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Pressureless Sintered High-Strength Mullite from Commercial Powder

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High-strength monolithic mullite ceramics were prepared from commercial-grade power by carefully controlled processing of the powder followed by pressureless sintering at 1700 °C. Mullite powder was mechanically and chemically dispersed, ball milled, and screened prior to slip casting. Specimens were sintered to 97% of theoretical density under pressureless conditions. The furnace ramp and soak schedule was an important variable. Four-point flexural strengths of 250 MPa were achieved, exceeding literature values for pressureless sintering of Baikowski mullite powder.[a] Pore sizes were small and were not strength limiting. Griffith calculations suggest a critical flaw size of 20 µm, in good agreement with the maximum observed crystal size in the microstructure.

1. Introduction

EFFORTS to obtain a high-temperature oxidation-resistant matrix material for SiC fiber composites led to a processing study of mullite. Mullite has several properties in addition to inherent oxidation resistance that are valuable in ceramic composites. The strength of mullite, although low at room temperature, increases with temperature[1,2] to the point where mullite is stronger than commercial Si_3N_4 above 1200 °C.[3] The excellent thermal shock properties of mullite result in part from its low coefficient of thermal expansion. High-temperature strength is attributed to the needle-like interlocking "jigsaw" grain structure.[4] Thus, mullite has significant potential as an engineered ceramic, either as a monolithic structural ceramic or as the matrix for ceramic matrix fiber composites.[5,6]

Notwithstanding the fundamental advantages of mullite ceramics, the processing and densification of mullite powders are difficult tasks and are limited by the poor sintering behavior of mullite due to the presence of acicular morphology and the tendency for grain growth in systems with silica-rich stoichiometry. Numerous investigators have recently studied the mullite system[7-9] and have greatly enhanced the understanding of these materials and the technology of producing engineering-quality mullite ceramics.

Many of the studies in the literature have described methods for preparing mullite from sol-gel precursors or other chemical means and for hot pressing the compacts to full density. The goal of the present study was to determine an improved method for processing commercial mullite powder using slip casting and/or tape casting and to densify the green compacts by pressureless sintering. Ultimately, the authors plan to prepare fiber composites from commercial mullite powders, and a moderately high strength mullite matrix is required.

2. Experimental Procedure

2.1 *Powder Preparation*

After considerable trial and error experimentation, the material with optimum performance to date is processed according to the formulation given in Table 1. A casting slip was prepared from Baikowski mullite powder by mixing the constituents in a blender in the order given in the table. Darvan 821A,[b] an ammonium polyacrylate electrolyte dispersant, and glycerol,[c] an easily volatilized weak binder, were added, and the pH was adjusted to a value of 10 with ammonium hydroxide[d] to produce a slip with minimum viscosity. After a homogeneous mixture was obtained, the slip was ball milled for 96 hr in a polyethylene ball mill with alumina balls. Milling promoted the dispersion of the powders and also reduced the particle size of the mullite from a 2 µm average size to approximately 1 µm, as measured by standard sedimentation techniques.[e] Agglomerates remaining in the slip were removed by screening through 325 mesh. The resulting slip was homogeneous, and the viscosity was 250 to 350 cps as measured with a Brookfield viscometer.[f] Test pieces were prepared either by casting in a plaster mold or by drying the slip and pressing parts at 35 MPa.

3. Sintering and Mechanical Testing

The firing schedule for these materials consisted of a 30-min soak at 500 °C, 1-hr soaks at 1275, 1600, and 1700 °C. All

Table 1 Composition of Mullite Slip

Component	Composition wt.%	vol.%
Water	35.8	60.4
Mullite powder	59.5	31.7
D-821A, 10%	1.3	2.2
NH_4OH, concentrated	1.7	3.2
Glycerol	1.7	2.5

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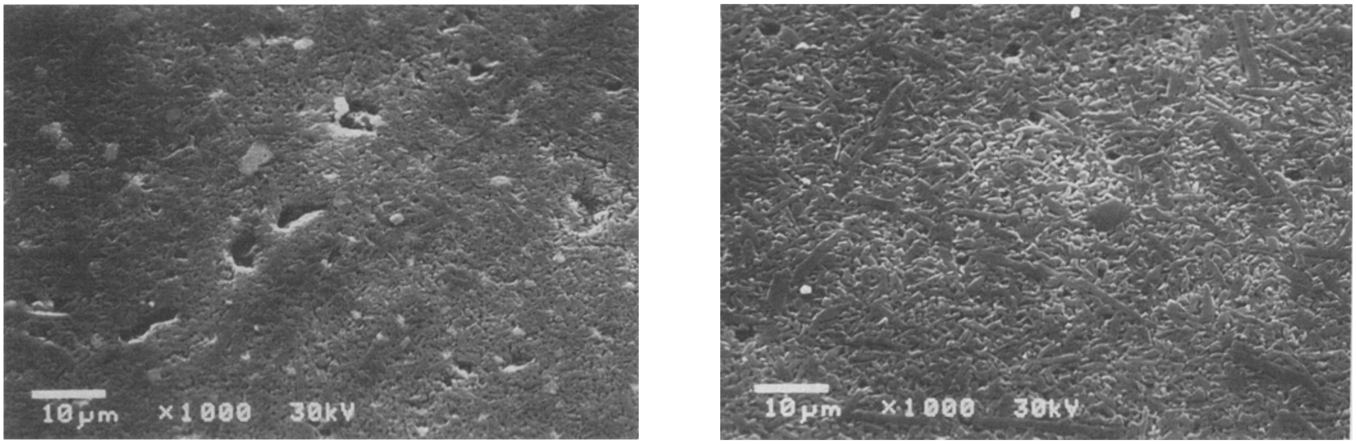

Fig. 1 Microstructure of pressureless sintered mullite. (**a**) Prepared from dry pressed granules. (**b**) Prepared by slip casting.

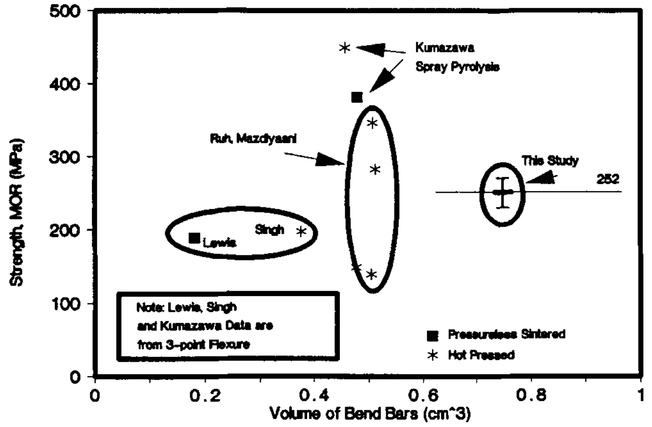

Fig. 2 Mullite strengths compared to product literature data[13,14].

soaks were reached at ramp rates of 850 °C/hr. Principal densification occurs within the 1600 °C soak period, and the final elimination of porosity occurs at 1700 °C. The soak at 1700 °C was kept to a minimum to avoid excessive grain growth. The flexural test specimens were diamond cut from sintered specimens. Edges of the test specimens were chamfered to avoid stress concentration. All sides of the specimens were SiC grit polished to 600 grit. The tensile side and the chamfered edges were diamond polished with a series of diamond pastes, the final polish was conducted with a 0.25-µm paste. Scanning electron microscope examination of surfaces prepared according to this procedure showed no polishing-related flaws larger than 1 µm. The mechanical behavior of the sintered mullite monoliths was characterized using a four-point bend fixture with a lower span of 1.9 cm and upper span of 0.64 cm. Crosshead speed was controlled at 0.005 cm/min, and the chart speed was set at 2.5 cm/min.

4. Discussion of Results

Careful control of the powder processing procedures was found to be critical to preparing high-strength mullite specimens. Generally, long ball milling times, secreening to remove agglomerates, and slip casting with a minimum of organic additives favored the preparation of superior materials. The results of pressureless sintering cycle studies were most interesting. Although the literature indicates that isothermal soaks in the 1250 to 1300 °C range are beneficial for mullite precursor (or amorphous) powders, the authors found that similar soaks were useful for Baikowski materials also. Furthermore, heating rate was an important variable. When specimens were heated at 400 °C/hr to the soak temperatures, poor densification occurred. The present 850 °C/hr rate has not been optimized, and slightly greater or lesser rates may offer further improvements.

The samples prepared by dry pressing the mullite powder were inferior in properties to the slip cast samples and had higher levels of porosity, as shown in Fig. 1, which compared dry pressed and slip cast microstructures. The dry pressed sample contained large pores and agglomerates compared to the more uniform and finer microstructure of the slip cast specimen. Only slip cast specimens will be discussed further.

The most notable result of this research is the achievement of 250-MPa flexural strengths for mullite specimens prepared from off-the-shelf commercial powder (Baikowski) without the use of hot pressing. This flexural strength is compared to other strengths reported in the literature in Fig. 2. The data for the present study are comprised of the average of ten specimens, and the error bar is the 95% confidence interval for the mean value. By comparison, the majority of strength data from other investigators are lower. Osendi *et al.*[10] fabricated mullite in a similar manner (Baikowski mullite, pressureless sintering), but densities were low and the finished material had flexural strengths of 191 MPa. The Osendi work is also subject to the criticism that the flexural data were from three-point rather than four-point flexure. Hot pressing and chemical preparation methods produce stronger materials, as expected.

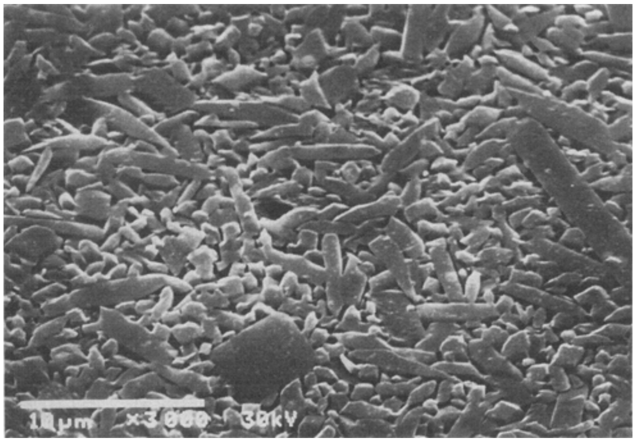

Fig. 3 High-magnification microstructure of slip cast mullite.

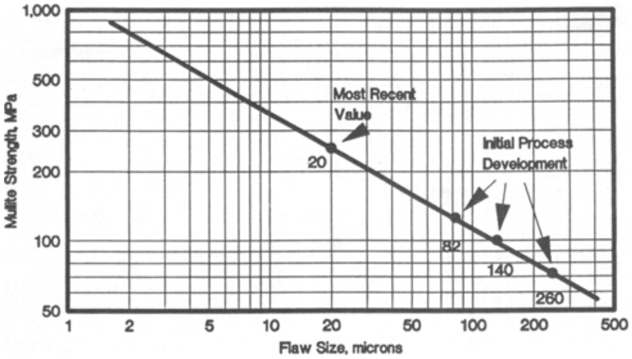

Fig. 4 Mullite processing improvements illustrated on strength/flaw size coordinates. The line is drawn from Eq 1 and strength values achieved from process improvements were placed on the line to illustrate corresponding flaw sizes.

Hot pressed mullite, with porosity of less than 1%, resulted in a strength of 202 MPa.[11] The volume of test bars is an important parameter for materials such as most ceramics, which have moderate or low Weibull modulus values. If failure-inducing flaws are randomly distributed throughout the ceramic, the probability of encountering a critical flaw at a low test load increases with increasing specimen volume. Thus, for specimens cut from the same material, larger volume test bars will fail at a lower average applied stress.

During the sintering studies, data not presented in this article showed that porosity was not the strength-limiting parameter for these materials. Samples with porosity in the range of 96 to 98% had identical strengths. An examination of the microstructure (Fig. 1b and a higher magnification photomicrograph in Fig. 3) illustrates the very fine character of the existing porosity for this 97% dense specimen. The morphology of the mullite crystals is quite acicular, and the crystal sizes range from 0.5 to 10 μm, although some crystals have grown to near 15 μm.

An important and useful technique in process research is the monitoring of flaw sizes calculated from strength data and the comparison of these values to observed microstructural detail. Given the properties of mullite ($E = 145$ GPa, $K_{IC} = 2.2$ MPa $\cdot$ $m^{0.5}$),[12] the surface energy per unit area is calculated as 13.1 J/m^2. Flaw size versus strength curves can subsequently be calculated from the Griffith equation for planar stress:

$$\sigma_f = \left[\frac{2E\gamma_o}{\pi c}\right]^{1/2} \qquad [1]$$

The flaw size calculated from the maximum mullite strength of 250 MPa is 25 μm. The photomicrograph in Fig. 3 illustrates the microstructure of the 250 MPa mullite. The crystal morphology is acicular, and crystals nearly 25 μm in size are visible. Of course, the sample area shown by the micrograph is small compared to the sample volume tested during flexure and the presence of a 25-μm critical flaw in the test volume seems reasonable. The observation of highly acicular crystals in these materials suggests the presence of a liquid phase at the grain boundaries.[5] More equiaxed grains of mullite are observed in some systems, such as sintered refractories, in which the glass phase is substantially absent. Evidently, the presence of a glass phase promotes transport processes, which result in growth of the mullite crystals along the *c*-axis. Similarly, glassy phases may be expected to promote exaggerated grain growth. Baikowski mullite powder is produced to a specification of 1% excess silica. Analysis of typical production material indicates a range of approximately 0.5 to 1.5% excess silica. Thus, during sintering of this powder, one anticipates the existence of a silica-rich glassy phase at the mullite grain boundaries.

The evolution of mullite strengths in this research program is illustrated in Fig. 4. Initial processing procedures produced material with large flaws generated by agglomerates and porosity, as shown in the photomicrographs of Fig. 1(a) and as represented by the low strengths of Fig. 4. Ultimately, it is the goal of the present research to increase strengths to 350 MPa, a value that will require flaw sizes of less than 10 μm. Achievement of this grain size under pressureless sintering for commercial powders will require the use of grain growth inhibitors or improved mullite stoichiometry.

5. Summary and Conclusions

High-density mullite ceramics can be prepared from commercial mullite powder by milling powders to approximately 1 μm average size, dispersing well in aqueous media, screening out very large agglomerates, slip casting in plaster molds, followed by pressureless sintering. Four-point flexural strengths of 250 MPa were achieved, which exceed literature values for commercial mullite. Porosity was reduced to 2 to 3% in these samples, and the maximum pore size, as observed in photomicrographs, was approximately 1 to 2 μm. Acicular mullite crystals were observed in the sintered microstructure, indicating the presence of a liquid grain boundary phase during sintering. Flaw size calculations based on the observed strength suggest a critical flaw size of 20 μm. The flaw size is consistent with the observed microstructure, which revealed that the flexural strength was limited by acicular crystal flaws rather than by porosity. Considerable opportunity exists to further improve the strength of these materials via grain growth inhibition and improved stoichiometry.

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Names and Addresses of Suppliers

[a] Mullite Powder
Baikowski International Corp.
1833B Crossbeam Dr.
Charlotte, NC 28217
704-357-3770

[b] Darvan 821A
R.T. Vanderbilt Co.
30 Winfield St.
Norwalk, CT 06855
203-853-1400

[c] Glycerol
Product G-33
Fisher Scientific Co.
711 Forbes Ave.
Pittsburgh, PA 15219
412-562-8300

[d] Ammonium hydroxide
Product A-669
Fisher Scientific Co.
711 Forbes Ave.
Pittsburgh, PA 15219
412-562-8300

[e] Sedigraph Particle Size Analyzer
Micromeritics Instrument Corp.
Micromeritics Dr.
Norcross, GA 30093-1877
404-662-3633

[f] Brookfield viscometer
LVT Spindle No. 1
Brookfield Engineering
240 Cushing St.
Stoughton, MA 02072
617-344-4310