Preparation, characterization and uses of mullite grain

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The properties were compared of grain formed at low temperature from a homogeneous mullite precursor gel, and grain formed from the manufactured material produced at high temperature by fusion or by sintering. A homogeneous precursor gel with the oxide stoichiometry of mullite was prepared by treating technical ethyl silicate with aluminium chlorohydrate, with or without dibutyltin oxide as hydrolysis/gelation catalyst. The gel was dried and heated for 5 h at 700° C to remove organic residues then ground to 8 μm nominal size to obtain a mullite precursor grain. Crystallites form even at this moderate temperature. Commercially produced fine mullite grain manufactured by fusion or by high temperature sintering was also ground to a give a grain of 8 μm nominal size to provide a comparative standard with well known material. Each of the three grain materials, homogeneous precursor gel, fused mullite and sintered mullite, each ground to 8 μm nominal size, representative of the 'fines' fraction of a grain mix to be used in producing refractory shapes, was made into compacts which were sintered, and, when cold, tested for compressive and bend strength. Materials of this size were chosen for comparison because of their significance in applications where properties at temperature are important. The precursor gel compacts were 95% crystalline mullite and reached 86% of theoretical density. At 1500° C, heated in a 90 deg min^{-1} schedule, they had strength comparable to sintered mullite; both materials were much stronger than fused mullite. The results show that sintering procedure has a profound effect on strength, and indicated that in the absence of binder, fused mullite is less reactive than sintered mullite. Some properties of refractory shapes and bricks made from the sintered or fused mullite grain are discussed and some uses in refractory shapes are considered.

1. Introduction

Mullite, ideally $3Al_2O_3 \cdot 2SiO_2$, is a high-melting crystalline aluminosilicate material which has long been used in heavy-duty refractories. Our extensive investigations into its formation [1, 2 and references therein] prompt us to report more specifically on mullite grain, which is important in being the form of this material which finds wide industrial application. Thus a clear comparison can be made between the characteristics of materials which are available commercially and grain produced by the sol–gel route. The commercial manufacture [3] is by fusion or by sintering at high temperature. Mullite precursor materials may also be obtained [1] by sol–gel procedures such as precipitation processes in which hydrous silica is deposited on hydrous alumina (or vice versa), or from gels having the oxide stoichiometry required for mullite. These precursor materials convert to mullite on firing, the temperature necessary for conversion being

much lower than the high temperature required to form mullite in the commercial manufacture by sintering or by fusion. When the mullite precursor material is a gel formed from a technical ethyl silicate (silica equivalent 40% w/w) and an aluminium chloride species, homogeneous gels give the best yield of mullite and require the lowest conversion temperature. Crystallites form at a temperature as low as 690° C, which is significantly lower than previously reported conversion temperatures [1]. Non-homogeneous precursor gels give a poor yield of mullite [1]. The homogeneous mullite precursor gels are obtained when the gel is formed by heat or via an organotin hydrolysis/gelation catalyst (e.g. dibutyltin oxide). A comparison between grain formed from a homogeneous mullite precursor gel and grain obtained from the material formed at the high temperature required in the manufacture of fused mullite or sintered mullite is therefore of interest.

The present paper describes the preparation of fine

SINTER ROUTE

Blend of refined → Briquette and stack → Sinter at 1700° C in high → Cool, crush, → SINTERED MULLITE GRAIN
raw materials   onto kiln car   temperature tunnel kiln   classify and mill

FUSION ROUTE

Blend of refined → Feed → Fuse at 2000° C in → Cool, crush, → FUSED MULLITE GRAIN
raw materials   an electric arc furnace   classify, and mill

PRECURSOR GEL ROUTE

Ethyl silicate and → co-hydrolysis → Gelation → Mullite → Dry, sinter at 700° C → MULLITE
aluminium chlorohydrate   precursor gel   crush and mill   PRECURSOR GRAIN

Figure 1 Flow diagrams for the production of mullite materials.

grains (average particle size $\sim 8 \mu$m) from a mullite precursor gel which is homogeneous, obtained from technical ethyl silicate and aluminium chlorohydrate and gives the properties of these grains and the properties of the fine grain obtained from the commercially available sintered mullite and fused mullite materials. Fig. 1 is a flow sheet showing the preparation of the various grains of 8μm average size. In a refractory body, the fine grains, grain size 8μm being typical, help to form the 'matrix' which binds the coarser grains and is crucial in determining the properties of a refractory body. Compacts were prepared from the grain obtained from the precursor gel, and also from the fine sintered mullite material and from the fine fused mullite material, each after grinding to a nominal 8μm gain size, to evaluate their behaviour during sintering, which defines the properties of refractory shapes manufactured from mullite grain. Some properties of refractory bricks made from the fused mullite grain and from the sintered mullite grain are also described and the uses of mullite grain in manufacturing refractory shapes are summarized.

2. Experimental details
2.1. Materials preparation
A homogeneous precursor gel with oxide stoichiometry in the mullite range was prepared as described previously [1, 2, 4] from technical ethyl silicate, aluminium chlorohydrate, ethanol, water and dibutylin oxide, then dried. The dried gel was heated to 700° C for 5 h in a flowing oxygen atmosphere to remove organic material and initiate the crystallization process [1, 5], then dry-milled in a tungsten carbide Fritsch Pulversiette for 0.5, 1.0, and 1.5 h in three separate batches. Each batch of milled grain and a sample of the unmilled precursor was compacted by uniaxial compression in a cavity of dimensions 26 mm height × 4.5 mm radius. Four compaction pressures were used: 75, 135, 155 and 310 MPa. Some compacts were sintered in air or in an inert atmosphere in an electrically heated furnace for 1, 2, 5, and 20 h at 1500° C at a heating rate of 9 deg min^{-1}. Four specimens were used for each firing, one specimen being removed after 1, 2, 5, or 20 h. Other compacts prepared by milling for 1 h and compacting at 310 MPa were sintered at 1300, 1400, or 1500° C at heating rates of 9 or 90 deg min^{-1}. Two samples of heat-treated precursor grain, milled for 1 h but uncompacted, were heated for 2 h at 1300 and 1500° C. All firing schedules were carried out in duplicate at least.

A homogeneous precursor gel with the oxide stoichiometry in the mullite range was prepared as previously described [1, 6] from aluminium chlorohydrate, technical ethyl silicate, ethanol and water. A precursor solution was made by adding an aqueous solution of aluminium chlorohydrate to a solution of technical ethyl silicate in ethanol. The resulting precursor solution (pH = 4.7) was held at 60° C until gelation occurred ($\sim$ 40 min). After drying and milling, the gel was fired as previously described [1, 6] to form crystalline mullite.

The production of fused mullite grain and sintered mullite grain has been described previously [3]. The fine sintered mullite grain and the fine fused mullite grain were each milled to a particle size as close as possible to that obtained by milling the heat-treated precursor gel. Compacts were prepared from the milled grains by uniaxial compaction at 310 MPa and sintered at 1300, 1400 and 1500° C for 5 h at heating rates of 9 or 90 deg min^{-1}.

2.2. Analytical procedures
The particle size of milled materials was determined with a Fisher sub-sieve analyser. The density of both green and fired components was determined by weighing, then measuring the dimensions to ± 0.5 mm using a micrometer. After firing, compacts obtained by processing the pre-heated precursor gel were examined microscopically (optical and SEM with EDAX analysis as appropriate). A Phillips PW1033 X-ray diffractometer was used to obtain X-ray diffraction data. The percentage crystalline material was estimated [1, 5] from the peak height and width of the major diffraction peaks for the particular material. Specimens for optical microscopy were mounted in epoxy resin and, after grinding using coarse and fine diamond polishing laps, were polished on graded (6μm → 1μm) diamond polishing cloths. Specimens for electron microscopy were gold-shadowed. Grain size was determined with a Zeiss particle size analyser and pore size was determined by a Quantimet 726 image analysing computer. Internal grain structure was observed by breaking the compacts and then examining the broken compacts on a Phillips 505 scanning electron microscope. A further check on grain size was obtained from at least ten fractographs taken from the fracture surface.

The texture of the commercially available fine fused mullite and fine sintered mullite was assessed by optical microscopy (thin sections viewed using polarized

TABLE I Properties of materials from which fine grains having oxide stoichiometry required for mullite, $3Al_2O_3 \cdot 2SiO_2$ were made

	Grain for heat-treated homogeneous precursor gel	"Fused" grain (as manufactured)	"Sintered" grain (as manufactured)
Minor impurity	~1% Sn	~0.25% Na	~1.7%, K, Fe, Ca, Mg
Apparent porosity	3%	0.5%	2.5%
Glass phase	–	3.2%	11.2%
Phases present	At least 95% conversion to crystalline mullite and a small amount of cristobalite on heating to 1500°C	Crystalline mullite 95.7%	Corundum 7.9% crystalline mullite 80.9%
Structure	Network of laths	large needle-like crystals	Interlocking network of laths
Grain size	~8 μm	~8 μm	8 μm
BET	42 m² g⁻¹	–	–

light). The diametral compression disc test procedure [7] was used to determine the strength of compacts.

3. Results and discussion

Table I gives the properties of grain formed by milling for 1 h the pre-heated precursor gel obtained using dibutyltin oxide as hydrolysis and gelation catalyst, together with the properties of the commercially available fine fused mullite grain material and the fine sintered mullite grain material. No attempts were made to optimize the particle size distribution of the grain boundary compacted. No binder (fugitive or permanent) was used in preparing the compacts as these could influence densification and grain growth.

The compression disc test used [7] measures the tensile strength in compressive loading mode. In this test, a biaxial stress state is produced within the specimen. Fracture initiates internally rather than at a free surface. Multiplying by a factor of 2.5 converts diametral compression strength to bending flexure strength for these materials [7]. This is a convenient method for determining the strength of brittle materials

prepared from fine grains because the specimen is easy to prepare and to load.

3.1. Grain from the pre-heated mullite precursor gel

X-ray diffraction data for grain from the pre-heated mullite precursor gel prepared using dibutyltin oxide as hydrolysis/gelation catalyst, milled for one hour and fired at 1500°C for 20 h showed (from peak height-to-width ratio measurements) that more than 95% conversion to mullite is obtained. Firing the preheated and milled gel to 1300°C gives an equally high conversion to crystalline mullite. EDAX examination of the precursor gel after firing showed the presence of tin on the surface of the grain. No evidence of a crystalline tin(IV) species was obtained from the X-ray data, confirming our previously reported observations [1, 2, 4]. Table II gives X-ray diffraction data for grain obtained when mullite precursor gel formed by heat is fired, together with X-ray diffraction data for the fused mullite grain, showing a practically quantitative conversion of the precursor gel to mullite.

TABLE II Comparison of X-ray diffraction of mullite products from sol-gel and fused materials

| 2θ	sol-gel d-spacing	RI (%)	2θ	fused d-spacing	RI (%)
16.5	5.3679	48	16.3	5.4333	62
26.0	3.4241	100	25.9	3.4371	100
31.0	2.8823	15	30.8	2.9005	26
33.5	2.6727	28	33.0	2.7120	42
35.5	2.5266	39	35.0	2.5615	33
37.0	2.4275	9	36.8	2.4402	9
39.2	2.2962	15	39.0	2.3075	18
41.0	2.1994	50	40.6	2.2202	35
42.7	2.1157	20	42.5	2.1252	15
48.5	1.8754	4	47.8	1.9012	4
49.5	1.8398	11	49.0	1.8574	9
54.0	1.6966	13	53.5	1.7113	11
55.5	1.6543	4	57.5	1.6014	6
57.8	1.5938	13	58.0	1.5888	4
60.7	1.5244	33	60.5	1.5290	36
63.7	1.4597	7	63.5	1.4638	7
64.7	1.4395	15	64.5	1.4435	18
66.5	1.4048	4	65.5	1.4238	7
67.5	1.3864	4	66.0	1.4142	5
69.7	1.3479	2	69.5	1.3513	4
70.5	1.3346	9	70.3	1.3379	16
74.2	1.2769	11	74.0	1.2799	11
75.2	1.2624	9	74.8	1.2682	9
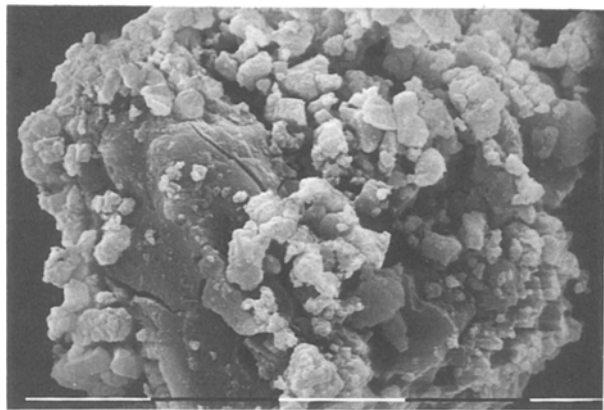
Figure 2 Particle size distribution in pre-heated precursor gel after milling for 0.5 h (bar = 10 μm).

The non-homogeneous gel formed [1, 6] at pH = 7 or 8 gave a low conversion to mullite on firing.

Crystallites form in the mullite precursor gel at a temperature as low as 690° C, a conversion to crystalline mullite of more than 95% being obtained at 1300° C. A gel having the oxide stoichiometry of mullite, prepared from technical ethyl silicate and aluminium chlorohydrate–polyol complex also shows [8] an equally high conversion to mullite at 1300° C. These observations agree with the tentative diagram proposed by Stacey [9] from data obtained by Espie and Vickerman [10] for the intermediate phase systems occurring during the heating of silica–alumina systems formed by sol–gel procedures. For comparison, a mullite precursor powder prepared [11] by precipitation of the oxides was completely converted to crystalline mullite on heating to 1250° C, but remained amorphous after heating for 4 h at 1150° C. Homogeneous gels prepared [12] from organoaluminosiloxanes such as $Al(Oi–Pr)_2OSiMe_3$, gave aluminosilicate glasses by thermal treatment at 900° C and above 1000° C gave optically transparent glass ceramics by crystallization of mullite in an amorphous silica network.

Independent of the method of preparation of the gel, all material obtained from the pre-heated homogeneous precursor gel crystallized after firing to form a regular mullite with the 3:2 alumina:silica molar ratio and an X-ray diffraction pattern typical of the orthorhombic crystalline structure. The strongest diffraction line (210) corresponds to the most densely packed family of planes in the orthorhombic lattice and appears at the initiation of crystallization; subsequent growth parallel to (210) increases order to a stage where (121) reflections are next observed as crystallization proceeds. Despite this progressive crystallization, when dibutyltin oxide was used as hydrolysis/gelation catalyst, amorphous material existed even after 20 h at 1500° C, so the progress of

crystallization is hindered (a) at low temperatures because there is insufficient thermal energy to maintain growth as diffusion distances increase, and (b) at higher temperatures where competitive and selective grain growth and volume changes due to previous loss of volatiles result in the creation of porous structures in which amorphous material is trapped. Crystalline phases other than mullite were formed; these were silica-rich and most showed a major diffraction line of cristobalite (4.1 Å). Other lines not clearly identified on firing at 1300° C (4.067 Å) and on firing at 1500° C (4.055 Å) were also probably cristobalite. Interestingly, the proportion of cristobalite decreased with increased firing temperature, showing that silica reacted with alumina to form mullite from both the amorphous state and previously crystallized cristobalite.

Fig. 2 shows the particle size distribution in the pre-heated precursor gel (prepared using dibutyltin oxide as hydrolysis/gelation catalyst) after milling for 0.5 h. There are large irregularly shaped particles to which the smaller particles are attached. During milling, the smaller particles are removed from the surface of the larger particles and the larger particles are fractured to produce smaller particles. The material shown in Fig. 2 had a BET surface area of $42 \, m^2 g^{-1}$. If the material comprised solid particle spheres, this would correspond to a particle size of 0.02 μm. However, the particle size is of the order of 8 μm so the particles must either be porous or irregularly shaped. Table III shows the effect of compaction pressure on the density of the compacts. The results show that, at a low compaction pressure, increasing the milling time gives a large increase in the density of the compact; this is much less significant at high compaction pressure.

Table IV shows the effect of sintering time on the density of sintered compacts, at a given temperature and sintering time. The effect of time and temperature on the density of sintered compacts prepared from material milled for 1 h and compacted at 310 MPa is given in Table V. The influence of temperature and heating rate on the grain size, pore size, and density of sintered compacts prepared from material compacted at 310 MPa after milling for 1 h is given in Table VI. Fig. 3 is an optical micrograph showing the texture of a compact prepared from pre-heated precursor gel material milled for 1 h, compacted at 310 MPa, then sintered for 5 h at 1500° C, the heating rate being 90 deg min^{-1}. The grain size and pore size are shown in Fig. 4. Optical and SEM micrographs of other compacts are given in [5]. The average pore size increased with increased heating rate at all sintering temperatures and sintering times, although the total pore volume decreased (i.e. density increased). The

TABLE III Density of "green" compacts

Compaction pressure (MPa)	Density (kg m^{-3}) at milling time				Density increase
	0 h	0.5 h	1.0 h	1.5 h	
75	–	1350	1590	1680	
135	1310	1500	1700	1780	470 (36 %)
155	1480	1670	1740	1800	320 (28 %)
310	1620	1780	1790	1820	200 (12 %)

TABLE IV Effect of time of sintering on density of sintered compacts (compaction pressure 310 MPa; heating rate 9 deg min^{-1}; to temperature of 1500° C). The figures in brackets are the density increase

Sintering time (h)	Density (kg m^{-3}) at milling time			
	0 h	0.5 h	1.0 h	1.5 h
1	1830 (210)	2280 (500)	2330 (540)	2430 (610)
2	1880 (260)	2290 (510)	2350 (560)	2430 (610)
5	1900 (280)	2350 (570)	2350 (560)	2430 (650)
20	1970 (350)	2370 (590)	2440 (610)	2476 (650)

activation energy for densification [1, 4] is between 12 and 42 kJ mol^{-1}. From optical observation of the closure of fissures (produced during the pre-treatment) during fast firing it is clear that this was mainly responsible for the higher bulk densities; in this context the adverse phenomenon of increased micropore size was insignificant. As expected, increasing time at temperature favoured grain growth. The results show that the rapid heating rate of 90 deg min^{-1} gives higher density after sintering at higher temperature, also that density increases with the temperature of sintering. Given the right choice of conditions, a sintered compact which is at least 95% converted to crystalline mullite, with a density of 86% of the density of natural mullite (taken as 3156 kg m^{-3} [13]) may be obtained from the homogeneous mullite precursor gel material. Based on the above observations, the sintering conditions of 5 h at 1500° C and a heating rate of 90 deg min^{-1} were chosen in determining the strength of compacts prepared from the milled homogeneous precursor gel. The results are given in Table VII.

3.2. Grain from sintered mullite and fused mullite

3.2.1. Manufacture
"Fused" mullite grain is manufactured by fusion in an electric furnace to produce ingots which are allowed to cool and then crushed and graded. Crystals in fused mullite can be several centimetres long and more than 1 mm wide. Fused mullite grain down to 1.5 mm size can often be single crystal and grain smaller than this must be virtually all single crystal particles (Fig. 5). These crystals are, however, not perfect. The grain t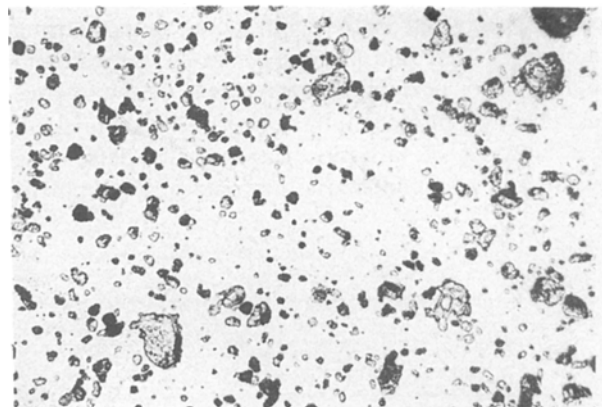ends to be block-shaped averaging between 30 and 60 μm which pack well. The fused mullite material [3] contains over 95% crystalline mullite, with a small amount of corundum and glass. (see Table I).

"Sintered" mullite grain is very different. The best material is made by sintering at high temperature in a tunnel kiln, then crushing and grading the resulting sintered material. In large sintered mullite grain, the mullite crystals are in the form of an interlocking network of laths; the crystallite size varying over a wide range, between 500 and 5–10 μm, averaging between 30 and 60 μm. The alumina crystallizes in small colonies, usually clustered round a pore. The glass pockets are only a few microns in size between the crystals. This structure (Fig. 6) results in a grain which crushes to give a significant proportion of acicular particles from the conchoidal fracture and they tend to be flaky. All grains larger than 100 μm contain a number of mullite crystallites, some of which were large. Milling the grain to an average particle size of 8 μm destroys the arrangement of glass, crystalline mullite and crystalline alumina. The sintered mullite grain [3] contains ~80% crystalline mullite, together with corundum (~8%) and glass (~11%). The mullite crystals are well-developed small needles which interlock. A complete reaction to give mullite crystals would not be expected because the rate of diffusion between the reactants is usually insufficient [12]. In contrast, the grain obtained by sintering a pre-heated mullite precursor gel contains over 95% crystalline mullite, as does the fused mullite material.

3.2.2. Mullite bricks and refractory shapes
Mullite has much to recommend it as a material for manufacturing refractories and ceramics. It is refractory to 1800° C; compared with the alternatives
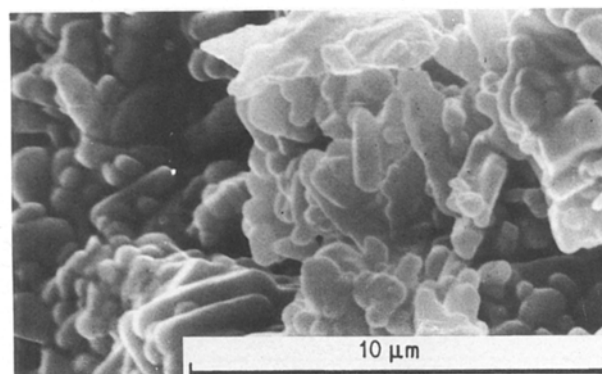

Figure 3 Optical photomicrograph of compact sintered at 1500° C for 5 h, heating rate 90 deg min^{-1}, compacted at 310 MPa. Density 83.5% of theoretical (magnification × 236).

Figure 4 SEM micrograph of compact prepared from powder milled for 1 h, compacted at 310 MPa and sintered 1500° C for 5 h, heating rate of 90 deg min^{-1} (bar = 10 micron).
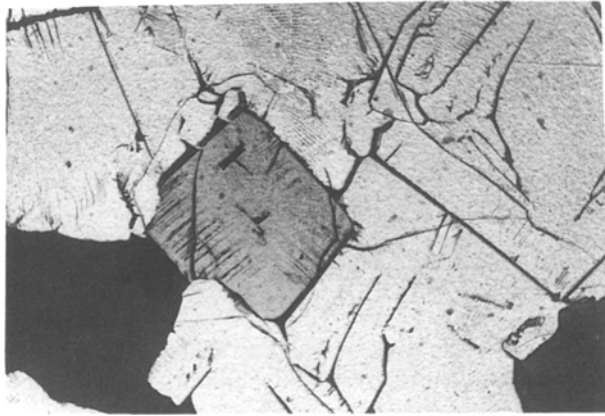
Figure 5 "Fused" mullite grain: a thin section viewed using polarized light (magnification × 32).

Figure 6 "Sintered" mullite grain: a thin section viewed using polarized light (magnification × 32), showing the interlocking network of mullite crystals and clusters of alumina crystals.

alumina, magnesia, silica and zirconia, it goes through no disruptive phase changes, it has a remarkably low thermal expansion which is reversible, a low thermal conductivity and a good resistance to molten metals, slags, glass batch materials and the like. It has to be synthesized commercially because no adequate mineral deposit exists. Two processes are used, electric arc fusion and high temperature sintering, to give fused and sintered mullite respectively. The best sintered mullite is made by sintering in a tunnel kiln.

The two materials each exhibit the good features of mullite in general, but each has its own particular merits, which are related to their microstructure. The massive crystal structure of fused mullite leads to particularly good high temperature creep resistance, while the interlocking network of small crystallites in sintered mullite confers a high hot modulus of rupture. Bricks and refractory shapes made from mullite grain generally show good resistance to spalling, withstanding the shock of heating and cooling exceptionally well and resistant to slag erosion. Examples of shapes made from mullite grain are burner quarls, element carriers, crucibles and high duty casting pit refractories. Conventional methods (e.g. hand ramming, slip casting, uniaxial or isostatic pressing) are used. Bricks may be made [14] by dry and semi-dry pressing. Mullite grain is particularly suitable for use in the ethyl silicate bonding process. For instance, large single piece well blocks for ladles fitted with a sliding gate system, to be used in steel casting, may be made [15] from ethyl silicate-bonded sintered mullite grain (coarse fraction) plus calcined alumina grain ("fines" fraction).

3.3. Sintering behaviour of mullite grains
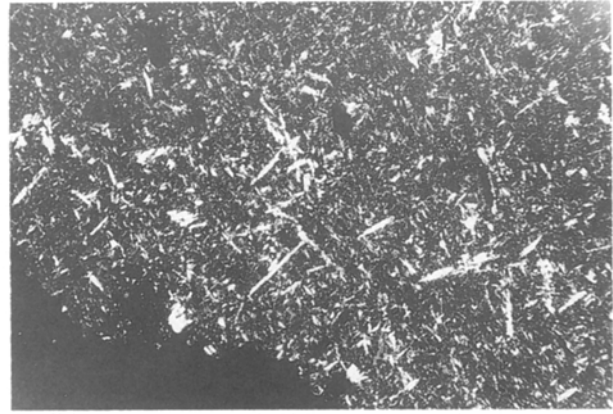
Mullite is not an easy material to sinter [16]. A fast heating rate is desirable and the molar ratio Al_2O_3: SiO_2 is critical. Compositions high in alumina show Al_2O_3 present as corundum, To evaluate the sintering behaviour of mullite grains, the strength of sintered compacts prepared from the various grains, each milled to an average particle size of 8 μm was determined.

Details of the preparation and sintering, together with the strength after firing, are given in Table VII. For compacts prepared from the fine sintered mullite grain milled to an averaged particle size of 8 μm, the maximum strength is obtained at 1500° C at a heating rate of 90 deg min^{-1}. This could be due to crystallization of glass and grain growth together with the elimination of defects. Our observation that maximum strength is obtained at a rapid heating rate agrees with previous work [16]. Comparable compacts prepared from fused mullite grain are generally weaker when fired up to 1500° C.

The value of 274 MPa obtained for the bending flexure strength of compacts prepared from the commercially available fine sintered mullite grain after milling can be compared with the value [17] of 319 MPa for the bending flexure strength of sintered mullite bars ground longitudinally and 259 MPa for the bending flexure strength of the same bars ground transversely, also with the value of ~ 200 MPa given [18] for the strength of mullite ceramics. The results given in Table VII show that the sintered mullite grain, provided it is sufficiently fine, gives good development of strength in refractory shapes during sintering. This could be due to grain growth and elimination of defects. Reinforcement of the viscous glass phase in sintered mullite material by interlocking of a network of lath-like, substantially defect-free crystals can also contribute to strength development

TABLE V The effect of time and temperature on the density of sintered compacts (compaction pressure 310 MPa; heating rate 9 deg min^{-1}; temperature 1500° C). The figures in brackets are the density increase.

Time at temperature (h)	Density (kg m^{-3}) at temperature		
	1300° C	1400° C	1500° C
1	2090 (300)	2140 (350)	2330 (540)
2	2140 (350)	2190 (400)	2350 (560)
5	2150 (360)	2230 (440)	2350 (560)
20	2200 (410)	2280 (490)	2440 (580)

TABLE VI Grain size, pore size and density of sintered compacts (compaction pressure 310 MPa; milling time 1 h, 5 h at temperature). The figures in brackets are the density increase.

Heating rate to temperature (deg min^{-1})	Temperature (° C)	Average grain size (μm)	Average pore size (μm)	Density (kg m^{-3})
9	1300	1.38	0.96	2150 (360)
9	1400	0.47	2.45	2220 (430)
9	1500	0.86	1.71	2490 (700)
90	1300	0.47	2.46	2230 (440)
90	1400	–	–	2350 (560)
90	1500	0.61	2.56	2720 (930)

during sintering. This interlocking of crystals explains [19] the strength of mullite refractory bodies.

Fig. 5 and the data given in Table I show that the the fused mullite grain contains large crystals. The size of the crystals, and the absence of a significant amount of glass, explains the low development of strength in compacts made from fine fused mullite grain, milled to 8 μm nominal size. To obtain strength development in refractory bodies made from fused mullite grain without a binder, the sintering temperature must be at least 1700° C. The fused mullite grain is less reactive during sintering than the sintered mullite grain.

The value of 225 MPa obtained for the bending flexure strength of compacts prepared from the homogeneous mullite precursor gel milled to 8 μm nominal size can be compared with the value of $\sim$200 MPa given [18] for the strength of mullite ceramics. It is interesting to note that a rapid heating rate was used and that the rapid heating rate gives higher density after sintering. A high conversion to crystalline mullite, like that found in mullite prepared by fusion, together with a bending flexure strength similar to that found for compacts made from mullite prepared by high temperature sintering, are obtained in compacts made from the homogeneous precursor gel milled to 8 μm nominal size. These values may be compared with the values of 117 MPa at 95% density and 152 MPa at 98% density given [20] for the bending flexure strength of bars made from a mullite precursor powder obtained by a precipitation process, milled to a particle size of 4 μm and fired at $\sim$1700° C for 1 h after uniaxial compression at 155 MPa, using a polybutyl methacrylate fugitive binder.

The cold strength of sintered compacts prepared from fused or sintered mullite, average size 8 μm, relates to properties at temperature because the sintering of the matrix of a brick or refractory shape is much influenced by the finer-sized material. The inference from this work that fused mullite will generally require firing to a significantly higher temperature than sintered mullite to optimize its properties has some foundation in practice, because to obtain strength development in refractory bodies made from fused mullite grain without a binder the sintering temperature must be at least 1700° C.

4. Conclusions

(i) Homogeneous precursor gels with the oxide stoichiometry required for mullite, prepared from technical ethyl silicate and aluminium chlorohydrate with or without dibutyltin oxide as hydrolysis/gelation catalyst, give good conversion to mullite on firing.

(ii) A mullite precursor grain may be prepared from the precursor gel by firing to 700° C to remove organic material and initiate crystallization, then grinding to an average particle size of 8 μm.

(iii) In compacts made from the mullite precursor grain, a fast firing rate (90 deg min^{-1}) to 1500° C increases density, giving small grain size but comparatively large micropores.

(iv) With the right choice of conditions, compacts having at best 95% conversion to crystalline mullite and 86% of the true density of mullite can be prepared from grain made from the homogeneous precursor gel.

(v) The fused mullite grain and grain made from the

TABLE VII Diametral compression strength and bending flexural strength of compacts prepared from sintered or fused mullite grain or mullite precursor grain, each milled to 8 μm nominal size, after sintering for 5 h at temperature. Compaction pressure was 310 MPa (SM = sintered mullite, FM = fused mullite, PG = precursor gel).

Grain type	Temperature (° C)	Heating rate (min^{-1})	Diametrical compression strength (MPa)	Bending flexure strength (MPa)
SM	1300	9	3	8
SM	1400	9	10	25
SM	1500	9	15	38
SM	1300	90	15	38
SM	1400	90	16	40
SM	1500	90	109	274
FM	1300	9	2	5
FM	1400	9	3	8
FM	1500	9	4	10
FM	1300	90	1	3
FM	1400	90	1	3
FM	1500	90	4	10
PG	1500	90	90	225

homogeneous mullite precursor gel by sintering at 1300° C or higher each contain at least 95% crystalline mullite.

(vi) The properties of fine sintered mullite grain and fine fused mullite grain show that during sintering fused mullite grain is less reactive than sintered mullite grain and that sintered mullite grain gives good development of strength during sintering.

(vii) Compacts made from mullite precursor grain, or from the fine sintered mullite grain, each ground to 8 μm nominal size, fired at a heating rate of 90 deg min^{-1} to 1500° C for 5 h, have similar bending flexure strength.

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