JOURNAL OF MATERIALS SCIENCE 24 (1989) 4488–4494

Crystallization and properties of Li–Al–B–Ti–Zn–silicate system glass-ceramic fibres

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Phase separation, nucleation, crystallization and micro-crack extension and their affects on the tensile strength and alkaline resistance of TiO_2 nucleating Li_2O–Al_2O_3–B_2O_3–ZnO–SiO_2 system glass–ceramic fibres are studied by DTA, XRD, TEM and SEM. Phase separation, temperature range of nucleation, T_g, sequence and kinetics of crystallization, sizes of microstructure and surface microcracks, tensile strength and weight loss of alkali corrosion of glass–ceramic fibres are also studied. The mechanism of crystallization and the process of microcrack extension during the preparation of glass–ceramic fibres are discussed in detail. The glass prepared for glass–ceramic fibres should be characterized by the temperature of phase separation, nucleation and crystallization of the glass ought to be low, as near T_g as possible, corresponding to its basic properties and the rate of dense bulk crystallization must be closely controlled. The microstructure of small and concentrated crystallites, about, 25 nm in size while the diameter of the glass–ceramic fibres is 16 μm, produced in the glass–ceramic fibres increases its tensile strength and alkaline resistance. A suitable coupling agent covering the surface of the glass–ceramic fibres and tensile stress exerted on them during heat treatment benefit its mechanical and chemical properties.

1. Introduction

Glass–ceramic fibres are a new kind of artificial inorganic non-metallic material. It has been indicated [1] that controlled crystallites existing in glass–ceramic fibres can improve their properties. Since Booth and Rindone's [2] glass–ceramic fibres study in 1964, other researchers such as Plaskon [3], Tetsuro Yoshida [4], Trojer [5], Aslanova [6], McMillan [7] and Meriani [8–13] have done some interesting work in this field. The very large surface-to-volume ratio of glass fibres makes research difficult and there have still been few publications. There is a shortage of systematic knowledge about the mechanisms of the microstructure forming process of glass–ceramic fibres. The kind of nucleation and crystallization process suitable for glass–ceramic fibres and the relationship between heat treatment and tensile strength of glass–ceramic fibres are explored in this paper.

2. Experimental details

2.1. Preparation of glass–ceramic fibres

The chemical composition of glass is shown in Table I, ignoring the quantities of TiO_2 and ZnO, is like that of β-eucryptite.

Glass is melted in an electric furnace, glass fibres of diameter 16 μm are drawn from a one-hole platinum crucible. Some of the glass fibres are covered with coupling agent A151 immediately. Glass fibres are heated in a tube-furnace having a 20 cm length of constant temperature zone. One end of the glass fibre is fixed, while the other end is kept straight by being pulled by a constant weight through a pulley.

2.2. DTA

DTA curves [14, 15] are recorded by a DT-30 thermo analyser and 300 mesh powdered sample and powdered α-Al_2O_3 used as reference, both samples of 25 mg, are used in analysis. T_g and the temperature range of nucleation of glass fibres are determined by DTA [14].

2.3. Measurement of tensile strength of glass–ceramic fibres

The tensile strength of glass–ceramic fibres is measured by a DX-500 tensile testing machine. The pull rate is 5 mm min^{-1} and the gauge length is 10 mm. The temperature is about 20° C and the relative humidity is approximately 70%. The tensile strength is the average of 15 measurements for every glass–ceramic fibre sample.

2.4. Weight loss of alkali corrosion

Weight loss of alkali corrosion [16] is measured after the sample of glass–ceramic fibres has been left to

TABLE I Chemical composition of glass

	Li_2O	Al_2O_3	SiO_2	B_2O_3	TiO_2 (extra)	ZnO (extra)
wt %	10.1	17.3	62.0	10.6	8.1	4.8
mol %	20.0	10.0	61.0	9.0	6.0	3.5

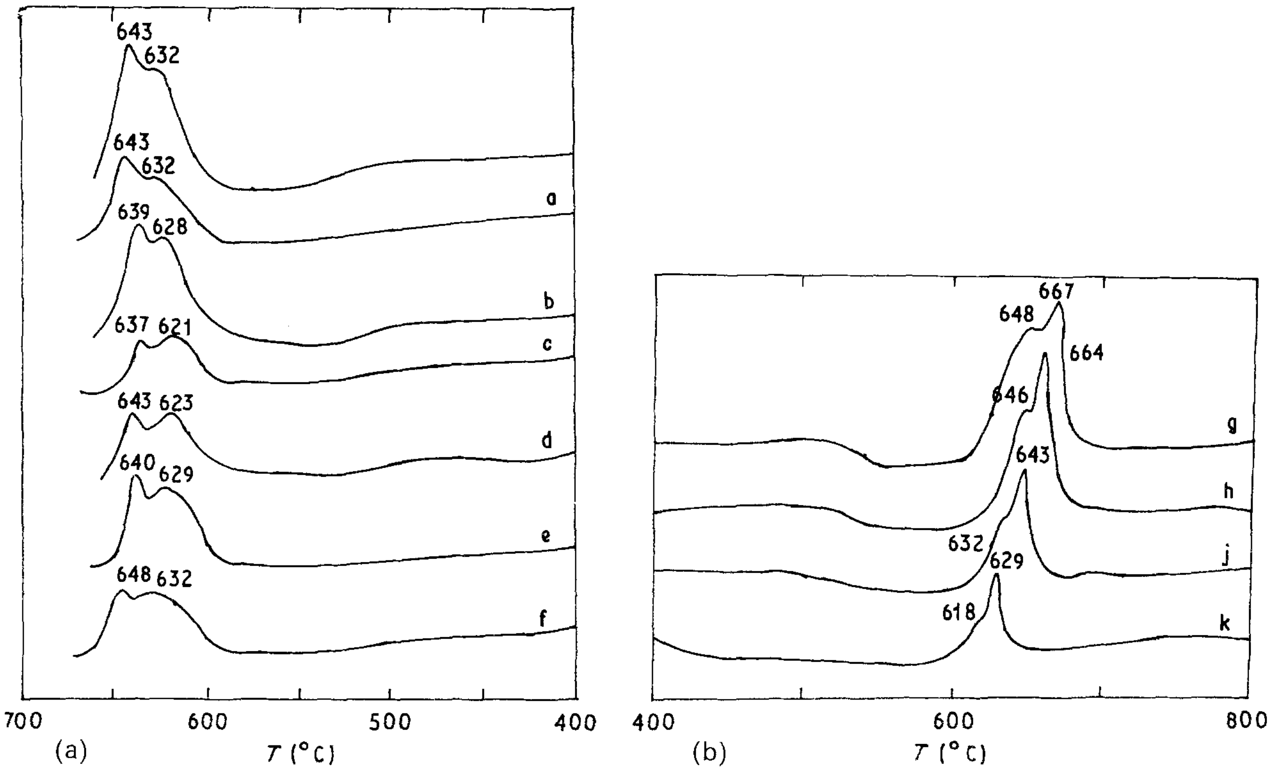

Figure 1 DTA analysis of glass-ceramic fibres (a) in various heat treatments for 1 h (a 450° C, b 470° C, c 510° C, d 520° C, e 530° C, f 540° C) (b) at various rates of heating (g 20° C min^{-1}, h 15° C min^{-1}, j 10° C min^{-1}, 5° C min^{-1}).

corrode in a supersaturated solution of $Ca(OH)_2$ for 10 h.

2.5 XRD

Greigerflex D/max-rA XRD [12] is used in conditions of 40 KV, 60 mA, copper target and scanning rate of $2\theta = 1\ \mathrm{deg\,min^{-1}}$.

2.6. TEM and SEM

JEM 200CX (TEM) and JEM 100CX (STEM) electron microscopes were used to observe glass-ceramic fibres and their cross-section was studied by a T-20 SEM.

3. Results and discussion

3.1. Nucleation mechanism of glass-ceramic fibres

The results of DTA of glass-ceramic fibres [14] are shown in Figs 1a and b. It can be concluded that the temperature range of nucleation of this glass system is

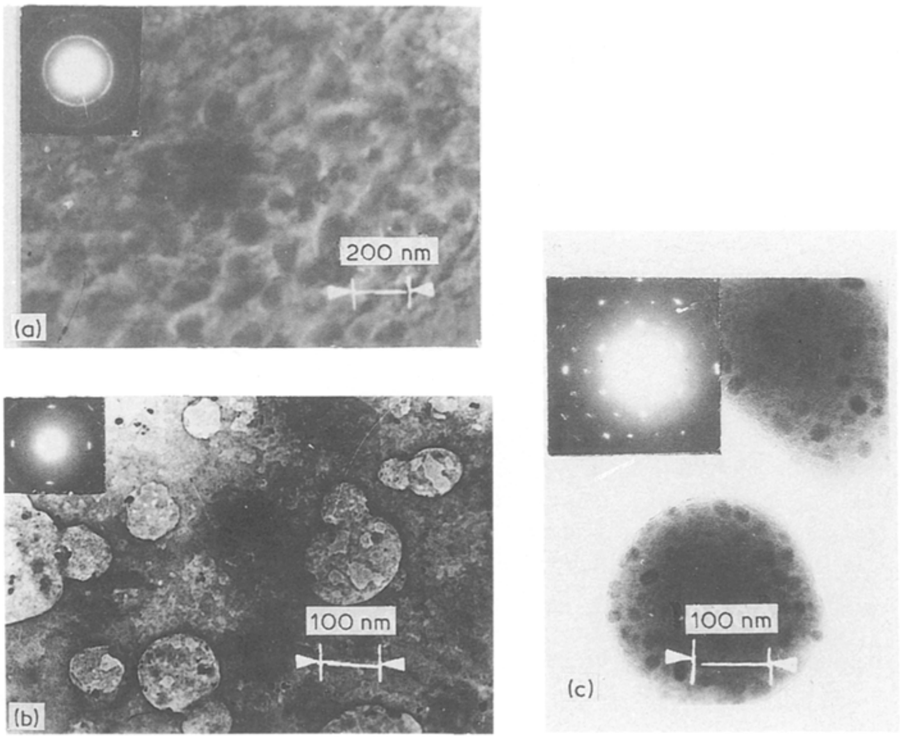

Figure 2 (a) Phase separation in glass-ceramic fibres. (200CX, TEM, 480° C 3 min, × 24500). (b) Precipitation of rutile particles in glass-ceramic fibres (200CX, TEM, 480° C 15 min, × 52500). (c) β-eucryptite appearance in glass-ceramic fibres as an initial crystalline phase. (200CX, TEM, 480° C 35 min, × 65800).

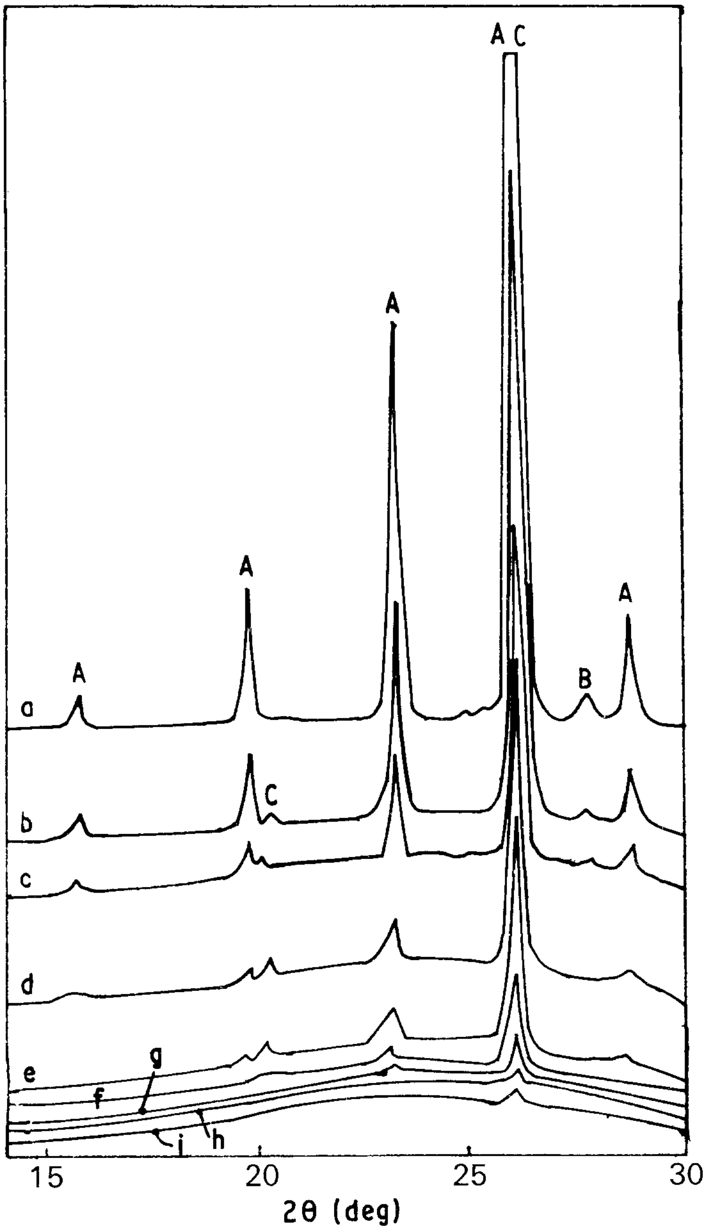

Figure 3 XRD of glass–ceramic fibres in various time of crystallization at 600° C (480° C 0.5 h). (A β-spodumene, B rutile, C β-eucryptite, a 13 min, b 10 min, c 8.5 min, d 7 min, e 5 min, f 3.5 min, g 2.5 min, h 2 min, i 1.5 min).

from 450 to 540° C. T_g is about 470° C determined by the turning point of the first endothermic peak in the DTA curve.

The results of TEM observation show that the nucleation process of glass–ceramic fibres is after phase separation had occurred in the glass fibres, see Fig. 2a, the rutile particles precipitate in one phase, see Fig. 2b, and lead to the appearance of the β-eucryptite as an initial crystalline phase in another phase, see Fig. 2c).

3.2. Sequence and kinetics of crystallization of glass–ceramic fibres

The XRD results of glass–ceramic fibres are shown in Fig. 3. The sequence of crystallization is as follows. First, β-eucryptite separates out then while β-eucryptite is separating at a constant rate, part of it transforms to β-spodumene simultaneously. Finally, β-spodumene crystallites grow up with rutile crystallites.

The process of crystals growth in glasses can be described by a Johnson–Mehl–Avrami equation

$$X = 1 - \exp(-kt^n)$$

where X is the volume fraction of crystallized phase at time t, n a kinetic parameter related to the mechanisms of the process. k is a constant related to the absolute temperature T, by the Arrhenius equation

$$k = AN\exp(-E_a/RT)$$

where E_a is the activation energy for crystallization, R the gas constant, N the number of nuclei and A a pre-exponential constant.

From the results of DTA of glass–ceramic fibres, according to the DTA method [15], the activation energy of β-eucryptite crystallization in one dimension E_1 is 70.0 kcal mol^{-1} and the activation energy of β-eucryptite transforms to β-spodumene in one dimension E_2 is 54.5 kcal mol^{-1} and the apparent activation energy, E', of β-eucryptite crystallization is 196.5 kcal mol^{-1}. Then, the kinetic parameter can be determined by

$$n_1 = E'/E_1 = 196.5/70.0 = 2.8$$

$$n_2 = E'/E_2 = 196.5/54.5 = 3.6$$

It shows that β-eucryptite crystallizes in three dimensions, for $n_1 = 2.8$, near 3, bulk crystallization. The

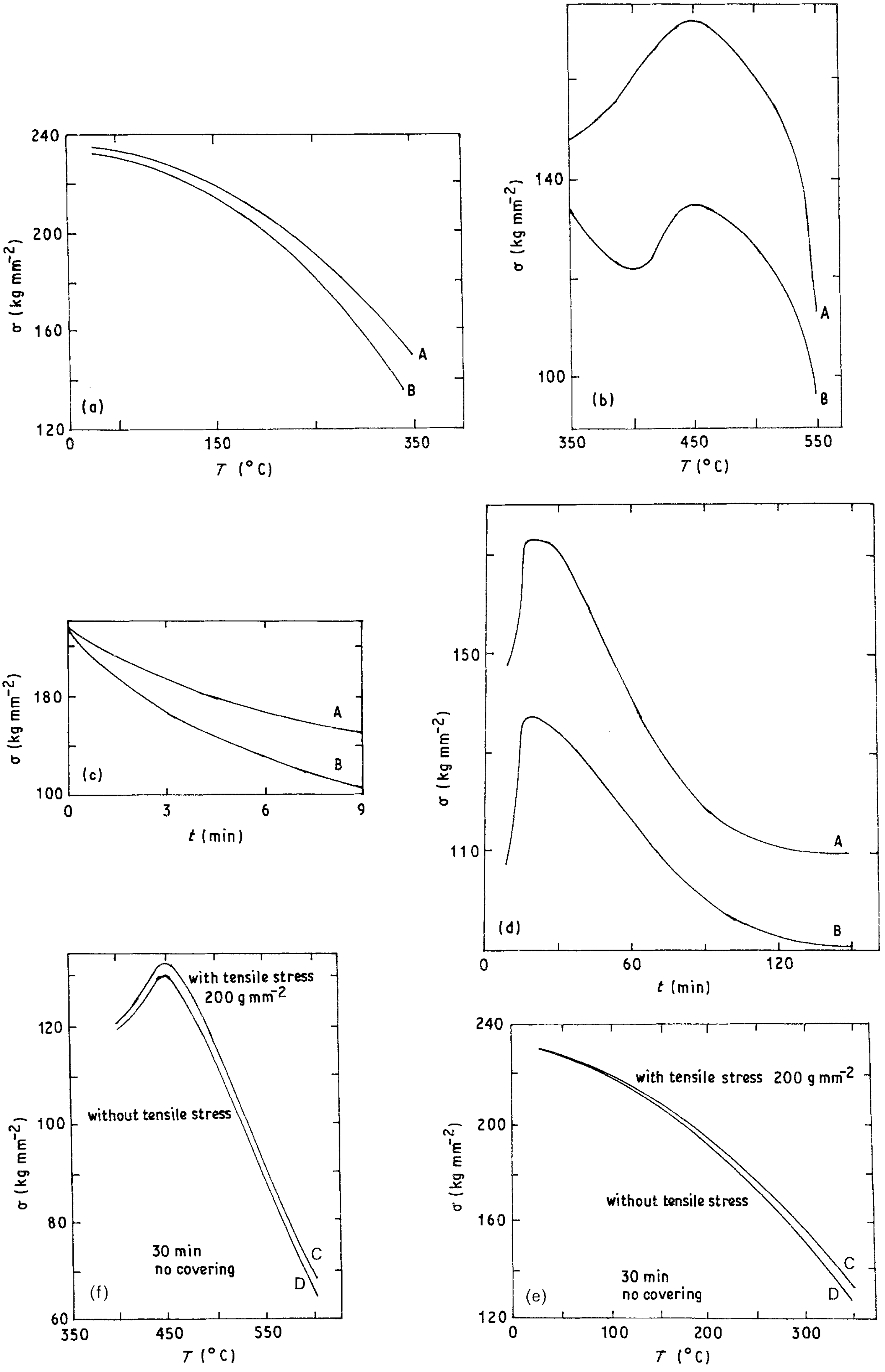

Figure 4 The relationship between tensile strength and heat treatment temperature of glass–ceramic fibres. (a) $T < 350°$C. (b) $T > 350°$C. (c) $t < 9$ min. (d) $t > 9$ min. (A covering with A151, B no covering). Tensile strength of glass–ceramic fibres with and without tensile stress exerted on the glass fibres during heat treatment. (e) $T < 350°$C. (f) $T > 350°$C (C with tensile stress 200 g mm^{-2}, D without tensile stress, 30 min no covering).

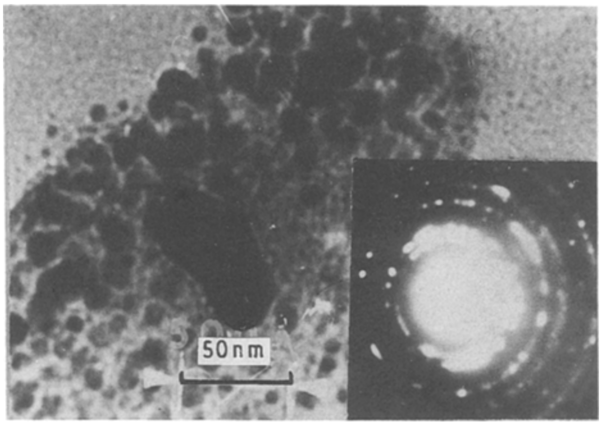

Figure 5 Phase separation in glass–ceramic fibres. (200CX, TEM, 420° C 15 min, × 16720).

datum from the second exothermic peak can not be easily explained, $n_2 = 3.6$, it is due to the fact that not only the process of β-eucryptite transforms to β-spodumene but also the process of crystallization of β-eucryptite occurs simultaneously, besides, we find that n is in the range of 2.25 to 2.83 [17] from the results of XRD quantitative analysis of glass–ceramic fibres. This shows that crystallization is almost in three dimensions, but is accompanied by some one-dimensional crystallization.

3.3. Tensile strength and microcrack extension process of glass–ceramic fibres during crystallization

The results of tensile strength of glass–ceramic fibres after heat treatment at various temperatures is shown in Fig. 4a. The tensile strength of glass–ceramic fibres decreases as the temperature increases below 350° C. This can be explained by the existence of a compressive stress in the surface layer of rapidly cooled glass–ceramic fibres which vanishes when the fibre is reheated. This causes the extension of microcracks and results in the decrease of tensile strength of glass–ceramic fibres. This result is consistent with that of Jones and McMillan [7].

Above 350° C, see Fig. 4b, the tensile strength of glass fibres begins to increase and reaches a maximum at about 450° C and then decreases again. The reason of the appearance of the maximum is mainly due to nucleation and crystallization in the glass fibres. The microstructure of the glass–ceramic fibres with maximum tensile strength is shown in Fig. 5. Small concentrated crystallites about 25 nm in size increases the tensile strength and prevent microcrack extension. The time of heat treatment of glass fibres also has an important affect on its tensile strength. Jones and McMillan have reported that the tensile strength of glass–ceramic fibres decreases with crystallization

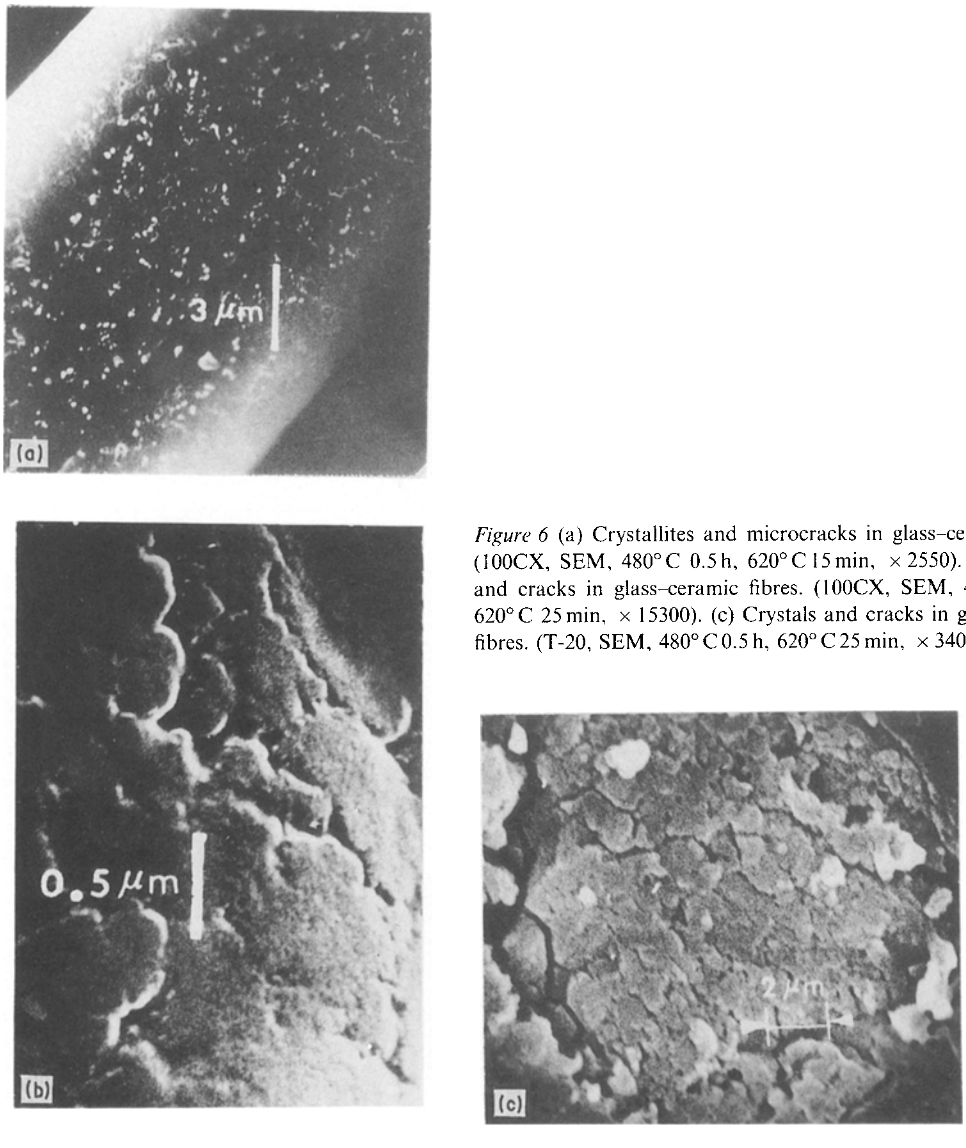

Figure 6 (a) Crystallites and microcracks in glass–ceramic fibres. (100CX, SEM, 480° C 0.5 h, 620° C 15 min, × 2550). (b) Crystals and cracks in glass–ceramic fibres. (100CX, SEM, 480° C 0.5 h, 620° C 25 min, × 15300). (c) Crystals and cracks in glass–ceramic fibres. (T-20, SEM, 480° C 0.5 h, 620° C 25 min, × 3400).

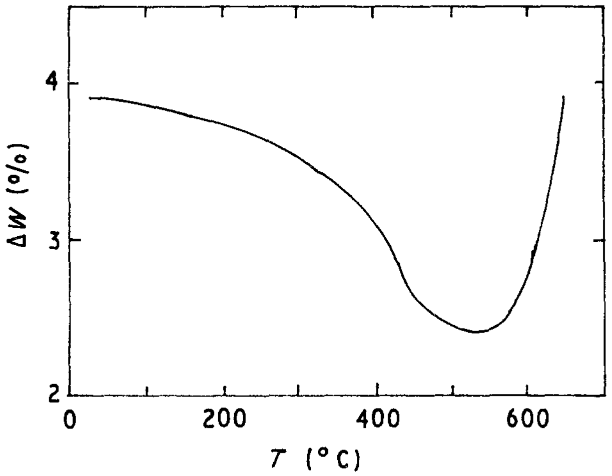

Figure 7 The relationship between weight loss of alkali corrosion and heat treatment temperature of glass–ceramic fibres.

time for any given temperature of crystallization. From the results of Figs 4c and d, we discover that, there exists a range of heat treatment times, (15 to 30 min) for which the tensile strength of glass–ceramic fibres increases with heat treatment time. This is also due to the appearance of the microstructure of small and concentrated crystallites in glass–ceramic fibres. This result implies that despite the tensile strength dropping below 350° C, it is worthwhile choosing an optimum temperature and time of heat treatment for glass–ceramic fibres having higher tensile strength than the original tensile strength of glass fibres.

We now investigate the process of microcrack extension of glass fibres during heat treatment. First, well distributed microcrystallization occurs in the separated phase of glass fibres and the microcrack is not clearly visible. Secondly, microcracks extend from point defects to a considerable size, see Fig. 6a, the size of microcracks is about 0.5μm, and this results in the immediate decrease of tensile strength of glass–ceramic fibres. Finally, crystallites grow into thick crystals and microcracks extend to wide cracks resulting in the almost complete loss of tensile strength of glass–ceramic fibres, see Figs 6b and c.

3.4. The affect of coupling agent on the tensile strength of glass–ceramic fibres

In spite of the ability to increase the tensile strength of glass–ceramic fibres by appropriate crystallization, the surface microcracks are the cause of the decrease in tensile strength. The coupling agent A151 is used to improve the surface of glass–ceramic fibres preventing microcracks extension by the formation of a layer of organic silicon surface covering. The tensile strength of glass–ceramic fibres with and without coupling agent A151 on the surface of glass–ceramic fibres are shown in Figs 4a, b, c and d which shows that the tensile strength of glass–ceramic fibres can be increased about 10 to 30% by the use of the coupling agent. The coupling agent A151 is, however, not ideal for glass–ceramic fibres as it cannot withstand the heat treatment temperature of up to 500° C.

3.5. The affect of tensile stress exerted on glass fibres during heat treatment

It has been reported that tensile stress exerted on glass fibres during heat treatment increases the tensile strength of the glass fibres after crystallization [18]. We exert a 200 g mm^{-2} tensile stress on the glass fibres during heat treatment. The result is shown in Figs 4e and f. It may be thought that the tensile stress exerted on the glass fibres leads to the production of a microstructure not only in the bulk of glass fibres but also on the surface to balance the tensile stress exerted. After heat treatment, relaxation of the tensile stress results in a compressive stress in the glass fibres which increases the tensile strength of the glass fibres.

3.6. Chemical durability of glass–ceramic fibres

The result of weight loss in alkali after heat treatment at various temperature is shown in Fig. 7. The glass–ceramic fibres which have been heat treated at 475 to 600° C have the best chemical durability. This is due to the microstructure of small and concentrated crystallites also produced in glass–ceramic fibres. An increase in the temperature of heat treatment leads to the extension of microcracks, which results in an increase of the reaction surface and further increases the weight loss of alkali corrosion of glass–ceramic fibres.

4. Conclusions

The conclusions are as follows.

(1) The glass prepared for glass–ceramic fibres should be characterized by the temperature of phase separation, nucleation and crystallization of the glass ought to be low, as near T_g as possible, corresponding to its basic properties and the rate of dense bulk crystallization must be closely controlled.

(2) The microstructure of small and concentrated crystallites, of about 25 nm (while the diameter of glass–ceramic fibres is 16 μm) produced in glass–ceramic fibres is of benefit to the increase in tensile strength and alkaline resistance.

(3) A suitable coupling agent covering the surface of the glass–ceramic fibres together with tensile stress exerted on the glass–ceramic fibres during heat treatment is of benefit to its mechanical and chemical properties.

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Received 7 March 1988
and accepted 20 January 1989