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The interface, microstructure and mechanical properties of C_f/LAS glass-ceramic composites

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Carbon fibre (C_f)-reinforced lithium aluminium silicate (LAS) glass-ceramic matrix composites were prepared by using LAS ultrafine powders and LAS sol as starting materials and binder, respectively. The effects of fibre content, hot-pressing temperature and pressure on the mechanical properties of the composites were studied. By means of SEM and theoretical calculation, the effects of thermal mismatching between fibre and matrix, and the microstructure on the mechanical properties of the composites were analysed and discussed. The flexural strength and fracture toughness of C_f/LAS glass-ceramic matrix composite prepared were 740 MPa and 19.5 MPa $m^{1/2}$, respectively. The wettability of carbon fibre with matrix was also investigated.

1. Introduction

There are many factors which affect the mechanical properties of ceramic-matrix composites, such as thermal matching and chemical compatibility between fibre and matrix, microstructure, technical parameters of the hot-pressing process, etc. Generally, fibres (f) or whiskers (w) are used to reinforce a ceramic matrix with a thermal expansion coefficient lower than that of the fibre or whisker, in order to meet the thermal matching between the reinforcer and matrix, such as SiC_w/Si_3N_4 [1], SiC_f/lithium aluminium silicate (LAS) glass-ceramic system [2–5] etc. Coating of the fibre was studied in order to improve the compatibility and wetting of the fibre with a ceramic matrix [6, 7]. In the present work, by adjusting the chemical composition of the LAS glass-ceramic, matrixes with different thermal expansion coefficients were obtained to meet the thermal matching with carbon fibre. At the same time, the effects of fibre content, hot-pressing process and microstructure on the mechanical properties of C_f/LAS glass-ceramic composites were studied.

2. Experimental procedure

2.1. Preparation of materials

The matrix used in this work was ultrafine LAS glass-ceramic powders. Its preparation and related properties are reported elsewhere [8]. The composition and properties of LAS glass-ceramics are given in Table I. Carbon fibres, manufactured by the Shanghai Carbon Materials Factory, and Toray Industries, Inc., were used as reinforcer; their properties are listed in Table II. LAS sol solution, having perfect wetting with carbon fibre, was used as binder to prepare C_f/LAS glass-ceramic composites. First, the carbon fibres were uniformly distributed into the LAS slurry in a mould, and then the preshaping body was formed through the sol-to-gel transition of LAS binder. After being dried and preheated at 300–350 °C in air to remove organic solvents, C_f/LAS glass-ceramic composites were fabricated by hot-pressing the preshaping bodies at 1260–1340 °C for 10–60 min under a compressive stress of 6–20 MPa.

2.2. Characterization of C_f/LAS glass-ceramic composites

Mechanical properties of C_f/LAS glass-ceramic composites were determined from three-point bend tests using an Instron 1195 universal materials-testing machine. The dimensions of the samples were $2.5 \times 5 \times 30 mm^3$. The loading speed was 0.5 mm min^{-1} for the flexural strength test and 0.05 mm min^{-1} for the fracture toughness test. The coating on the carbon fibre, microstructure and interface of the C_f/LAS glass-ceramic composites were observed using a Cambridge Stereoscan 250-MK3 SEM.

3. Results and discussion

3.1. Study of improvement of the wetting between carbon fibre and matrix

Pores often appeared in interface of C_f/LAS glass-ceramic composites owing to the poor wetting between carbon fibre and matrix. This has a great effect on the compactness and mechanical properties of the composites. In the present work, the wetting between carbon fibre and LAS sol solution was investigated by SEM. The preparation of the LAS sol solution and the dip-coating process were described elsewhere [7, 8].

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TABLE I Compositions and properties of LAS glass-ceramics

	Composition (wt %)				Main crystalline phases	Density ($g\,cm^{-3}$)	Elastic modulus (GPa)
	Li_2O	Al_2O_3	SiO_2	TiO_2 + Minor component			
LAS1	4.1	22.2	67.2	6.5	β-spodumene	2.44	60.5
LAS2	5.5	34.5	54.5	5.5	β-spodumene + β-quartz solid solution	2.56	59.0
LAS3	3.8	21.4	68.8	5.7	β-quartz solid solution + β-spodumene	2.45	62.0

TABLE II Properties of carbon fibres

	Manufacturer	Tensile strength (GPa)	Elastic modulus (GPa)	Diameter (μm)	Density ($g\,cm^{-3}$)	Axial expansion coefficient ($10^7\,°C^{-1}$)
PAN	Shanghai Carbon Materials factory	2.0	135	7–9	1.79	− 0.7
T300C	Toray Industries, Inc.	3.6	240	6–7	1.82	− 1

TABLE III Constitution and related properties of LAS1 coating solutions

	L-1	L-2	L-3	L-4
$V_{\text{surface-active agent}}/V_{\text{TEOS}}$	0.3	0.7	1.0	2.0
pH	1.4	2.2	2.7	4.5
Viscosity (cP)	3.0	3.8	4.2	7.0

The constitution and related properties of the LAS coating solution are given in Table III. Scanning electron micrographs of the LAS coating on the carbon fibre are shown in Fig. 1. The wetting between the carbon fibre and the LAS sol solution was poor when the addition of surface-active agent was low, but improved on increasing the content of surface-active agent. A uniform LAS film on the carbon fibre was prepared when the volume ratio of surface active agent to TEOS was 0.7–1.0. The thickness of the film was about 1 μm. Further increasing the content of surface-active agent made the uniformity of coating on the carbon fibre poor.

According to Young's wetting equation, the contact angle of a liquid with a solid can be represented as

$$\cos\theta = (\sigma_{SG} - \sigma_{SL})/\sigma_{LG} \qquad (1)$$

where θ is the contact angle, $0 \leqslant \theta \leqslant 180°$; σ_{SG}, σ_{SL} and σ_{LG} are the interface tension for the gas–solid, liquid–solid and gas–liquid interfaces. The addition of a surface-active agent caused the interfacial tension of the liquid with the solid to decrease. Thus, the contact angle became smaller. Wetting by the LAS coating solution of the carbon fibre was improved. However, the viscosity of the coating solution increased obviously with increasing addition of surface active agent to it. This had a poor effect on the uniform LAS coating on the carbon fibre.

Using LAS sol solution, which has perfect wetting with carbon fibre, as binder to prepare LAS slurry can decrease the pores in the interface of the C_f/LAS glass-ceramic composites, thus, improving the compactness and enhancing the mechanical properties of the composites.

3.2. The effect of the hot-pressing process on the mechanical properties of C_f/LAS glass-ceramic composites

The relation between flexural strength and hot-pressing temperature for C_f/LAS glass-ceramic composites is shown in Fig. 2. It can be seen that the strength increased from 45 MPa to 530 MPa on increasing the hot-pressing temperature from 1240 °C to 1340 °C. When the hot-pressing temperature was higher than 1340 °C, the LAS glass-ceramic softened and bound to the graphite mould. This result was different from that reported by Zhang Yufeng *et al.* [9]. In their work, the flexural strength of SiC_f/LAS glass-ceramic composites first increased and then decreased with increasing hot-pressing temperature.

Fig. 3 shows the dependence of mechanical properties of C_f/LAS glass-ceramic composites on the hot-pressing pressure. The composite had the highest flexural strength and fracture toughness, that is 646 MPa and 20.1 $MPa\,m^{1/2}$, respectively, when the hot-pressing pressure was 10 MPa. The reasons for this are that there existed a certain number of pores in the interface of the composites when the hot-pressing pressure was lower, resulting in the carbon fibre effectively being unable to load the force exerted on the matrix. Higher pressure caused more damage to the carbon fibre, therefore, both the strength and toughness of the composite decreased.

In theory, the mechanical properties of ceramic-matrix composites increase with increasing the fibre

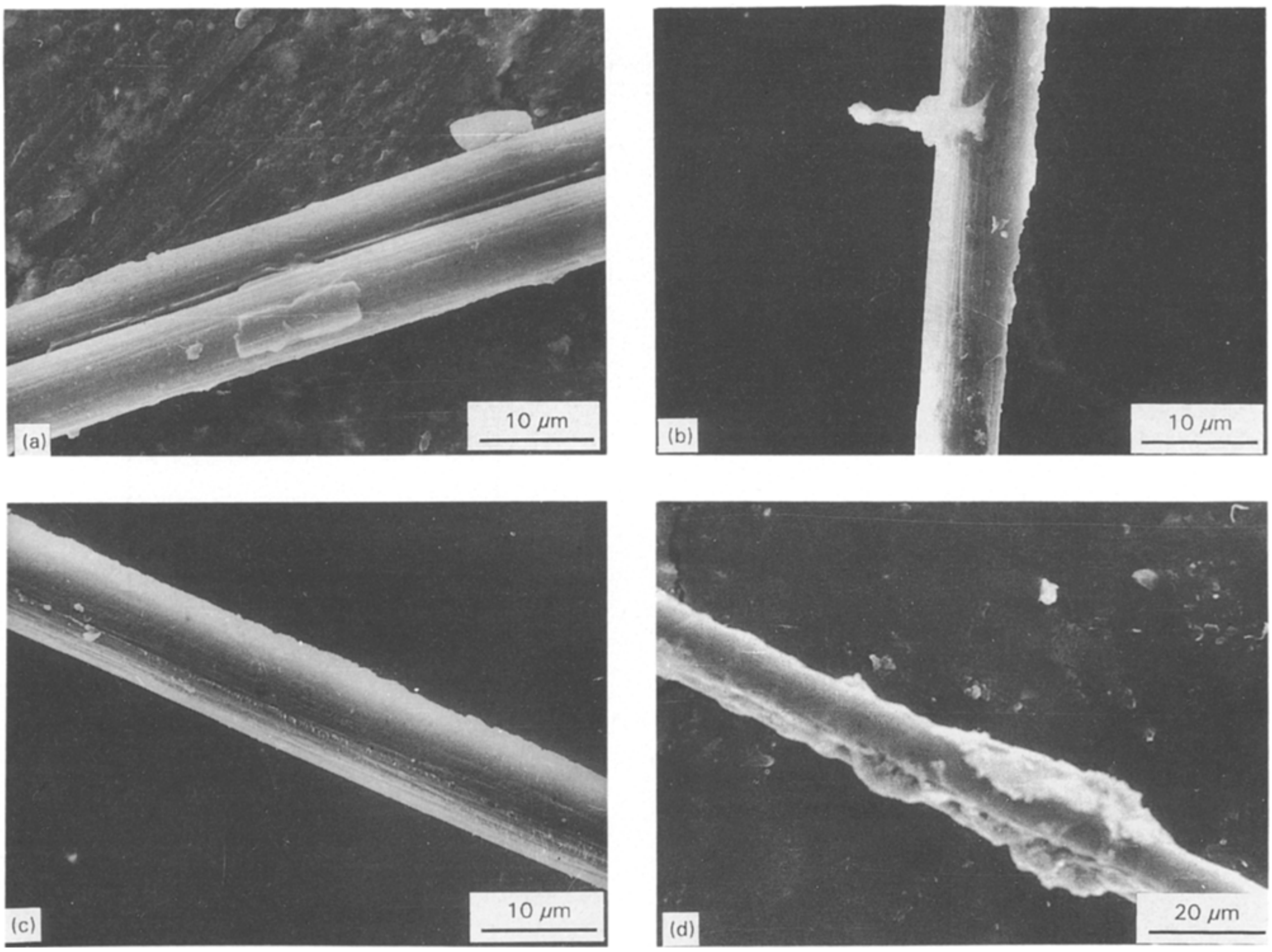


Figure 1 Scanning electron micrographs of LAS coatings on carbon fibre: (a) L-1, (b) L-2, (c) L-3, (d) L-4.

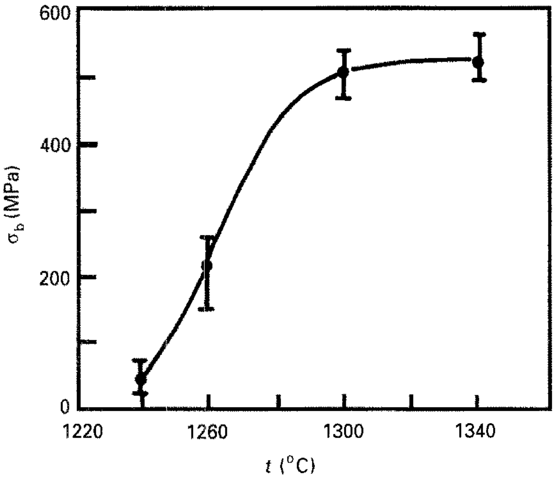


Figure 2 Relation between flexural strength of C_f/LAS glass-ceramic composites on hot-pressing temperature. PAN fibre, LAS1 matrix, $V_f = 30\%$.

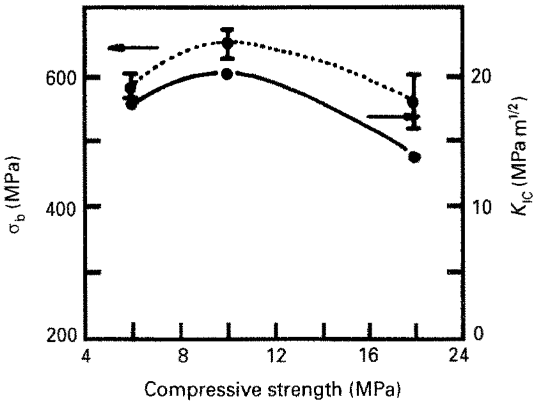


Figure 3 Dependence of mechanical properties of C_f/LAS glass-ceramic composites on hot-pressing pressure. T300C fibre, LAS1 matrix, $V_f = 30\%$.

content. In practice, it is very difficult uniformly to distribute fibre into the matrix for composites with higher fibre content. This results in decreasing strength of the ceramic-matrix composites. The dependence of the properties of C_f/LAS glass-ceramic composites on the carbon fibre content is shown in Fig. 4. The flexural strength of the composites first increased with increasing carbon fibre content and then decreased owing to the poor distribution of fibre in the matrix and the high porosity when the fibre content was higher than 35 vol%, while the fracture toughness of the composites increased with increasing fibre content in the range 25–40 vol%. Fracture of C_f/LAS glass-ceramic composites follows the Cook–Gordon model (Fig. 5). That is, the fibre separates from the matrix under the action of tensile or shear stress before the crack tip reaches the interface. Then the crack tip becomes blunt and changes its direction when the crack reaches the ceramic

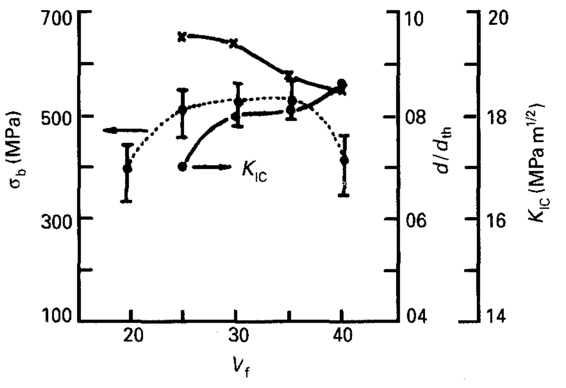


Figure 4 Dependence of properties of C_f/LAS glass-ceramic composites on carbon fibre content. PAN fibre, LAS1 matrix.

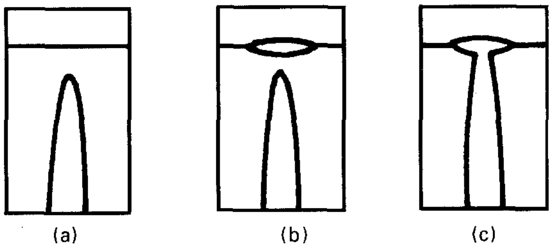


Figure 5 Interaction between an advancing crack and an interface: (a) an advancing crack; (b) interaction between an advancing crack and an interface; (c) a blunt crack.

composite interface. The greater the fibre content, the greater is the barrier potential preventing crack propagation. Thus, the fracture toughness of C_f/LAS glass-ceramic composites can be improved.

3.3. The effect of interfacial stress on the mechanical properties of C_f/LAS glass-ceramic composites

The thermal expansion coefficient of the matrix varies with the composition of the LAS glass-ceramic on which the thermal stress in the interface of the C_f/LAS glass-ceramic composites depends. The axial thermal stresses, σ_a, in the matrix were calculated from Equation [10]

$$\sigma_a = (\alpha_m - \alpha_f)\Delta T\left[E_fV_f\Big/V_f\left(\frac{E_f}{E_m}-1\right)+1\right] \qquad (2)$$

The thermal stress was tensile for $\sigma_a > 0$, and microcracking would occur in the matrix near the interface if $\sigma_a > \sigma_m$. The matrix was subjected to compressive stress for $\sigma_a < 0$. The calculated results are given in Table IV. The tensile stress in the matrix decreased with decreasing thermal expansion coefficient. When α_m was lower than α_f, the thermal stress was compressive. In the present work, the tensile stress in the matrix was lower than the strength of the LAS glass-ceramic. Microcracking would not occur in the matrix. Therefore, high strength and toughness were obtained for the three kinds of C_f/LAS glass-ceramic composites (Fig. 6). When $\Delta\alpha = \alpha_m - \alpha_f$ varied from 9.3×10^{-7} to -5.3×10^{-7} °C^{-1}, the flexural strength and toughness of the composites changed from 646 MPa and 20.1 MPa m$^{1/2}$ to 740 MPa and 19.5 MPa m$^{1/2}$, respectively, indicating that higher strength could be obtained when the axial thermal stress in matrix was compressive. However, the toughness decreased slightly due to the better binding of the fibre with the matrix in the radial direction. For LAS glass-ceramic, the thermal matching of the fibre with the matrix can be met by adjusting the matrix composition. For other ceramic systems, optimum matching between fibre and matrix may be achieved by adding a second phase to form a multi-phase ceramic.

TABLE IV Axial thermal stresses in the matrix for C_f/LAS glass-ceramic composites. $V_f = 30\%$

Matrix	σ_m (MPa)	α_m (10^7 °C^{-1})	$\alpha_m - \alpha_f$ (10^7 °C^{-1})	ΔT (°C)	σ_a (MPa)
LAS1	72.0	8.3	9.3	1330	48.1
LAS2	70.5	1.0	2.0	1330	10.4
LAS3	73.5	− 6.3	− 5.3	1330	− 27.4

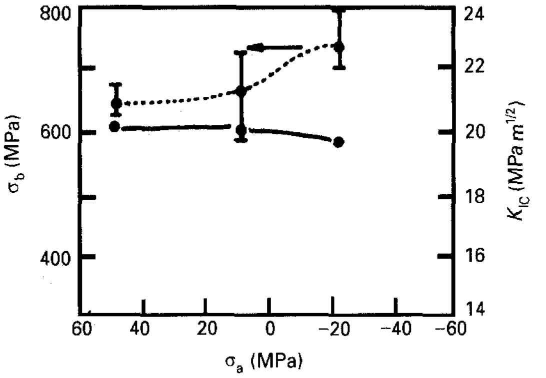


Figure 6 Dependence of mechanical properties of C_f/LAS glass-ceramic composites on axial thermal stresses. T300C fibre, $V_f = 30\%$.

3.4. The microstructure of C_f/LAS glass-ceramic composites

Scanning electron micrographs of C_f/LAS glass-ceramic composites hot-pressed at different temperatures are shown in Fig. 7. Many large and small pores were present in the matrix and interface for the sample hot-pressed at 1260 °C, but the number greatly decreased for the sample hot-pressed at 1340 °C, because the flowability of LAS powders was poor when the hot-pressing temperature was low. In this case, the shear stress in the interface of the composites was weak. The high porosity and poor binding of the fibre with the matrix resulted in poor strength of C_f/LAS glass-ceramic composites hot-pressed at low temperatures. The flowability of LAS powders increased with increasing hot-pressing temperature. The binding between fibre and matrix was improved, and the strength of the composites enhanced. Thus, the hot-pressing temperature is one of the most important technical parameters affecting the mechanical properties of C_f/LAS glass-ceramic composites. Fig. 8 shows scanning electron micrographs of C_f/LAS glass-ceramic composites prepared by different matrices. For

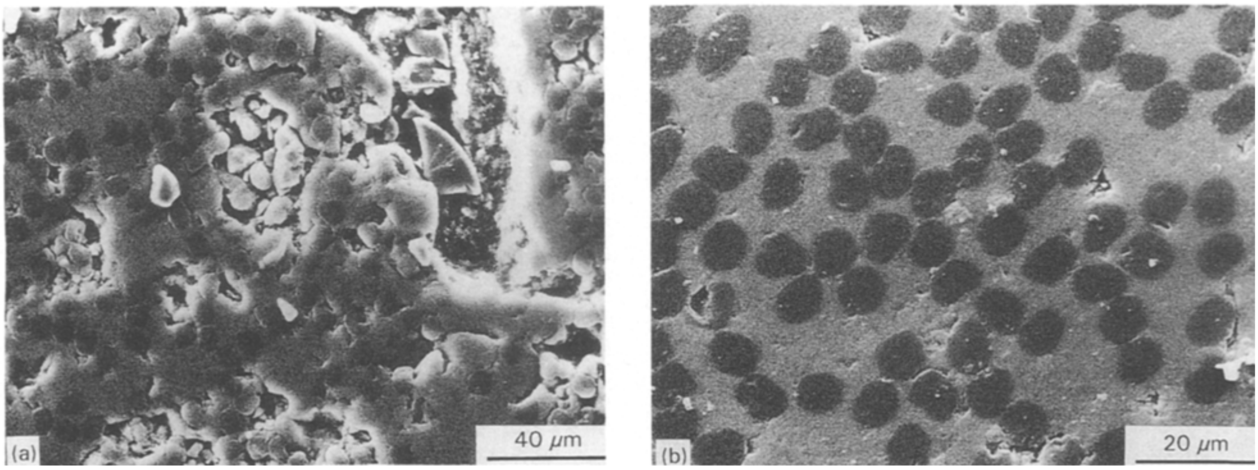
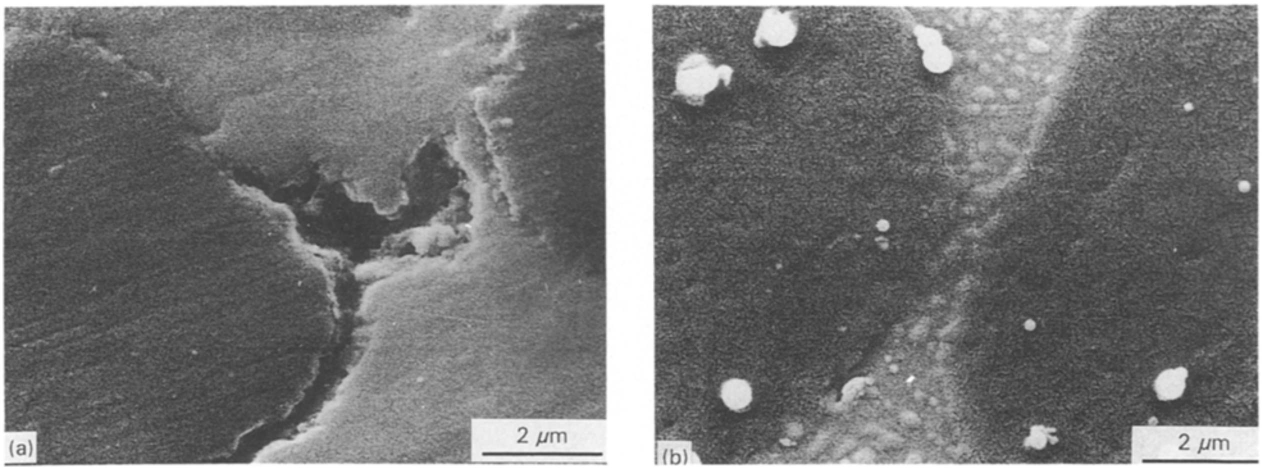


Figure 7 Scanning electron micrographs of C_f/LAS glass-ceramic composites hot-pressed at different temperatures: (a) 1260 °C, (b) 1340 °C.



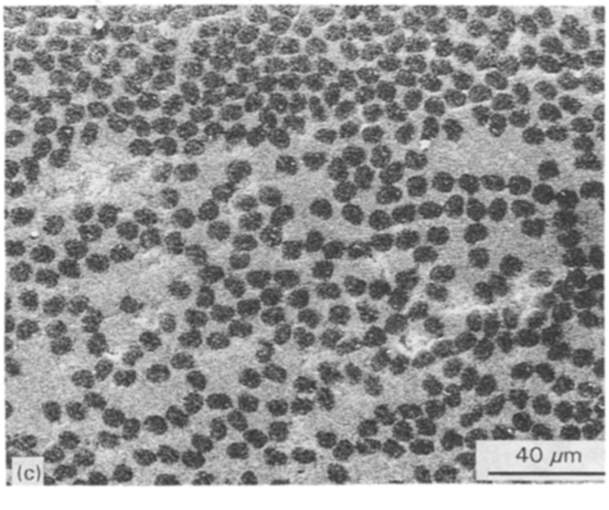


Figure 8 Scanning electron micrographs showing the interface of C_f/LAS glass-ceramic composites with different matrices: (a) LAS1, (b, c) LAS3 T300C fibre.

LAS1-matrix composite, interstices existed in the interface, resulting from shrinkage of the fibre and matrix in the radial direction. Stress could not therefore be effectively transferred from the matrix to the fibre in continuous carbon fibre composites. Thus, it was not advantageous to the improvement of mechanical properties of the composites. For LAS3-matrix composite, carbon fibre had better binding with the matrix and interstices in the interface were greatly decreased (see Fig. 8b and c). The stress could be effectively transferred from the matrix to the fibre in the composite. Thus, LAS3-matrix composite had the highest flexural strength (see Fig. 6). However, the fracture toughness decreased slightly owing to the strengthening of the binding between fibre and matrix. The above results can be explained as follows. Both carbon fibre and LAS1 matrix have positive thermal expansion coefficients in the radial direction, that is, 80×10^{-7} to 100×10^{-7} and 8.3×10^{-7} °C^{-1}, respectively. During cooling of the C_f/LAS glass-ceramic composites, shrinkage of the fibre and matrix resulted in a weak binding. However, the LAS3 matrix has a negative thermal expansion coefficient and during the cooling process, the expanding of this improved the binding between fibre and matrix in the radial direction.

Fig. 9 shows scanning electron micrographs of C_f/LAS glass-ceramic composites prepared from uncrystallized and crystallized LAS powders. There was a certain amount of porosity in the matrix and interface of the composite prepared from crystallized LAS

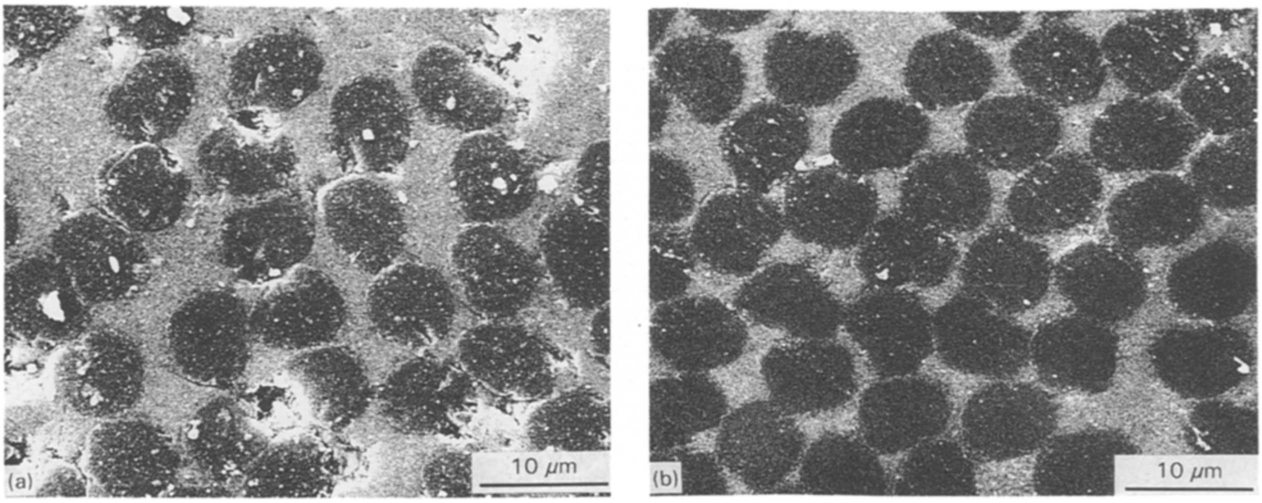


Figure 9 The effect of pre-treatment of LAS powders on the microstructure of C_f/LAS glass-ceramic composites: (a) sample prepared from crystallized powders, (b) sample prepared from uncrystallized powders.

powders, while the composite prepared from uncrystallized LAS powders had less porosity and more compactness. The reason for this was that, after crystallization, the grain size of the LAS powders increased owing to the sintering and aggregation between particles. During sintering, the shrinkage of ceramic bodies can be expressed as

$$(\Delta L/L_0)^{5/2} = Kr^{-3}t \qquad (3)$$

$$K = (5 v a_0^3 D)/kT \qquad (4)$$

where r is the grain size, t the sintering time, v is the surface tension, a_0 the lattice constant, D is the self-diffusion coefficient and T the sintering temperature. From Equation 3, it can be seen that the shrinkage rate of ceramic bodies is mainly determined by the grain size of the powders under given sintering temperature and time. The smaller the grain size, the higher is the surface energy of the powders. Under the action of high surface energy, viscous flow occurred for particles in the body, which was conducive to the densification of the bodies. Therefore, dense C_f/LAS glass-ceramic composite could be fabricated using uncrystallized LAS powders as starting materials.

4. Conclusions

1. Uniform LAS coating on carbon fibre was prepared by the sol–gel process. The thickness of the coatings was about 1 μm.

2. C_f/LAS glass-ceramic composites with high flexural strength and fracture toughness could be fabricated by using LAS ultrafine powders and LAS sol solution as starting materials and binder, respectively. The optimum technical parameters for the preparation of the composites containing 30–35 vol% fibres were 1340 °C for hot-pressing temperature and 10 MPa for hot-pressing pressure.

3. When the thermal expansion coefficient, in the axial direction, of the carbon fibre is higher than that of the matrix, the axial thermal stress in the matrix is compressive. In this case, the C_f/LAS glass-ceramic composite has the highest strength. Thermal mismatching in the radial direction may cause weak binding of the fibre with the matrix.

4. Dense C_f/LAS glass-ceramic composites could be prepared by using uncrystallized LAS powders as starting materials.

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