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Constitution of Mullite Glasses Produced by Ultra-rapid Quenching of Plasma-sprayed Melts

M. Schmücker,[a] H. Schneider,[a] M. Poorteman,[b] F. Cambier[b] & R. Meinhold[c]

[a]Institute for Materials Research, German Aerospace Research Establishment, D-51147 Köln, Germany
[b]Research Center of the Belgian Ceramic Industry, B-7000 Mons, Belgium
[c]New Zealand Institute for Industrial Research and Development, Lower Hutt, New Zealand

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Abstract

Spherical shaped spray-dried admixtures of chemical pure and very fine α-Al_2O_3 *and quartz powders with mullite composition (72 wt%* Al_2O_3*, 28 wt%* SiO_2*) were used as starting materials. The spray-dried powders (10–100 μm) were melted in a nitrogen plasma flame and subsequently quenched in water thus producing spherical, hollow, and porous particles (≤100 μm). The as-quenched spherules consist of mullite glass, some residual* α-Al_2O_3 *and quartz, and a very low amount of newly formed mullite. Double quenching of the material increases the glass content to >90 wt.%.* ^{27}Al *and* ^{29}Si *MAS NMR studies show that the rapidly quenched mullite glass is composed of a network of (SiO)-tetrahedra and (AlO)-octahedra, -pentahedra, and -tetrahedra. The frequency distribution of (AlO)-structural units is similar to those in metakaolinite, type I (polymer) mullite precursors, and in other melt-quenched aluminium-silicate glasses suggesting strong structural similarities of these phases. This has been supported by the exothermic mullite crystallization process taking place at ≈ 980°C in all cases.*

Introduction

Due to its excellent thermal shock and creep resistance, its high temperature strength and chemical stability mullite has become increasingly important as a structural high temperature material.[1,2] Various preparation methods have been investigated for mullite synthesis. The most important techniques are:

- mullite formation by reaction sintering of oxides or silicates,
- crystallization of mullite from melts,
- mullite formation from chemical precursors.

Conventional fabrication methods using powders or reaction sintering routes require high sintering temperatures (1600–1800°C) in order to produce dense ceramics. Ceramics with suitable densities can be achieved at much lower temperatures if chemical produced precursors are used as starting materials. An alternative method to process mullite ceramics at relatively low temperatures is densification of viscous glass particles with mullite composition and subsequent mullite crystallization.[3] However, preparation of glasses with mullite composition is difficult, since its glass forming ability is low, and extreme cooling rates are required to suppress crystallization during the quenching of the melt. This paper presents a possible glass formation route using ultra-rapid quenching of aluminium silicate liquids produced by melting the starting powder materials in a plasma flame. It also provides data on the structural constitution of Al_2O_3-rich aluminium silicate glasses.

Experimental

Starting material

An aqueous slip, corresponding to stoichiometric 3/2-mullite ($3Al_2O_3 \cdot 2SiO_2$) was prepared from chemically very pure α-Al_2O_3 (A16SG, ALCOA, USA) and quartz powders (SIPUR A1, Bremthaler Quarzitwerk, Germany). Mean grain size of the starting material as determined by laser diffraction was 0·68 μm for the alumina powder and 1·92 μm for the silica powder. The raw materials were admixed in water under conditions assuring high stability of the suspensions which was verified by zeta potential measurements (pH 10, dry matter content of 30%). Mixing took place in a vibration mill (Sweco) for 16 h using alumina balls. After milling the chemical composition of the raw materials was checked again. If there was enrichment in Al_2O_3 due to wear of α-Al_2O_3 milling balls the composition was adjusted to 3/2-mullite composition.

The slurry was spray-dried with a centrifugal rotating disc atomiser in an Anhydro Lab 1 spray dryer. By spray drying spherical agglomerates ranging from ≈ 10 to 100 μm in diameter were formed.

Plasma quenching experiments

The dried agglomerates were sprayed into a 24 kW DC plasma torch using nitrogen both as plasma and powder carrier gas (Fig. 1). The powder was introduced into the nozzle under a 70° angle. When leaving the plasma, the particles were quenched in water. Care was taken that the water surface was as close as possible to the plasma flame. A second batch of powders was prepared by sieving the already once quenched powder and quenching the fraction below 40 μm a second time. This double quenched material was used for subsequent structural investigations.

Characterization of plasma-quenched mullite glasses

The chemical composition of the starting material and of the quenched powders were determined by X-ray fluorescence analysis (ARL 8410). Differential thermal analyses (DTA) were performed with a computer-controlled Netzsch STA 409 apparatus (sensitivity: DTA: 50 mV) in air. About 80 mg of the samples and of the reference material (fired kaolinite), respectively, were heated up in Pt crucibles, with a constant heating rate of 10 K/min.

The contents of crystalline phases were determined by X-ray diffraction (Siemens D 5000 XRD equipment) comparing the diffraction line intensities of the quenched samples with those of a α-Al_2O_3 reference material.[4] Quenched powders were analyzed by optical microscopy, scanning-electron microscopy (SEM, Model 525 M, Philips) and transmission electron microscopy (Model 430 TEM, Philips, with LaB_6-filament, 300 kV accelerating voltage and a TRACOR system for energy dispersive X-ray spectroscopy (EDX)). Sample preparation for transmission electron microscopy was difficult, due to the small sizes and spherical, porous shapes of the quenched powder particles. However, by embedding the powders in epoxy and subsequent grinding and ion beam thinning electron transparent areas of a few microns were achieved.

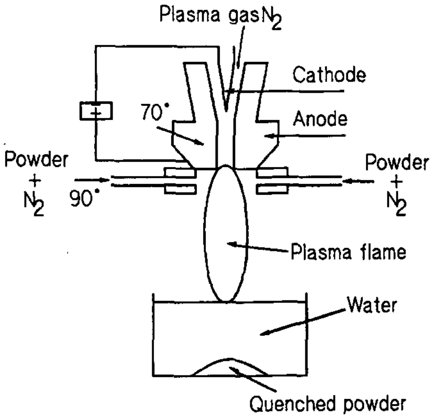


Fig. 1. Schematic diagram of the plasma spray technique used for the production of mullite glasses by ultra rapid quenching the melt droplets.

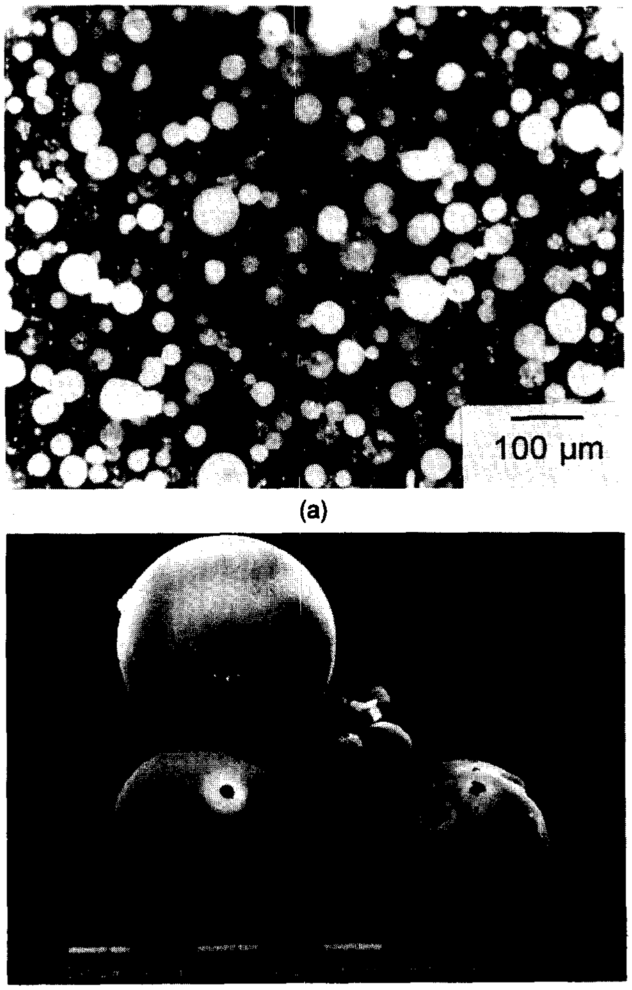
Nuclear magnetic resonance spectroscopy was performed in a Unity 500 spectrometer at 11.7T, using a Doty Scientific Magic Angle Spinning probe at a spinning speed of 10 kHz. For ^{29}Si 798 transients were accumulated with a delay of 100 s between 90° pulses. T_1 was found to be 52 + 9 s. Chemical shifts are referenced with respect to external tetramethylsilane. For ^{27}Al a 1 s delay between $\pi/12$ pulses was used and shifts referenced relative to a 0·1M aqueous aluminium sulfate solution.

Results and Discussion

The spray-dried powders used for the plasma quenching experiments consisted of spherules composed of an admixture of very small quartz and α-Al_2O_3-crystallites. The powder particles exhibit spherical shapes ranging between about 10 and 100 μm. After plasma melting and subsequent rapid quenching the batch consists of hollow and porous spherules (Fig. 2(a) and (b)) with a similar size distribution as the starting spray-dried powder. The formation of hollow and porous spherules is attributed to the fact that gas molecules incorporated in the starting spray-dried spherules rapidly expand in the plasma flame.

The smaller grain fraction (≤20 μm) of the plasma sprayed and subsequently ultra-rapidly quenched materials consists of an optically transparent glass, whereas the coarser particles (≥20 μm) frequently are non-transparent due to light scattering on crystalline phases. By means of TEM and XRD α-Al_2O_3, quartz (Figs 3 and 4), and mullite were detected. Obviously the former are relictic starting compounds, whereas mullite crystallized from the melt in regions of relative low quenching rates. The correlation between size and crystalline phase content of the quenched powders has been proved unambiguously by quantitative XRD.

In order to achieve a high degree of glass formation ultra-rapidly plasma-quenched materials with a particle size below 40 μm was plasma-sprayed again under the same experimental conditions as in the first quenching run. After double plasma quenching the amount of residual quartz



(a)

(b)

Fig. 2. Ultra-rapidly quenched mullite glasses. (a) Optical micrograph showing mullite glass spherules (transparent), and partially crystallized glass spherules (white). (b) Scanning electron micrograph showing hollow and porous glass spherules.

and α-Al_2O_3 is reduced considerably with respect to the powder quenched only once (crystalline phase content $\approx$10 wt%). On the other hand the amount of newly formed mullite slightly increases in double quenched materials probably due to the crystallization of liquid phase on already existing mullite nuclei produced by the first quenching procedure.

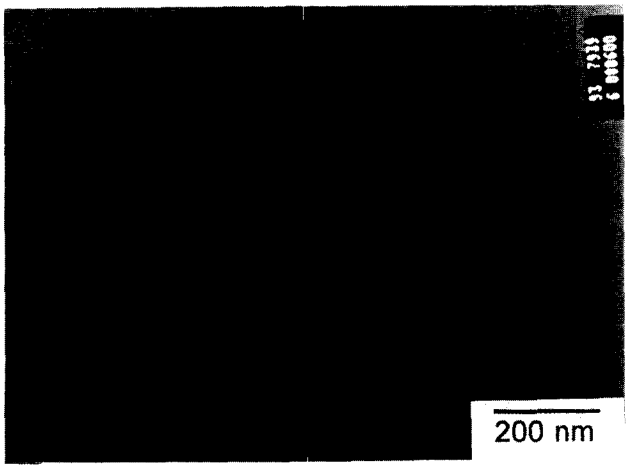


Fig. 3. Transmission electron (TEM) micrograph of ultra-rapidly quenched mullite glasses, showing a residual α-Al_2O_3 crystal embedded in a glassy matrix.

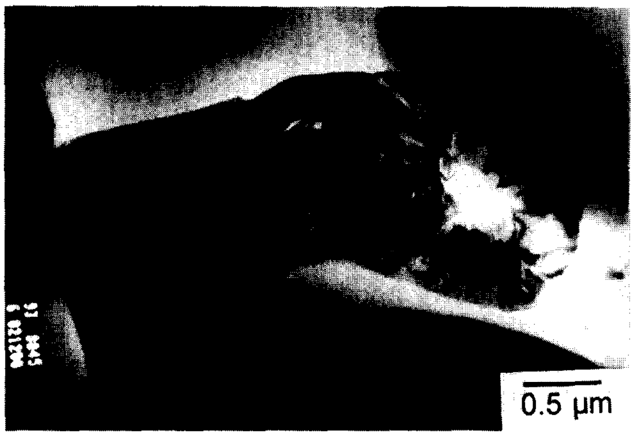


Fig. 4. Transmission electron micrograph of ultra-rapidly quenched mullite glass showing a large residual quartz crystal embedded in a glassy matrix.

The composition of the glass phase produced by plasma quenching as determined by EDX-analyses generally lies near 63 mol % Al_2O_3 and 37 mol % SiO_2 corresponding to a composition in between that of 3/2-mullite (60 mol % Al_2O_3) and of 2/1-mullite (66 mol % Al_2O_3). However, glass areas richer in SiO_2 are also detected. They are interpreted as to be due to unsufficient homogenization of the melt droplets during the short dwell time in the plasma flame. The fact that the bulk Al_2O_3 content of the plasma quenched powder is slightly higher than that of the starting material (74·5 wt% Al_2O_3 instead of 72 wt%) is attributed to a minor silica vaporization in the hot plasma flame.[5]

^{27}Al NMR spectra display broad signals near 2, 33, and 60 ppm and a sharp peak of higher intensity near 14 ppm (Fig. 5(a)). The broad 2, 33, and 60 ppm peaks are very similar to these described in some mullite precursors and in Al_2O_3-rich glasses in the system SiO_2–Al_2O_3.[6] They are assigned to octahedrally, pentahedrally, and tetra-

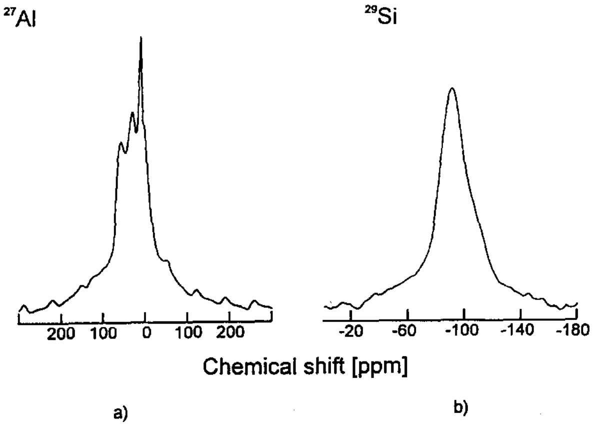


Fig. 5. Nuclear magnetic resonance (NMR) spectra of ultra-rapidly quenched mullite glass. (a) ^{27}Al; (b) ^{29}Si.

hedrally aluminium sites in the Al_2O_3-rich plasma-quenched glass, while the sharp and intense 14 ppm peak is due to the presence of α-Al_2O_3 (e.g. ref. 6). The broadness of ^{27}Al NMR-peaks associated with the glass phase show that the (Al O)-polyhedra may be distorted giving broadening by electric fields gradients or they may have a number of different environments. Though it is difficult to give quantitative approach of the relative abundance of the (Al O)-polyhedra in the glass, a predominance of (Al O)-pentahedra with respect to (Al O) octahedra and tetrahedra can be taken into account.

The ^{29}Si spectrum (Fig. 5(b)) shows a peak at –89·8 ppm and an upfield shoulder. The spectrum can be deconvoluted to show a peak at –89·3 ppm with 70% of the intensity and one at –104·8 with 23% of the intensity; the remaining 7% is a peak at –47·9 ppm. A slightly improved fit is found by fitting to four broad peaks with positions and intensities: –52·6 ppm (11%); –85·2 ppm (19%); –91·6 ppm (48%); –106·0 (22%). Thus about 22% of the Si occurs in a peak near –106 ppm with a width of 2300 Hz. This position is consistent with amorphous SiO_2 and the width indicates a variety of environments as often found in glasses, perhaps with contributions at more positive shifts from incorporation of Al. The main peak near –89 ppm is close to that in mullite itself. According to the studies of Engelhardt and Michel[7] and Mägi *et al.*[8] this is likely to arise from Si with a fully condensed oxygen network and perhaps surrounded by four Al cations; which fits well with the Al_2O_3-rich composition of the glassy phase. Again, the width of this peak (1900 Hz) indicates a variety of environments as often found in glassy materials. The peak near ≈50 ppm interestingly appears in the chemical shift region expected for silicon nitride or sialon which might form by high temperature reactions in the nitrogen plasma flame.

According to the ^{29}Si and ^{27}Al NMR studies the structural short-range-order of the (Si O)-tetrahedra, and of (Al O)-octahedra, -pentahedra and tetrahedra is very similar to these of metakaolinite, type I (polymer) mullite precursors and of melt quenched Al_2O_3-rich glasses of the system Al_2O_3–SiO_2 (see e.g. Schneider *et al.*[9]). The structural similarity of these materials also becomes evident by their crystallization behaviour. Differential thermal analysis (DTA) measurements carried out on corresponding powders all exhibit sharp and strong exotherms near 980°C which is associated with mullite crystallization in each case (Fig. 6). In a previous study on the constitution on non-crystalline mullite precursors it was suggested that the driving force of the 980°C reaction process is the dissappearence of (Al O)-pentahedra due to its sudden instability in this temperature range and subsequent crystallization either of mullite or γ-Al_2O_3.[9]

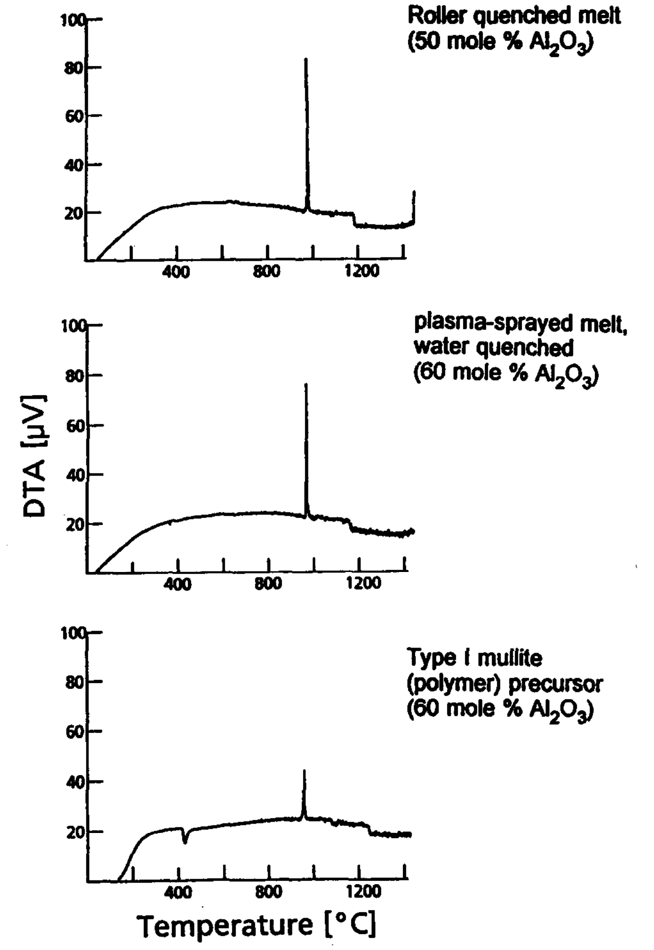


Fig. 6. Differential thermal analysis (DTA) curver of ultra-rapidly quenched mullite glass in comparison to type I (polymer) mullite precursor and roller-quenched aluminium silicate glasses.

It is an important result of the present study that mullite-type melt glasses can be produced under the extreme conditions of plasma spraying and subsequent water quenching, in spite of the extremely low viscosity of the melts.[10] However, glass formation is strongly influenced by particle size, which limits melting rate as well as quenching rate. Since the particles are melted in the plasma flame by propagation of a melting front from the outside to the inside of the particles[11] coarser grains cannot be completely melted in the plasma due to the low thermal conductivity (a few W/mK) of the material and the short dwell time in the plasma flame (about 1 ms[12]). On the other hand it is known from experiments of Gani and McPherson[3] that mullite formation by quenching melt droplets into water can be suppressed only if particle size remains below 19 μm. The size limit of glassy particles of ≈20 μm determined in our study agrees well with the observation of Gani and McPherson.

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