Original Paper

Thermal expansion behaviour of unidirectionally SiC fibre-reinforced MAS and BMAS glass-ceramics

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The thermal expansion behaviour of SiC fibre-reinforced Magnesium–Aluminium–Silicate (MAS) and Barium–Magnesium–Aluminium–Silicate (BMAS) glass-ceramics was studied in air as well as in argon furnace atmosphere. The results show that the coefficients of thermal expansion up to a temperature of 800 °C are influenced to a minor degree by the furnace atmosphere and to a major degree by the phase composition of the matrices and the fibre concentration. The largest values in air and argon atmosphere are obtained from BMAS(14)/SiC fibre composites with $\alpha_{150/800} = 3.92 \cdot 10^{-6}\,K^{-1}$ and $3.87 \cdot 10^{-6}\,K^{-1}$, respectively, at a fibre content of 52 vol.%, while the lowest values are found for BMAS(9)/SiC fibre composites in air with $\alpha_{150/800} = 3.24 \cdot 10^{-6}\,K^{-1}$ and in argon with $\alpha_{150/800} = 3.11 \cdot 10^{-6}\,K^{-1}$ at a fibre content of about 25 vol.%. Increasing fibre concentration leads to increasing thermal expansion. The experimentally determined values were compared with calculated ones by the mixing rule and a good agreement was found, particularly for the BMAS(14) composites.

Thermisches Ausdehnungsverhalten unidirektional SiC-faserverstärkter MAS- und BMAS-Glaskeramiken

Das thermische Ausdehnungsverhalten von SiC-faserverstärkten Magnesium–Aluminium–Silicat(MAS)- und Barium–Magnesium–Aluminium–Silicatglaskeramiken (BMAS) wurde sowohl in Luft- als auch in Argonatmosphäre untersucht. Die Ergebnisse zeigen, daß die Ausdehnungskoeffizienten bis zu einer Temperatur von 800 °C nur in geringem Maße von der Ofenatmosphäre, aber in stärkerem Maße von der Phasenzusammensetzung der Matrizes und der Faserkonzentration beeinflußt werden. Die höchsten Werte in Luft- und Argonatmosphäre werden für die BMAS(14)/SiC-Faserverbunde mit $\alpha_{150/800} = 3{,}92 \cdot 10^{-6}\,K^{-1}$ bzw. $3{,}87 \cdot 10^{-6}\,K^{-1}$ erhalten bei einem Faservolumenteil von 52 %, während die niedrigsten Werte für BMAS(9)/SiC-Faserverbunde in Luft mit $\alpha_{150/800} = 3{,}24 \cdot 10^{-6}\,K^{-1}$ und in Argon mit $3{,}11 \cdot 10^{-6}\,K^{-1}$ bei einem Faservolumenanteil von etwa 25 % gefunden wurden. Zunehmende Faserkonzentration bewirkt eine zunehmende thermische Ausdehnung. Die experimentell bestimmten Werte wurden mit den aus der Mischungsregel berechneten verglichen, wobei gute Übereinstimmung, besonders für die BMAS(14)-Verbunde, erhalten wurde.

1. Introduction

The thermal expansion behaviour of composite materials is, in addition to mechanical properties such as strength, Young's modulus and toughness, an important property for possible applications of low-expansion materials. Investigations in preceding papers [1 and 2] on fibre-reinforced glass-ceramics were related to optimum preparation parameters and mechanical properties of the composites. Only few papers [2 and 3] exist so far about the thermal expansion behaviour. In [2] a coefficient of thermal expansion of $\alpha = 2.8 \cdot 10^{-6}\,K^{-1}$ was measured and in [3] $\alpha = 2.4 \cdot 10^{-6}\,K^{-1}$ in fibre direction of a SiC fibre-reinforced LAS glass-ceramic (Lithium–Aluminium–Silicate).

The authors' measurements of thermal expansion on cordierite and osumilith glass-ceramics were performed in the temperature range 50 to 800 °C with respect to the applied temperatures up to 800 °C. It is known from literature [4 and 5] that the SiC fibres are surrounded by a thin carbon layer after the hot-pressing process which influences positively the ductility of the composites. Because this layer will be oxidized at temperatures above 400 °C in air, the measurements were extended to those in argon atmosphere in order to find out possible differences in thermal expansion behaviour.

The linear mixing rule (LMR) will be applied to calculate the coefficients of thermal expansion of the composites from those of the matrix (M) and fibres (F) and their Young's moduli (E) after [3]:

$$\alpha_{comp} = (\alpha_F V_F E_F + \alpha_M V_M E_M)/E_{comp} \qquad (1)$$

with α = coefficient of thermal expansion, V = volume portion. If the matrix of the composites is a homogeneous material such as a glass, the determination of the matrix properties is simple. If, however, the matrix is heterogeneous as is the case for glass-ceramics, one has to regard the various crystalline phases which have different coefficients of thermal expansion. Therefore, considering [6] the following equation was used to calculate α_M in equation (1):

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Table 1. Properties of the crystalline and glassy phases and of the SiC fibres

components	$\alpha_{20/800\,°C}$ in $10^{-6}\,K^{-1}$	density in g/cm^3	Young's modulus in GPa	literature
cordierite	1.50	2.50[1)]	120	[7]
barium osumilith	1.80[1)]	2.79[1)]	120	
mullite	5.00	3.17	120	[8]
celsian	3.30	3.38	120	[9]
glass phase MAS	4.50[1)]	2.64[1)]	80	
glass phase BMAS(9)	4.66[1)]	2.78[1)]	80	
glass phase BMAS(14)	4.35[1)]	2.76[1)]	80	
SiC fibre (Nicalon)	3.30	2.55	189	[10]

1) Author's measurements.

Table 2. Used glass powders and their stable crystalline phases

initial glass powder	abbreviations	main crystal phase	maximum temperature of application in °C
stoichiometric cordierite	MAS	cordierite	1450
MAS + 9 wt% BaO	BMAS(9)	cordierite + celsian	1450
MAS + 14 wt% BaO	BMAS(14)	barium osumilith	1250

$$\alpha_M = \left[\frac{\alpha_1 E_1 V_1}{D_1} + \frac{\alpha_2 E_2 V_2}{D_2} + \ldots\right] / \left[\frac{E_1 V_1}{D_1} + \frac{E_2 V_2}{D_2} + \ldots\right] \tag{2}$$

with E = Young's modulus, V = portion of the phase in wt%, D = density, α = mean linear coefficients of thermal expansion. In table 1 all needed properties of the single components are listed. The SiC fibres and the glassy phases show isotropic thermal expansion while that of the crystalline phases is anisotropic. The literature data in table 1 are related to the isotropic linear mean coefficient of thermal expansion for the crystalline phase. The authors' values (*) in table 1 were determined from polycrystalline materials.

2. Materials used

The prepregs were prepared by the sol-gel-slurry method [11] and densified to composites at 1200 °C and at a pressure of 10 MPa. All composites were treated by a temperature-pressure programme, called B in [12], which is characterized by heating up the prepregs to T_g of the used glass particles, loading the samples with the full pressure, heating up to the final temperature, and cooling down under pressure. SiC fibres NL-202 Nicalon (Nippon Carbon Comp., Tokyo (Japan)) were used as reinforcing components, which were incorporated unidirectionally. The glass powders had the compositions of the stoichiometric cordierite and cordierite with additions of either 9 or 14 wt% BaO, which in the following are called BMAS(9) and BMAS(14), respectively. BaO leads to crystallization of barium osumilith (table 2). The powders had a grain size distribution of 99 % < 40 µm and were prepared by Schott Glaswerke, Mainz (Germany).

Those composites have been selected for the present investigations which have high crystallinity and good mechanical properties. BMAS(9) and BMAS(14) composites were prepared with two fibre concentrations each, a low (=l) and a high (=h) fibre concentration. Some properties of the composites are listed in table 3. The coefficients of thermal expansion of the composites were determined parallel to the fibre direction.

3. Experimental

The determination of the coefficients of thermal expansion was done with the help of a difference dilatometer with an accuracy of $\pm 0.1 \cdot 10^{-6}\,K^{-1}$. The reference sample (standard) was a silica glass rod ($(50 \times 4 \times 4)\,mm^3$) with a well-known thermal expansion behaviour. The samples had the same dimensions as the silica glass rod. The difference principle eliminates some possible errors of the equipment. The error of the temperature measurements is ±2 K. The samples were heated and cooled several times, at least twice, with rates of +5 K/min and −2 K/min, respectively. The mean longitudinal coefficient, α, was calculated for selected temperature intervals from the relative elongations $(L - L_0)/L_0$.

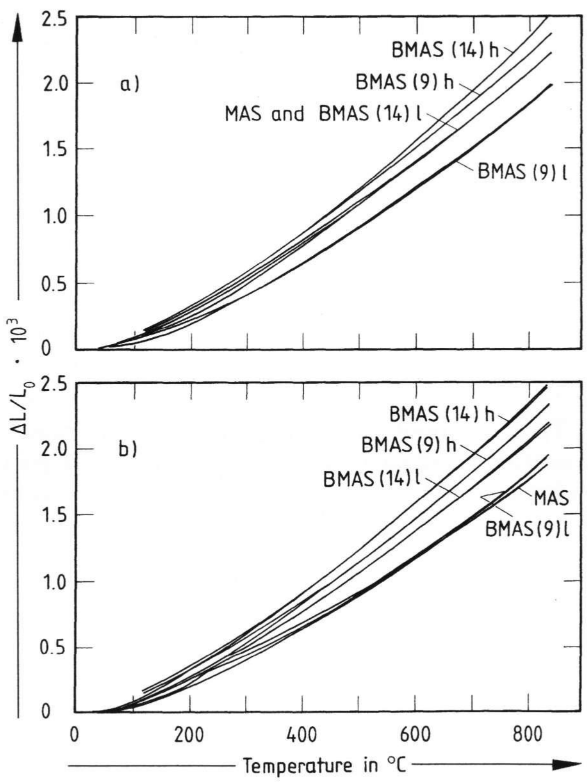
4. Results

The thermal expansion behaviour of the composites in air as well as in argon atmosphere are shown in figures 1a and b versus temperature. In both cases the differ-

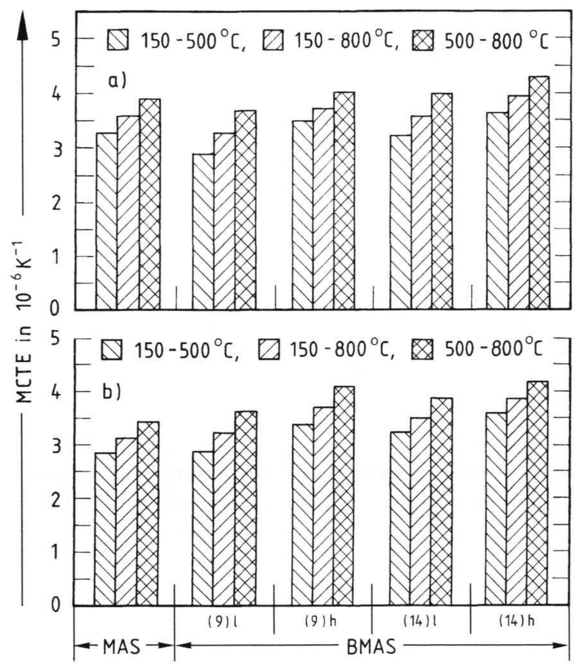
Table 3. Properties of the used composites

	MAS	BMAS(9) l	BMAS(9) h	BMAS(14) l	BMAS(14) h
σ in MPa	193 ± 34	282 ± 28	241 ± 9	534 ± 41	270 ± 57
D in g/cm^3 (s = ±0.4%)	2.48	2.57	2.56	2.61	2.59
Young's modulus in GPa	104 ± 3	122 ± 7	140 ± 10	115 ± 4	137 ± 5
V_f in vol.% (s = ±2%)	18	22	42	27	52
crystalline phases in wt%	cor (93) gl (7)	cor (77) cel (9) osu (5) gl (7)	cor (48) osu (36) cel (9) gl (7)	osu (34) cor (32) m (6) cel (6) gl (23)	osu (38) cor (29) m (10) cel (8) gl (15)

Explanations: σ = three-point bending strength; D = density; V_f = volume fibre content; cel = celsian; cor = cordierite; gl = glass; m = mullite; osu = barium osumilith; ( ) = concentrations in wt%; l = low, h = high fibre concentration; s = standard deviation.



Figures 1a and b. Thermal expansion behaviour of composites in air (figure a) and in argon (figure b); h = high fibre content, l = low fibre content (see table 3).



Figures 2a and b. Mean coefficients of thermal expansion (MCTE) for three temperature intervals in air (figure a) and in argon atmosphere (figure b).

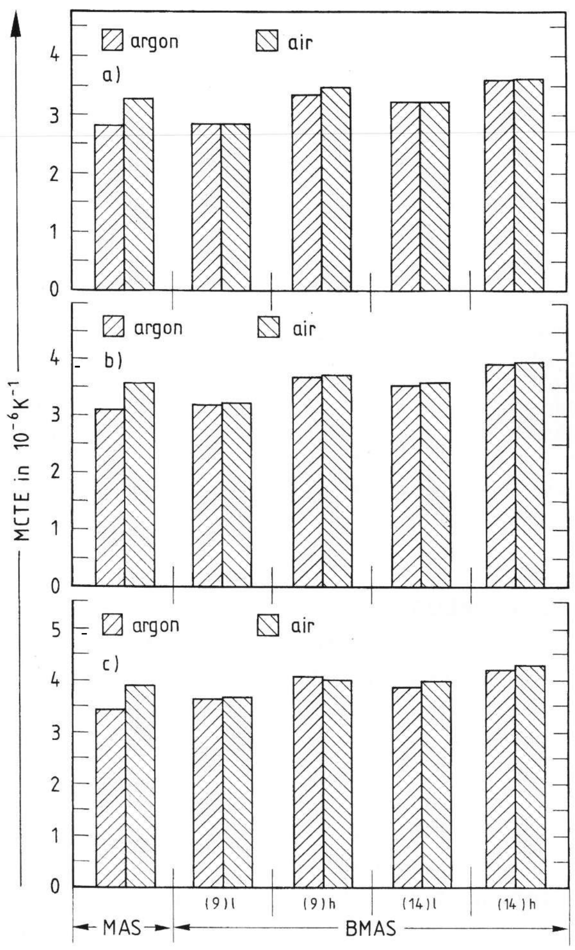
ences in thermal expansion of the composites are very small. The heating and cooling curves are practically identical which means that nearly no alterations took place by the thermal treatment in both cases. Only slight differences could be observed occasionally at low temperatures between heating and cooling curves.

Some of the composite matrices contain a glass phase up to 23 wt% (BMAS(14) l). The presence of the glass phase, however, is not detectable in the thermal expansion behaviour because no indication for the glass transition branch above T_g is found.

In order to compare the thermal expansion of the various composites the results of the dilatometer measurements are presented as longitudinal mean coefficients of thermal expansion (Mean Coefficient(s) of Thermal Expansion = MCTE). Three temperature intervals are regarded: 150 to 500 °C, 150 to 800 °C and 500 to 800 °C. The results of the MCTE in air and in argon are displayed in figures 2a and b. The largest values are obtained in the temperature interval 500 to 800 °C as expected and the lowest ones in the interval 150 to 500 °C. No extreme differences in MCTE are found among the composites. The lowest values are found for the BMAS(9) composites with a fibre content of V_f = 22 vol.% and the largest values for the

Table 4. Calculated values for α_M in $10^{-6}\,K^{-1}$ after equation (2)

	MAS	BMAS(9) l	BMAS(9) h	BMAS(14) l	BMAS(14) h
α_M	1.63	1.83	1.89	2.36	2.37



Figures 3a to c. Comparison of MCTE of composites measured in argon and air atmosphere for three temperature intervals; a) 150 to 500 °C, b) 150 to 800 °C, c) 500 to 800 °C.

BMAS(14) composites with V_f = 52 vol.%. The largest difference in the MCTE is $0.8 \cdot 10^{-6}\,K^{-1}$ within comparable temperature intervals.

The comparison between the MCTE measured in argon and in air (figures 3a to c) shows no significant differences for the BMAS(9) and BMAS(14) composites whereas lower values are obtained in argon than in air for the MAS composites. The origin of this difference is not yet clear. The influence of the fibre concentration is also seen from figures 3a to c. Composites with higher fibre content show larger MCTE values. In this connection the MCTE of the matrix, α_M, is of interest which influences also the thermal expansion behaviour of the composites. Therefore, the α_M values were determined after equation (2). The results are listed in table 4 and

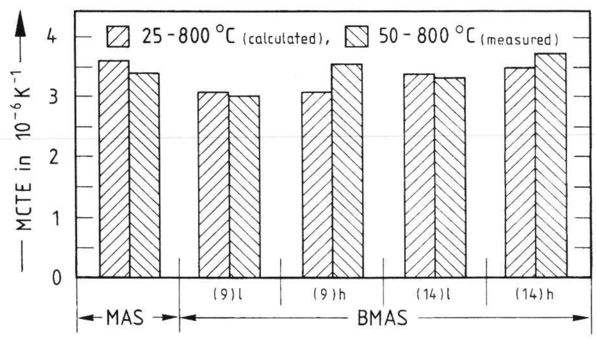


Figure 4. Comparison of MCTE of composites between calculated and measured values (in air).

show that the MCTE deviate only little among the BMAS(9) and the BMAS(14) matrices despite of the different concentrations of the various phases due to the high and low fibre concentrations (table 3). It is clear that the BMAS(14) matrices show larger MCTE than the BMAS(9) matrices due to the larger portion of glass phase.

The results of table 4 indicate that the thermal expansion behaviour of the composites is influenced mainly by the MCTE of the fibres (see table 1) because the MCTE of the composites do not vary much with varying phase composition and content of the matrix although the MCTE of the matrices are different from the MCTE of the fibres and different among each other.

5. Discussion

An interesting point is to calculate the MCTE by means of equation (1) and to compare them with the experimentally determined ones. Figure 4 shows this comparison between the calculated and measured values in air atmosphere within the temperature interval 25 to 800 °C and 50 to 800 °C, respectively, because the thermal expansion measurements started heating at 50 °C. A rather good agreement is obtained although the measured values are somewhat larger than the calculated ones. The deviations are relatively small for the BMAS(14) composites while those of the BMAS(9) and MAS composites are larger. The matrices of the latter ones consist mainly of cordierite and contain only small portions of glass phase (7 wt%) while the matrices of the BMAS(14) composites contain mainly barium osumilith and larger portions of glass phase (up to 23 wt%). Possible reasons for this behaviour are:

a) the real portion of glass phase may be higher than that of table 3. The MCTE of the glass phase is larger than those of the SiC fibres and of the main crystalline phases which would cause the larger MCTE of the composites.

b) The used literature value for the single cordierite crystal (table 1) refers to the mean linear coefficient of thermal expansion and does not regard the real anisotropy resulting from a lower negative and larger positive MCTE in the directions of crystallite axes measured by X-ray diffraction; but in reality polycrystalline aggregates are regarded, for which the anisotropy effects are compensated, somewhat larger MCTE values may result. For cordierite a value of $2.6 \cdot 10^{-6}\,K^{-1}$ [6 and 13] was found. For the second main phase in the composites, the barium osumilith, own measurements were used for the polycrystalline material which gave better results. The other crystalline phases such as mullite and celsian are present in such a low concentration that their influence is of minor degree on the composite properties.

In order to check possibility a) it was calculated how large must be the portion of the glass phase in the matrices to reach the measured values of the MCTE of the composites. These fictively calculated quantities for the glass phase portions are compared with the measured quantities (after Chung [14], see also [12]) in table 5. As is seen from the table an increase of the glass phase portion up to a factor of 5 to 8 would be needed to fit the calculated MCTE on the measured values, particularly for composites with a low portion of glass phase. This would mean an error for the quantitative determination of the phases in the matrix which is unrealistic. Thus, the glass phase portion (case a)) cannot be the reason for the difference between the calculated and measured MCTE.

In order to check possibility b) the larger MCTE for cordierite [13] may be introduced into equation (2) for the evaluation of α_M and for the calculation of α_{comp} after equation (1). The comparison between the calculated and measured MCTE of the composites is given in table 6 and shows a better agreement between calculation and experiment by use of the larger MCTE value for cordierite. Only for the BMAS (9) composites with high fibre concentration the difference between calculated and measured MCTE does not become significantly smaller. The matrix of these composites has a large crystalline portion (93 wt%) with a cordierite portion of 50 wt%, the rest is barium osumilith and celsian. It would be necessary to determine the MCTE of a pure polycrystalline material but this material is very different from that which crystallizes with the SiC fibre present. Therefore, the crystallized compact sample without fibre has another phase composition than that with a SiC fibre content [12]. Thus, it is impossible to prepare a matrix without fibres which is comparable to the fibre-containing matrix.

Table 5. Fictively calculated and measured portions of glass phase in the matrices (values in wt%)

	measured	fictively calculated	factor calc./meas.
MAS	7	42	6.0
BMAS(9) l	7	36	5.1
BMAS(9) h	7	59	8.4
BMAS(14) l	23	30	1.3
BMAS(14) h	15	44	2.9

Table 6. Comparison between calculated and measured values of α_{comp} (in $10^{-6}\,K^{-1}$)

	α_{comp1} (calc.)	α_{comp2} (calc.)	α_{comp} (meas.)
MAS	2.62	3.62	3.38
BMAS(9) l	2.54	3.14	3.00
BMAS(9) h	2.90	3.06	3.52
BMAS(14) l	3.21	3.42	3.33
BMAS(14) h	3.41	3.46	3.69

Explanations: α_{comp1} (calc.): with $\alpha_{cordierite} = 1.5 \cdot 10^{-6}\,K^{-1}$;
α_{comp2} (calc.): with $\alpha_{cordierite} = 2.6 \cdot 10^{-6}\,K^{-1}$.

6. Conclusion

It could be shown that the MCTE of the SiC fibres parallel to the fibre axis determine mainly the expansion behaviour of the composites because the MCTE of the composites do not vary much with varying phase composition and concentration of the matrix although the MCTE of the matrices are different from the MCTE of the fibres and different among each other. A possible reason may be the effect that the phase composition and the concentration of the various phases of the matrix depend very much on the presence and on the concentration of the SiC fibres [12], which indeed has a larger consequence for the strength than for the MCTE of the composites.

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