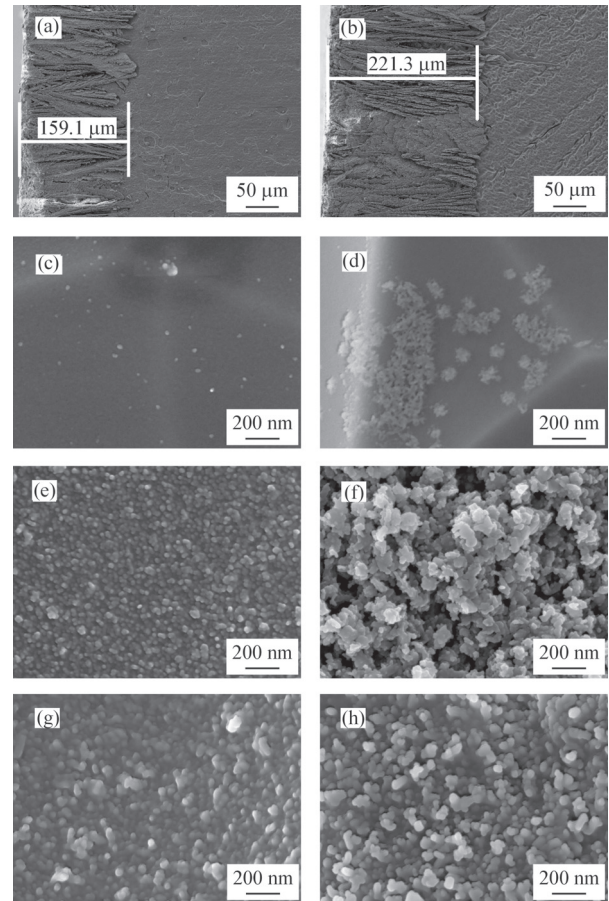

Fig.4 FESEM images of fracture section of CT0 ((a), (c)), CT4 ((b), (d)), CT8 ((e), (f)) and CT12 ((g), (h)) obtained by a single-step heat treatment

Figs.4(a), (b) show that the dendritic crystals grow from the surface of CT0 and CT4 towards the internal of the specimens. The crystallized surface layers of samples CT0 and CT4 are 159.1 and 221.3 μm in thickness, respectively. Figs.4(c), (d) show that CT0 and CT4 have a small amount of crystals in the bulk with the average diameter 36.2 and 79.6 nm, respectively. Both thickness of crystallized surface layers and average diameter of crystals in the bulk of CT4 are higher than CT0, which is due to that TiO₂ can reduce the viscosity of the glass and promote the crystal growth. Figs.4(e), (g) show that CT8 and CT12 suffer from a dramatic phase separation after heated

at their T_{p1}, but the average diameter of droplets in the bulk of CT12 is bigger than CT8. When heated at T_{p2}, the morphology of the interior of CT8 (Fig.4(f)) and CT12 (Fig.4(h)) is significantly different, which is due to the different crystalline phases.

It can be found that the activation energy of the surface crystallization is higher than E_c of the phase separation and less than that of augite precipitation in the bulk. When 8 wt% TiO$_2$ is adopted, phase separation occurs at lower temperatures, promoting the rapid formation of augite nucleus during the heating process. When heated to high temperatures, diopside dominates to grow up in the bulk, at the same time the precipitation of plagioclase on the surface is hindered. So glass ceramics obtained by a single-step heat treatment is realized with the addition of 8 wt% TiO$_2$. When 12 wt% TiO$_2$ is adopted, phase separation occurs at 800 ℃, and a small amount of MAT is detected by XRD analysis. Because the activation energy of crystallization for augite is much higher than that of MAT, the main crystalline phase becomes MAT in the bulk. Otherwise, plagioclase appears as the main crystalline phase on the surface of the glass again. In conclusion, the optimum addition amount of TiO$_2$ is 8 wt%, because the crystalline phase of the surface and interior is identical.

4 Conclusions

a) With the increase of TiO$_2$ content, the crystallization peak temperature, T_p decreases firstly, and then increases. The avrami parameter of the glass sample with 8 wt% TiO$_2$ is 3.25, suggesting a two-dimensional crystallization mechanism. The activation energies for phase separation and crystallization of augite are 321.75 and 698.83 kJ/mol, respectively.

b) Surface crystallization is predominant in CT0 and CT4, and the crystalline phase of the surface is plagioclase. With the addition of 12 wt% TiO$_2$, the main crystalline phases of the surface and interior are plagioclase and MAT, respectively. The optimum addition amount of TiO$_2$ is 8 wt%, because the crystalline phase of the surface and interior is identical. Glass ceramics are obtained by a single-step heat treatment at 924 ℃ for 1 h with augite as the only crystalline phase.

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