Diphasic mullite gel pressed at 1.5 GPa: Mechanical properties and microstructure of ceramics

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Mullite gels containing 72–85 wt% Al_2O_3 were prepared by mixing commercial boehmite and silica sols and gelled by heating. Powdered gels were either dried at 60 °C or calcined at 550 °C, and cold isostatically pressed under 0.5, 1.0 or 1.5 GPa. The effect of pressure is greater for the calcined gels than for the dried gels. The bulk density and room-temperature flexural strength of ceramics increased with increasing compacting pressure, while the fracture toughness is independent of the pressure. Mullite containing 75 wt% Al_2O_3 and sintered at 1500 °C for 3 h has a density which is about 99% of the theoretical density, a flexural strength of 523 ± 40 MPa and a fracture toughness of 3.5 MPa $m^{1/2}$.

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1. Introduction

Mullite ceramics are technologically attractive materials [1–3] because of their excellent mechanical, thermal, optical and chemical properties. Dense mullite and mullite composites have been studied for many different applications.

It is well known [4–8] that diphasic mullite gel precursors can be substantially densified starting at about 1200 °C and are subsequently transformed to crystalline mullite ceramics at temperatures of 1300–1350 °C. In spite of this advantage, direct transformation of gel to ceramics is not commonly used in large-scale technology because of the large volume change. In order to avoid large shrinkage the gel precursor is first calcined at mullitization temperatures (usually greater than 1250 °C) and then applied through classical approaches [9–13] such as milling pressing and sintering at temperatures over 1600 °C. Thus the material is twice sintered, first as grains, and then as a green body.

The purpose of this investigation was to take advantage of the low temperature and higher rate of direct sintering of the diphasic gels of mullite composition to produce mullite ceramics, and simultaneously to reduce the disadvantage of large shrinkage by using a high cold-isostatic-pressing (CIP) pressures (0.5, 1.0 and 1.5 GPa).

2. Experimental procedure

2.1. Sample preparation

Diphasic gels in the Al_2O_3–SiO_2 system containing 72–85 wt% Al_2O_3 were prepared using commercial boehmite (Pural, Condea; particle size, about 10 nm) and silica (Tosil, CZ; size, about 12 nm) sols. The silica sol was ammonia stabilized, even though it contained approximately 0.045 wt% Na_2O. The details of the method of preparation have been documented elsewhere [11]. The gels were dried at 60 °C and milled (less than 60 μm) using an agate mortar and pestle. About half of every powdered gel sample was calcined at 550 °C for 1 h. Both dried and calcined types of powder were die pressed (4 mm × 5 mm × 40 mm) at 150 MPa and subsequently subjected to CIP at 0.5, 1.0 on 1.5 GPa [12]. Green bodies formed from the dried gel were calcined at 550 °C for 1 h. Ten test bars of each gel composition were sintered for 3 h at 1350 and 1500 °C, respectively.

2.2. Characterization

The bulk density was determined by the mass and dimensions of the sample with error below ± 1.2%. The lattice parameters of mullite were measured with a Stoe Stadi P transmitting diffractometer using Co $K\alpha_1$ radiation. Calculations were carried out by means of the program equipment of the diffractometer. The compositions of the mullite solid solution were obtained from the lattice parameters of sintered bodies and from the known function of lattice parameters versus composition [13, 14]. The flexural strength was measured at room temperature (RT) in three-point bending on a 30 mm span using 4 mm × 5 mm × 40 mm test bars. The microstructure of sintered samples was examined by scanning electron microscopy (SEM) with a JEOL 840. Two types of surface were prepared for SEM observation: firstly the fracture surface (without finishing) created before sintering; secondly surfaces created after sintering and finished by polishing and etching with 5% HF for 5 min and/or etching, with boiling 50% NaOH solution for 5 min.

The fracture toughness was determined by an indentation method using the equation [15]

$$K_{\mathrm{Ic}} = 0.0899\left(\frac{HP}{4a}\right)^{1/2} \qquad (1)$$

where H is the Vickers hardness, P is the indentation load (100 N was used) and a is the mean radial crack length.

3. Results

3.1. The effect of composition

The concentrations of Na_2O and K_2O in silica sol were determined by flame photometry. The measured concentration of Na_2O in the Al_2O_3–SiO_2 studied system ranged from 0.030 to 0.042 wt% (Table I). The concentration of K_2O was significantly lower.

Figs 1 and 2 show the bulk densities and RT flexural strength of mullite after CIP at 1.5 GPa followed by sintering at 1350 and 1500 °C for 3 h as functions of the nominal Al_2O_3 content. The bulk densities (Fig. 1) of the green bodies were approximately the same for all the compositions but depended significantly on the pressure (CIP) and sintering temperature. The bulk density of die-pressed (150 MPa) samples was approximately only 1.16 g cm^{-3}. This value increased to about 1.9 g cm^{-3} (64%) by high CIP at 1.5 GPa.

The bulk densities of test samples sintered at 1350 or 1500 °C for 3 h depended significantly on the compacting pressure. Die-pressed (150 MPa) samples reached only about 76% of the theoretical density (TD), while cold isostatically pressed samples were nearly theoretically densified ($\rho_r > 99\%$ TD). The relative density decreased slightly for Al_2O_3 concentrations higher than about 75 wt%, since the TD increased with increasing Al_2O_3 concentration ($\rho_{Al_2O_3} = 3.99$ g cm^{-3}).

TABLE I Concentration of Na_2O, K_2O and Al_2O_3 in Al_2O_3–SiO_2 studied system

Na_2O (wt %)	K_2O (ppm)	Al_2O_3 (wt%)
0.042	19	72.0
0.038	17	75.0
0.033	15	78.0
0.030	14	80.0

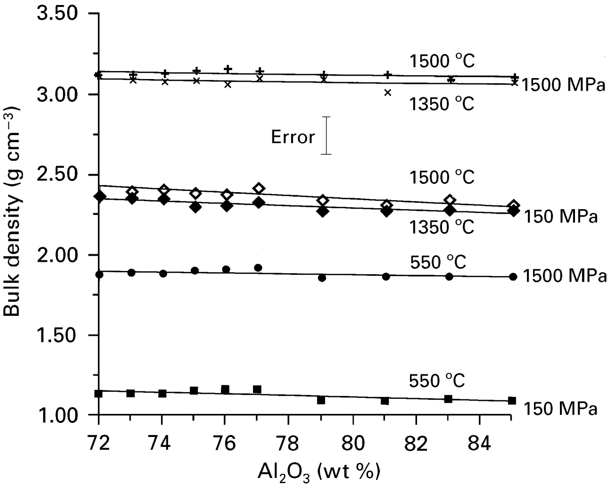

Figure 1 Variation in bulk density of calcined Al_2O_3–SiO_2 gels with compacting pressure (150 MPa and 1.5 GPa), Al_2O_3 concentration and sintering temperature (1350 and 1500 °C).

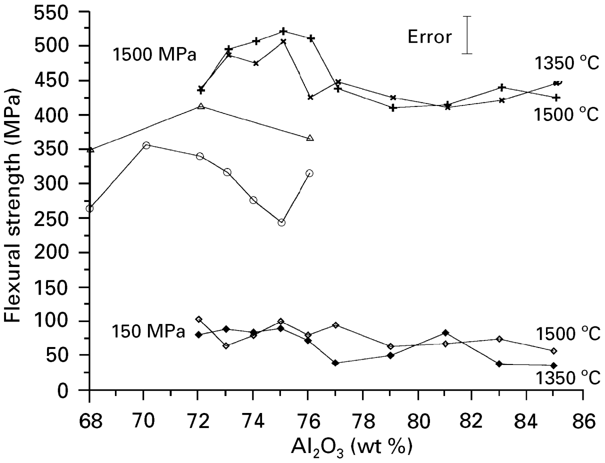

Figure 2 Variation in flexural strength of calcined Al_2O_3–SiO_2 gels with pressure (150 MPa and 1.5 GPa), Al_2O_3 concentration and sintering temperature (1350 and 1500 °C). The results of [18] (—△—) and [19] (—○—) were also included for comparison.

The RT flexural strength of mullite correlated with the bulk density (Fig. 2). The strength of the die-pressed samples was low (about 90 MPa) and almost independent of composition and sintering temperature (1350 and 1500 °C). Samples isostatically pressed (1.5 GPa) show high bending strengths, the best of which were 523 ± 40 MPa (samples containing 75 wt% Al_2O_3) and 500 ± 30 MPa (72 wt% Al_2O_3). The flexural strength is only slightly affected by the sintering temperature (1300–1500 °C). However, the strength is a function of composition. The strength slightly decreased at 77 wt% A_2O_3 and above. The measured RT strength is higher than values published for undoped mullite ceramics (350–420 MPa [9, 10, 16–21]) and are in the range for ZrO_2 (15–30 wt%)-doped mullite ceramics (500–630 MPa [10, 16, 20, 22]).

3.2. Effect of compaction pressure

The composition of mullite with the largest flexural strength (Fig. 2), containing 75 wt% Al_2O_3, was used for the second series, where the CIP pressure was varied between 0.5 and 1.5 GPa. Fig. 3 shows that the bulk density of green bodies increases with increasing compaction pressure. As expected, the bulk density of dried samples was higher than that of calcined samples. This can presumably be explained by easier transportation (reorganization) of particles with a higher concentration of OH groups [23] (dried sample). The dependence of the bulk density on pressure also had the same trend for sintered samples (1500 °C for 3 h). It was interesting that the sintered bulk densities of dried samples were almost the same,

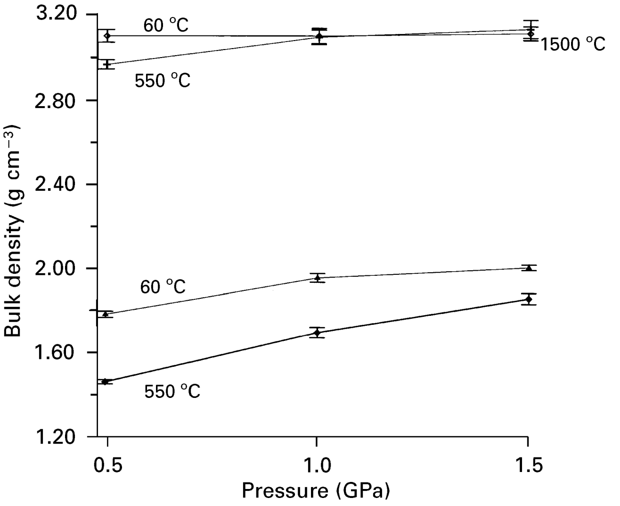

Figure 3 Green and sintered (1500 °C for 3 h) bulk densities of Al_2O_3–SiO_2 gels (dried at 60 °C or calcined at 550 °C) containing 75.0 wt% Al_2O_3 as a function of pressure (CIP).

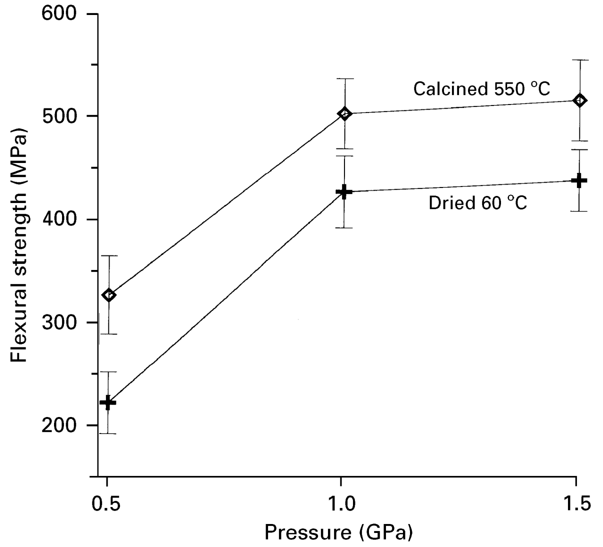

Figure 4 Flexural strength of Al_2O_3–SiO_2 gels containing 75.0 wt% Al_2O_3 sintered at 1500 °C for 3 h as a function of pressure (CIP).

for all three compacting pressures used (about 98% TD). The pressure effect on bulk density was observed only for calcined gel. The sintered bulk density of calcined samples pressed at 0.5 GPa was lower than that of dried samples. Both types of sample pressed at 1 and 1.5 GPa showed approximately the same bulk densities (98–99% TD).

The pressure effect on the flexural strength and the Vickers hardness (for dried samples) was significant (Fig. 4 and Table II) unlike the fracture toughness. The flexural strength of the calcined samples was higher than that of the dried samples for all applied pressure. The difference between them was about 80 MPa (Fig. 4) with that of the calcined samples being higher.

The strength particularly increased between pressures of 0.5 and 1.0 GPa for both types of sample. A further increase in pressure (1.5 GPa) had only a slight effect on the strength (Fig. 4).

TABLE II Bulk density, ρ, flexural strength, Vickers hardness and fracture toughness, K_{Ic}, after sintering at 1500 °C for 3 h as a function of the drying temperature, T_D, or calcination temperature T_c, and compacting pressure (CIP), P

T_D or T_C (°C)	P (GPa)	ρ (g cm^{-3})	Flexural strength (MPa)	Vickers hardness (GPa)	K_{Ic} (MPa m$^{1/2}$)
60	0.5	3.11	223	6.16	3.7
60	1.0	3.11	329	9.13	3.7
60	1.5	3.13	431	10.62	3.4
550	0.5	2.97	407	9.89	3.4
550	1.0	3.11	443	9.88	3.3
550	1.5	3.15	521	10.18	3.5

TABLE III Nominal composition of gels and the excess of Al_2O_3 or SiO_2 in sintered samples with respect to the composition of mullite solide solutions (75.71 wt% Al_2O_3 when sintered at 1350 °C and 72.80 wt% Al_2O_3 when sintered at 1500 °C)

Gel composition (wt%)		Excess (wt%)			
Al_2O_3	SiO_2	1350 °C		1500 °C	
		Al_2O_3	SiO_2	Al_2O_3	SiO_2
72	28	—	3.7	—	0.8
73	27	—	2.7	0.2	—
74	26	—	1.7	1.2	—
75	25	—	0.3	2.2	—
76	24	0.3	—	3.2	—
77	23	1.3	—	4.2	—

For the composition with the Al_2O_3 content in the range 72–77 wt% and sintered at 1350 or 1500 °C for 3 h, only the mullite phase was determined by X-ray diffraction. For the composition with 77 wt% Al_2O_3 or greater, and sintered at the same condition, α-Al_2O_3 was present in addition to mullite.

The Al_2O_3 content in mullite solid solutions were determined from the lattice constants *a*, utilizing the known linear relationship between *a* and the alumina content [13, 14]. Independent of the nominal composition, the alumina content 75.71 (± 0.52) wt% was estimated for samples sintered for 3 h at 1350 °C, and 72.80 (± 0.38) wt% for those sintered for the same time at 1500 °C.

3.3. Amorphous phase

With the assumption of equilibrium at a temperature, the existence of the amorphous phase in the system studied depended on an excess of SiO_2 and the presence of impurities. The SiO_2 excess beside the nominal composition depended also on the composition of the mullite solid solution [14]. In relation to the nominal composition and the Al_2O_3 content of mullite sintered at 1350 °C (75.51 wt%) and 1500 °C (72.82 wt%), the possible amount of excess SiO_2 is given in Table III. The table shows that, at a temperature of 1350 °C, SiO_2 is in excess even at the Al_2O_3 level of 75 wt%. At the sintering temperature of 1500 °C, the content of SiO_2 in mullite is higher; therefore the excess of SiO_2 ends, starting at an Al_2O_3 content of about 73 wt%.

3.4. Microstructure

Individual mullite crystals were not observable on the fracture surfaces of samples sintered at 1350 and 1500 °C (Fig. 5) and surfaces polished and etched with HF. They are visible on fracture surface created prior to sintering (Figs. 6–8) and polished surfaces etched with boiling 50% NaOH solution (Fig. 9).

Mullite grains of size 0.5–3 μm show intragrain microstructure (the size of the species about 0.2 μm) on the polished surfaces etched with NaOH (Fig. 9) and partly also on the surfaces created before sintering (Figs. 6–8). This microstructure was not observed on the polished surfaces etched with HF. There is no doubt that, by etching, the degradable part of the material was removed easily and the etching revealed grain boundaries (crystal) and intragrain porosity (Fig. 9). The features dissolved by etching are very probably partly a secondary crystallized (during cooling) amorphous glassy phase, which contains alkaline impurities and more SiO_2 than Al_2O_3. Subsequent research will provide the answer to whether the porous mullite grains observed are single crystals or whether they are aggregates of even smaller grains (0.1–0.2 μm).

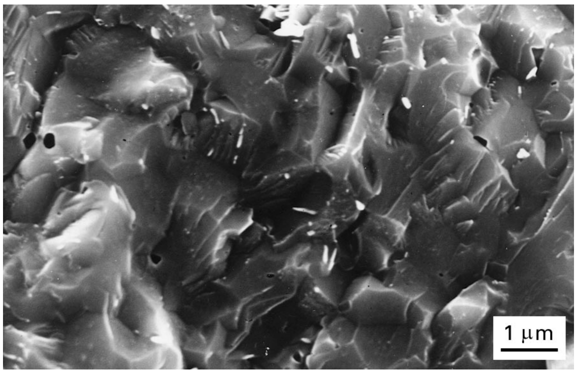

Figure 5 SEM picture of the fracture surface (created after sintering) of mullite with 75.0 wt% Al_2O_3 and sintered at 1500 °C for 3 h.

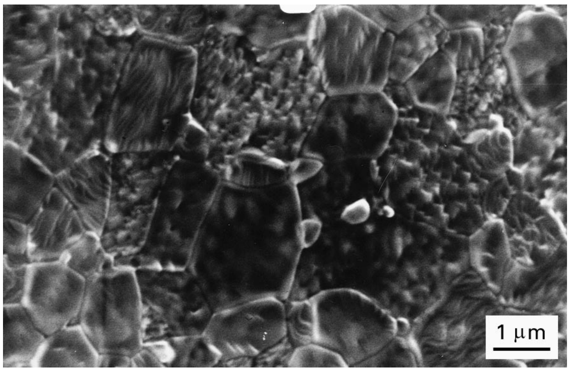

Figure 6 SEM picture of mullite with 75.0 wt% Al_2O_3 (surface created before sintering at 1500 °C for 3 h).

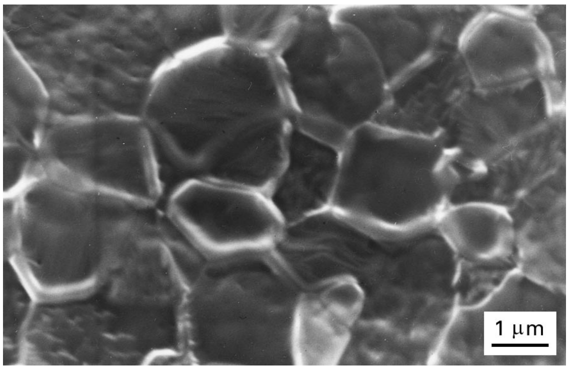

Figure 7 SEM picture of mullite with 75.0 wt% Al_2O_3 (surface created before sintering at 1350 °C for 3 h).

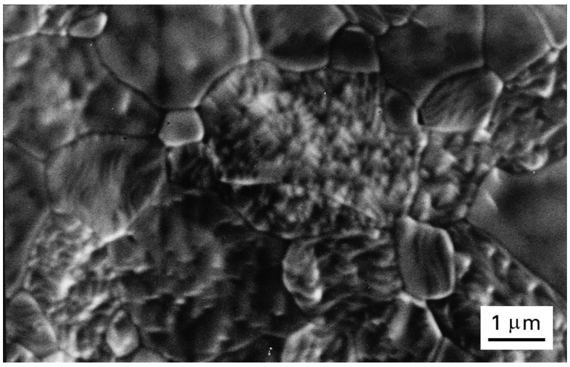

Figure 8 SEM picture of mullite with 76.0 wt% Al_2O_3 (surface created before sintering at 1500 °C for 3 h).

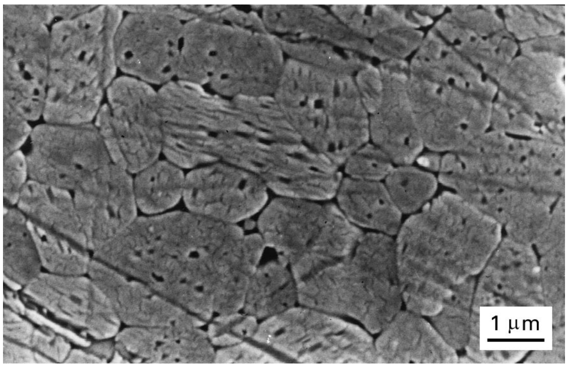

Figure 9 SEM picture of polished and etched (boiling 50 wt% NaOH for 5 min) surface of mullite with 75.0 wt % Al_2O_3. Sample sintered at 1500 °C for 3 h.

Some grains on the surfaces, created before sintering, were divided, surrounded (Figs 6 and 7) by the amorphous phase which failed to wet the mullite and squeezed out of the intergrain space. Grains were not observed to be surrounded when the Al_2O_3 content was 76 wt% (Fig. 8) and sintered at 1500 °C. On the other hand, it was more evident at the lower sintering temperature of 1350 °C (Fig. 7).

4. Discussion

The results presented proved that the alkali in gels from commercial sources, in a concentration of 0.03–0.04 wt% in the system, do not hinder the achievement of high RT flexural strength of mullite ceramics. The strength (an average, 523 MPa, but some about 550 MPa) was higher than the published strength of undoped mullite although most of the ceramics were prepared from cleaner sources, from alkoxides [18] or additionally purified sols [16]. The high strength of mullite samples was connected with the usage of high-pressure pressing of xerogels. The highest flexural strength was achieved with mullite having 75 wt% Al_2O_3.

The flexural strength depended significantly on the compacting pressure, especially between values of 0.5 and 1.0 GPa. The strength of calcined samples was higher than those of dried samples, although bulk densities were inverse to that function. This slightly contradictory finding can be explained by the dual effect of the pressure on the material. Besides the known macroeffect between pressure and bulk density, it can also be considered a pressure-dependent process on an atomic level related to the topotactic transformation of alumina ($AlOOH \rightarrow \gamma\text{-}Al_2O_3$) component of the system. A defect-containing $\gamma\text{-}Al_2O_3$ structure, as is known [24], contains vacancies on the OH sites in the original boehmite structure. Therefore, pressing of the gel after calcination ($\gamma\text{-}Al_2O_3$) and before calcination (dried gel, AlOOH) were not the same when considered in detail. High pressure could reduce the number of vacancies ($\gamma\text{-}Al_2O_3$ calcined gel) and, on the other hand, the low OH group content hindered the macroscopic densification. The pressure applied on gel dried at 60 °C had no effect on vacancies (they were not present), but only on the bulk density.

We did not find in the literature the microstructure of mullite grains observed in this work. According to SEM pictures (Figs 6–9), it seems to be true that formation of the characteristic microstructure depends on the energies of mullite–mullite (M–M) and mullite–amorphous phase (M–AP) interfaces. To squeeze out the amorphous phase from the grain boundary is possible when

$$\gamma_{\text{M–M}} < \gamma_{\text{M–AP}} \qquad (2)$$

where γ is the interface energy. For this condition the energy balance of the system demands the spread of the M–M grain boundary at the expense of the M–AP interface. Because the amorphous phase (glassy phase) is not present at the M–M grain boundary, but it is at the surface and pores, it does not significantly affect the flexural strength. It is generally assumed that the presence of the glassy phase lowers the strength of mullite [9] but, according to the presented results, the microstructure is more important for the achievement of high strength than the low glassy phase content.

5. Conclusions

Diphasic mullite gel, cold isostatically pressed up to 1.5 GPa, could be sintered at 1500 °C for 3 h to a density of 99% TD. The bulk density and flexural strength of ceramics increase with increased compacting pressure. The flexural strength of calcined and sintered samples is about 80 MPa higher than for dried and sintered samples at all the pressures used. The fracture toughness is nearly independent of the compacting pressure. The flexural strength reached a maximum (523 ± 40 MPa) for the calcined gel having 75 wt% Al_2O_3. The microstructure of ceramics is characterized by a special arrangement of the mullite crystals. The alumina content in mullite solid solutions increases with decreasing sintering temperature.

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