Journal of the European Ceramic Society 19 (1999) 2613–2618

PII: S0955-2219(99)00053-9
0955-2219/99/$ - see front matter

Fabrication of Mullite Ceramics by Rotary Forging and Pressureless Sintering

A. R. Boccaccini,[a]* M. Bücker,[b] T. K. Kahlil[b1] and C. B. Ponton[c]

[a]Fachgebiet Werkstofftechnik, Technische Universitat Ilmenau, PF 100565, D-98684 Ilmenau, Germany
[b]Technisches Institut, Friedrich-Schiller Universität Jena, D-07743 Jena, Germany
[c]School of Metallurgy and Materials, and IRC in Materials for High Performance Applications, The University of Birmingham, Birmingham B15 2TT, UK

(Received 11 December 1998; accepted 13 February 1999)

Abstract

Mullite ceramics were fabricated from boehmite/silica diphasic gels using a rotary forging compaction technique and pressureless sintering. Almost fully dense mullite samples were obtained after sintering at 1350°C for 2 h. The microstructure of sintered samples comprised fine (average size $<1\,\mu m$), equiaxed grains. The samples showed superior sintering behaviour in comparison to those fabricated using conventional uniaxial and isostatic pressing. Powder compaction by rotary forging is thought to generate viscous deformation of the contact points increasing the interparticle contact area as well as increasing the packing density by breaking down hard agglomerates more effectively with concomitant rearrangement of the primary powder particles, thus promoting greater densification at relatively low temperatures. © *1999 Elsevier Science Limited. All rights reserved*

Keywords: rotary-forging, sintering, sol-gel processes, mullite.

1 Introduction

Considerable progress in the synthesis of mullite via sol-gel and colloidal processing has been made in recent years.[1–3] Both single phase and diphasic gels have been used successfully to fabricate high-purity mullite ceramic materials with controlled microstructures.[4–17] Single phase gels are characterised by the mixing at the molecular scale of alumina and silica, obtained by hydrolysis of metal alkoxides or coprecipitation of aluminum and silicon salts.[4–7] On the other hand, diphasic gels are obtained from a colloidal mixture, where the mixing of the alumina and silica precursors occurs at the nanometre scale.[6–17] Usually, the silica and alumina precursors are amorphous and poorly crystallised, respectively. Hybrid gels, consisting of diphasic and single phase gels, have also been prepared.[8]

The principal advantage of preparing powder compacts from diphasic gels is the ability to densify the powder compacts through the viscous flow of the amorphous silica at temperatures $<1250°C$, prior to the diphasic gel's conversion to fully crystalline mullite at temperatures above 1250°C.[6–17] Using this fabrication approach, mullite ceramics with fine, isotropic and homogeneous microstructures have been obtained.[11–17] The principal benefit of this processing technique is the ability to produce very dense pressureless-sintered ceramic bodies at relatively low temperatures ($<1400°C$). In order to achieve a high sintered density, however, it is essential that the powder particles are densely and uniformly packed together.[18] Thus, the green density is a very important processing parameter, particularly when pressureless sintering is used to densify a powder compact. A smaller sintered grain size and smaller residual pore size are usually obtained when the green density is uniformly high throughout the powder compact. The green density of and green density distribution within a powder compact depends strongly on the powder compaction procedure employed. By using very high pressure (0·5–1·5 GPa) cold-isostatic pressing, closely packed green compacts with green densities in the range of 60–70% theoretical density (TD), have been obtained recently.[14,19,20] These mullite compacts could be densified to >95% TD

*To whom correspondence should be addressed. Fax: +49-3677-691597; e-mail: aldo.boccaccini@maschinenbau.tu-ilmenau.de

Permanent address: Hot Labs Center, Atomic Energy Authority, Cairo, Egypt.

by sintering at 1500°C for 2 h. Other powder compaction techniques, such as uniaxial die pressing and rotary forging, were used to investigate the effect of different "green" density values (in the range 15–68% TD) on the densification and mullitisation of transiently sintered mullite by Wang *et al.*[18]

Rotary forging is a powder compaction technique frequently used to fabricate metal and ceramic magnets,[21] but apart from its use by Wang *et al.*[18] to fabricate mullite ceramics and its use in the fabrication of platelet reinforced glass-ceramics,[22] it has received little attention as a ceramic green body fabrication technique.

In the present work rotary forging has been used to fabricate mullite precursor powder compacts which are then pressureless sintered. The mullite precursor powders were produced by a diphasic gel route, employing two fumed silicas and a boehmite sol as starting materials.[12,13] The densification behaviour observed and the resultant microstructures were compared with the corresponding results obtained for samples prepared by conventional uniaxial cold-pressing and cold isostatic pressing during a previous investigation.[12] Furthermore, both Vickers hardness and indentation fracture toughness measurements were made as an initial mechanical property characterisation.

2 Experimental Procedure

Two grades of fumed amorphous silica (Aerosil OX50 and Aerosil 200, Degussa Ltd., UK) and a boehmite (γ-A1OOH) sol (Remal A20, Remet Corp., USA) were used as precursors. The Aerosil OX50 powder had a broad particle size distribution in the 10–100 nm range and an average particle size of 40 nm, while the Aerosil 200 material had a narrow particle size distribution and an average particle size of 12 nm. The boehmite sol comprised 20 wt% of 50 nm particles of fibrillar morphology suspended in an aqueous medium at pH 4. These precursors were mixed in proportions such that the resulting ceramic after sintering would be stoichiometric mullite, i.e. 72 wt% alumina and 28 wt% silica. Preparation of the diphasic gel has been described in detail previously.[12,13] The fumed silica nanopowders were added slowly to the boehmite sol, firstly the Aerosil OX50 silica and then the Aerosil 200 silica in equal proportions. The sol was stirred constantly. On addition of the Aerosil 200 silica, the mixture gelled immediately due to the strong electrostatic attraction between the silica and boehmite particles that occurs at the working pH. After having been dried slowly at 80°C, the gel was ground using a mortar and a pestle and sieved to obtain a powder with a nominal particle size $< 63\,\mu$m. Figure 1 shows a transmission electron microscope (TEM) image of the dried sol particles.

Rotary forging was used to produce green compacts of relatively high green density. A schematic diagram of the rotary forging apparatus is shown in Fig. 2. It consists of an upper conical tool and lower tool, both of which are adjusted to suit the desired rotary forging conditions and the final compact dimensions. The angle of forging (θ) can be altered with an adjusting screw. Loads in the range 0–100 MN can be used and angular velocities up to 200 rpm are possible. To achieve a given contact pressure between the upper tool and the powder being compacted, a much lower overall load is needed when rotary forging as compared with uniaxial die pressing.[21] In fact, when rotary forging, using an excessive load may result in end-capping (i.e. the formation of a hemispherical shaped hole on the top surface) or radial cracking.[21] A nominal pressure of 30 MPa was applied without the use of a binder to obtain mullite precursor powder green compacts 25 mm in diameter and 5 mm high.

The green density of the samples was measured geometrically. The compacts were then sintered for a fixed time of 2 h at temperatures between 1000 and 1450°C, using a heating rate of 20°C/min, and the

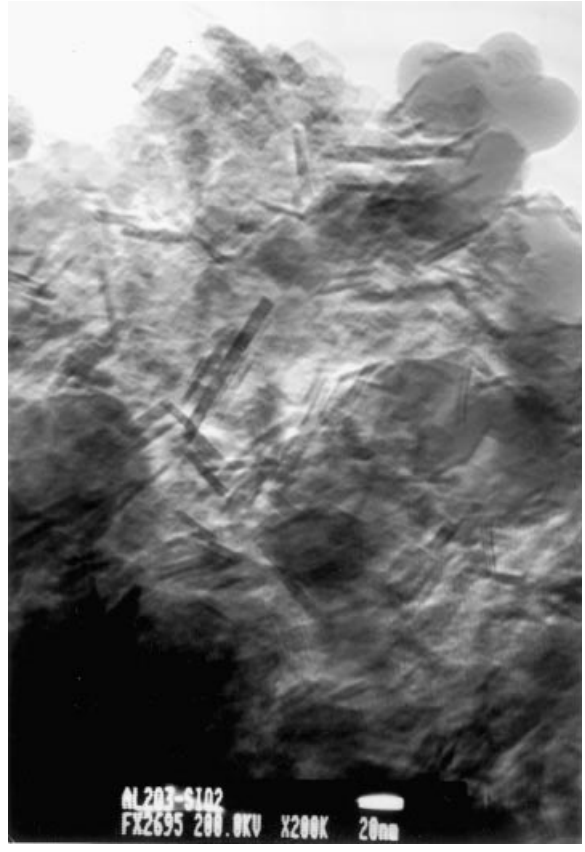

Fig. 1. TEM micrograph of the diphasic sol used, showing the nanoscale mixing of the spherical silica and fibrillar (rod-like) boehmite particles.

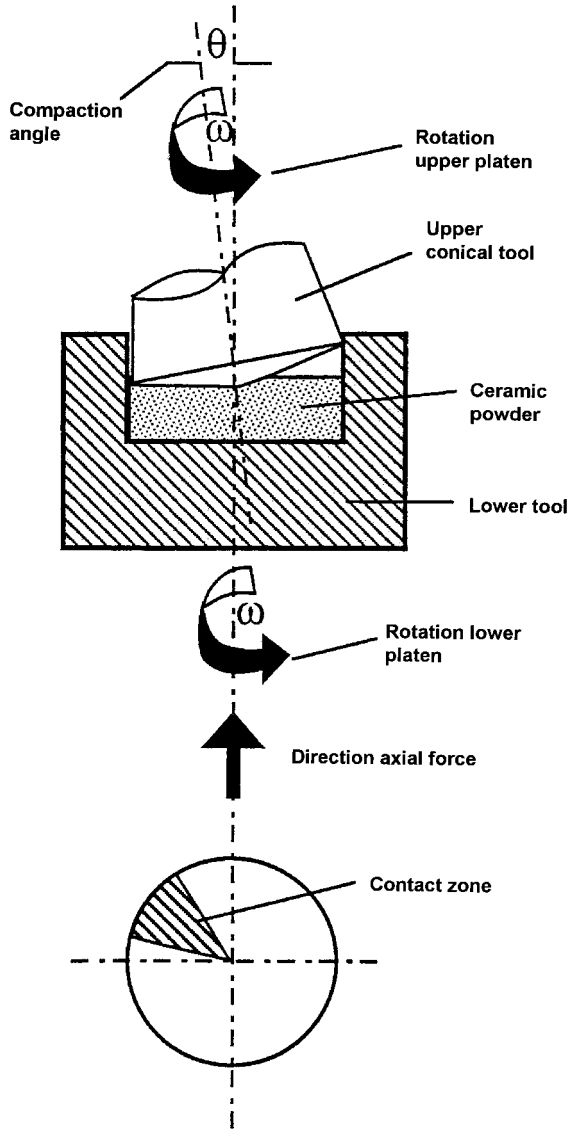

Fig. 2. Schematic diagram showing the rotary forging compaction process.[21]

sintered density was determined geometrically. Selected sintered samples were cut, polished and thermally etched for scanning electron microscopy (SEM) observation. SEM fractography was also carried out. X-ray diffraction (XRD) phase analysis of the sintered bulk samples was also done. The indentation fracture toughness (K_{Ic}) of sintered samples was determined using the following equation:[23]

$$K_{Ic} = 0{\cdot}0899\left(\frac{HP}{4a}\right)^{1/2} \quad (1)$$

where H is the Vickers hardness, P is the indentation load ($10\,N$) and a is the mean radial crack length.

3 Results and Discussion

The XRD patterns for samples that were sintered at 1200 and 1300°C are shown in Fig. 3. Up to a temperature of 1200°C, no mullite formation was detected but the presence of δ-alumina was noted. At 1300°C and higher sintering temperatures, mullite was the only crystalline phase detected.

Moreover, no cristobalite formation was detected over the temperature range investigated, which is a positive aspect of using the present diphasic gel route, i.e. silica viscous flow-led sintering.

The mullitisation behaviour of the present samples is in broad agreement with that observed in previous studies on mullite derived from diphasic-gels.[7–17] In a recent investigation using differential thermal analysis (DTA) at different heating rates, it was shown that such diphasic gels exhibit an activation energy for mullitisation of $E = 880 \pm 30\,\mathrm{kJ\,mol^{-1}}$, and that mullitisation starts at temperatures between 1250 and 1350°C, depending on the heating rate used.[24] In colloidal sols such as that prepared here, the alumina and silica precursors are present as discrete entities, and any chemical reaction between them during gelation is minimal. Only at temperatures above ~1250°C, does mullite crystallise from a mixture of poorly crystallised transition (pre-α) aluminas (i.e. δ- or θ-alumina) and amorphous silica.[6–17] In previous XRD-studies on similar diphasic gels,[13] it was also shown that no transitional Al-Si spinel phase at ~960°C is formed. It must be noted that given the phase proportion limit (2–5 wt%) of XRD, there is a possibility for an intergranular glassy phase and/or a silica rich aluminosilicate crystalline phase to exist in the sintered compacts, which would result in poorer high temperature creep resistance. TEM observations of grain boundaries and triple points junctions should clarify this behaviour, but this has not been conducted in the present study.

The XRD-patterns in Fig. 3 are very similar to those obtained for samples prepared by cold-isostatic pressing and cold uniaxial pressing at pressures of 250 and 450 MPa, respectively.[12] This indicates that for the range of compaction pressures investigated, the method of compaction does not affect the crystallisation behaviour. Furthermore, the previous study[12] showed that in the case of the mullite precursors used, the green density has little influence on the development of crystalline phases during sintering. This is in contrast to the behaviour reported for transiently sintered mullite produced from α-alumina particles coated with an amorphous silica layer;[18] namely, that the crystallisation and subsequent mullitisation behaviour was influenced strongly by the green density. Both the crystallisation temperature of the amorphous silica layer and the subsequent mullitisation temperature were shown to be lower for the more highly compacted, i.e. higher green density materials. In the case of mullite ceramics made from diphasic

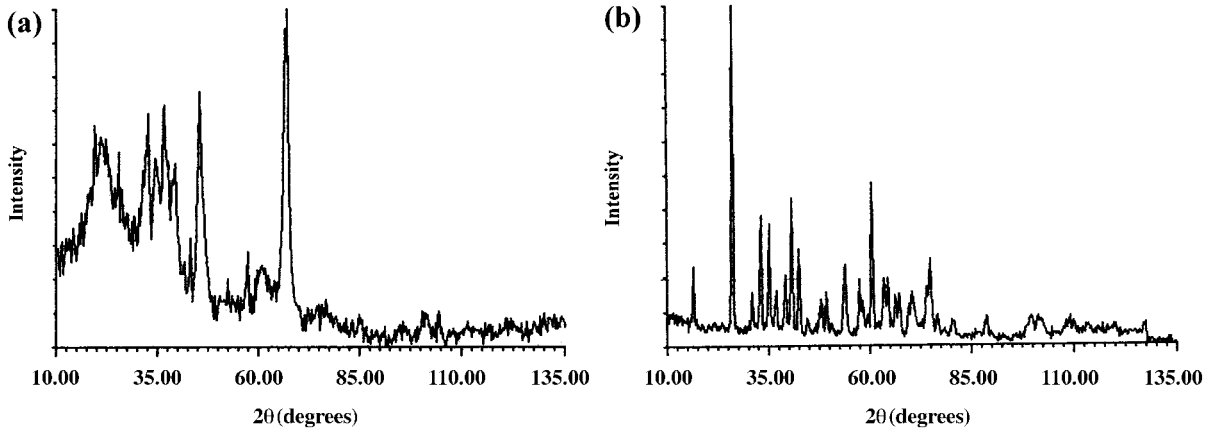

Fig. 3. XRD patterns for the powder compacts produced by rotary forging and sintered for 2 h at (a) 1200°C and (b) 1300°C. In (a), all peaks are attributed to δ-alumina, while in (b), all the peaks are attributed to mullite. Note the absence of a background amorphous halo in (b), indicating that no significant aluminosilicate amorphous phase is present (within the phase-detection limits of detection of XRD).

gels similar to that used here,[15] however, only a slight decrease in the mullitisation temperature (of about 20°C) was observed for samples isostatically compacted at 1·5 GPa, in comparison with non-pressed gels. While this is in qualitative agreement with our results, a detailed DTA study should be conducted to assess quantitatively the effect of compaction pressure on crystallisation temperature and subsequent mullitisation temperature in diphasic gels, this being the focus of current studies.

By careful adjustment of the rotary forging parameters, crack-free powder compacts of relatively high green densities were produced. Figure 4 shows the sintered density as a function of sintering temperature for green samples produced by rotary forging. Data from a previous study[12] on green samples produced by cold-uniaxial and cold isostatic pressing are also presented for comparison. The sintering behaviour of mullite powder compacts fabricated from diphasic gels has been discussed in the literature and there is broad agreement that densification occurs by a viscous flow-led mechanism prior to mullitisation.[7–17] Indeed, the degree of viscous flow-led densification increases as the green compact density increases, as Fig. 4 shows, in agreement with previous studies.[14,16,18–20]

The results presented in Fig. 4 indicate that the rotary forging technique is more effective in producing green compacts of relative high density (61% TD, with TD = 3·17 g cm^{-3}, Ref. 11), which require lower sintering temperatures than samples prepared by other conventional compaction techniques. This result is well-known in the area of magnetic materials fabrication,[21] and is in agreement with previous investigations on the rotary forging of mullite[18] and composite glass-ceramics.[22] It is probable that using rotary forging on poorly crystalline, i.e. pseudo-amorphous powders, results in the viscous deformation of the inter-particle contact

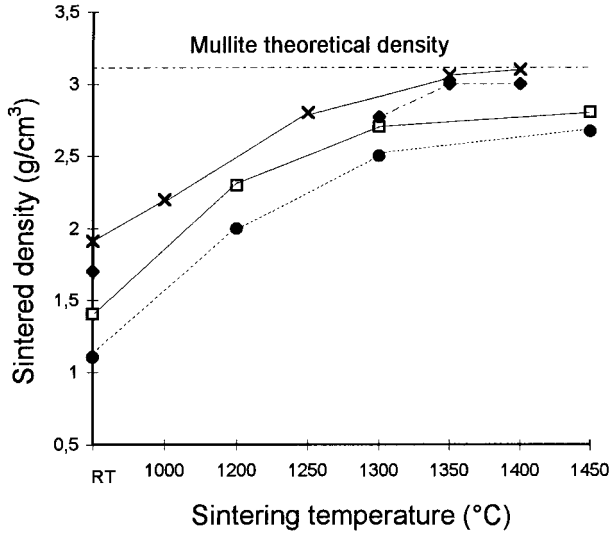

Fig. 4. Sintered density of mullite compacts as a function of sintering temperature and a fixed sintering time of 2 h for different powder compaction processes: (✕) rotary forging (this work), (●) uniaxial pressing, 170 MPa,[12] (□) uniaxial pressing, 450 MPa,[12] (◆) isostatic pressing, 250 MPa.[12]

points, increasing the inter particle contact area, as well as increasing the packing density by breaking down hard agglomerates more effectively with concomitant rearrangement of the primary powder particles, thus promoting greater densification at relatively low temperatures. This is because during rotary forging very high shear stresses are produced, which facilitate particle rearrangement and hence pore elimination to a greater extent than is certainly possible with uniaxial pressing, and probably even isostatic pressing. Although, viscous deformation of the inter-particle contact points has been observed by Kamiya *et al.* during high-pressure isostatic compaction of similar mullite precursor powders.[20] As suggested by these authors,[20] viscous deformations of the contact points may lead to the generation of new defects in the primary

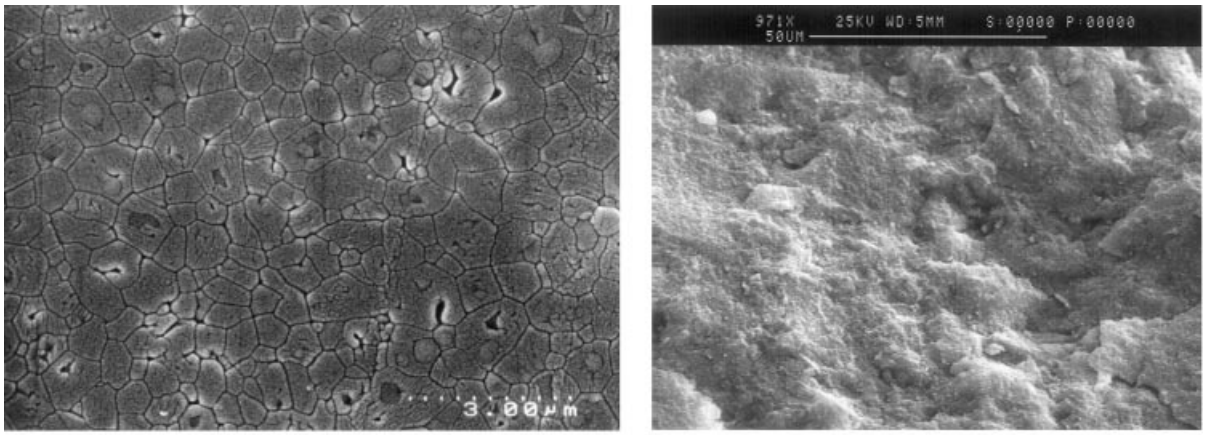

Fig. 5. (a) SEM micrograph of a polished and thermally-etched section of a sample obtained by rotary forging and pressureless sintering (2 h, 1350°C). Note the very fine and homogeneous, equiaxed microstructure and low level of intra- and intergranular residual porosity, (b) SEM fractograph, confirming the high sintered density of the sample.

particles near the contact points, increasing the "pseudo-amorphous" nature of the contact regions, which would promote viscous flow-led sintering at relatively low temperatures (starting below 1000°C in our material; see Fig. 4). Furthermore, the high shear stress generated during rotary forging may also be more effective than conventional uniaxial or isostatic pressing in destroying hard agglomerates by causing greater agglomerate fragmentation and particle microfractures. According to Kara and Little,[16] the elimination of hard agglomerates in the green compact, which will eliminate large inter-agglomerate pores, enables full densification at relatively low temperatures (< 1400°C). Hence, the effectiveness of rotary forging shown in Fig. 4.

Given the axial rotation and relative motion of the lower die and upper tool during rotary forging, the possibility of producing a degree of anisotropy in the green compact and hence in the sintered microstructure must be considered.[21] However, this effect did not seem to be very pronounced in the present samples after sintering, as SEM observations of polished surfaces showed. Figure 5(a) shows, for example, the microstructure of a sample sintered at 1350°C for 2 h. Note the almost pore-free, fine and homogeneous microstructure comprising equiaxed grains with average grain size under 1 μm. Only some small discrete intragranular pores are observed. The SEM fractograph shown in Fig. 5(b), confirms the high sintered density of the sample. The microstructure of the present material resembles that of mullite ceramics obtained by pressureless sintering at 1600°C (2 h) and 1500°C (3 h) after cold isostatic pressing at very high pressures of 1 GPa[19] and 1·5 GPa[14], respectively. This confirms that by using rotary forging at much lower compaction pressures, satisfactory results in terms of the green and sintered density as well as the microstructure of mullite

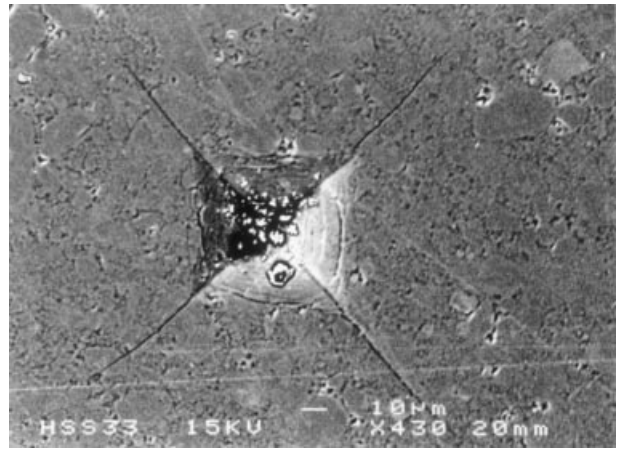

Fig. 6. Vickers indentation (indentation load = 10 *N*) in a mullite sample fabricated by rotary forging and pressureless sintering (2 h, 1350°C).

ceramics made from diphasic gels are possible. Average values of the Vickers hardness and indentation fracture toughness [eqn (1)], determined from indentations similar to that shown in Fig. 6, were: $H = 11$ GPa and $K_{Ic} = 1{\cdot}7$ MPm$^{1/2}$, respectively. These data are in agreement with the literature results for dense mullite ceramics.[25] Moreover, the equiaxed grain microstructure (Fig. 5) suggests that the present material should exhibit good mechanical properties at high temperature.

4 Conclusions

Powders of mullite composition obtained from diphasic gels were used to fabricate mullite ceramics employing a rotary forging compaction technique and pressureless sintering. Near-theoretical density mullite ceramics with a fine and highly homogeneous microstructure were obtained after sintering at only 1350°C for 2 h. The superior

sintering behaviour of the present rotary forged green powder compacts, as compared to those green compacts fabricated from similar diphasic gel precursor but using conventional uniaxial and isostatic pressing, is attributed to both the increased viscous deformation of the contact points (and hence larger inter-particle contact area) and the higher packing density resulting from the very high shear stresses generated during rotary forging.

Acknowledgements

The rotary forging experiments were carried out with the support of Dr. A. J. Williams (School of Metallurgy and Materials, The University of Birmingham). The authors also acknowledge the assistance of Dr. I. MacLaren (IRC in Materials, The University of Birmingham) during the TEM observations.

References

1. Somiya, S. and Hirata, Y., Mullite powder technology and applications in Japan. *Am. Ceram. Soc. Bull.*, 1991, **70**, 1624–1632.
2. Somiya, S., Davies, F. and Pask, J. A. (Eds.), *Mullite and Mullite Matrix Composites, Ceramic Trans.* Vol. 6, The American Ceramic Society, Westerville, OH, 1990.
3. Schneider, H., Okada, K. and Pask, J., *Mullite and Mullite Ceramics*, Wiley, New York, 1994.
4. Sonuparlak, B., Sol-gel processing of infrared transparent mullite. *Adv. Ceram. Mat.*, 1988, **3**, 263–267.
5. Hoffman, D. W., Roy, R. and Komarneni, S., Diphasic xerogels, a new class of materials: phases in the systems Al_2O_3–SiO_2. *J. Am. Ceram. Soc.*, 1984, **67**, 468–471.
6. Sundaresan, S. and Aksay, I. A., Mullitization of diphasic aluminosilicate gels. *J. Am. Ceram. Soc.*, 1991, **74**, 2388–2392.
7. Wei, W.-C. and Holloran, J. W., Phase transformation of diphasic aluminosilicate gels. *J. Am. Ceram. Soc.*, 1988, **71**, 166–172.
8. Huling, J. C. and Messing, G. L., Epitatic nucleation of spinel in aluminosilicate gels and its effects on mullite crystallisation. *J. Am. Ceram. Soc.*, 1991, **74**, 2374–2381.
9. Li, D. X. and Thomson, W. J., Kinetic mechanisms for mullite formation from sol-gel precursors. *J. Mat. Res.*, 1990, **5**, 1963–1969.
10. Sacks, M. D., Bozkurt, N. and Scheiffele, G. W., Fabrication of mullite and mullite-matrix composites by transient viscous sintering of composite powders. *J. Am. Ceram. Soc.*, 1991, **74**, 2428–2437.
11. Jeng, D. and Rahaman, M. N., Sintering and crystallization of mullite powder prepared by sol-gel processing. *J. Mat. Sci.*, 1993, **28**, 4904–4909.
12. Boccaccini, A. R., Trusty, P. A. and Telle, R., Mullite fabrication from fumed silica and boehmite sol precursors. *Mat. Lett.*, 1996, **29**, 171–176.
13. Boccaccini, A. R., Trusty, P. A., Taplin, D. M. R. and Ponton, C. B., Colloidal processing of a mullite matrix material suitable for infiltrating woven fibre preforms using electrophoretic deposition. *J. Eur. Ceram. Soc.*, 1996, **16**, 1319–1327.
14. Pach, L. and Mankos, P., Diphasic mullite gel pressed at 1·5 GPa: mechanical properties and microstructure of ceramics. *J. Mat. Sci.*, 1997, **32**, 3195–3199.
15. Pach, L., Iratni, A., Hrabe, Z., Svetic, S. and Komarneni, S., Sintering and crystallisation of mullite in diphasic gels. *J. Mat. Sci.*, 1995, **30**, 5490–5494.
16. Kara, F. and Little, J. A., Sintering behaviour of precursor mullite powders and resultant microstructures. *J. Eur. Ceram. Soc.*, 1996, **16**, 627–635.
17. Rahaman, M. N., De Jonghe, L. C., Shinde, S. L. and Tewari, P. H., Sintering and microstructure of mullite aerogels. *J. Am. Ceram. Soc.*, 1988, **71**, C-338–C-341.
18. Wang, J. G., Ponton, C. B. and Marquis, P. M., Effects of green density on crystallization and mullitization in the transiently sintered mullite. *J. Am. Ceram. Soc.*, 1992, **75**, 3457–3461.
19. Cho, Y. I., Kamiya, H., Suzuki, Y., Horio, M. and Suzuki, H., Processing of mullite ceramic from alkoxide-derived silica and colloidal alumina with ultra-high cold isostatic pressing. *J. Eur. Ceram. Soc.*, 1998, **18**, 261–268.
20. Kamiya, H., Suzuki, H., Ichikawa, T., Cho, Y. I. and Horio, M., Densification of sol-gel derived mullite ceramics after cold isostatic pressing up to 1 GPa. *J. Am. Ceram. Soc.*, 1998, **81**, 173–179.
21. Rowlinson, N., A Study of Rotary Forged Nd-Fe-B Permanent Magnets, Ph.D. thesis, The University of Birmingham, UK, 1989.
22. Boccaccini, A. R., Pearce, D. P. H. and Trusty, P. A., Pressureless sintering and characterization of Al_2O_3-platelet reinforced barium-magnesium-aluminosilicate glass-ceramic composites. *Composites Part A*, 1997, **28A**, 505–510.
23. Ponton, C. B. and Rawlings, R. D., Vickers indentation fracture toughness test—Part 1 review of literature and formulation of standardised indentation toughness equations. *Mater. Sci. Tech.*, 1989, **5**, 865–872.
24. Boccaccini, A. R., Kahlil, T. K. and Bücker, M., Activation energy for the mullitization of a diphasic gel obtained from fumed silica and boehmite sol. *Mat. Letters*, 1999, **38**, 116–120.
25. Tkalcec, E., Nass, R., Krajewski, T., Rein, R. and Schmidt, H., Microstructure and mechanical properties of slip cast sol-gel derived mullite ceramics. *J. Eur. Ceram. Soc.*, 1998, **18**, 1098–1099.