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Preparation and crystallization of ultrafine Li_2O–Al_2O_3–SiO_2 powders

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Ultrafine powders of Li_2O–Al_2O_3–SiO_2 (LAS) glass-ceramic were prepared by the sol–gel process using tetraethoxysilane, titanium butoxide, lithium, magnesium, aluminium (and zinc) inorganic salts as starting materials. The effect of pH on the sol–gel transition and particle sizes of the Li_2O–Al_2O_3–SiO_2 system was studied. The nucleation and crystallization process of LAS powders were also investigated by differential thermal analysis and X-ray diffraction. The results show that a surface nucleation process occurs for ultrafine LAS powders. The LAS glass-ceramics fabricated from ultrafine LAS powders have a low thermal expansion coefficient, $\alpha < 10 \times 10^{-7}$ °C.

1. Introduction

Many authors have studied the crystallization theories and manufacturing process of glass-ceramics since the appearance of the first glass-ceramic product in the 1950s. Glass-ceramic products with different compositions and properties have been produced. LAS glass-ceramic is one of the most important glass-ceramic systems, and because of its many excellent properties, it has been widely used. Since the end of the 1960s, investigation of ceramic-matrix composites has been made in order to improve the fracture toughness of ceramics. SiC fibre-reinforced LAS glass-ceramic has been considered to be one of the most challenging candidates for medium-temperature-structural materials because of its high strength, high fracture toughness and low thermal expansion coefficient, etc. [1]. For the SiC_f/LAS system, bending strength and fracture toughness as high as 1380 MPa [2] and 17 MPa m$^{1/2}$ [3], respectively have been obtained.

In present work, LAS ultrafine powders were prepared by the sol–gel process. The powders can be used to manufacture LAS ceramic products or as a matrix of ceramic-matrix composites.

2. Experimental procedure

2.1. Preparation of ultrafine powders

The nucleus agent TiO_2 in LAS glass-ceramic can react with SiC and cause a decrease in strength and toughness of the composites [4]. Thus, LAS ultrafine powders using TiO_2 and ZrO_2 as nucleating agents were prepared. The composition and preparation process of LAS powders are shown in Table I and Fig. 1, respectively. The starting materials used in the present work were tetraethoxy silane (TEOS) (SiO_2 28.0 wt %), titanium butoxide (purity $\geqslant$ 98.0%), zirconium chloride ($ZrCl_4 \geqslant 98\%$), lithium chloride (purity $\geqslant$ 97.0), aluminium nitrate (purity $\geqslant$ 99.0), magnesium acetate (purity $\geqslant$ 97.0) and zinc acetate (purity $\geqslant$ 98.0).

2.2. Characterization of LAS powders and ceramics

Nucleation and crystallization of LAS powders were studied by X-ray diffractometry (D/MAX-II) and DTA (CRY-1). The particle size of the LAS powders was examined by SEM (JSM-35C) and a size analyser (BI-90). The bending strength of LAS glass-ceramics was determined using an AG-2000A universal materials testing machine with a three-point single-edge notched beam.

3. Results and discussion

3.1. Preparation of LAS gel and ultrafine powders

LT sol with the composition shown in Table I was prepared, and the effect of pH on the gelation and powder sizes was also studied (see Table II). It is shown that the gelling time decreased with increasing pH value. When the pH value was 2.0, the transition of sol to gel occurred only 3 min after the addition of catalyst. At the same time, a small amount of precipitation appeared in the gel. Therefore, the suitable pH value of the sol solution is 1.0–1.5 in order to obtain homogeneous gel and to control the sol to gel transition easily. Scanning electron micrographs of LAS powders, obtained by ball milling after calcining at 300 °C, are shown in Fig. 2. The particle size of LAS dried gel powders was larger when the pH was 0.5 (without catalyst), about 5–20 μm. The amount of smaller particles increased with increasing pH value.

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TABLE I Composition of LAS powders

	Composition (mol%)						
	Li_2O	Al_2O_3	SiO_2	MgO	TiO_2	ZnO	ZrO_2
LT	8.8	13.8	71.0	2.4	4.0	–	–
LZ	8.8	13.8	71.6	2.4	–	1.4	2.0

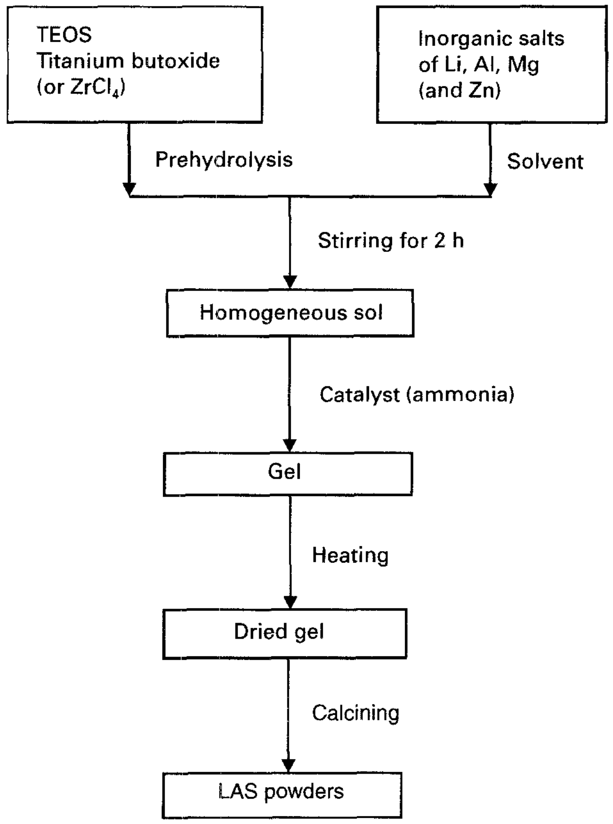

Figure 1 Preparation process of LAS ultrafine powders.

TABLE II Effect of pH values on gelation of LAS sol

	pH value	Gelling time (h)	Homogeneity of the gel
LT-0	0.5	12	Good
LT-1	1.0	5	Good
LT-2	1.5	0.5	Good
LT-3	2.0	0.05	Bad

The average size of the powders was about 1–5 μm when the pH was 2.0. Because the sol solution catalysed by ammonia partially hydrolysed, and the condensation rate was quicker, the obtained gel powders had a low density and large pores. Thus, LAS powders with small size and narrow particle-size distribution could easily be prepared.

In the preparation of ultrafine powders by the sol–gel process, many secondary particles were found which were aggregates of many small initial particles. Fig. 3 shows a secondary particle, about 2 μm in size, composed of 0.05–0.2 μm initial particles. Both the technical parameters of the sol–gel transition and the drying, calcining, and ball milling of the dried gel powders, can affect the appearance of the secondary particles. When calcining, a bridge may be formed between powders with increasing temperature, because of sintering and solid state reaction [5]; this is called hard aggregation. By using the correct preparation process and the addition of a surface-active agent. Both soft and hard aggregation can be eliminated. In the present work, ultrafine LAS powders with a particle size smaller than 0.5 μm were prepared. Fig. 4 shows that the average particle size for LT and LZ powders are 130 and 180 nm, respectively, and the range of particle sizes is 34–500 and 34–1000 nm, respectively. The specific surface areas of LAS ultrafine powders are 160 $m^2 g^{-1}$ for LT and 155 $m^2 g^{-1}$ for LZ.

The wetting of the fibre with slurry, the homogeneity of distribution of the fibre in the matrix, as well as the mechanical properties of the composites, can be greatly improved by using LAS ultrafine powders as starting materials in the preparation of LAS/SiC_f (C_f) composites.

3.2. Nucleation and crystallization of LAS ultrafine powders

Fig. 5 shows differential thermal analysis (DTA) curves of LT powders. An exothermic peak of crystallization occurred at around 900 °C on the DTA curves. This peak shifted to low temperature and became sharp with increasing temperature of heat-treatment. Then the peak became weak and finally disappeared after LT dried gel powders were treated at temperatures higher than 600 °C. The growth of crystals can be described by the Johnson–Mehl–Avrami equation during crystallization [6]:

$$-\ln(1-\alpha) = (kt)^n \tag{1}$$

$$k = AN\exp\left(-\frac{E_c}{RT}\right) \tag{2}$$

where α is the volume fraction of crystallized phase at time t, n is a parameter related to the mechanism of the process, E_c is activation energy for crystal growth, A is a constant, and N is the number of nuclei ($N = N_s + N_h + N_n + N_c$, N_s is surface nuclei, N_h is bulk nuclei formed during the DTA run, N_n is bulk nuclei formed during a previous heat treatment of nucleation, N_c is heterogeneous bulk nuclei).

A relationship exists between the shape of the crystallization peak and the parameter n: the higher the parameter n, the sharper is the peak. The value of parameter $n = 1$ for surface nucleation and 3 for volume nucleation. LT powders prepared in this work have a high specific surface area. At first, crystallites precipitated on the surface during crystallization, so surface crystallization predominated, and $n = 1$. Thus, the crystallization peaks on the DTA curves are not sharp and the crystallization temperature decreased by about 100 °C compared with bulk LAS glass-ceramic with similar composition [7].

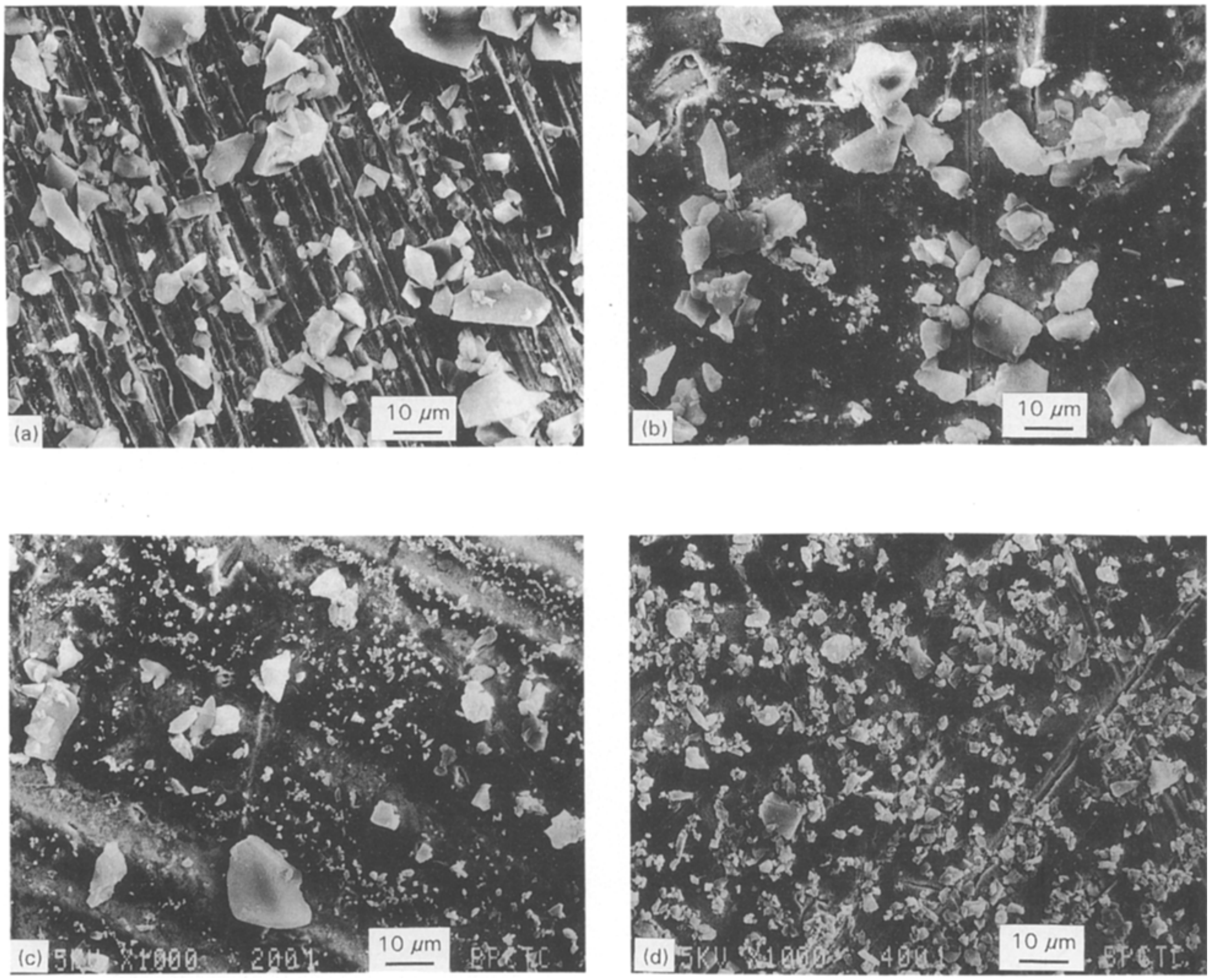

Figure 2 Scanning electron micrographs of LT powders: (a) LT-0, (b) LT-1, (c) LT-2, (d) LT-3.

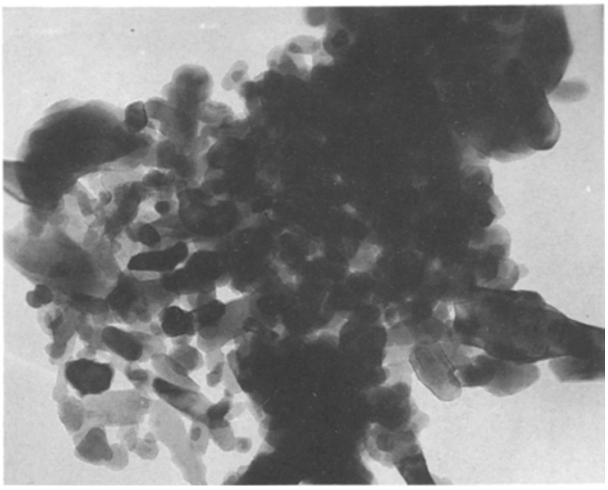

Figure 3 Transmission electron micrograph of secondary particles in LAS powders (magn. ×40 000).

For samples with the same composition, the following relationship exists between the number of nuclei N and the crystallization temperature, T_p, when the heating rates are the same in the DTA run

$$\ln N = \frac{E_c}{R}\frac{1}{T_p} + \text{constant} \quad (3)$$

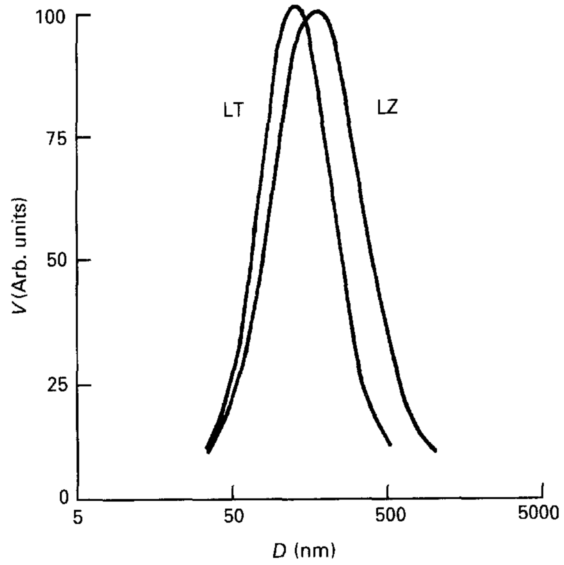

Figure 4 Curves of grain-size distribution for LAS ultrafine powders.

That is, the greater the number of nuclei, the lower is the crystallization temperature. Therefore, the best nucleation temperature for LT powders can be determined as 600 °C from Fig. 5. When LAS powders were

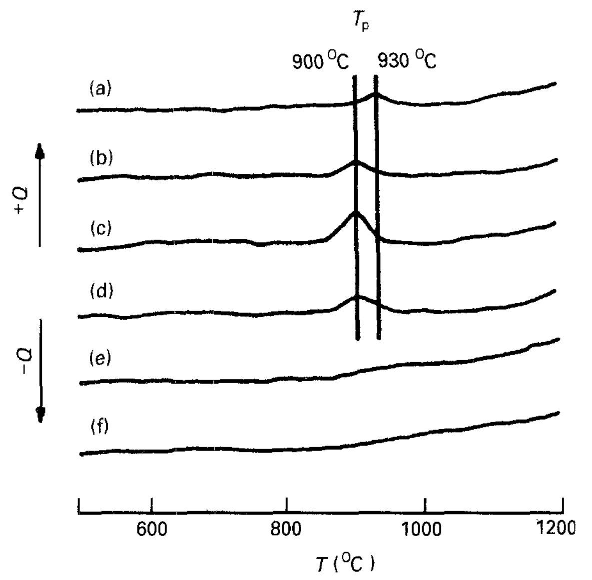

Figure 5 DTA curves of LT powders heat treated at different temperatures, (a) without heat treatment, (b) 500 °C, (c) 600 °C, (d) 700 °C, (e) 800 °C, (f) 900 °C.

heat treated at temperatures higher than 700 °C, a large amount of crystalline phase was precipitated. Thus, the crystallization peak on the DTA curves became weak and finally disappeared.

X-ray diffraction (XRD) experiments indicated that both LT and LZ powders were amorphous after heat treatment at 600 °C (Fig. 6). β-quartz solid solution occurred at 700 °C. The crystallization temperature decreased by 100–200 °C compared with bulk glass-ceramics with a similar composition [8]. A small amount of β-spodumene occurred at 800 °C. β-quartz solid solution transformed to β-spodumene completely at 1200 °C. From the X-ray diffraction patterns of samples heated at 900 °C, it is also seen that the transformation from β-quartz solid solution to β-spodumene was easier for LZ powders than LT.

3.3. Preparation of LAS ceramics from LAS ultrafine powders

Powders produced by the sol–gel process must be calcined in order to eliminate alkoxyl and acid radicals, and to avoid large shrinkage of samples when sintering at high temperature. However, the calcining temperature should be appropriate. With increasing calcining temperature, the specific surface area and reactivity of powders decreased because of the sintering between particles. Table III shows the weight loss of LT powders after calcining at different temperatures, from which the appropriate calcining temperature can be determined to be 500 °C.

Table IV gives related properties of LAS ceramics sintered at different temperatures. Ceramics prepared from both LT and LZ powders have similar thermal expansion coefficient because of having the same

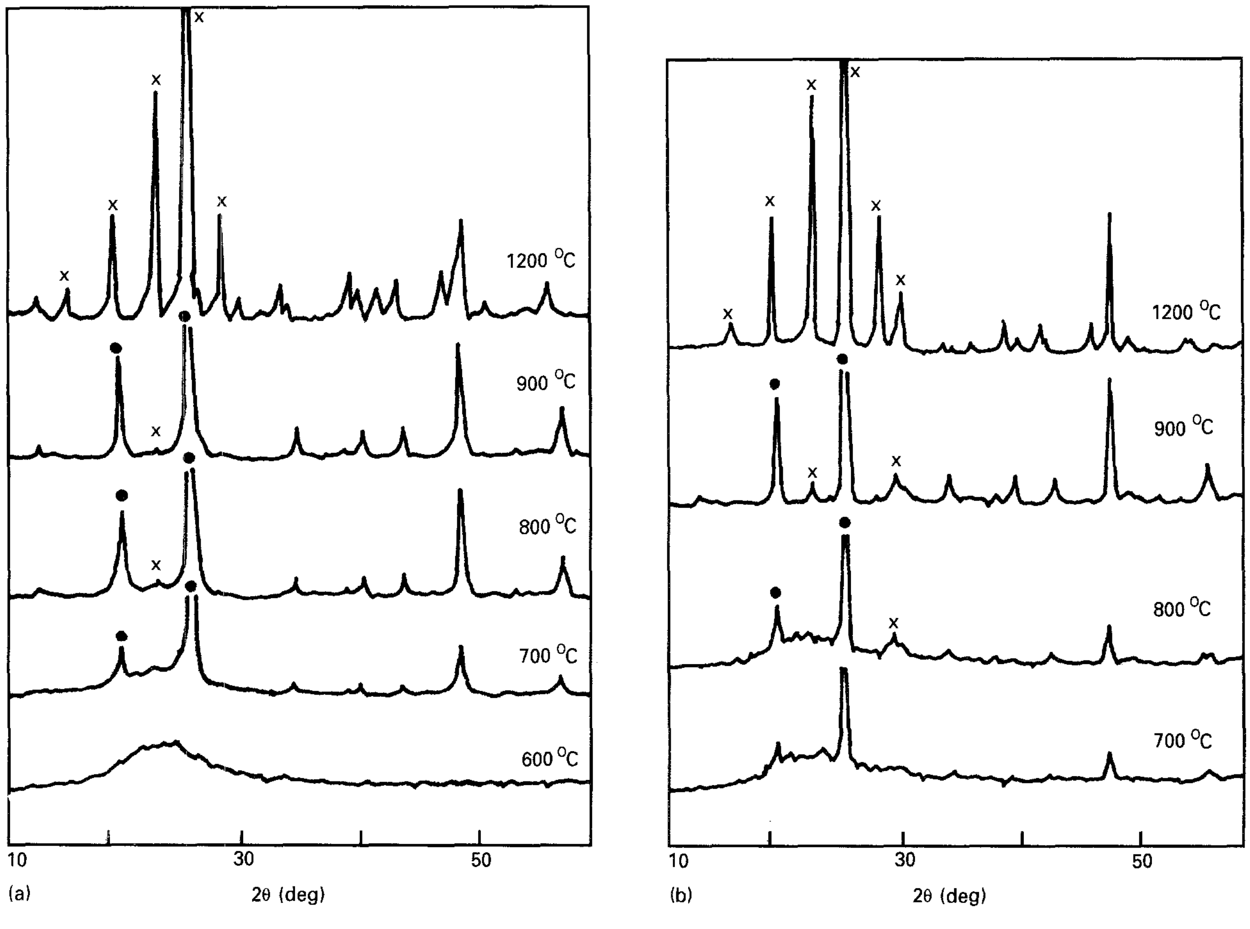

Figure 6 X-ray diffraction patterns of LT and LZ powders heat treated at different temperatures: (●) quartz solid solution, (×) spodumene. (a) LT, (b) LZ.

TABLE III Weight lose of LT powders calcined at different temperatures

Calcining temperature (°C)	400	500	600
Weight (g)	1.2661	1.0377	1.0336
Weight loss (%)		18.04	18.36

Weight loss (%) = $(W_{400} - W_t)/W_{400} \times 100\%$; W_{400} = Weight of powders calcined at 400 °C; W_t = weight of powders calcined at temperature, *t*.

TABLE IV Properties of LAS glass-ceramics

Sintering temperature	LT		LZ	
	1200 °C	1250 °C	1200 °C	1250 °C
$\alpha_{\text{RT-500}\,^\circ\text{C}}$ (10^7 °C)	7.7	8.3	8.3	6.9
σ_b (MPa)	15	72	11	31

crystalline phase. At sintering temperatures, samples manufactured from LZ powders sintered poorly, thus its bending strength was also poor. The LAS ceramics prepared in the present work have low thermal expansion coefficients, and resistance to high temperature, and can be used as thermal shock materials. In addition by adjusting the composition of LAS glass-ceramic, we can obtain LAS matrices with different thermal expansion coefficients to match the reinforcing fibres or whiskers, such as carbon and SiC fibres. Thus, LAS matrix composites with high bending strength and fracture toughness can be obtained by using the LAS ultrafine powders prepared in this work as starting materials.

4. Conclusion

By adjusting the pH values of LAS sol and controlling the technical parameters of drying, calcining, and ball milling of the dried gel powders, ultrafine LAS glass-ceramic powders were prepared. The average particle size and specific surface area of the powders were 130 nm and 160 $\text{m}^2\,\text{g}^{-1}$, respectively. Compared with a bulk LAS glass-ceramic having a similar composition, the nucleation temperature and crystallization temperature decreased by 100 °C and 100–200 °C, respectively. The optimum nucleation temperature was about 600 °C. The LAS glass-ceramics prepared from the ultrafine LAS powders have low thermal expansion coefficients, $\alpha < 10 \times 10^{-7}$ °C.

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