Journal of the European Ceramic Society 18 (1998) 1729–1735

PII: S0955-2219(98)00105-8
0955-2219/98/$—see front matter

Effect of Changing TiO_2 Content on Structure and Crystallization of $CaO–Al_2O_3–SiO_2$ System Glasses

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(Received 24 December 1997; accepted 20 March 1997)

Abstract

This paper studied that the influence of changes in the TiO_2 content on the glass structure of $CaO–Al_2O_3–SiO_2$ system and the formation of crystalline phases on reheating. The activation energy (E) for crystal growth and the Avrami parameter (n) have also been evaluated by means of differential thermal analysis (DTA) techniques. The value of the Avrami parameter (n) agrees well with scanning electron microscopy (SEM) observations of dendritic crystal growth from surface nuclei. In all the $CaO–Al_2O_3–SiO_2$ system glasses studied, dendritic crystals were observed. The greater the TiO_2 content, the lower were the glass transition temperature, T_g, and crystallization peak temperature, T_p. The high value of T_p did not mean that value of E was large. The most effective addition of TiO_2 was about 10·8% (by mass) in the $CaO–Al_2O_3–SiO_2$ system glasses. The difference of E between the base glass (no TiO_2 added) and the glass containing most effective addition of TiO_2 was very little. The experimental results suggest that in the studied samples, TiO_2 cannot promote the crystallization very effectively. © 1998 Elsevier Science Limited. All rights reserved

1 Introduction

Glass-ceramics are microcrystalline materials obtained from a parent glass by almost complete devitrification, that generally have low coefficients of linear thermal expansion together with high chemical and thermal shock resistance, and have a wide variety of applications.[1–4] The ternary $CaO–Al_2O_3–SiO_2$ system has a wide range of glass-forming compositions, and contains inexpensive components, so glass-ceramics obtained from the crystallization of glassy compositions belonging to the ternary $CaO–Al_2O_3–SiO_2$ system are very universal. However, $CaO–Al_2O_3–SiO_2$ system glasses are difficult to crystallize and they require the addition of nucleating agents for crystallization. Stookey[5] studied compositions in the wt% range: 5–20 CaO, 14–40 Al_2O_3, 50–80 SiO_2 which were nucleated with 11 wt% TiO_2, and found that TiO_2 was one of a series of effective nucleating agents. Toropov and Tigonen[6] studied nucleated anorthite-rich compositions along the anorthite–wollastonite binary join and found that Cr_2O_3 was a better nucleating agent than CaF_2, Fe_2O_3 or TiO_2. Topping[7,8] studied nine compositions in the wt% range: 24–48 CaO, 0–42 Al_2O_3, 54–62 SiO_2, and found that by using 18 wt% TiO_2 as a nucleating agent, the composition range in which good glass ceramics materials could be made was extended significantly. TiO_2 are one kind of the most common nucleating agents. Although TiO_2 is vital in the preparation of practical glass-ceramics, its mechanism of nucleation is by no means clear in many cases. McMillan[9] realized that the role of TiO_2 in many glass-ceramics is to form compounds with other oxides, which precipitate as high density fine crystals, usually by a process involving prior liquid phase separation. These crystals act as heterogeneous nuclei for crystallization of the remaining glass. Barry and Hillig *et al.*[10,11] suggested that, in certain circumstances, for example in the $Li_2O–Al_2O_3–SiO_2$ system, TiO_2 may act as a surface active agent and increase the nucleation rate. TiO_2 content in some system glasses can be reached in amounts ranging from 2 to 20 wt%;[9] when used in large contents, TiO_2 is a major component in the glasses and it is questionable to describe it as simply a nucleating agent. However, for some certain system glasses the action of TiO_2

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is abnormal, for example with small amounts of TiO_2 added to the $BaO{\cdot}2SiO_2$ composition, the bulk nucleation rates are reduced markedly.[11,12]

In general, currently there is still a great controversy regarding the use of TiO_2 as a nucleating agent. So, this paper attempts to overcome this controversy regarding the role of TiO_2 and deals with the effect of changing the TiO_2% on the structure and crystallization of the CaO–Al_2O_3–SiO_2 system glasses.

2 Experimental

2.1 Glass preparation

The glassy components studied are shown in Table 1. The glass components, very pure (99·9%) $CaCO_3$, Al_2O_3, SiO_2, and TiO_2, were mixed well together and then the mixtures were transferred to alumina crucibles, which were heated at 1450–1500°C in an electrically heated furnace with $SiMo_2$ elements for 4 h. After that some glass melts were quenched in water and simultaneously other glass melts were quenched in air and annealed at 600°C. The glass quenched in water was dried and then ground to produce a fine powder in order to do the DTA experiments.

2.2 Differential thermal analysis

Differential thermal analysis (DTA) experiments were performed by instrument of model Dupont 2100 made in America, and Al_2O_3 powders were the reference material. The sample nos 1 and 2 (Table 1) were heated at a rate of 5, 8, 10, 15°C min^{-1}, respectively, whereas the sample nos 3 and 4 (Table 1) at heating rates of 5, 8, 10, 15, 20°C min^{-1}, respectively. The sample no. 4 quenched in water was transferred to an electrically heated furnace with SiC elements for 8 h at 770, 800, 830, and 860°C, respectively, which were conducted at a rate of 10°C min^{-1}.

2.3 Glass heat-treatment

The sample nos 1, 2, 3, and 4 quenched in air were transferred to an electrically heated furnace with SiC elements for 2 h at the temperature about the maximum nucleation rate which was derived from the DTA experiments (Fig. 2), and then continued to heat to the crystallization peak temperature (Fig. 3) for 2 h at a rate of 10°C min^{-1}.

Table 1. Compositions (wt%) of various glass samples

Sample name	*$CaCO_3$*	*Al_2O_3*	*SiO_2*	*TiO_2*
No. 1	42 ± 1	20 ± 1	57 ± 1	0
No. 2	42 ± 1	20 ± 1	57 ± 1	5
No. 3	42 ± 1	20 ± 1	57 ± 1	10
No. 4	42 ± 1	20 ± 1	57 ± 1	20

2.4 Scanning electron microscopy (SEM)

The sample were polished and etched in 1·0% hydrofluoric acid for 1–2 min. After that the samples were washed, dried and coated with gold in an ion beam coater and then were analyzed by scanning electron microscopy of Hitachi S-450.

3 Theoretical Analysis

3.1 Kinetic equations

The process of crystal growth in a glass is well described by a Johnson–Mehl–Avrami equation:[13,14]

$$-\ln(1-\beta) = (kt)^n \tag{1}$$

where β is the volume fraction of crystallized phase at time t, and n is a parameter related to the mechanism of the process ($n = 1$, surface crystallization; $n = 3$, bulk crystallization). The k is a constant related to the absolute temperature, T, and can be described by an Arrhenius type equation:

$$k = AN\exp\left(-\frac{E_c}{RT}\right) \tag{2}$$

where E_c is the activation energy for crystal growth, A is a constant, and N is the number of nuclei, which can be described as:

$$N = N_S + N_h + N_n + N_c \tag{3}$$

where N_s is the number of surface nuclei per unit volume, N_h is the number of bulk nuclei formed during the DTA run per unit volume, N_n is the number of bulk nuclei formed per unit volume during a previous heat treatment, and N_c is the number of heterogeneous bulk nuclei per unit volume. The values of N_s, N_h, N_n, and N_c are proportional to the sample specific surface, S, the reciprocal of DTA heating rate, α, the time, t_n, of the nucleation heat treatment and the amount of nucleating agent, respectively.

The shape of the peak of DTA curve is related to the parameter n. The higher the value of n, the narrower is the peak. At each temperature T, the ΔT deviation from the baseline of the DTA curve to the line of the peak is proportional to the instantaneous reaction rate $d\beta/dt$,[15]

$$\Delta T = k^n t^{n-1}(1-\beta) \tag{4}$$

At the crystallization peak temperature T_p

$$\frac{d\Delta T}{dT} = \frac{d}{dT}\left(\frac{d\beta}{dt}\right) = 0 \tag{5}$$

which leads to[16,17]

$$kt = 1 \tag{6}$$

Assuming that the heating time is proportional to the reciprocal of the DTA heating rate, α, and α is a constant and taking into account eqn (3), the logarithms of eqn (6) lead to the following equation

$$\ln N - \ln\alpha = \frac{E_c}{R}\frac{1}{T_p} + \text{const.} \tag{7}$$

3.2 Activation energy and mechanism of crystal growth

When a glass crystallizes at temperatures well above the temperatures of high nucleation rates, the number of nuclei already present in the glass cannot appreciably increase during the crystallization, so N is a constant.

The following two equations, (8) and (9), can be derived from (7) and (4), respectively:

$$\ln\alpha = -\frac{E_c}{R}\frac{1}{T_p} + \text{const.} \tag{8}$$

$$\ln\Delta T = -\frac{nE_c}{R}\frac{1}{T} + \text{const.} \tag{9}$$

The kinetic parameter E_c and n can be obtained from the above two equations.

3.3 Temperature of maximum nucleation rate

It is assumed that there is not the heterogeneous bulk nuclei, N_c, in the samples. The samples have same specific surface, S, and the DTA is carried out at the same heating rate, α, so the sum, N_0, of surface nuclei, N_s, and bulk nuclei, N_h, formed during the DTA run is constant. From (7) we can derive the equation:

$$\ln(N_0 + N_n) = \frac{E_c}{R}\frac{1}{T_p} + \text{const.} \tag{10}$$

For an as-quenched sample ($N_n = 0$)

$$\ln N_0 = \frac{E_c}{R}\frac{1}{T_p^0} + \text{const.} \tag{11}$$

From eqns (10) and (11), the following equation can be drawn

$$\ln\frac{N_0 + N_n}{N_0} = \frac{E_c}{R}\left(\frac{1}{T_p} - \frac{1}{T_p^0}\right) \tag{12}$$

The number of nuclei N_n is related to the time t_n of nucleation heat-treatment by

$$N_n = It_n^b \tag{13}$$

where I is the kinetic rate constant of nucleation and b is a parameter related to the nucleation mechanism. If the samples are held the same time t_n (a long time) at each temperature T_n of the heat-treatment and the DTA runs are carried out at a high heating rate, the following approximated equation can be derived from (12):

$$\ln I = \frac{E_c}{R}\left(\frac{1}{T_p} - \frac{1}{T_p^0}\right) + \text{const.} \tag{14}$$

A plot of $\frac{1}{T_p} - \frac{1}{T_p^0}$ versus T_n can give the temperature of maximum nucleation rate.

4 Results

Table 2 shows the values of the crystallization peak temperature, T_p, of DTA experiments of samples at different heating rates. The activation energy, E, for crystal growth for each sample derived from the plots of $\ln\alpha \sim 1/T_p$ (Fig. 1) are listed in Table 3. The values of crystallization peak temperature, T_p, of the sample no. 4 heat-treated at the different temperature are listed in Table 4, and the DTA experiments were conducted at a rate of 10°C min^{-1}. The plot of $[1/T_p - 1/T_p^0]$ versus T_n (Fig. 2) shows that the temperature corresponding to the maximum nucleation rate of sample no. 4 is about 780°C. Figure 3 shows the curves of DTA experiments carried out at a rate of 10°C min^{-1}. The ΔT values from the baseline of the DTA curve to the line of the peak are listed in Table 5. The parameters, n, related to the mechanism of the process are listed in Table 3, which are derived from the plot of $\ln\Delta T$ versus $1/T$ (Fig. 4). Figure 6 show the SEM photographs of the samples.

5 Discussion

With the increase of the TiO_2 content in the CaO–Al_2O_3–SiO_2 system glasses, the glass transition temperature, T_g, and crystallization peak temperature, T_p, gradually decrease (Fig. 3, Table 2). Some researchers[18,19] realized that the TiO_2 entered as the glass network formers in the form of [TiO_4], whereas some other researchers[20,21] pointed out that the TiO_2 entered as the glass network modifiers in the form of [TiO_6]. We realize that at high temperature the TiO_2 enter as the glass network modifiers in the form of [TiO_6] but at low temperature the TiO_2 enter as the glass network formers in the form of [TiO_4],[22] that may be the reason of the decrease of T_g and T_p with the increase of TiO_2 content in this paper. When the amounts of Ti^{4+} ions changed from the network formers to network modifiers increase with the development of temperature, the aggregation extent of glass network decreases and the viscosity also decreases. Table 3 shows that when a low amounts of TiO_2 such as 5% (by mass) are added to the base glasses, the activation energy, E, for the crystal growth has an obvious increase, whose value is about two times that for base glasses, which means that adding a low TiO_2 content to the base glasses depresses the crystallization. With the increase in TiO_2 amounts added to the CaO–Al_2O_3–SiO_2 system glasses, the activation energy, E, decreases gradually. After activation energy, E, attains a minimum value, with the continuous increase of TiO_2, the value of E starts to increase again. So, the variation of E with TiO_2 content does not correspond to that of T_p with TiO_2 content. That the glass crystallization peak temperature, T_p, is high or low does not mean that the glass crystallization is difficult or easy. The plot of E versus TiO_2 content (Fig. 5) shows that the most effective TiO_2 content corresponding to the minimum value of E is about 10·8 wt%. It is well known that thermodynamics and kinetics govern glass crystallization.[9] With the increase of TiO_2 content in the CaO–Al_2O_3–SiO_2 system glasses, the kinetics barrier of glass crystallization decreases gradually but the thermodynamics barrier, which is related to the constitution, property of nuclei and base glass, does not decrease as much as the

Table 2. The values of T_p at different heating rates α of DTA

	$\alpha=5°C\ min^{-1}$	$\alpha=8°C\ min^{-1}$	$\alpha=10°C\ min^{-1}$	$\alpha=15°C\ min^{-1}$	$\alpha=20°C\ min^{-1}$
No. 1 (K)	1324	1349	1358	1369	—
No. 2 (K)	1283	1288	1287	1303	—
No. 3 (K)	1226	1241	1245	1265	1281
No. 4 (K)	1196	1211	1219	1228	1234

Table 4. The values of crystallization peak temperature T_p of the sample no. 4 heat-treated at the different temperature

T (heat-treatment) (°C)	770	800	830	860
T_p (crystallization peak) (K)	1182·97	1209·76	1216·45	1316·90

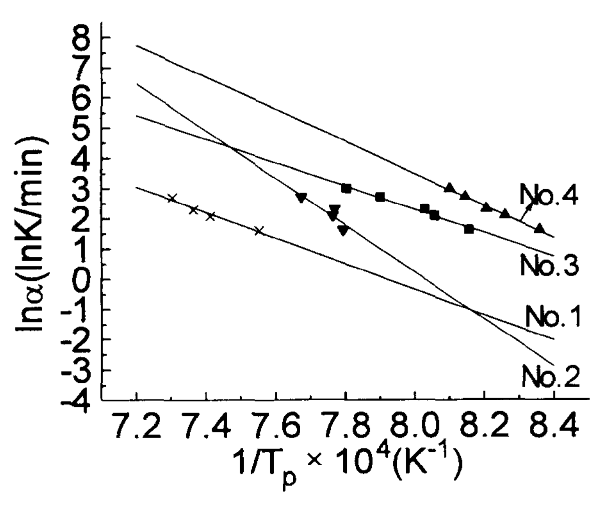


Fig. 1. The plots of $\ln\alpha \sim 1/T_p$ for the glass samples nos 1, 2, 3 and 4, from which the activation energy values, E, for crystal growth for each sample can be derived.

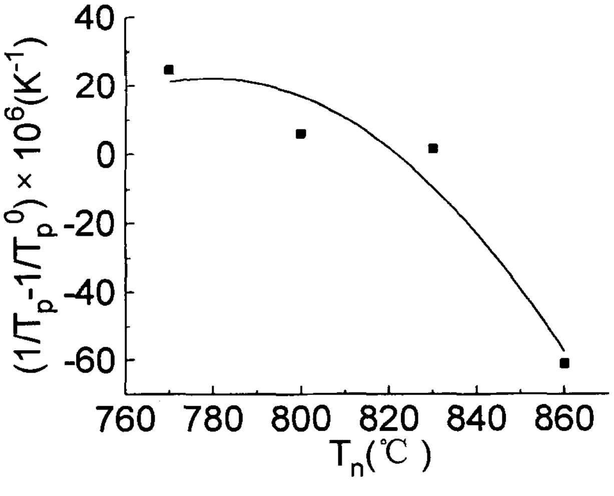


Fig. 2. The plot of $\left[1/T_p - 1/T_p^0\right] \sim T_n$ for the glass sample no. 4. The temperature corresponding to the maximum nucleation rate is about 780°C.

Table 3. The values of activation energy E for crystal growth and parameter n related to the mechanism of the crystallization process

	No. 1	No. 2	No. 3	No. 4	No. 3 (800°C, 8 h)	No. 4 (800°C, 8 h)
E ($J\,mol^{-1}$)	$3{\cdot}489\times10^5$	$6{\cdot}488\times10^5$	$3{\cdot}267\times10^5$	$4{\cdot}431\times10^5$	$3{\cdot}267\times10^5$	$4{\cdot}431\times10^5$
n	1·88	0·70	1·33	1·29	1·32	1·02

kinetics barrier. The activation energy, E, corresponding to the most effective TiO_2 content is $3{\cdot}167\times10^5\,J\,mol^{-1}$, and its value is close to that of the activation energy E ($3{\cdot}489\times10^5\,J\,mol^{-1}$) of the base $CaO–Al_2O_3–SiO_2$ system glasses (Table 3). The above description shows that TiO_2 does not effectively promote the crystallization of $CaO–Al_2O_3–SiO_2$ system glasses, and TiO_2 is not an effective nucleating agent.

Table 3 shows that the parameters, n, related to the mechanism of the crystallization process are less than 2, which means that the crystallization of all samples mainly start from the surface.[23,24] The TiO_2 addition to the $CaO–Al_2O_3–SiO_2$ system glasses cannot help change the crystallization mode from surface to bulk crystallization. The above description further shows that the TiO_2 is not one kind of effective nucleating agent.

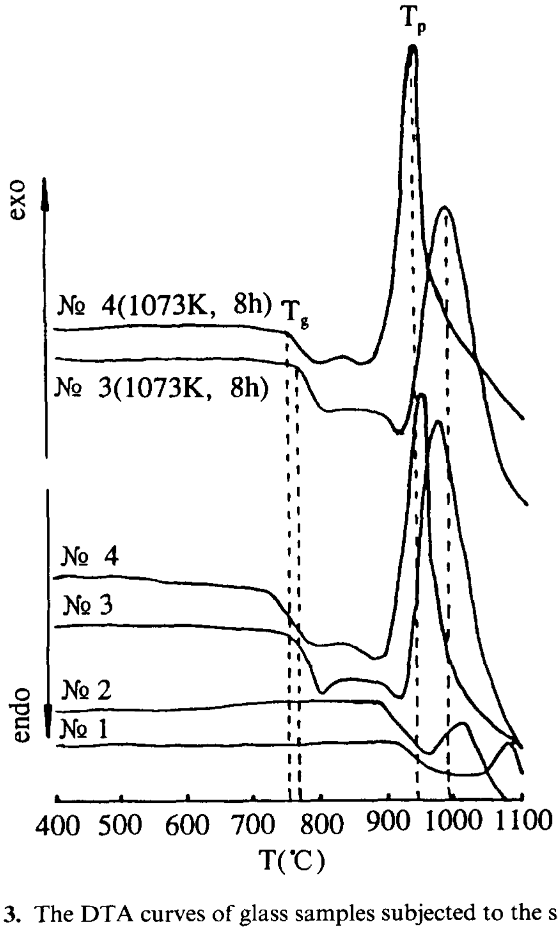


Fig. 3. The DTA curves of glass samples subjected to the same heating rate, $\alpha = 10°C\,min^{-1}$.

The temperature corresponding to the maximum nucleation rate for the sample no. 4 is about 780°C (Fig. 2). When the samples nos 3 and 4 are heat-treated for a long time (8 h) at the temperature corresponding to the maximum nucleation rate, the glass transition temperature, T_g, of these two samples slightly increase (Fig. 3) but the parameters, n, decrease (Table 3), and the glass crystallization

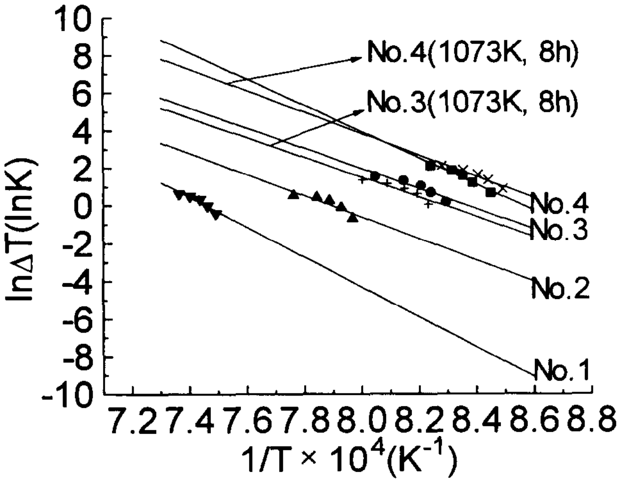


Fig. 4. The plots of $\ln \Delta T \sim 1/T$ for the glass samples (nos 1, 2, 3 and 4) quenched in water and the glass samples (no. 3 and 4) firstly quenched in water and secondly heat-treated at 1073 K for 8 h, from which the parameters, n, related to the mechanism of the glass crystallization can be derived.

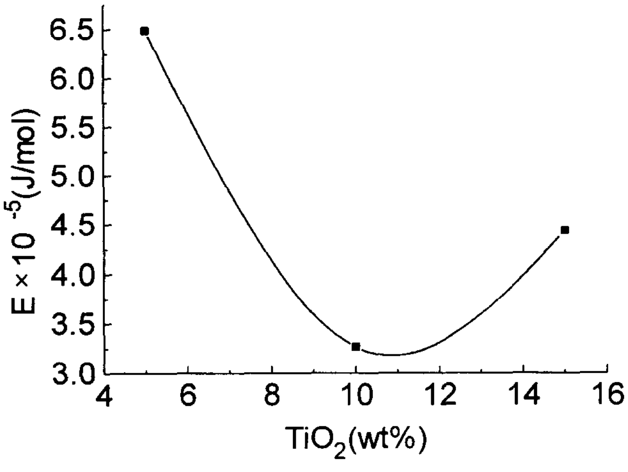
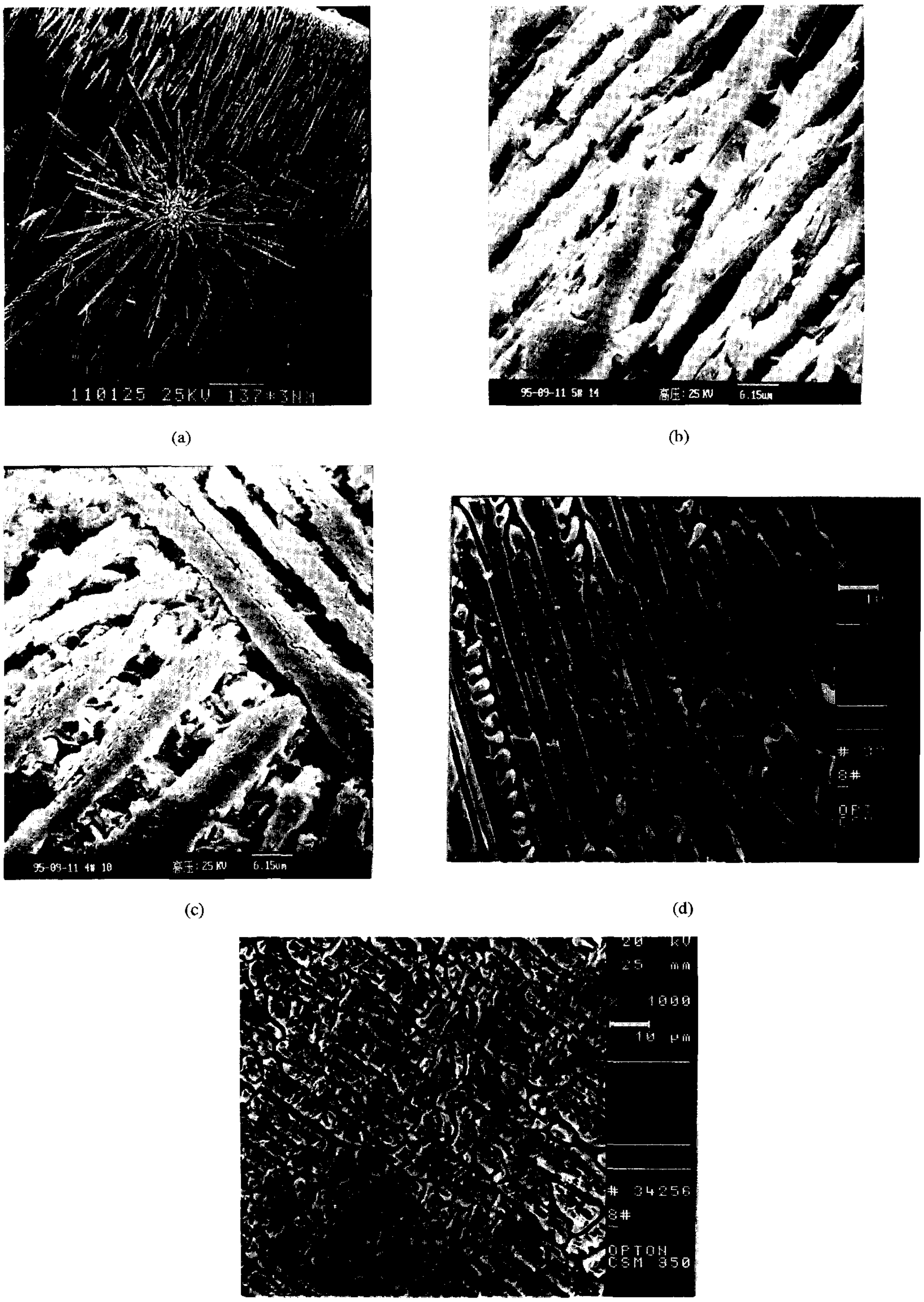


Fig. 5. The plot of activation energy E for crystal growth versus TiO_2 content for the $CaO–Al_2O_3–SiO_2$ system glasses.

Table 5. The values of ΔT at different temperatures T

No. 1		*No. 2*		*No. 3*		*No. 4*		*No. 3* (800°C, 8 h)		*No. 4* (800°C, 8 h)	
T (K)	ΔT (K)	T (K)	ΔT (K)	T (K)	ΔT (K)	T (K)	ΔT (K)	T (K)	ΔT (K)	T (K)	ΔT (K)
1334·58	0·660	1255·05	0·500	1205·84	1·232	1183·63	2·000	1215·05	1·068	1177·91	2·480
1339·82	1·000	1261·25	0·900	1213·53	2·054	1192·67	3·386	1220·77	1·879	1185·05	4·040
1344·58	1·420	1267·91	1·316	1218·82	2·955	1197·44	4·977	1227·44	2·510	1189·82	5·312
1350·77	1·660	1275·05	1·566	1227·96	3·904	1202·67	6·456	1236·48	3·263	1196·96	6·832
1357·91	1·880	1288·39	1·733	1242·86	4·864	1213·63	8·363	1249·82	3·942	1207·91	8·480

peak temperature, T_p, of the sample no. 3 slightly increase but the T_p of sample no. 4 decreases (Fig. 3). The reason for this is that some nuclei formed in the interior of glass after the heat-treatment slightly change the constitution and structure of base glass and lead to the variation of the glass transition temperature, T_g, and crystallization peak temperature, T_p. Although the TiO$_2$ content of the sample no. 4 is 2 times for that of the sample no. 3, the parameters, n, of these two samples are very near ($n_{no.3} = 1{\cdot}33$, $n_{no.4} = 1{\cdot}29$). After the heat-treatment, the parameter, n, of no. 3



(a) (b) (c) (d) (e)

Fig. 6. Scanning electron micrographs of glass samples treated under the conditions of: (a) the schematic diagram of crystal growth in all glass samples; (b) the glass sample no. 1 heat-treated firstly at about 900°C for 2 h and then at about 1050°C for 2 h; (c) the glass sample no. 2 heat-treated firstly at about 900°C for 2 h and then at about 1050°C for 2 h; (d) the glass sample no. 3 heat-treated firstly at about 780°C for 2 h and then at about 1000°C for 2 h; (e) the glass sample no. 4 heat-treated firstly at about 780°C for 2 h and then at about 1000°C for 2 h.

does not change nearly (from 1·33 to 1·32), and the parameter, *n*, of no. 4 slightly decreases from 1·29 to 1·02. This indicates that TiO_2 does not help in changing the surface crystallization to bulk crystallization for the glass forming compositions in the $CaO–Al_2O_3–SiO_2$ ternary system. On the contrary, after nucleation heat-treatment, the higher the TiO_2 content, the stronger is the surface crystallization.

Figure 6(a) shows that the crystals in all samples grow mainly from the surface nuclei. In the interior of the glasses, there are a few sites from which the crystals grow. All crystals formed are dendritic in shape. These are in agreement well with the above analysis to the parameters, *n*, which are less than 2 in all glass samples studied. The description again proves that the TiO_2 play a little role in improving the crystallization of the $CaO–Al_2O_3–SiO_2$ system glasses. The greater the TiO_2 content, the finer are the dendritic crystals [from Fig. 6(b)–(e)]. The morphology shown in the SEM photograph of no.1 is nearly same as that of no.2, and the morphology shown in the SEM photograph of no. 3 is nearly same as that of no. 4, but the morphologies of nos 3 and 4 are very different from those of nos 1 and 2, what shows that when TiO_2 content exceeds a certain amount, they become a major component in the glasses and are not a simply nucleating agent.

6 Conclusions

1. Adding TiO_2 to the $CaO–Al_2O_3–SiO_2$ system glasses leads to that the glass transition temperature, T_g, and crystallization peak temperature, T_p, decrease. That the glass crystallization peak temperature, T_p, is high or low does not mean that the glass crystallization is difficult or easy.
2. Whether the TiO_2 are added to the $CaO–Al_2O_3–SiO_2$ system glasses or not, or whether the TiO_2 content is high or not, the glasses begin crystallizing mainly from the surface and TiO_2 are not one kind of effective nucleating agent.
3. After the sufficient nucleation heat-treatment, adding TiO_2 to the $CaO–Al_2O_3–SiO_2$ system glasses cannot also lead to the bulk crystallization. On the contrary, the higher the TiO_2, the stronger is the surface crystallization.

References

1. Levitt, S. R., *Journal of Mater. Sci.*, 1973, **8**, 793–806.
2. Doremus, R. H., *Glass Science*. Wiley, New York, 1973, p. 75.
3. Beall, G. H. and Duke, D. A., In *Glass-ceramic Technology—Glass Science and Technology*, Vol. 1, ed. D. R. Uhlmann and N. J. Kreidl. Academic Press, New York, 1983, pp. 403–445.
4. Brennan, J. J. and Prewo, K. M., *Journal of Mater. Sci.*, 1982, **17**, 2371–2383.
5. Stookey, S. D., Method of making ceramics and product thereof. US Patent No. 2,920,971, 1960.
6. Toropov, N. A. and Tigonen, G. V., *Inorg. Mater. (USSR)*, 1967, **3**(11), 1789–1792.
7. Topping, J. A., *Journal of Can. Ceram. Soc.*, 1976, **45**, 63–67.
8. Idem, *Amer. Ceram. Soc. Bull.*, 1977, **56**(6), 574–577.
9. McMillan, P. W., *Glass Ceramics*, 2nd edn. Academic Press, London, 1979, p. 74.
10. Barry, T. I., Clinton, D., Lay, L. A., Mercer, R. A. and Miller, R. P., *Journal of Mater. Sci.*, 1969, **4**(7), 596; *Journal of Mater. Sci.*, 1970, **5**(2), 117–126.
11. Hillig, W. B., In *Symposium on Nucleation and Crystallization in Glasses and Melts*, ed. M. K. Reser, G. Smith, and H. Insley. American Ceramic Society, Columbus, OH, 1962, pp. 77–89.
12. Isard, J. O., James, P. F. and Ramsden, A. H., *Phys. Chem. Glasses*, 1978, **19**(1), 9–13.
13. Johnson, W. A. and Mehl, R. F., *Trans. AIME*, 1939, **135**, 416–458.
14. Avrami, M., *Journal of Chem. Phys.*, 1939, **7**, 1103–1112.
15. Borchardt, H. J. and Daniels, F., *Journal of Amer. Chem. Soc.*, 1957, **79**, 41–46.
16. Ozawa, T., *Polymer*, 1971, **12**, 150–158.
17. Augis, J. A. and Bennett, J. E., *Journal of Therm. Anal.*, 1978, **13**, 283–293.
18. Henderson, G. S. and Fleet, M. E., *Canadian Mineralogist*, 1995, **33**, 399–408.
19. Wu, H. F., Lin, C. C. and Shen, P. Y., *Journal of Non-Cryst. Solids*, 1997, **209**, 76–86.
20. Villegas, M. A., Depablos, A. and Navarro, J. M. F., *Journal of Mater. Sci.*, 1995, **30**, 995–999.
21. Farges, F., *Am. Mineralogist*, 1997, **82**, 36–43.
22. Duan, R. G., Liang, K. M., Gu, S. R. and Wan, J. L., *Journal of Chin. Ceram. Soc.*, 1997, **25**, 305–311.
23. Amista, P., Cesari, M., Montenero, A., *et al.*, *Journal of Non-Cryst. Solids*, 1996, **192–193**, 529–533.
24. Duan, R. G. and Liang, K. M., *Journal of Inorganic Mater.*, 1997, **12**, 257–264.