Optimized preparation parameters of unidirectionally C fibre-reinforced glass ceramics of the systems MAS and BMAS

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For reinforcement with high strength C fibres, the optimized preparation parameters of two glass ceramics in the system $MgO-Al_2O_3-SiO_2$ (MAS) and $BaO-MgO-Al_2O_3SiO_2$ (BMAS) were investigated. The optimized preparation is related mainly to the mechanical properties of composites having a high portion of crystalline matrix microstructure. As a first step, the temperature ranges were determined at which the glass matrix crystallizes to a high degree. The optimized mechanical properties of the composites were obtained by systematic variation of the temperature–pressure profile for the densification of the prepregs. The best results were obtained by densifying the composition of each composite in the glass temperature region, T_g, before the matrix started to crystallize. Optima mechanical properties exist also for composite fibre concentrations observed in the range of 31–33 vol%.

1. Introduction

Great effort has been made in the last ten years for the development of fibre reinforced materials on the basis of non-metallic inorganic matrices. While glass matrices were reinforced by SiC and C fibres as well, glass ceramic matrices were reinforced mainly by SiC fibres. The C fibres, indeed, have a larger reinforcement potential than the SiC fibres, but they are limited for applications to temperatures below 400 °C in air due to their low oxidation resistance. This is the reason why C fibre reinforced glass ceramics are relatively rarely prepared so far [1–5]. However, in vacuum or in a protected gas atmosphere, C fibre can be applied up to 1200 °C. Thus, ceramic or glass ceramic matrices are necessary for these applications. Therefore, and due to good results with C fibre reinforced glasses [6–8], glass ceramic compositions were selected in the present paper for C fibre reinforcement, which have been used successfully for SiC fibre reinforcement [9].

2. Experimental procedure
2.1. Glass ceramics

Two glasses were selected with stoichometric compositions of cordierite (MAS: $2MgO-2Al_2O_3-5SiO_2$) and barium osumilith (BMAS: $BaO-MgO-2Al_2O_3-5SiO_2$), thus, corresponding crystalline phases could be expected. The glasses were powdered to grain sizes with 99% < 40 μm. The compositions of the two glasses are given in Table I.

2.2. Preparation of the prepregs and composites

The prepregs were prepared by the slurry sol–gel method which is described extensively in [10]. It is based on the dispersion of glass powder in an Si–alkoxide solution, through which the C fibre bundles were drawn and loaded by glass particles. Polycondensation, hydration and gelation lead to well handlable and workable prepregs.

The densification of the prepregs was made by an inductively heated pressure device with various temperature–pressure programmes according to Fig. 1. For programme A, a pressure of 5 or 10 MPa was applied at about 50 K before the final maximum temperature was reached. The schedules B and C differ from A in the temperature range of glasses, T_g, where a portion of the pressure (programme B) or the total pressure (programme C) was applied. The samples were cooled without any holding time after the maximum temperature was reached.

Testing rods were cut by a diamond saw with a cross-section of about $3 \times 3 \, mm^2$ from the compressed $10 \times 10 \, cm$ plates of the composites.

2.3. Investigation methods
2.3.1. Three point bending test

The mechanical properties of the composites were determined by a universal testing machine (Zwick, Ulm) with a three point bending load. The span length was 75 mm and the bending rate 10 mm min^{-1}. In such a way, Young's modulus, the strength (maximum fracture stress, σ_{max}) and the bend over stress, σ_{bend}, which indicates the end of the elastic (el) range of the composites, as well as the corresponding strains, ε_{max} and ε_{bend}, were measured from stress–strain diagrams. The corresponding energies, W_{el}, the work of elastic deformation up to the bend over stress, W_{Fmax}, the work up to the maximum strength, and W_{total}, the

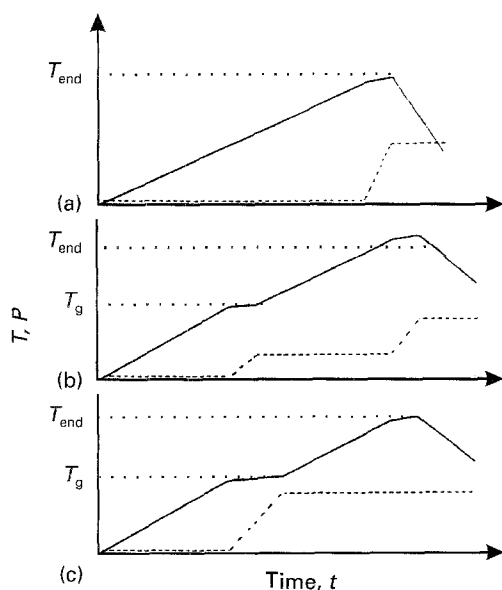|	Initial glass powder	Composition in (wt %)				Main crystal phases	Maximum temperature of application (°C)
		SiO_2	Al_2O_3	MgO	BaO		
MAS	Stoichiometric cordierite	51.3	34.9	13.8	–	Cordierite	1450
BMAS	Stoichiometric Ba osumilith	50.0	28.3	7.5	14.2	Ba osumilith	1250

Figure 1a–c The applied temperature (———) pressure (– – – –) programmes A, B and C respectively.

whole work of fracture, were determined from the area below the stress–strain curves. Of special interest for the toughness of the composites is the part of the stress–strain diagram after reaching the maximum strength. If the stress shows a slow decrease with a final strength level at high strains the toughness is good and W_{total} will be large. The error beams in the Figs 2–8 refer to five to ten samples from the same plate.

2.3.2. X-ray diffraction

The qualitative determination of the crystalline phases in the composites was done by usual X-ray diffraction techniques, within a Bragg angle range of 5–50°. For the quantitative determination of composites crystalline phases, the method of Chung [11] for multiphase glass ceramic systems was applied. This method works without knowledge of the mass absorption coefficients of the single crystal phases by mixing the pure crystal phase in the mass ratio 1:1 with the standard, α-Al_2O_3, and by determining the integral intensity of a selected peak in each case. In order to determine the mass portions of the crystal phases in the composites the milled sample was mixed with the standard, also in the mass ratio 1:1, and the integral intensities of the selected peaks of the various crystalline phases were determined.

2.3.3. Density

The density of the composites was measured by the Archimedes' method in distilled water. Porous samples were sealed with a lacquer of known density before measurement.

2.3.4. Fibre concentration

The fibre content of the composites was determined from samples which were cut, ground and polished perpendicular to the fibre direction by light microscopy combined with a semi-automatic image analyser (type: 40–10, Al Tektron).

3. Results

With respect to the goal of this paper to determine the optimized preparation parameters, three selective steps were chosen for which the temperature, compressive load application and fibre content were varied successively. In the first step a variation of the pressing temperature was made in order to obtain a matrix with a crystalline portion as high as possible. Variation of the temperature–pressure profile was made in a second step with the optimal pressing temperatures from the first step, in order to find the optimized mechanical properties. In the third step the fibre concentration was varied with respect to the best parameters found in the second step in order to find the optimal ratio of fibres to matrix. In the first two optimizing steps a fibre content was chosen (about 20–30 vol %) which has been successful in SiC fibre reinforced corresponding glass ceramics [9].

3.1. Variation of pressing temperatures

The experiments were done with pressures of 5 and 10 MPa according to temperature–pressure profile A (Fig. 1). The limits of the temperature variation were given on the one hand by melting of the crystalline phases resulting in a low viscous melt and in a non-reproducible fibre concentration due to matrix losses during pressing and on the other hand by too high viscosities below the T_g of the corresponding glass matrix.

Temperatures above 1300 °C were found to be too high for the two kinds of matrices because low viscous primary melts occurred and matrix losses made reproducible fibre concentrations impossible in such a way that the fibre content increased.
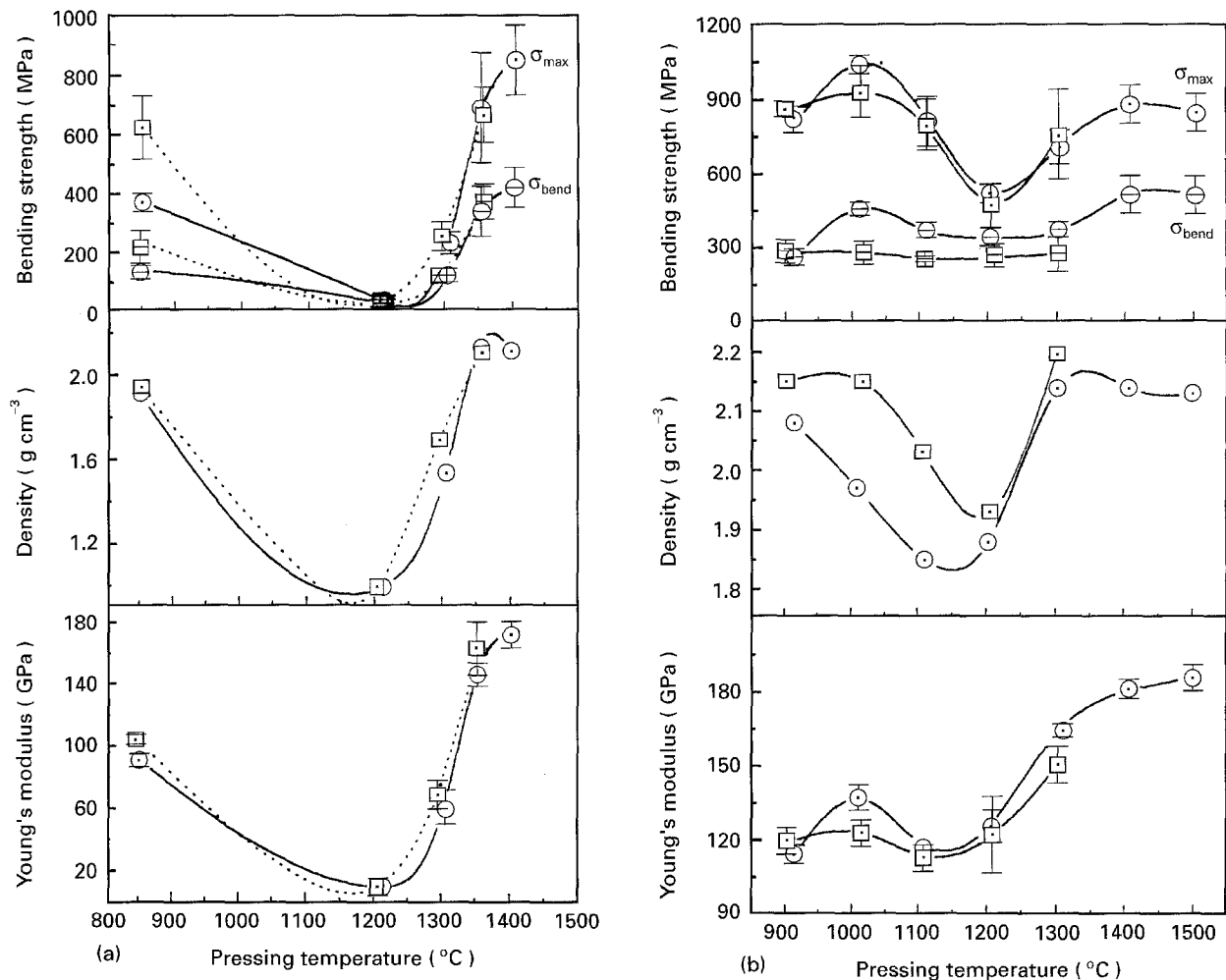
Figure 2 Bending strength, σ_{max}, bend over stress, σ_{bend}, density and Young's modulus versus pressing temperature at (O) 5 and (□) 10 MPa for programme A: (a) MAS, and (b) BMAS matrix.

At temperatures above 1000 °C, mainly cordierite was found in the MAS matrices and towards high pressing temperatures small quantities of mullite were also present. At the lower pressing temperatures, high-quartz solid solution crystals, the metastable primary phase of cordierite (μ-cordierite), was found.

Ba-osumilith was the main quantity in the composites with BMAS composition; additionally cordierite and low amounts of celsian, mullite and the high-quartz solid solution phase were found.

Fig. 2a, b shows the relevant mechanical data plotted versus the corresponding preparation temperatures. The strength, σ_{max}, exhibits a characteristic minimum which coincides with the largest degree of crystallization of the matrices at 1100 and 1200 °C. The bend over stresses, however, are influenced only slightly by the preparation temperatures, as long as the matrices have not yet melted ($T < 1300$ °C). Difficulties due to the fast crystallization of the matrices become evident, particularly for the MAS matrix. The density behaviour indicates clearly that a very poor densification of the composites and therefore also low mechanical values are obtained by the applied temperature–pressure profile; which allows the rapid crystallization of cordierite at 1100–1200 °C before the matrices of the prepregs are densified at all. Possibly, the late application of pressure even causes predamage of the matrices and/or of the

fibres. Best densification values and also best mechanical properties are found when the crystallinity of the matrix is low at the moment of pressure application. These are the temperatures around T_g and those at which the matrices begin melting again ($T > 1300$ °C). Also, Young's modulus shows a behaviour closely related to the densification and microstructure of the matrices. The low values of Young's modulus at the lowest pressing temperatures, despite high densities, are caused by inhomogeneities of the matrix, which is comparable to a well densified sintered glass powder with interfaces still present.

Nevertheless, from the relatively high densification of the composites around T_g it was concluded that the mechanical properties can be improved by improving the microstructure and densification. Therefore, the temperature–pressure profiles B and C were chosen in the second optimizing step, which were coupled to partial or full pressure application in the T_g ranges of the matrices.

3.2. Variation of the temperature–pressure profile

The pressing temperatures with the largest degrees of matrix crystallization (1100 and 1200 °C for BMAS and 1200 and 1300 °C for MAS) were used for the
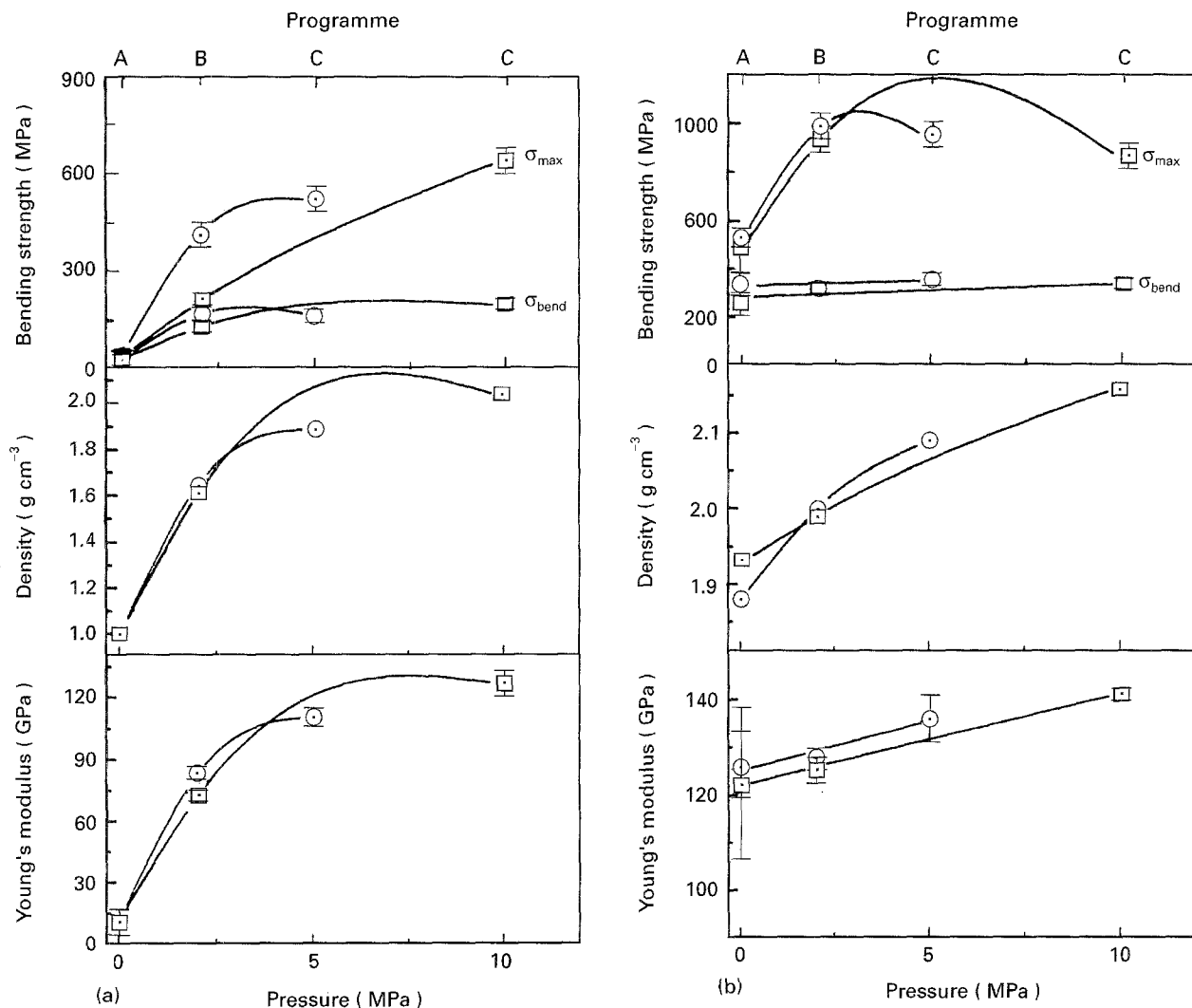
Figure 3 Bending strength, σ_{max}, bend over stress σ_{bend}, density and Young's modulus versus the applied pressure at T_g, and heating up to 1200 °C maintaining pressures of (O) 5 or (□) 10 MPa: (a) MAS, $V_f = 24 \pm 2$ vol %, and (b) BMAS matrix, $V_f = 30 \pm 2$ vol %. The various applied temperature pressure programmes A, B and C are indicated as the top line of the diagrams.

second optimizing step. The temperature–pressure profile is varied now according to the pressing variants B and C (Fig. 1) at final pressures of 5 and 10 MPa and at the two final temperatures for each matrix. The results are exemplified in Fig. 3a, b for one temperature of each composition. It is evident that the pressure application within the T_g range of the glasses is very advantageous for the composite properties. Better mechanical properties result from better densification of the composites. Especially, a remarkable increase of the mechanical values of the MAS composites is observed. The application of total pressure at T_g (profile C, see Fig. 1) gives the best values generally for the composites of both matrices, because the best densification is obtained in the viscous state before crystallization of the glass particles takes place. The second stage of the pressure application at about 50 K, before the final maximum temperature (profile B), seems to have no influence on the enhancement of the properties. Rather, this final stage of pressure application produces predamage of the matrix or fibres, which is confirmed by the fact that lower values are always obtained with profile B when the larger compressive stress was applied.

The bend over stress, σ_{bend}, does not show a significant influence of different pressures around T_g. The

enhanced densification of the composites does not lead to a clearly increase of the load transfer toward the fibres, because the C fibres shrink remarkably due to the large coefficient of radial thermal expansion of 29×10^{-6} K^{-1} (the matrix only around $3-5 \times 10^{-6}$ K^{-1}). Only when the first cracks in the matrix are produced does the load transfer on the fibres become better the larger the densification of the composites.

In total, Fig. 3a, b shows that the very bad values resulting from programme A can be improved by application of programme C but not in temperature regions at and below 1000 °C and beyond 1300 °C because this would cause a high portion of the glassy phase. The large difference between the application of programmes A and C is that the matrices from programme A with good mechanical values contain high concentrations of the glassy phase, whereas those from programme C are highly crystalline and therefore much more thermodynamically stable at elevated temperatures.

3.3. Variation of fibre concentration

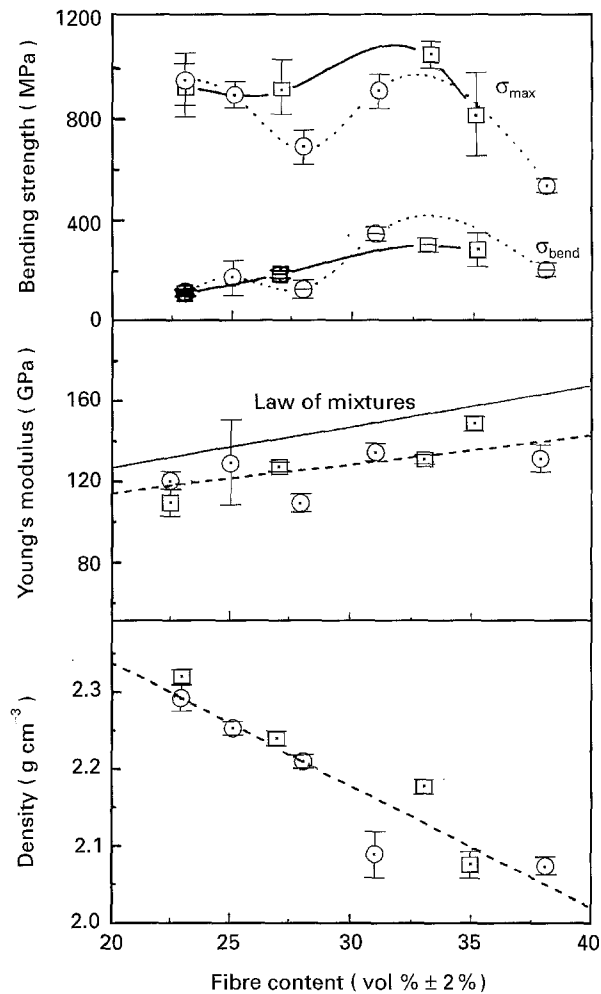The fibre content, V_f, of the composites is the final process parameter which is varied between 20 and

Figure 5 Optical microscope photograph of a polished and etched cross-section of a composite with a fibre content of 38 ± 2 vol % prepared after programme C at 1200 °C; matrix, BMAS; various fibre–fibre contacts (see arrows).

Figure 4 Bending strength, σ_{max}, bend over stress, σ_{bend}, density and Young's modulus versus fibre concentration: matrix, BMAS; pressing temperatures, ($\square$) 1100 and ($\bigcirc$) 1200 °C; programme C.

Figure 6 Stress–strain diagram of composites with different fibre content: (a) 23 ± 2 vol % fibres, BMAS, programme C, $T = 1100$ °C, and (b) 38 ± 2 vol % fibres, BMAS, programme C, 1200 °C.

40 vol % by different ratios of the glass powder to the Si alkoxide solution. The temperature–pressure profile C was applied because this profile resulted from the preceding preparation steps as the optimum. The resulting mechanical properties versus fibre content are shown in Fig. 4. The optimum strength values are in the range 31–33 vol %. The decrease of strength towards higher fibre concentrations is remarkable. The reason for this is the local contacts between the fibres in the composites, as seen from Fig. 5. At these contact areas stress concentrations and friction lead to a preferred crack propagation. This can lead to the delamination of whole fibre (bundle) plains which were observed in these samples. Towards lower fibre concentrations the decrease of strength and bend over stress is much lower. Young's modulus increases with fibre content according to the linear mixing rule; the absolute values, however, are smaller than those calculated from the linear mixing rule. The density of the composites decreases with increasing fibre content due to the lower density of the fibres. The fracture behaviour becomes more brittle with decreasing fibre content, as seen from Fig. 6 for samples with fibre concentrations of 23 and 38 vol %. At low fibre concentrations the fracture behaviour is widely catastrophic after reaching the maximum value of bending strength, while towards higher fibre concentrations
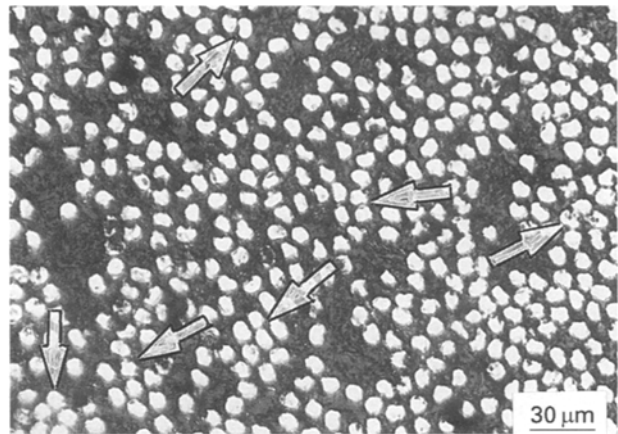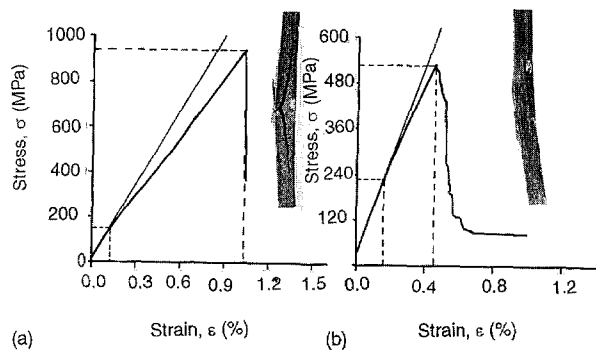
a certain final strength level is preserved. This difference is also seen from the geometry of fracture propagation, as shown in Fig. 6. At low fibre concentrations, crack deflection into the fibre direction occurred; but the crack rapidly increased and propagated over large matrix regions. At high fibre concentrations, pronounced multiple crack formation occurred at the fibres. At too high fibre concentrations the already mentioned delamination of wide fibre (bundle) plains takes place caused by fibre–fibre contact areas, although the strength decreased. This effect resulted in a lower strength of the composites. The fracture behaviour according to Fig. 6, right side, corresponds to fibre concentrations of 31–33 vol % and to those composites with the best "quasiductile" quality.

Another interesting effect is observed from composites with the matrix BMAS. The ratios of the various crystallized phases in the matrix are influenced by the variation of the fibre content. Ba osumilith crystallizes stoichiometrically only at low fibre concentrations as the main phase. With increasing fibre content more and more cordierite appears (Fig. 7). The two minor phases, celsian and mullite, are influenced unessentially by changes in the fibre concentration.
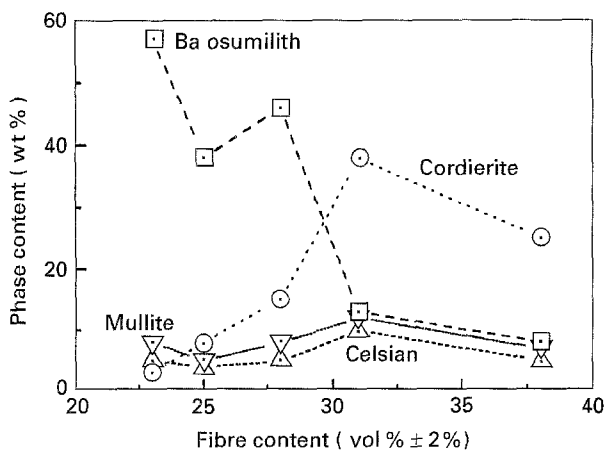
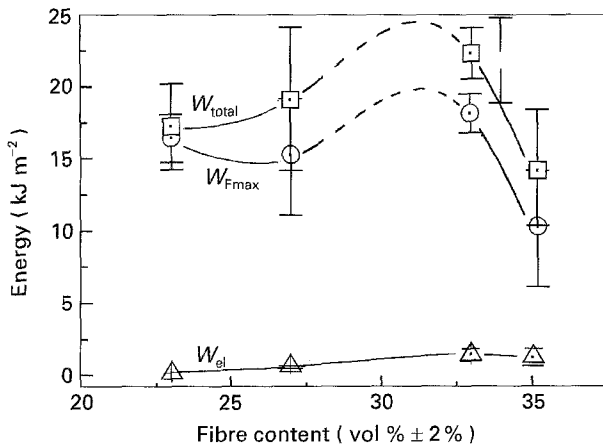*Figure 7* Crystalline phases in the BMAS matrix versus fibre concentration.

Figure 8 Work of deformation, W_{el}, and work of fracture, W_{Fmax} and W_{total}, versus fibre concentration: matrix, BMAS; pressing temperature, 1100 °C; programme C.

3.4. Work of fracture

The enhancement of toughness caused by the fibre reinforcement can be proved best by means of the measured energies (work of fracture). The work of fracture of unreinforced samples of BMAS is between 0.05 and 0.15 kJ m^{-2} (where $W_{el} = W_{Fmax} = W_{total}$ because of the totally brittle fracture behaviour). The values of W_{total} for optimized BMAS composites are in the range 20 kJ m^{-2} and even the values of W_{el} are about a factor of ten larger. The energies were influenced by the variation of the processing parameters essentially in the same way as the corresponding stresses. This is shown, for example, in Fig. 8 for the variation of the fibre concentration at one pressing temperature. Also the already mentioned change to a more brittle fracture behaviour at low fibre concentrations can be seen from this figure. At the lowest fibre concentration the values of W_{total} and W_{Fmax} are nearly the same, which indicate brittle fracture after reaching the maximum strength (see also Fig. 6, left side).

4. Discussion

The results of this investigation have shown a strong dependence of the composite properties on the preparation parameters (temperature–pressure profiles) and on the fibre content. Large strength values are obtained from well densified composites. Maximum strength values result preferably when the pressure is applied in a temperature range where the matrix is still vitreous or remelted again. In particular, the variant of pressure application in the still vitreous state of the matrix around T_g is of interest because a final crystalline product is obtained with remarkable strength values which are of the same order of magnitude as those with a glassy remelted matrix. Therefore it can be concluded that no significant damage of the pressure-sensible C fibres takes place due to the high viscosity of the matrix grains during the early application of pressure around T_g, at least in the systems investigated here.

The fracture behaviour of the composites corresponds to that shown in Fig. 6, right side. The composites still show a remarkable strength potential after the appearance of the first matrix cracks characterized by the bend over stress, σ_{bend}, from which no non-linear stress–strain behaviour exists up to the maximum stress of fracture, σ_{max}. The end of the pure elastic range, σ_{bend}, is about one-third of σ_{max}, thus, the composites have a large safety reserve after the appearance of the first matrix damage at loadings above σ_{bend}. This reserve is about two times larger $(\sigma_{max} - \sigma_{bend})$ than σ_{bend}.

When σ_{max} is reached, a more or less sudden decrease of stress due to fracture takes place depending on the fibre content to a stress level of about σ_{bend}, which is preserved up to somewhat larger strains. The failure of the composites is connected to only a low fibre pull out effect. This indicates low fibre–matrix bonding and low interfacial friction stress. The reason for this is the thermal expansion behaviour of C fibres with large radial $(\alpha_r \sim 30 \times 10^{-6} \text{ K}^{-1})$ and very low longitudinal coefficients $(\alpha_1 \leqslant 0)$. Therefore, during cooling from the hot pressing temperature, fibres tend to shrink away from the surrounding matrix in a radial direction connected with low adhesion between fibre and matrix. Thus, the matrix will be relieved of stress by the fibres only to a relatively low extent. Better load transfer towards the fibres is obtained after the first cracks in the matrix appear at the crystal boundaries and between the structured fibre surface and the matrix. Also, further fracture energy consuming mechanisms occur, such as fibre debonding and multiple crack formation, which are responsible for the additional increase of stress beyond σ_{bend}. The more or less uncontrolled failure without fibre pull out at σ_{max} is again a consequence of the weak adhesion between fibre and matrix.

The influence of the fibre concentration on the phase composition of the matrix may be explained in two ways. On the one hand, the fibres may catalyse the formation of cordierite or the high quartz solid solution (hqss) phase, respectively, the latter one anyway occurring as the primary crystalline phase [e.g. 12]. This assumption is not improbable by reason of the well known tendency of cordierite and its metastable primary phase to crystallize from the surface by heterogeneous nucleation [13, 14]. On the other hand, the preferred crystallization of cordierite with increasing

fibre content may be caused by the SiO_2 coating of the fibres. This SiO_2 content increases with increasing fibre content because of the larger ratio of Si alkoxide solution to glass powder during the preparation of the prepregs. Therefore, the SiO_2 portion is increased, particularly around the fibres, with increasing fibre concentration. Since the metastable primary phase (hqss) of cordierite is a solid solution with high quartz structure, the larger amount of SiO_2 around the fibres can cause a preferred creation of hqss crystals.

5. Conclusions

It has been shown that it is possible to obtain fibre reinforced glass ceramics with predominant crystalline portions of the matrix and good mechanical properties. An optimum of the mechanical properties was found at a fibre content of 31–33 vol %. Preparation temperatures of 1200–1300 °C for the MAS matrices and 1100–1200 °C for the BMAS matrices lead to optimum crystalline contents. Full pressure at T_g up to 10 MPa produces significant increase in strength. In this manner it was possible to obtain strength values of composites with crystalline matrices which exceeded the level of composites with glassy matrices. The bend over stress values, however, could not be influenced significantly by the different temperature pressure variants. The larger strength values as compared to the SiC fibre reinforced composites with the same matrix compositions [9] is mainly a consequence of the larger mechanical tensile strength of the C fibres.

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