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Hot pressing ‘window’ for (P_2O_5, B_2O_3)-containing magnesium aluminosilicate reinforced with SiC fibres

CHAO ZHAO, KONSTANTZA LAMBRINOU, OMER VAN DER BIEST
Department of Metallurgy and Materials Engineering, Katholieke Universiteit Leuven, de Croylaan 2, B-3001 Heverlee, Belgium

Unidirectional magnesium aluminosilicate (MAS) glass-ceramic matrix/silicon carbide (SiC) fibre composites were produced, employing the slurry infiltration-hot pressing technique. The densification and crystallisation behaviour of the (P_2O_5, B_2O_3)-containing MAS glass-ceramic matrix was studied in depth. The major result of the matrix study was the construction of a two-dimensional hot pressing ‘window’ within which MAS/SiC composites were successfully processed. The ‘window’ dimensions, namely temperature and time, were shown to depend on each other. © *1999 Kluwer Academic Publishers*

1. Introduction

In the past 25 years, fibre-reinforced glass-ceramic matrix composites (e.g. lithium aluminosilicate (LAS), calcium aluminosilicate (CAS), magnesium aluminosilicate (MAS) and barium magnesium aluminosilicate (BMAS)) have received much attention for high temperature structural applications. Cordierite (MAS) glass-ceramics, in particular, have been considered as potential matrix materials due to their attractive properties, such as the low thermal expansion coefficient mismatch with SiC fibres and the high softening point.

Cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$) occurs in one metastable and two stable forms [1–5]: α-cordierite, also known as the mineral indialite, is the “disordered”, hexagonal polymorph, which is stable between 1450 °C and 1465 °C (melting point). Below 1450 °C, the metastable α-cordierite transforms sluggishly to β-cordierite. β-cordierite, known as the mineral cordierite, is the “ordered”, orthorhombic form and is stable below 1450 °C. μ-cordierite is the metastable polymorph, which crystallises below 900 °C from glasses, and is a high-quartz solid solution with a hexagonal β-quartz crystal structure. The metastable μ-cordierite invariably forms first and transforms irreversibly to α-cordierite by increasing either the temperature or the isothermal holding time [1–3, 5].

The first results on the room temperature mechanical behaviour of a MAS glass-ceramic reinforced with SiC (Nicalon$^{®}$ fibres were reported in 1985 by Mah *et al.* [6]. In 1989, an interface analysis of Nicalon fibre-reinforced MAS matrix composites (with or without Ba, Nb, Zr, Li and Li-Zr-Nb cation additions) was presented by Chen *et al.* [7]. Metcalfe *et al.* [8] reported on the properties of Tyranno$^{®}$ (SiC with 2–4% Ti) fibre-reinforced MAS composites. The use of a (P_2O_5, B_2O_3)-containing MAS glass-ceramic as matix for fibre-reinforced composites was introduced by Greengrass and Ridealgh in 1993 [9]. Recently, Glendenning and Lee reported on the crystallisation mechanism of a (P_2O_5, B_2O_3)-containing MAS glass-ceramic [1], while Kumar and Knowles focused on the relationship between microstructure and properties of (P_2O_5, B_2O_3)-containing MAS/Nicalon composites [10, 11].

Processing fibre-reinforced MAS matrix composites at temperatures higher than the liquidus (“melt pressing”) is impossible, due to the primary crystallisation of mullite upon cooling. The crystallisation of mullite shifts the melt composition away from that of stoichiometric cordierite and causes the co-precipitation of cristobalite (SiO_2). Cristobalite undergoes a displacive phase transformation around 200–250 °C accompanied by a considerable volume reduction (≅3.9%), which can be detrimental for the composite’s mechanical properties due to extensive matrix microcracking [10].

An alternative processing method for MAS matrix composites is the so called “window pressing”, which takes place in the temperature range between the glass transition temperature (T_g) and the onset of crystallisation temperature (T_c) of the MAS glass-ceramic. Within this temperature range, the viscous flow characteristics of the matrix ensure the composite’s densification. Another advantage of the ‘window pressing’ of MAS glass-ceramics is the fact that phase nucleation takes place on inhomogeneities which were initially present on the powder surfaces and are still retained within the dense compact [1, 9]. Consequently, nucleating agents, such as titania (TiO_2) or zirconia (ZrO_2), are not required.

The ‘window pressing’ of large composite components of stoichiometric cordierite matrix composition (MAS) is also very difficult to accomplish, due to the narrow temperature zone within which the pressing can take place (only 63 °C between T_g and T_c). Heating of fairly big components usually creates large temperature gradients, resulting in matrix areas which

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either have started crystallising or have not yet softened and are, thus, too hard to press. However, addition of P_2O_5 and B_2O_3 to the MAS glass-ceramic results in a wider hot pressing 'window' (188 °C between T_g and T_c) by inhibiting the onset of crystallisation [1, 2, 9, 10]. Moreover, the addition of B_2O_3 and P_2O_5 in MAS glass-ceramics accelerates the transformation of μ- to α-cordierite [1, 2, 9] and limits the formation of μ-cordierite [1].

The transformation of μ- to α-cordierite in the matrix of SiC fibre-reinforced MAS is desirable, because it defines the residual stress state at the fibre/matrix interface. The thermal expansion coefficient of μ-cordierite is $4.72 \times 10^{-6}\ °C^{-1}$ from 25 to 870 °C, of α-cordierite is $1.2 \times 10^{-6}\ °C^{-1}$ from 25 to 1000 °C and of SiC (Nicalon) fibres is $3.1 \times 10^{-6}\ °C^{-1}$ from 25 to 1000 °C. Consequently, in SiC fibre-reinforced composites with pure α-cordierite matrix, the residual stresses at the fibre/matrix interface are tensile [11]. This excludes the formation of the detrimental radial matrix cracks upon cooling from the processing temperature.

To the authors' knowledge, the 'window pressing' of MAS/SiC composites has never been studied with respect to the time dimension. It is, nevertheless, important for the accurate determination of the processing conditions that both the temperature and the time dimension of the 'window' are defined. The present work aims at the determination of the hot pressing 'window' of (P_2O_5, B_2O_3)-containing MAS matrix/SiC (Nicalon) fibre-reinforced composites. The MAS/SiC composites were processed according to the slurry infiltration-hot pressing technique.

2. Experimental procedure

2.1. Starting materials

The composite system studied consisted of a MAS glass-ceramic reinforced with continuous SiC (Nicalon NL-200) fibres. The MAS glass-ceramic, which was ordered from the University of Sheffield, UK, was produced based on a patent owned by Pilkinton plc. UK [9]. The nominal composition of the MAS matrix material was 53.4 wt % SiO_2, 21.3 wt % Al_2O_3, 22.3 wt % MgO, 2.0 wt % P_2O_5 and 1.0 wt % B_2O_3. The glass, quenched from the melting temperature, was milled for 10 hours on a planetary ball mill (Fritsch GmbH, Germany), using alumina balls in alumina containers down to a mean particle size of approximately 5 μm.

2.2. Slurry infiltration-hot pressing method

A slurry was prepared, consisting of 350 g powdered matrix material, 1 *l* solvent (distilled water), 70 g binder (polyvinylalcohol, 88%, MW 124,000) and a small amount of dispersing agent (few drops of TEEPOL). The SiC fibre tow was first introduced into the slurry, where it got infiltrated by the matrix material. The impregnated tow was subsequently wound around a rotating drum, forming 'prepreg' sheets, which after having been dried in air were cut into the proper dimensions for composite production. For every composite plate, 12 'prepreg' sheets were placed unidirectionally in a graphite die and then heat treated for binder burn-out.

Both monolithic MAS glass-ceramics as well as MAS/SiC composite samples ($26 \times 12\ mm^2$) were hot pressed (KCE Sondermaschinen GmbH, model 8633, Rödental, Germany) in vacuum, the monolithic ones being previously cold pressed under a pressure of 12 MPa. Two different hot pressing schedules were adopted (Fig. 1). In schedule 1, the sample was heated at 100 °C min^{-1} to the 'soaking' temperature, T_{soak}, where the glass-ceramic was subjected to a 'softening' period, t_{soft}. A pressure of 12 MPa was applied on the sample for a period t_{press}, before the sample was cooled at about 10 °C min^{-1} to room temperature. The sum of the 'softening' period, t_{soft}, and the pressing period, t_{press}, was defined as the 'soaking' period, t_{soak}. In schedule 2, the sample was first heated at 100 °C min^{-1} to 900 °C, where it was maintained for a 'softening' period of 5 min. As will be shown in Section 3.2, 900 °C is in the center of the hot pressing window where the onset of crystallisation takes more than one hour. The sample was subsequently heated at 100 °C min^{-1} to the 'soaking' temperatue, T_{soak} , under a pressure of 12 MPa. The hot pressing cycle was again concluded by cooling at 10 °C min^{-1} to room temperature. Schedule 1 was employed for preparing both monolithic MAS specimens and MAS/SiC composites, while schedule 2 was only used to produce composite specimens.

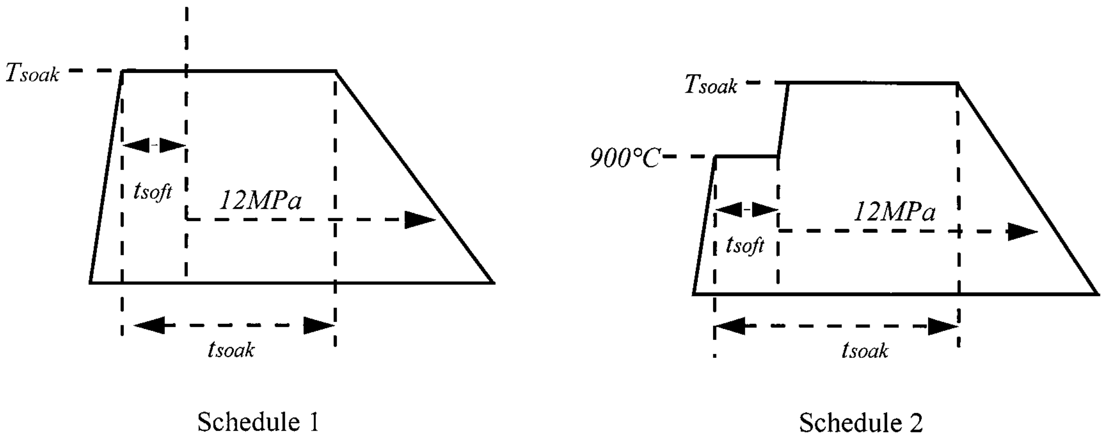

Figure 1 Hot pressing schedules.

TABLE I MAS glass-ceramic crystallisation degree versus XRD peak intensity

Crystallisation degree	XRD peak intensity
Amorphous-zone I[a]	Absence of crystallisation peaks
Initial crystallisation-curve AB[a]	Very low peak intensities (about 1–5% of the peak intensities in cases of completed crystallisation)
Intermediate crystallisation-zone II[a]	Peak intensities between initial and complete crystallisation
Complete crystallisation-curve CD and above (zone III)[a]	Very high peak intensities; no increase of intensity when increasing either T_{soak} or t_{soak}

[a] Curves AB and CD, zones I, II and III (Fig. 8) are extensively discussed in Section 3.2.

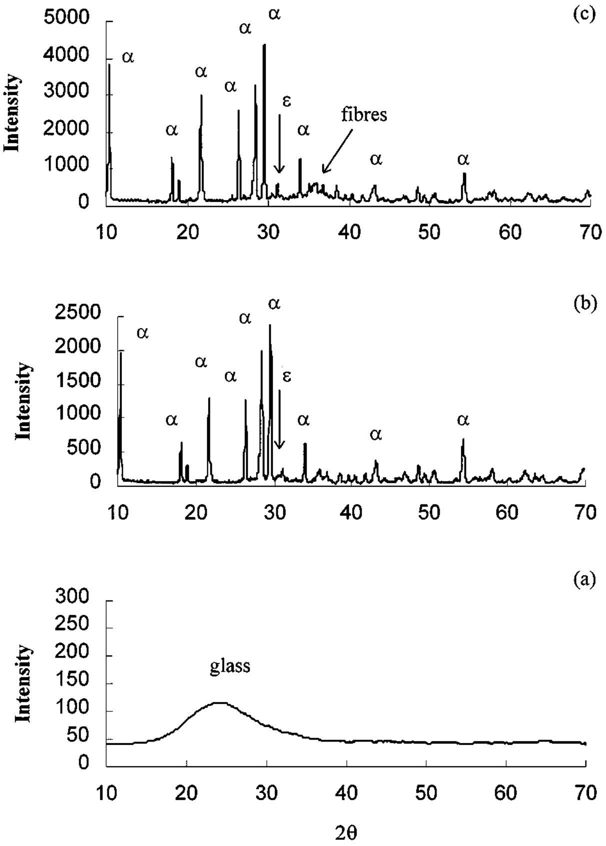

Figure 2 XRD spectra of: (a) monolithic MAS glass sample hot pressed at 900 °C for 45 min, (b) monolithic MAS ceramic sample hot pressed at 1150 °C for 60 min, (c) MAS/SiC composite hot pressed at 1150 °C for 60 min; $\alpha = \alpha$-cordierite, $\varepsilon =$ orthoenstatite.

2.3. Densification and crystallisation studies

X-ray diffraction (XRD) measurements were performed on both monolithic MAS glass-ceramic and composite specimens in the 9° to 79° 2θ interval. The XRD measurements were done on a diffractometer (Model PW-1010, Philips Electronic Instruments Co., Eindhoven, Holland) operating at 34 kV and 20 mA using monochromatic CuK_α radiation at a scan speed of 1°/min^{-1}. Phase identification was achieved by using the following JCPDS cards: 13–293 for α-cordierite, 14–249 for μ-cordierite and 19–768 for enstatite. The β-SiC phase in the fibres was identified with reference to published work [12, 13]. The matrix crystallisation degree was qualitatively estimated by comparing the peak intensities of the crystalline phases as they appeared in the acquired XRD spectra (Table I).

Differential thermal analysis (DTA) measurements were performed on 8.62 mg MAS glass samples, employing a Netzsch DSC-404 instrument (Netzsch, Salb/Bayern, Germany). The samples were heated in argon (Ar) from 600 to 1100 °C at 5 °C min^{-1}. The samples were contained in a Pt pan, while an empty Pt pan was used as reference. Data were recorded using a computer-driven data acquisition system. The dimensional change of composite specimens during hot pressing was monitored by the plunger displacement with a LHM data logger (DTL 1214). The density of all hot pressed samples was measured using the Archimedes principle.

2.4. Mechanical testing and examination of composites

Bars (27 × 4 × 1.5 mm^3) were cut from the produced composite plates using a diamond cutting wheel. The bars were tested on a three-point bending jig (Instron 1196, UK) with a 20 mm span and at a crosshead speed of 10 mm min^{-1}. The work of fracture was calculated by integrating the area under the load-displacement curve up to an arbitrary displacement limit of 4 mm. This was considered to be a good approximation because at such a displacement, the load has decreased to a negligible level.

Polished cross sections of composite plates were observed with an optical microscope and the fibre volume fraction was determined by quantitative image analysis. Scanning electron microscopy (Philips XL 30 FEG, Philips, Eindhoven, Holland) was also used to examine the composites' microstructure.

3. Results and discussion

3.1. Crystallisation behaviour of the MAS glass-ceramic matrix

XRD spectra acquired from MAS glass samples revealed the presence of a broad peak near $2\theta = 24°$, which is typical for silicate glasses (Fig. 2a). The (P_2O_5, B_2O_3)-containing MAS glass-ceramic crystallised towards μ-cordierite, α-cordierite and orthoenstatite after a high temperature heat treatment, whether in the monolithic (Fig. 2b) or in the fibre-reinforced composite samples (Fig. 2c). The amount and type of crystalline phases depended upon the soaking temperature and time. The XRD spectra of MAS/SiC composites showed additional β-SiC peaks from the SiC fibres and a broad peak at $2\theta = 34°$, which was attributed to the amorphous material in those fibres (Fig. 2c).

Using XRD is not sufficient to distinguish between α- and β-cordierite because of their similar interplanar spacings. However, α-cordierite was considered to be the phase present in all the crystalline MAS samples produced in this study, since the transformation of μ- to α-cordierite under similar processing conditions is well documented [1–3, 5].

Figs 3 and 4 show the influence of the soaking temperature and time, respectively, on the matrix crystallinity of MAS/SiC composites produced based on

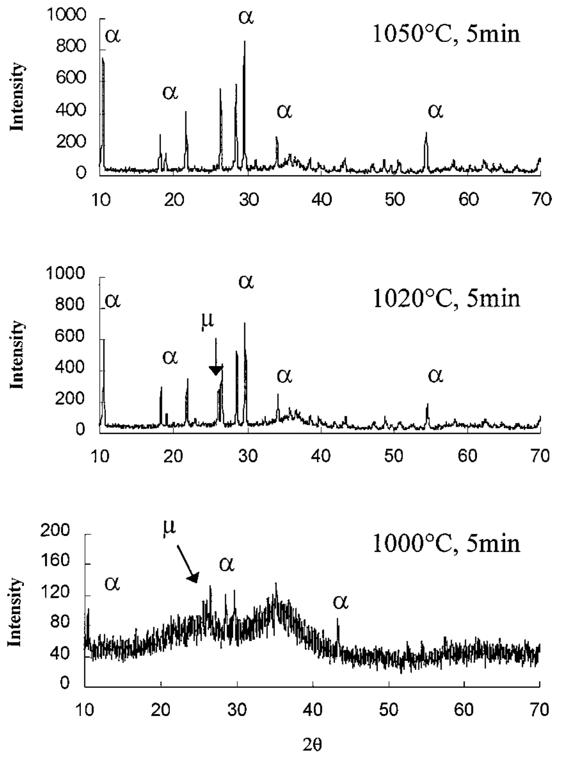

Figure 3 XRD spectra showing the phase evolution in MAS/SiC composites due to the increase in the soaking temperature; $\alpha = \alpha$-cordierite.

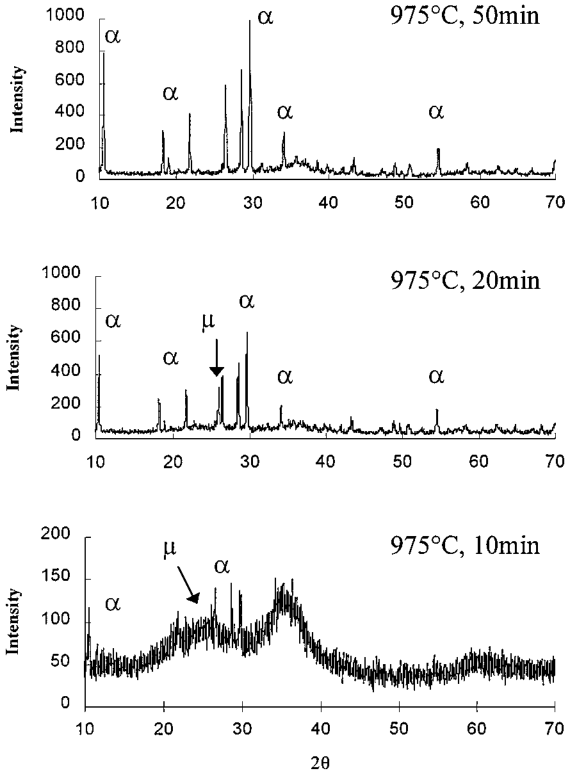

Figure 4 XRD spectra showing the phase evolution in MAS/SiC composites due to the increase in the soaking time; $\alpha = \alpha$-cordierite.

schedule 1. Fig. 3 shows that, the amount of amorphous phase present in the matrix decreased as the soaking temperature increased at a constant soaking time, while the amount of crystalline phase increased. A similar evolution of phases was observed in the matrix, when the isothermal soaking was prolonged (Fig. 4).

XRD measurements performed on MAS/SiC composites processed according to schedule 1 revealed the primary crystallisation of μ-cordierite. In Fig. 3, a small μ-cordierite peak can be distinguished in the spectra of the samples sintered at 1000 and 1020 °C for 5 min, while in Fig. 4, a similar peak can be seen in the spectra acquired at 975 °C for 10 and 20 min. However, in both cases, the amount of μ-cordierite is limited and is even further decreased due to its transformation to α-cordierite when the soaking temperature or time increases. In the spectra of the samples sintered at 1050 °C for 5 min (Fig. 3) and at 975 °C for 50 min (Fig. 4), the μ-cordierite peak disappears, accompanied by the intensity increase of the α-cordierite peaks. Fig. 5 provides a clear and convincing evidence of the primary crystallisation of μ-cordierite and its transformation to α-cordierite.

3.2. Hot-pressing ‘window’ for MAS/SiC composites

The determination of the ‘window’ started by measuring the softening point (T_g) of the glass-ceramic matrix. Fig. 6 shows a DTA trace from the MAS glass-ceramic according to which, the softening point is approximately 800 °C. Similar information regarding the softening point was acquired from the shrinkage curve of MAS/SiC hot pressed composites (Fig. 7). The pressing of fibre-reinforced composites should take place above the softening point, where the viscosity of the matrix is sufficiently low to ensure densification without any fibre damage.

The construction of the ‘window’ was completed by hot pressing several composite plates according to schedule 1 in the temperature range between 825 and 1150 °C for different soaking times. XRD measurements on those specimens allowed the construction of a time-temperature-transformation (TTT) diagram of the matrix crystallisation (Fig. 8). The TTT diagram is divided into three zones (I, II and III) by two curves (AB and CD). The phases observed in the matrix of MAS/SiC composites pressed in each one of the three zones are given in Table II.

The hot pressing ‘window’ is the grey area expanding between the softening point ($T_g \cong 800$ °C) and the onset of crystallisation temperature. The high-temperature limit of the ‘window’ (curve AB) is a function of the isothermal soaking time: the higher the soaking temperature, the shorter the time (Fig. 8). For example, at 1000 °C the MAS matrix needs only a few minutes to become fully crystalline, while at 900 °C it needs more than 1 hour. Above 1000 °C the MAS glass-ceramic can no longer be in the glassy state.

TABLE II Matrix composition of MAS/SiC composites

Zone	Matrix composition[a]
I (below curve AB)	G
II (between curve AB and CD)	$\mu + \alpha + G$
III (above curve CD)	$\alpha + e$

[a] G = glass, $\mu = \mu$-cordierite, $\alpha = \alpha$-cordierite, e = enstatite.

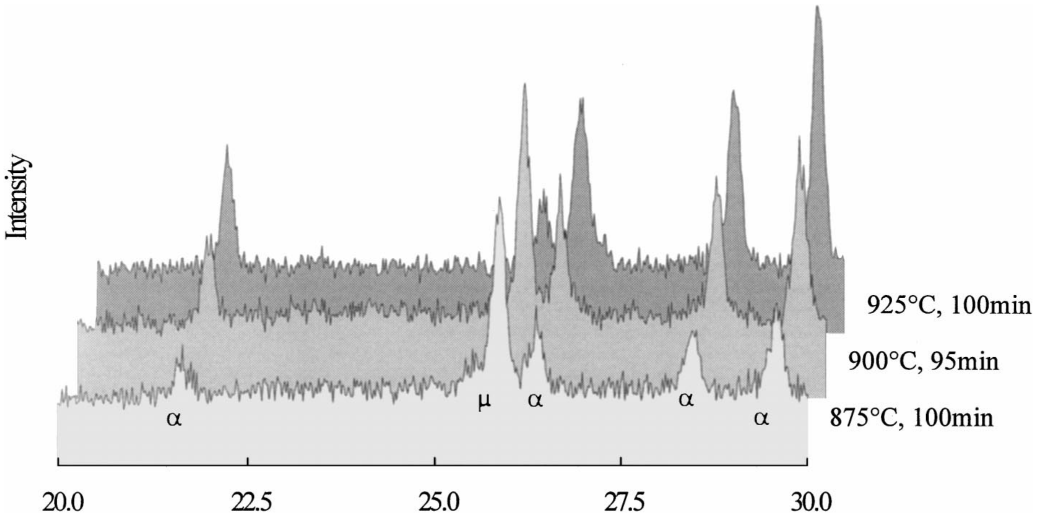

Figure 5 XRD spectra showing the transformation of μ-cordierite to α-cordierite in the matrix of MAS/SiC composites; $\alpha = \alpha$-cordierite, $\mu = \mu$-cordierite.

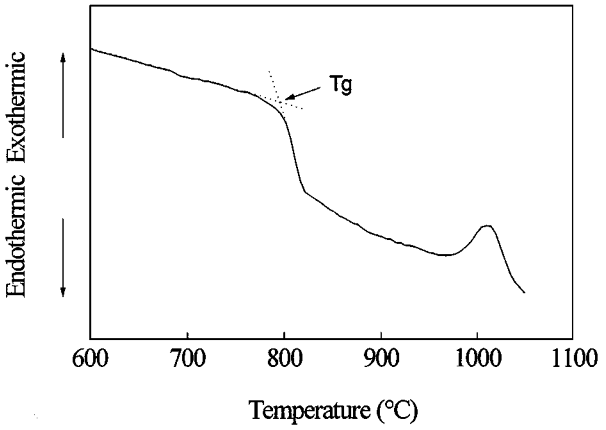

Figure 6 DTA trace from MAS glass-ceramic powder; heating rate 5 °C min^{-1} in Ar.

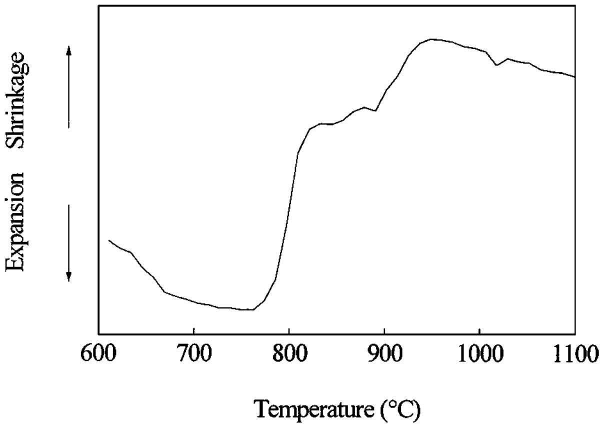

Figure 7 Shrinkage curve obtained during the hot pressing of MAS/SiC composites.

3.3. Densification behaviour of the MAS glass-ceramic matrix

Defining the hot pressing 'window' is crucial for the production of dense fibre-reinforced MAS matrix composites. With respect to the TTT diagram of Fig. 8, the composite densification should preferably be completed inside the 'window' (below curve AB). In zone II (between curves AB and CD), densification becomes more difficult, since the amount of the viscous, amorphous material decreases very fast. In zone III (above curve CD), the matrix is completely solid and the possibility of densification is excluded.

Fig. 9 shows the density values of two groups of monolithic MAS glass-ceramic samples prepared according to schedule 1: for one group, the softening time (before the application of pressure) was 5 min and for the second group, the softening time was 50 min. The density of the hot pressed samples decreased rapidly as the hot pressing conditions approached curve AB (the high-temperature limit of the 'window'). Outside the 'window' (above curve AB), the crystal growth rates were high, increasing melt viscosity and hindering densification. This was proven by the low density values of the matrix samples pressed within zones II and III.

The choice of an optimal softening time, which should be neither very short (fibre damage due to the hard glass particles) nor very long (fibre degradation due to a long heat treatment) is very important for the production of composites. In the case of MAS/SiC composites, a softening period of 5 min at 900 °C appears to be sufficient to ensure densification. This conclusion was based on density measurements done on two groups of composite plates produced according to schedule 2 (Table III). One group of specimens was softened at 900 °C for 5 min, while the other was pressed without a softening stage. Both groups of specimens were subsequently ceramed at 1150 °C for 1 hour. The group of specimens produced with a softening stage before the application of pressure had a higher average density (5 measurements per group) in comparison to the group where the softening stage was not incorporated.

TABLE III Density of MAS/SiC composites versus processing conditions

Softening time at 900 °C (min)	Soaking temperature (°C)	Soaking time (min)	Average density (g cm^{-3})	Relative density (%)
5	1150	60	2.60 ± 0.18	98.2 ± 0.07
0	1150	60	2.14 ± 0.11	80.8 ± 0.04

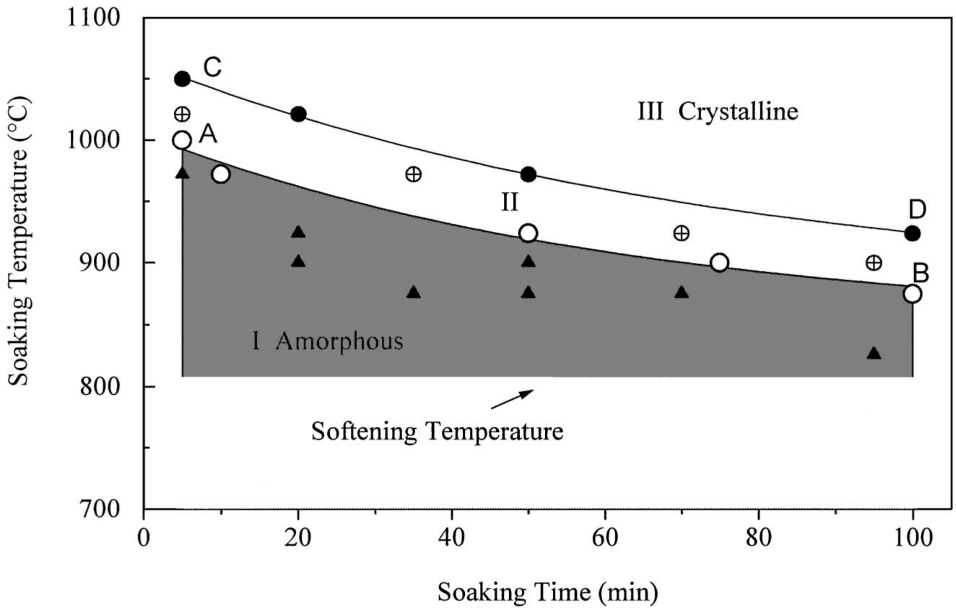

Figure 8 Hot pressing 'window' of MAS/SiC composites processed according to schedule 1; ▲: amorphous matrix, ○: matrix at the initial crystallisation stage, ⊗: matrix at an intermediate crystallisation stage, ●: matrix after the crystallisation is completed.

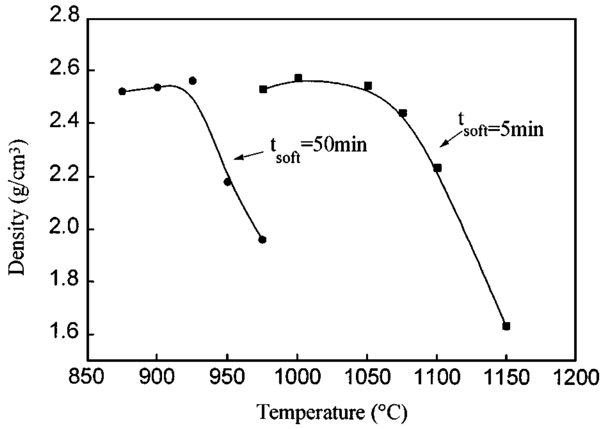

Figure 9 Density of monolithic MAS samples prepared according to schedule 1 as function of the softening time, t_{soft}.

3.4. Suggested hot pressing cycle for MAS/SiC composites

Although there is no unique 'optimum hot pressing cycle' for the production of MAS/SiC composites, the processing conditions may be defined based on the following suggestions:

1. A softening time of at least 5 min should be allowed before the application of pressure so as to avoid fibre damage from the hard glass particles due to premature pressing. Once applied, the pressure is maintained for a period, which must be long enough to attain densification but not so long so as to cause fibre degradation. The pressing temperature should preferably lie inside the 'window' (defined in Fig. 8).

2. During the processing of large composite tiles, heat flow considerations should also be taken into account. In that sense, the composites should be pressed at a temperature, where the time width of the 'window' is large enough to avoid the existence of crystallising matrix areas due to temperature overshoot.

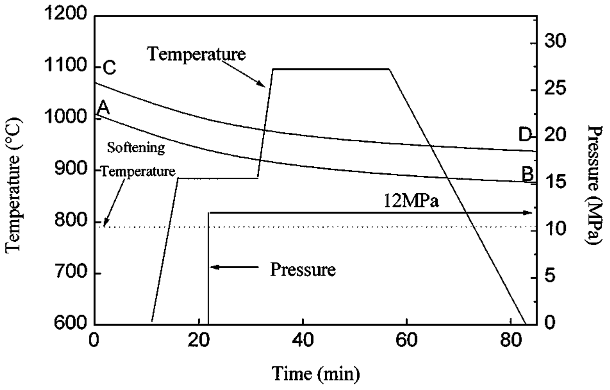

Figure 10 Suggested hot pressing cycle for MAS/SiC composites.

3. After densification, the composite article must be heated rapidly to the soaking temperature to limit the formation of metastable μ-cordierite. The 'ceraming' treatment should be engineered in such a way, so as to yield a polycrystalline matrix consisting of fine α-cordierite grains.

The suggested hot pressing cycle presented in Fig. 10 is based on the above considerations and was applied to produce large MAS/SiC composite plates ($15 \times 7\ \text{cm}^2$). The composites, which were produced on an industrial size hot press (Balzers, type TYP VSG 30HP, Asslar, Germany), had a fibre volume fraction of approximately 30%, flexural strength values up to 830 MPa with an average value of 370 ± 106 MPa (10 measurements per composite plate) and an average work of fracture equal to $11 \pm 2\ \text{kJ}\,\text{m}^{-2}$. The backscattered electron micrograph of Fig. 11 shows the characteristic microstructure of such a MAS/SiC composite.

4. Conclusions

This study defined the hot pressing 'window' for processing (P_2O_5, B_2O_3)-containing MAS/SiC composites. The 'window' is the two-dimensional (temperature-time) space, where the application of pressure

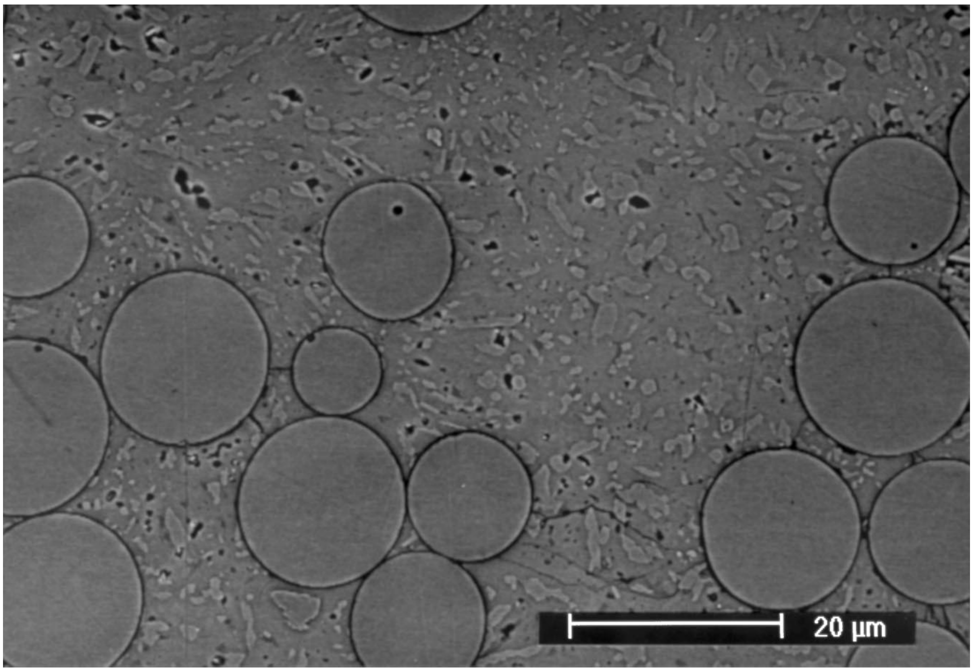

Figure 11 Backscattered electron micrograph revealing the microstructure of a MAS/SiC composite prepared with the hot pressing cycle of Fig. 10.

leads to the densification of fibre-reinforced composites. Before the application of pressure, a 'softening' period is foreseen, in order to allow the glass particles to soften and avoid fibre damage during pressing. The 'window' expands between the glass transition temperature (≅800 °C for the (P_2O_5, B_2O_3)-containing MAS used in this study) and the onset of crystallisation temperature, which is a function of the isothermal soaking time. The time dimension of the 'window' varies between 90 min at 825 °C and 5 min at 975 °C. Beyond the high-temperature limit of the 'window', crystallisation starts and is completed within maximum 40 min. The matrix crystallises initially towards μ-cordierite, which subsequently transforms to α-cordierite as the processing conditions (temperature and time) become more severe.

MAS/SiC composites were successfully prepared with a hot pressing cycle derived from the acquired data.

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