SiC Fibre/Borosilicate Glass Composite (Part 1)

——Matrix Devitrification——

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SiC 紡維/ホウケイ酸ガラス複合材（第1報）
——マトリックスの変性——

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The crystallization behaviour of borosilicate glass (Pyrex) with and without a continuous SiC fibre reinforcement has been investigated as a function of heat treating time (10 min to 20h), temperatures (800 to 1050°C) and particle sizes. The tendency to crystallize into cristobalite was found to be very sensitive to the particle size of Pyrex glass. Finer particles exhibited a higher amount of cristobalite than coarse particles for the same heat treating conditions, indicating that crystallization of Pyrex resulted from heterogeneous nucleation and growth on the surface of each particle. For the SiC fibre/Pyrex composite, the presence of fibres appeared not to contribute significantly to the devitrification of matrix, since (1) nearly same degree of devitrification occurred in the Pyrex powder compact alone compared with the degree of crystallization in the SiC fibre/Pyrex composite with same size of Pyrex particle, and (2) devitrification occurred randomly rather than occurring preferentially at the matrix-fibre interfaces. The devitrification of Pyrex matrix to cristobalite under processing conditions used for composites gave rise to extensive microcracking. The thermal mismatch stress originating from both a higher coefficient of thermal expansion of devitrified cristobalite and ~3.9% volume change at the phase transition temperature (~250°C) of cristobalite was calculated using the particle sphere model. The magnitude of stress calculated was high enough to cause cracking in and around a cristobalite particle surrounded by a Pyrex matrix.

Key-words: Fibre composite, Borosilicate glass, Matrix devitrification, Cristobalite, Thermal stress

1. Introduction

SiC fibre (Nicalon)-reinforced borosilicate glass (Pyrex) composites have received a great deal of attention because this material can exhibit both high strength (600-1200 MPa), and a high work of fracture (WOF) of the order of 70 kJ/m² mainly through fiber pull-out, up to the matrix softening point (560°C). In addition, the combination of SiC fibre and Pyrex matrix is considered to be a model system for ceramic matrix composites, since Pyrex matrix has a Young's modulus one third of SiC fibers and a similar thermal expansion to that of the fibres. Nicalon fibre-reinforced Pyrex glass is also of interest for basic research in glass-ceramic matrix composites, because of its easy fabrication at low temperature.

However, there has been little research on how the devitrification behaviour of the matrix itself affects the mechanical properties of the composites. This is particularly important in Pyrex glass where the temperatures used for consolidation of the prepreg (850-1200°C) can induce crystallization of cristobalite. For this reason the crystallization behaviour of a commercial Pyrex glass with and without the SiC fibre-reinforcement has been studied with three main objectives: (1) the role of the fibre/matrix interface on the devitrification of a Pyrex powder compact. (2) the mechanism of crystallization of a Pyrex powder compact to cristobalite during sintering. (3) the magnitude of thermal stresses occurred between the devitrified cristobalite and Pyrex matrix.

2. Experimental procedure

In order to study the crystallization behaviour of Pyrex glass, commercial Pyrex glass*1 fragments were milled to pass through mesh <250 μm, and pressed uniaxially to make a pellet shape (diameter ≈15 mm) prior to heat treating. These green bodies were heat-treated at temperatures from 700 to 1050°C for different times (10 min to 20h) under vacuum of 1.333 × 10⁻² Pa, in order to simulate an inert atmosphere for fibre composite processing. The heating rate was ~15°C/min. The role of fibre/matrix interface for the crystallization of Pyrex matrix was investigated using the composites where

*1 Pyrex glass beaker manufactured by Corning Co., U.S.A. was used as a starting materials. This glass has the composition: SiO₂ 81 mass%, B₂O₃ 13 mass%, Al₂O₃ 2 mass%, Na₂O 4 mass% and traces of CaO and K₂O.
the Pyrex was ground to <44 μm particle size and mixed with type NL-202 Nicalon fibre. These mixtures were heat-treated for short times at temperatures between 800°C and 1050°C to simulate the processing temperatures used for consolidation of the composites. Comparison of the degree of crystallization in the Pyrex alone and that in the Pyrex mixed with fibres was made to show the contribution of presence of fibre/matrix interface to the matrix crystallization.

The prepreg and consolidated SiC fibre\textsuperscript{62,63} reinforced Pyrex\textsuperscript{62} composite were supplied by Pilkington Plc., U.K. This prepreg was fabricated by a slurry impregnation route.\textsuperscript{6} Pyrex glass powder was ball-milled to pass through 325 mesh (<44 μm) screen, and the Nicalon fibres (∼50 vol%) were aligned uniaxially into prepregs containing Pyrex matrix dispersed on the fibres. The prepregs were heat-treated at the same conditions applied to the Pyrex glass alone in order to investigate the effect of reinforcements on the crystallization of matrix.

Further experiments were then performed at 850 and 900°C to simulate the effect of particle size on the devitrification behaviour of Pyrex. For these experiments the powders were divided into three size groups by passing through stacked sieve screens: The size distributions of ‘fine’ and ‘medium’ groups are given in Fig. 1. The ‘coarse’ particles were in the size range 250–1400 μm.

A powder X-ray diffraction method was applied for the quantitative analysis of crystalline silica generated from Pyrex. Calibration mixtures for external standards were prepared by mixing Pyrex powder and pure cristobalite powder with a constant particle size (<5 μm) in various proportions.\textsuperscript{7,8} A Philips diffractometer with Cu Kα radiation was used for X-ray diffraction (XRD) measurement. A calibration curve was made by plotting the relative intensities of the 0.405 nm reflection from the (101) α-cristobalite planes (which occurs at 2θ = 21.97° for the Cu Kα radiation used) in a mixture to that of pure cristobalite, against the weight fractions of cristobalite in the powder mixtures. All sample conditions for XRD measurement such as the sample weight, compacting condition in the sample holder and mixing time were fixed.

The calibrated mixtures for the Pyrex-containing fibres were also prepared by mixing in various proportions finely ground SiC fibres (taken as 50 vol% of the whole for simulating the content of fibre in prepreg), Pyrex powder and pure cristobalite powder prepared from silica gel. Although care was taken to ensure that the powder mixtures were each finely ground for the same length of time prior to X-ray examination, the X-ray intensity from the (101) α-cristobalite planes was found to vary within ±2 mass% error. Optical and scanning electron microscopy (SEM) micrographs were taken to show the fibre distribution in the composite and the effect of matrix devitrification on the microstructure, respectively.

3. Results and discussion

3.1 Devitrification of Pyrex glass

X-ray powder diffraction patterns of (a) Pyrex glass powder, (b) as-received Nicalon fibre, (c) prepreg and (d) a typical consolidated sample are shown in Fig. 2. The as-received Nicalon fibres and Pyrex powder consist of amorphous SiC and a typical glass structure, respectively. The diffraction pattern of the prepreg composed of about 50 vol% each of fibres and matrix material shows broad amorphous diffraction peaks from the Pyrex glass and the Nicalon fibres at about half the intensities seen in

![Particle Size Distribution](image)

**Fig. 1.** Size distributions of the ‘fine’ and ‘medium’ Pyrex powders.

\textsuperscript{62} Nicalon supplied by Nippon Carbon Co., Ltd., Tokyo, Japan; Tyrano fibre supplied by Ube Industries, Tokyo, Japan.

\textsuperscript{63} Pyrex glass supplied by J. A. Jobling and Co., Ltd., Durham, U.K.
Figs. 2(a) and (b), as might be expected from the volume fraction of fibres. However, the powder diffraction pattern Fig. 2(d) obtained from the composite hot-pressed at 960°C for 10 min reveals that this sample contains not only matrix glass, but also some peaks readily attributable to $\alpha$-cristobalite.

This tendency for the Pyrex glass to devitrify was examined initially as a function of temperature and time in vacuum on powders sieved to $<250\,\mu m$ particle size (Fig. 3). The crystallization behaviour of Pyrex powder to cristobalite can be divided into two regimes by considering greater than and less than 5h-heat-treating time. For heat-treating less than 3h, the maximum devitrification occurred at around 850–900°C, to the extent that about 20 mass% of the Pyrex glass had transformed to $\alpha$-cristobalite within 3h. Reducing the temperature decreased the rate of devitrification so that less than 10 mass% of Pyrex crystallized to cristobalite at 800°C. Below 700°C there is negligible devitrification, and above 1050°C the Pyrex glass is above its liquidus and so clearly devitrification did not occur. The general tendency of crystallization of Pyrex powder within the first 3h is in accord with the experimental work of Petruš [9] where the maximum devitrification of the Pyrex glass powder having 2 mass% of $Al_2O_3$ which is closest of the glass composition used for our experiment occurred at around 850–900°C during sintering.

The tendency to crystallize into cristobalite can be understood as a consequence of crystallization of the immiscible silica-rich glass phase together with surface devitrification of silica-rich glasses through phase separation into boron-rich and silica-rich phases. [10–12] In the phase-separated Pyrex glass, the free-surface in the bulk glass and particle surface of the powder compact can be preferred sites for the formation of cristobalite, because these surfaces can reduce the barrier to nucleation represented by the surface energy. In order to demonstrate that surface devitrification is likely to be one of crystallization mechanisms, the effect of particle size on devitrification was then studied, the results of which are shown in Figs. 4(a) and (b). The finer particles showed a faster rate of crystallization. This result shows the clear trend of increasing devitrification with decrease in particle size. In addition, a comparison of the amount of cristobalite between the glass compact heat-treated at 850 and 900°C for the fine particles showed that the glass compact heat-treated at 900°C has the higher degree of crystallization.

When the Pyrex powder compact is subjected to prolonged heat treatment, a reduced crystallization was observed at temperatures beyond 900°C. This may be arisen from the evaporation of some of volatile constituents. While heat treating in a vacuum of $1.333 \times 10^{-2}$ Pa, some volatile ions such as Na$^+$ and B$^{3+}$ can easily evaporate. [13] The degree of volatilization can be accelerated by increasing the temperature. Since the rate of crystallization of Pyrex glass is found to decrease with decreasing Na$_2$O and B$_2$O$_3$ contents, [9] the loss of these elements during heat treating can reduce the equilibrium amount of cristobalite which can form. Increasing the temperature below liquidus can increase the diffusion rate for growth of cristobalite, but also increase the evaporation rate. Thus, the amount of cristobalite formed could result from the compensation between the increased diffusion rate and increased evaporation rate with temperature. In practice, an increased porosity was observed in the Pyrex glass compact heat-treated at high temperature for long time.

Thus, at certain temperature, i.e., 900°C, the evaporation rate can become faster than the rate of crystallization, thus resulting in the reduction in the rate of crystallization for the powder compact. More clear evidence of changing the maximum crystallization temperature can be seen in the Time–Temperature–Transformation (T–T–T) curve (Fig. 5). The rate of crystallization at 900°C in comparison with
the crystallization rate at 850°C, which can be calculated easily by dividing the amount of crystallization by the time interval between the data located in isothermal line, is relatively fast in the beginning but slows with increasing heat-treating time. Furthermore, the nose of T-T-T curve shifts from ~900°C to 850°C with increasing heat-treating time. When considering the crystallization tendency shown in the T-T-T diagram together with the increased porosity observed in the powder compact, the reduction of the temperature at which the maximum rate of crystallization occurs for the powder compact can be attributed to the evaporation of some volatile elements during heat-treating at high temperature for long time in vacuum condition.

3.2 Devitrification of Pyrex matrix in the fibre composites

The crystallization behaviour of the matrix in the SiC fibre-reinforced Pyrex glass was also studied as a function of temperature and time (Fig. 6), where glass particles less than 45 μm were used to fabricate the prepreg. Although the overall tendency for crystallization of Pyrex matrix in the prepreg is similar to that of Pyrex alone, the rate of crystallization is faster than that of Pyrex glass alone. Thus, a larger amount of cristobalite occurred within a relatively short time in the fibre composites compared to Pyrex powder with size of <250 μm as shown in Fig. 3. For the heat treatment within initial one hour, the crystallization behaviour of glass composites seems to be a more complex function of temperature than in Pyrex glass alone. Devitrification of glass matrix within the first one hour of heat-treating time, and T-T-T curve up to the 10% of transformation of matrix are shown in Figs. 7 and 8, respectively. The fastest rate of transformation occurs at 1000°C to extent that about 10 mass% of matrix has crystallized to α-cristobalite within the initial 30 min. Increasing the time up to 1h decreases the temperature at which maximum crystal growth is observed to 950°C. When heat treating for longer time than 2h, the maximum crystallization appears at 850°C as was seen in Pyrex glass powder alone.

The changes of the maximum devitrification temperature from 1000 to 850°C depending on the heat-treating time can be understood as a result of the evaporation of some volatile constituents of Pyrex glass with an emphasis on the behaviour of much
smaller glass particles less than 44 μm used to make prepregs compared with the particles (<250 μm) in glass compact. Finer particles in the prepreg can provide a faster reactivity, higher driving force for diffusion of each element and larger surface area so that the incubation time for crystallization can be reduced. This may be the reason that the crystallization can occur within relatively short time for finer particles, and that the degree of crystallization increases with increasing temperature near to the liquidus. On the other hand, the rate of evaporation can also be increased with increasing temperature and decreasing the particle size. Assuming that the rate of crystallization results from the compensation between the rates of diffusion and evaporation, and also that the evaporation is more dominant with extending heat-treating time because of increased porosity, the reduction of crystallization begins at certain time, before the crystallization reaches the maximum value which is able to obtain if there is no evaporation. Increasing temperature near to liquidus at which dissolution of crystals occurs can reduce the time needed for the initiation of decrease of crystallization.

The occurrence of cristobalite in the glass composite at 1050°C is somewhat unexpected because the liquidus temperature of Pyrex glass is 1046°C, and so the crystallization did not occur in the Pyrex glass compact heat-treated at same temperature, as shown in Fig. 3. If there is any crystalline phase which formed on heating to 1050°C with the heating rate of ~15°C/min, this should be dissolved while heating at 1050°C for long time. However, some of Pyrex glass crystallizes at the order of 5 mass% at a temperature supposed slightly above the liquidus and do not dissolve into the glass matrix. The crystallization of Pyrex matrix at temperature supposed above the liquidus has also been found in the work of Davies et al.4) where they mentioned that the carbon fibre/borosilicate glass composites heat-treated even at 1200°C showed small traces of crystalline material occasionally visible on the surface of fibres. Therefore, the crystallization of Pyrex glass at this temperature may be due to either the presence of fibre or more likely slow cooling through devitrification temperature regime.

In order to determine the degree of contribution of fibre/matrix interface to the crystallization of Pyrex matrix, Pyrex particles less than 45 μm prepared by ball-milling and then passed through a 325-mesh screen were heat-treated at 850°C for 1h and 3h, since glass powder with same particle sizes was used in the prepreg. Nearly the same amount of cristobalite was generated as in the prepreg heat-treated under the same conditions. In addition, SEM micrographs of the polished surface of the composite consolidated at ~960°C reveal that crystallization does not occur preferentially at the fibre surfaces, but is generated homogeneously within the matrix, as shown in Fig. 9. These results indicate the presence of fibres is not the dominant factor in determining the degree of crystallization when the composite is held in the temperature range of 850–1000°C for a period of time of the order of hours, but may contribute to the small amount of crystallization near to the liquidus temperature.

3.3 Effect of matrix devitrification on the microstructure

The differences in the coefficients of thermal expansion (CTE) between α-cristobalite, β-cristobalite and borosilicate glass (19.68 × 10⁻⁶ K⁻¹) parallel to the ‘a’ and ‘b’ axes and 53.92 × 10⁻⁶ K⁻¹ parallel to the ‘c’ axis for α-cristobalite, 5.65 × 10⁻⁶ K⁻¹ for β-cristobalite4) and 3.3 × 10⁻⁶ K⁻¹ for borosilicate glass) can induce severe radial tensile stress within cristobalite particles and in the matrix.

For the simple case of an isolated spherical α-cristobalite single crystal in a large volume of borosilicate matrix, the stress field in the matrix on cooling through the β → α transformation will consist of a radial tensile stress and a compressive tangential stress around the particle. The variations of radial (σ₁) and tangential (σ₄) stresses in the matrix as a function r can be predicted quantitatively from the formulas suggested by Selsing.15)

When the Pyrex matrix containing cristobalite polycrystals is cooled from the consolidation temperature of the composites of ~960°C, the stress starts to be accumulated from the temperature for strain of Pyrex glass (520°C).16) Assuming that the transition temperature of β → α phase is 250°C, and that the stress relief does not occur during cooling, the maximum thermal mismatch stress developed between Pyrex matrix and cristobalite can be obtained from following equation,

\[
P = \frac{1}{1 + \frac{1}{v_p} - \frac{2v_p}{E_p}} \left[ \int_{20}^{250} (\alpha_{c-960} - \alpha_m) \, dT \
+ \left( \frac{\Delta V}{3V} \right) \int_{250}^{250} (\alpha_{c-960} - \alpha_m) \, dT \right]
\]

where P the hydrostatic pressure acting on the spher-
Table 1. Coefficient of Thermal Expansions and Elastic Properties of Pyrex and Cristobalite

<table>
<thead>
<tr>
<th></th>
<th>Pyrex matrix (1)</th>
<th>α-cristobalite (2)</th>
<th>β-cristobalite (2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E (GPa)</td>
<td>65</td>
<td>T ≤ 250°C</td>
<td>T ≥ 250°C</td>
</tr>
<tr>
<td>v</td>
<td>0.2</td>
<td>-100</td>
<td>-100</td>
</tr>
<tr>
<td>CTE (× 10−6/K)</td>
<td>3.3</td>
<td>31.4(1)</td>
<td>5.65</td>
</tr>
</tbody>
</table>

(1) Data from Ref. 16
(2) The elastic property of cristobalite is not available, so the data quoted are taken from range of values of silica-based ceramics (Ref. 19)
(3) Average CTE = (α_a + α_m + α_t)/3

The cubic cristobalite particle of radius a, ΔT the difference in CTEs of glass matrix and cristobalite particle, i.e., ΔT = α_m - α_p, ΔV the cooling range, ΔV the volume change at the phase transition temperature of cristobalite, and ε and E are Poisson's ratio and Young's modulus, respectively. Using the material parameters given by Table 1 and ΔV/ V = 0.039 at 250°C, then P = −1407 MPa. Thus, the maximum radial tensile stress and tangential compressive stress in the matrix near by cristobalite particle will be 1407 MPa and 703 MPa, respectively. These stresses formed in and around the cristobalite crystal would be high enough to cause a circumferential crack in the matrix around crystal and also cracking within the crystal, as shown in Fig. 9.

Thus the presence of large volume fractions of cristobalite particles in the borosilicate matrix causes the extensive microcracking in and around the particles and will also lead to a marked weakening in the tensile strength of the matrix (in the absence of fibres) and also stiffness of the matrix in comparison with that of the same matrix where devitrification has been prevented.

The main effect of matrix devitrification is to compound any deleterious effect of thermal cycling of these materials between room temperature and temperatures above the α→β phase transformation by providing further pathways for the environment to attack the composite.18

4. Conclusions

In SiC fibre-reinforced Pyrex composite, the presence of fibres appeared not to contribute significantly to the devitrification of matrix. Some of evidence for this are (1) nearly same degree of devitrifications occurred in the Pyrex powder compact alone compared with degree of crystallization of SiC fibre/Pyrex composite with same size of Pyrex particle. (2) nucleation of cristobalite occurred homogeneously rather than occurring preferentially at the matrix-fibre interfaces.

The radial tensile stress and tangential compressive stress were developed in the matrix near by cristobalite particles due to the difference in thermal expansions between the Pyrex matrix and cristobalite. The magnitude of stresses generated in and around cristobalite particle were calculated using the model of a spherical crystal in a continuous glass phase. This showed that the radial tensile stresses occurred both in the matrix and within the cristobalite are high enough to cause a circumferential cracks in the matrix around cristobalite and cracking within the crystal.

References