

Graded compositions and microstructures by infiltration processing

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Mullite/alumina particulate composites were fabricated by infiltrating porous alumina preforms with an SiO_2 -containing sol followed by a heating step to cause mullite formation and densification. Electron microprobe analysis was performed to obtain concentration profiles across sections of the sintered composites. These analyses revealed the existence of concentration gradients, the mullite content decreasing with increasing distance from the surface of the bodies. Analyses with a scanning electron microscope also indicated a microstructural effect; the alumina grain size in composite bodies tended to increase with distance from the surface of the sample. These two effects (microstructural and compositional) have been related and it has been concluded that while the presence of mullite limits grain growth in alumina, the mullite content must be at least ~ 5 wt % in order for grain growth to occur in a controlled fashion. The results point out the potential of the infiltration approach as a means for tailoring the composition and microstructure of ceramic bodies.

1. Introduction

The surfaces of ceramic bodies are often subjected to treatments for the purpose of improving some of the properties and hence the overall performance of the components. For example, coatings are sometimes applied on dense ceramics using thermal spraying, dip coating, chemical vapour deposition or other techniques. In addition, ceramic bodies may be engineered by the laminating of layers in which the concentration of the constituents has been varied or by the sequential casting of slips varying in composition. Many of these modification processes yield bodies in which there is an abrupt change in composition across the boundary between the modified region and the bulk or between the layers. In addition to the possibility of a chemical incompatibility between the materials on either side of the interface, the existence of a mismatch in the properties (e.g. thermal expansion coefficient) may give rise to stresses which can disrupt the integrity of the bond between the two zones or lead to failure within the zones. Therefore, from this stand-point, it is preferred that the transition from one zone to the other be a gradual one.

In this study, an infiltration process was used to incorporate mullite into alumina bodies. One of the advantages of the infiltration process is that preforms containing a significant amount of open porosity may be used and this allows for relatively broad control over both the depth and composition of the modified zone. Other parameters can also be varied for the purpose of regulating the infiltration process. For

example, the composition of the infiltrant, the number of infiltrations and the amount of time the preform is exposed to the infiltrant can be used to control the amount and distribution of the phases. In addition, infiltration can be enhanced (or hindered) by the use of vacuum and/or pressure at various points during the process. Following infiltration, preforms can be subjected to a heat treatment to bring about such processes as decomposition of the infiltrant, formation of new phases and densification.

The actual process whereby mullite is introduced into alumina using the infiltration approach has been discussed in detail previously [1]. The purpose of this paper is to point out the potential of the infiltration approach for controlling both the distribution of phases and the microstructural development in materials. Infiltration may, therefore, provide another means for designing materials and tailoring them for a specific application.

2. Experimental procedure

A schematic outline of the various steps in the fabrication of the samples by the infiltration process is shown in Fig. 1. Preforms were prepared by pressing alumina powder (RC-HP DBM without MgO , Reynolds, Bauxite, AS, USA) uniaxially at 28 MPa and isostatically at 138 MPa. The resulting compacts were heated to 1200°C (4°C min^{-1} , 2 h soak) thereby producing cylindrically shaped preforms with a relative density of 72%, height of 2.6 cm and diameter of

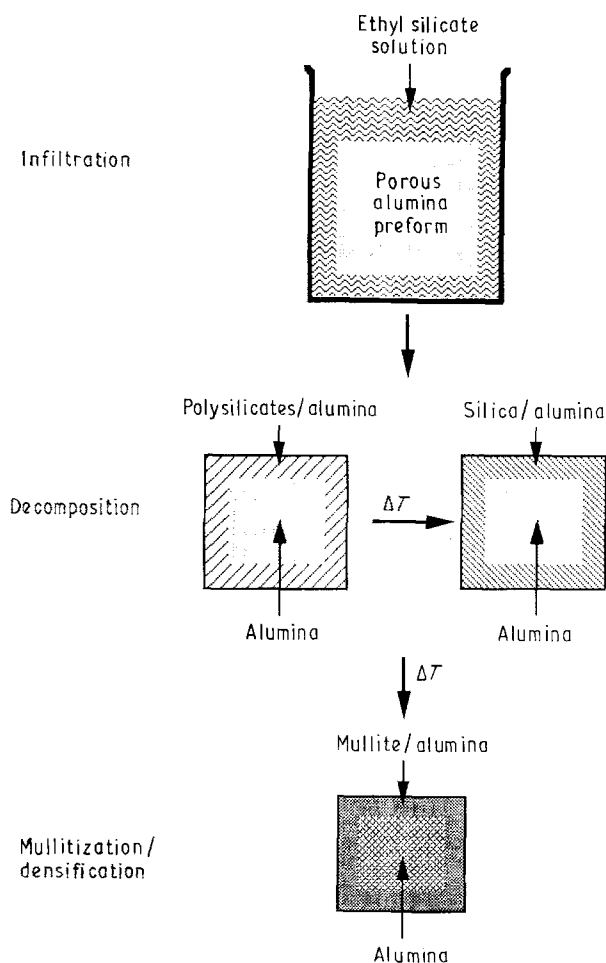


Figure 1 Schematic illustration of the main processing steps for the fabrication of mullite/alumina composites by the infiltration approach.

2.5 cm. These preforms were infiltrated by fully immersing them in a prehydrolysed ethyl silicate solution (Ethyl silicate, R-25, Remet, Chadwicks, NY, USA) containing 25 wt % SiO_2 , for times varying from 5 s to 144 h. Following removal from the infiltrating solution, samples were allowed to dry for 24 h at room temperature. Decomposition of the infiltrant was carried out by heating the samples in air to 1200°C (to 600°C at 1°C min^{-1} , 2 h soak; $600\text{--}1200^\circ\text{C}$ at 2°C min^{-1} , 0.5 h soak). Mullite formation and densification took place during a final heating step (in air) to 1650°C (2°C min^{-1} , 4 h soak). Mass changes were recorded after each step of the process. Densities of the sintered samples were determined using Archimedes' approach in distilled water. The bulk mullite content of the fired bodies was determined by noting the mass difference between the sintered sample and the preform prior to infiltration. By assuming that this change in mass was due solely to SiO_2 , which reacted with some of the alumina already present in the preform to form stoichiometric mullite, the bulk mullite contents were calculated using densities for alumina and mullite of 3.98 and 3.18 g cm^{-3} , respectively.

The bodies were sectioned and a selection of samples covering a range of infiltration times were polished for further observation. For some samples the microstructure at different points within the body was studied using a scanning electron microscope.

Analysis was also performed using an electron microprobe to determine the distribution of the phases. Point-by-point analysis using wavelength dispersive spectroscopy with a beam size of $50 \mu\text{m}$ was performed at 50 or $75 \mu\text{m}$ intervals across the surface of the samples. The elemental contents were converted and reported as the amounts of oxide present, SiO_2 and Al_2O_3 . These SiO_2 contents were then used to determine a corresponding mullite content by using a similar calculation to that outlined above.

3. Results and discussion

A photograph showing the interior of several of the (sectioned) sintered samples is shown in Fig. 2. The mullite-containing and pure alumina zones were readily distinguishable by the difference in colour – the alumina zone being beige (grey in the picture) and the composite zone, white. X-ray diffraction patterns of the exterior surface and of the interior of sintered samples which had been infiltrated for long periods indicated that the only phases present were mullite and alumina. Fig. 2 gives some idea of the rate at which the infiltration process occurred. Although it is not obvious in the figure, it has been shown previously that the infiltration front reached the centre of these samples 2–4 h after being immersed in the infiltrant [1]. No effort was made in this work to modify the chemistry of the infiltrating solution in order to change the rate of infiltration. Changing the solution chemistry could either enhance or limit infiltration which, depending on the desired outcome, could be advantageous.

Information on the depth of the composite zone and bulk mullite content for samples prepared using a range of infiltration times is given in Table I. The results of the electron microprobe analyses for these same samples are shown in Fig. 3. One of the significant things about these analyses is that they indicate the presence of concentration gradients in the samples.

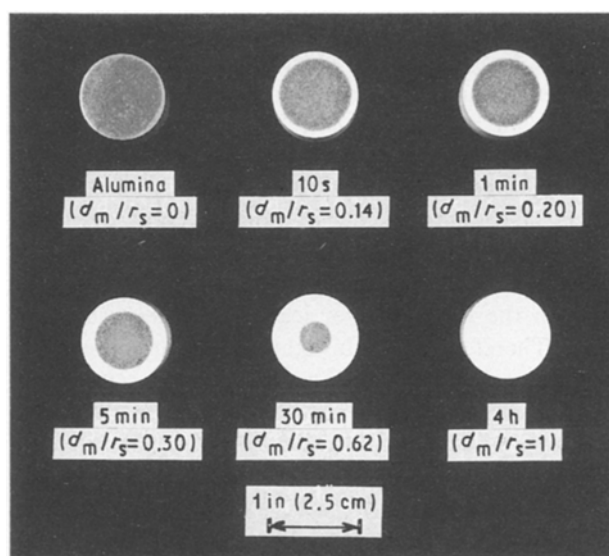


Figure 2 Photograph showing cross-sections of sintered samples and revealing both the mullite/alumina zone (white) and alumina region (grey).

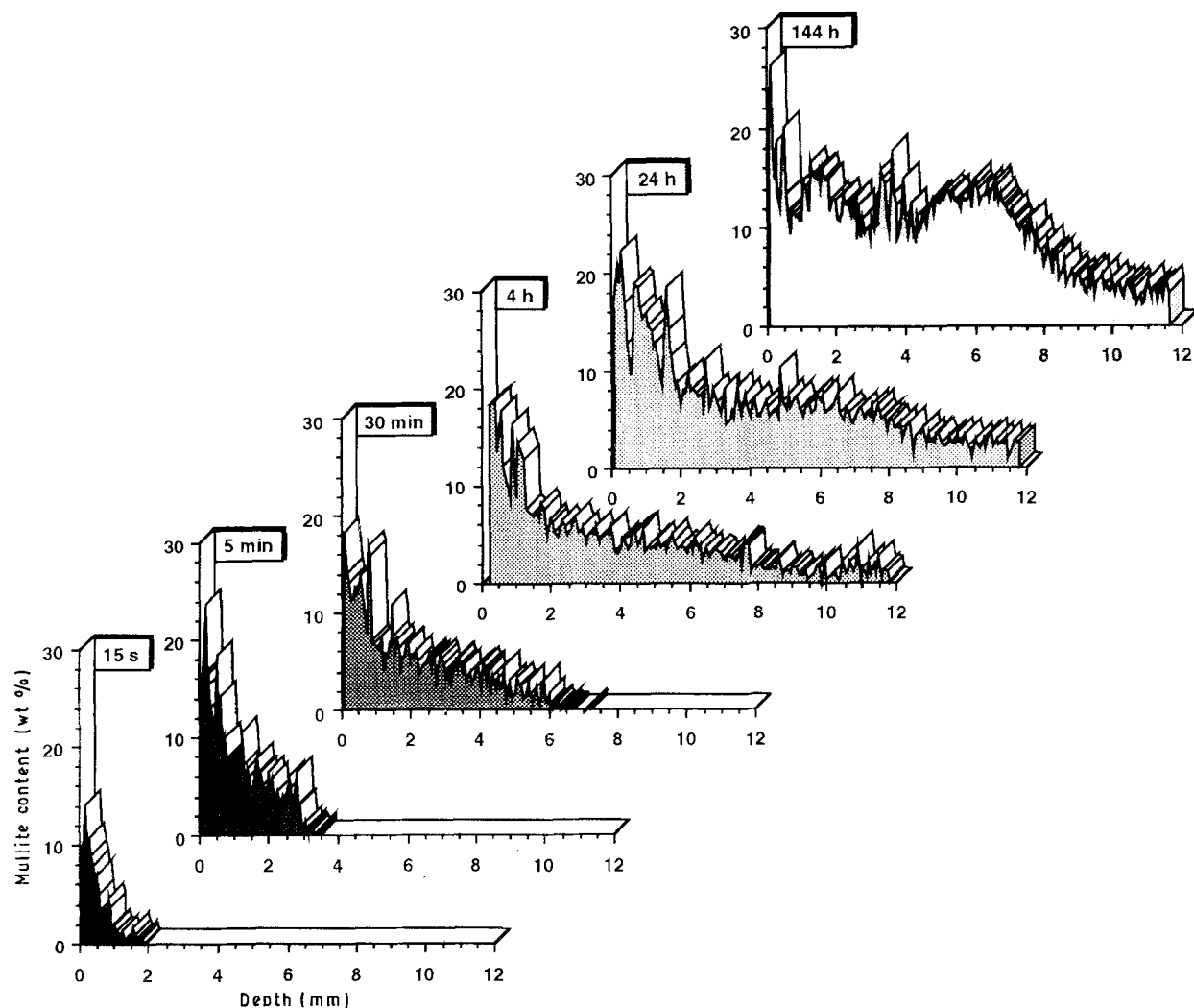


Figure 3 Concentration profiles showing the distribution of mullite within a selection of mullite/alumina samples. The infiltration time is noted on each graph.

TABLE I Depth of the composite zone and bulk mullite content in mullite/alumina samples

Infiltration time	Modified depth after sintering, d_m (mm)	Relative modified depth, ^a d_m/r_s	Bulk mullite content ^b (wt %)
15 s	1.85	0.16	1.7
5 min	3.50	0.30	4.6
30 min	7.28	0.62	6.8
4 h	11.85 (complete)	1	7.5
24 h	11.85 (complete)	1	8.7
144 h	11.85 (complete)	1	10.2

^a d_m and r_s are, respectively, the modified depth and radius of the sample after sintering.

^b Content with respect to the entire body as calculated from the weight gain.

The mullite content is higher in the surface region and decreases towards the interior of the bodies. This effect has been noted previously [2] and three possible explanations for this result have been proposed: (1) filtering of the sol as it infiltrates the body, (2) incomplete filling of the pores initially, with back-filling behind the infiltration front, and (3) liquid redistribution within the preform at some point in the processing after the infiltration step. Contributions

from any or all of these could give rise to gradients in composition.

The infiltration approach for introducing mullite into alumina was chosen for this work because it was felt that the formation of a composite layer in the surface region (with a lower coefficient of thermal expansion) could lead to the formation of residual compressive surface stresses during heat treatment and, hence, strengthening. Indeed, it has been shown that substantial increases in strength can be achieved by introducing mullite into alumina by the infiltration process [3] and that these increases can be related to the presence of a residual compressive stress [4]. Two things are clear from Fig. 3: (1) for bodies in which only the surface region is modified, the existence of the concentration gradient reduces the abruptness of the compositional change at the interface between the modified and unmodified zones, and (2) for bodies in which the infiltration front has reached the centre, the concentration gradients which still exist indicate the potential of the infiltration approach for creating bodies which are composite throughout and simultaneously introducing residual surface compression. Further work is required to determine to what degree this process can be refined and controlled to tailor the compositional changes in any given system.

The incorporation of mullite into alumina significantly affected the densification and microstructural development as compared to pure alumina. It has been reported previously that mullite/alumina composites containing up to ~20 vol % mullite required temperatures in the range 1600–1650 °C to achieve relative densities greater than 98% [2, 5]. Typical soak times to achieve these densities were 12 h at 1600 °C and 2–4 h at 1650 °C. Earlier work also showed that mullite limited grain growth in mullite/alumina composite bodies [5]. In the present study, the microstructure at various points within the sintered composite bodies was observed to determine if differences existed. Results of this work are presented in Figs 4–8 where micrographs of several composite samples fabricated using different infiltration times are presented. While no grain-size analysis was performed to quantify changes in the microstructure, these figures show that the grain size tended to increase with distance from the surface. This increase was most pronounced for partially infiltrated samples. For example, in the body infiltrated for 15 s, with a resulting modified depth of 1.9 mm, a relatively uniform, small-grained region was evident at a depth of 100 μm but at 500 μm a non-uniform microstructure with elongated alumina grains had developed. For samples modified to greater depths, this uniform microstructure and grain-growth control extended further into the sample.

In the two composite samples shown in Figs 1–8 the infiltration time was sufficient to allow the infiltration

front to reach the centre of the body. In the sample infiltrated for 144 h, a relatively uniform microstructure existed at a depth of 8–9 mm; for the sample infiltrated for 4 h, at a depth greater than 2–3 mm, a less-uniform microstructure became evident.

The microstructural development in these samples is obviously related to the presence of mullite. It has been shown in other work that second-phase particulate dispersions can hinder grain growth in the resulting composite body [6]. In the mullite/alumina composites, the presence of mullite at the multigrain junctions inhibits grain growth of the alumina. The concentration profiles of mullite for the composite bodies shown in Figs 4–8 were presented in Fig. 3. By comparing these two figures it can be concluded that in regions where the mullite content was greater than ~5 wt % (~6 vol %) the microstructure developed in a controlled fashion. At mullite contents below this, asymmetric, elongated alumina grains evolved and frequently these had mullite grains trapped within them.

The growth of large grains in the interface region (with their long axes often perpendicular to this boundary) of partially infiltrated samples (Fig. 4) has been discussed previously [2]. It was suggested that this effect was due to the presence of impurities which led to the formation of a low-melting-temperature glass phase. While this “interface effect” may have potential as a means of texturing materials, it has not been studied in any detail. However, it is worth noting that in addition to the potential for using infiltration

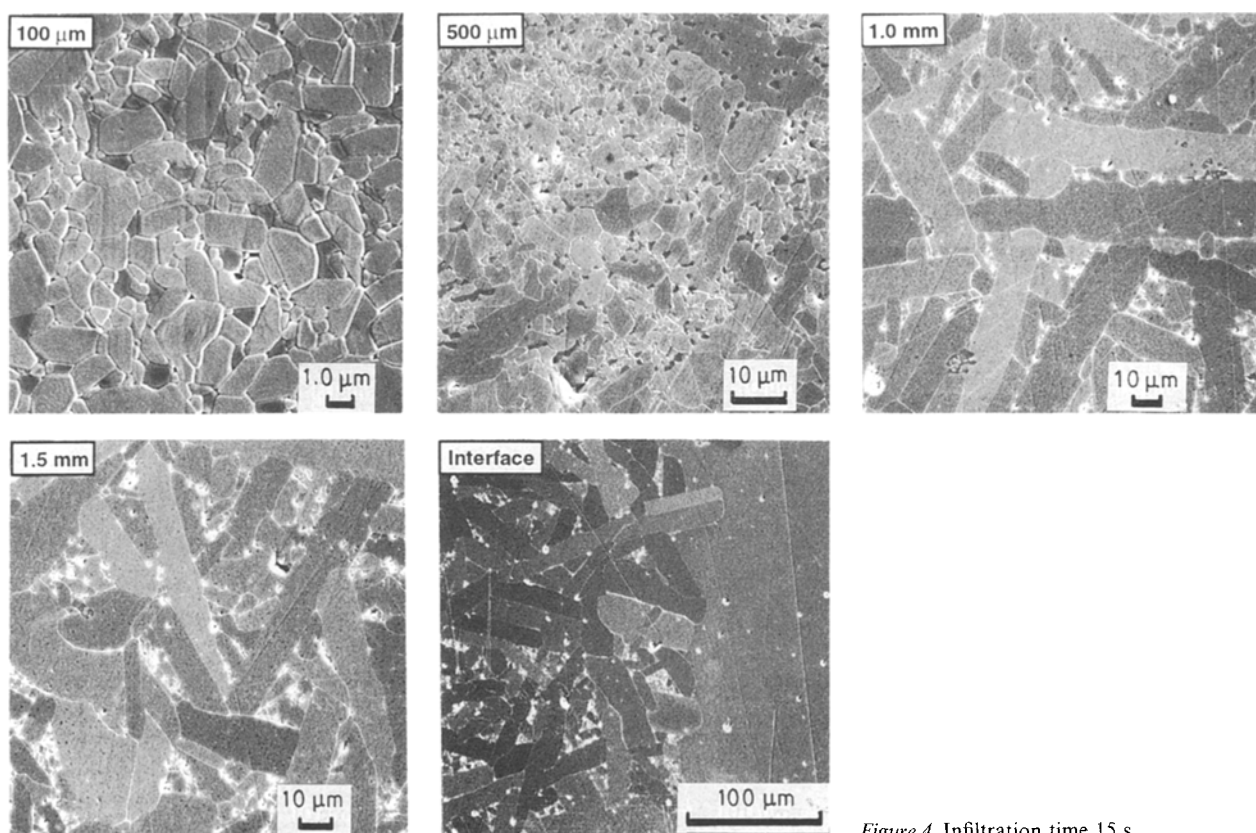


Figure 4 Infiltration time 15 s.

Figures 4–8 Microstructure at various points within mullite/alumina composite bodies prepared using infiltration times of 15 s, 5 min, 30 min, 4 h, and 144 h, respectively. The region being displayed is indicated on the upper left-hand corner of each micrograph where the distance from the surface is shown.

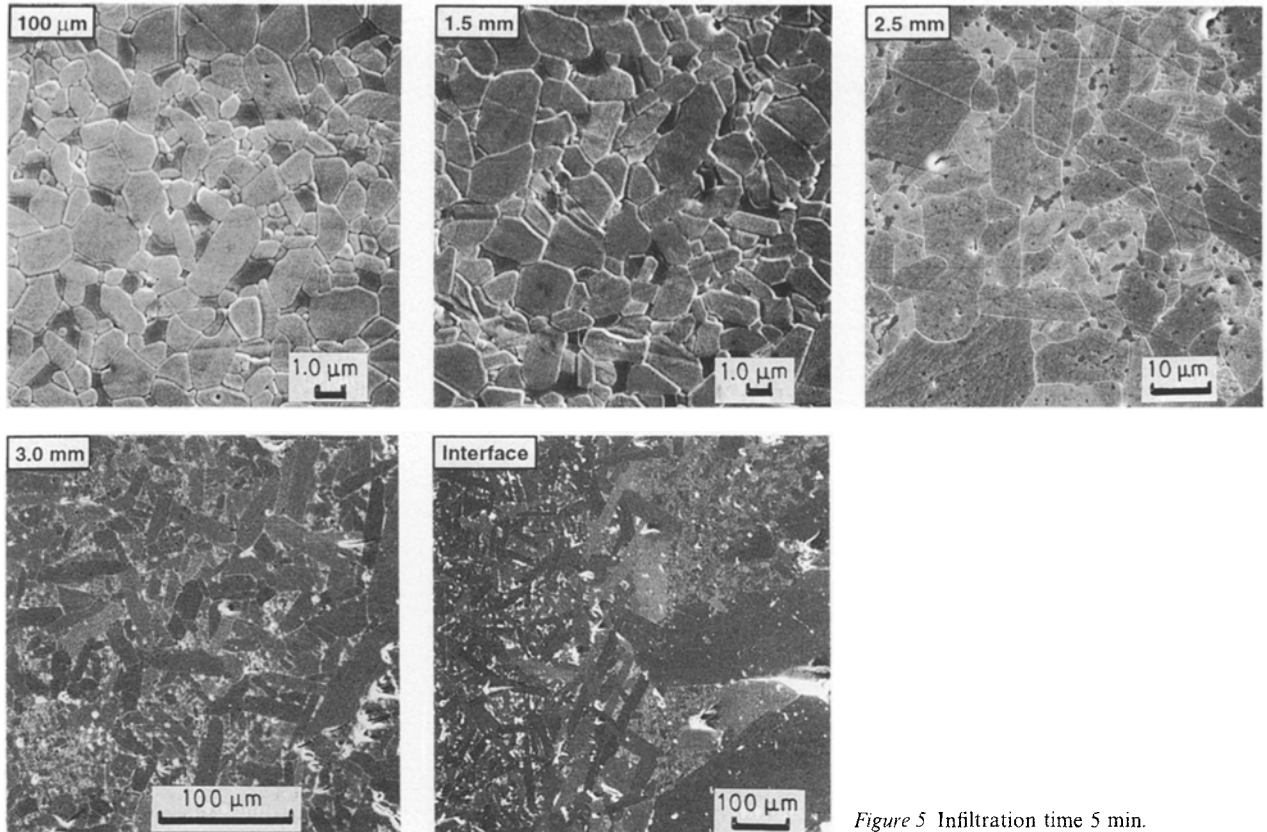


Figure 5 Infiltration time 5 min.

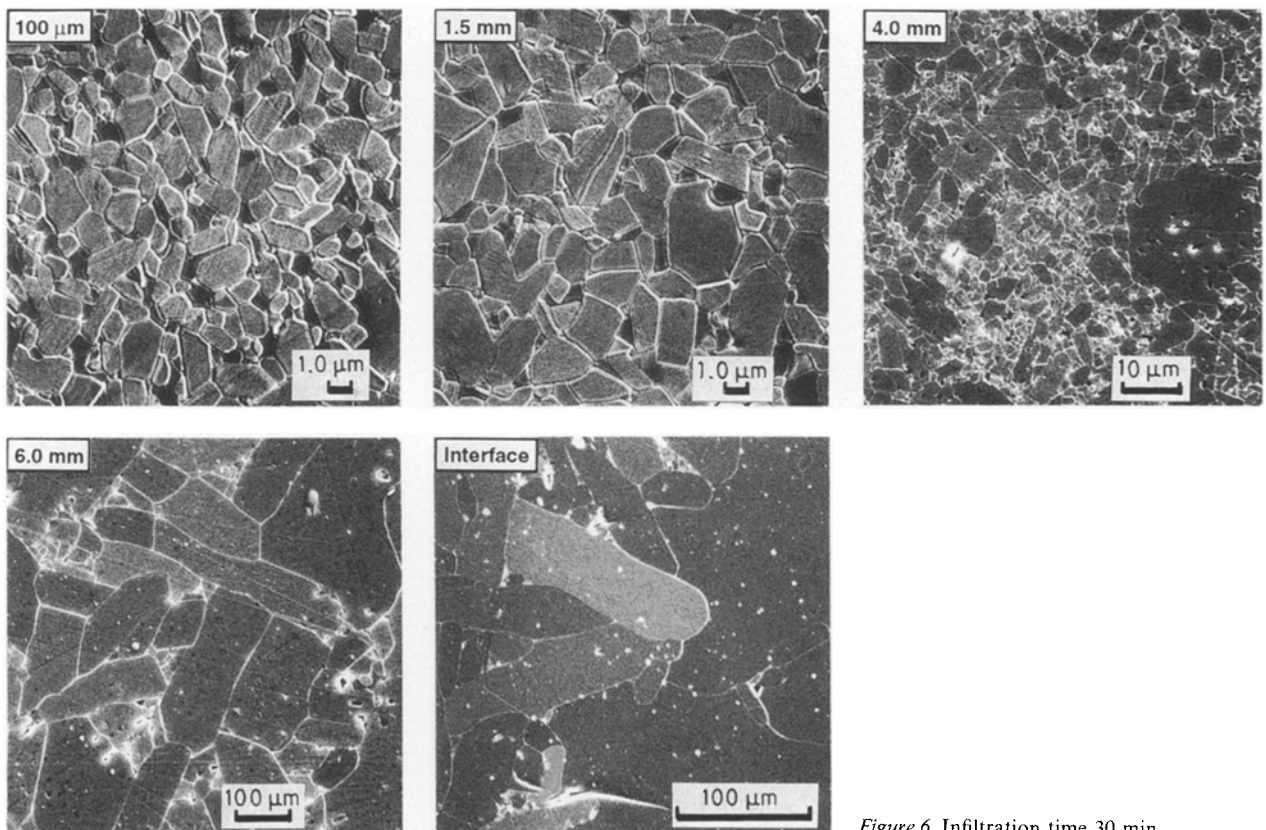


Figure 6 Infiltration time 30 min.

processing to engineer ceramic bodies with gradients in the composition and microstructure, the process may also be a means of producing materials in which the grains have a preferred orientation.

The ability to fabricate graded materials is attractive for both functional and structural applications.

For example, for high-temperature application, limiting grain growth in the surface region could have a positive effect on strength while a larger scale microstructure in the bulk could improve creep resistance. Strength can also be enhanced if the gradient in composition results in a residual compressive stress in

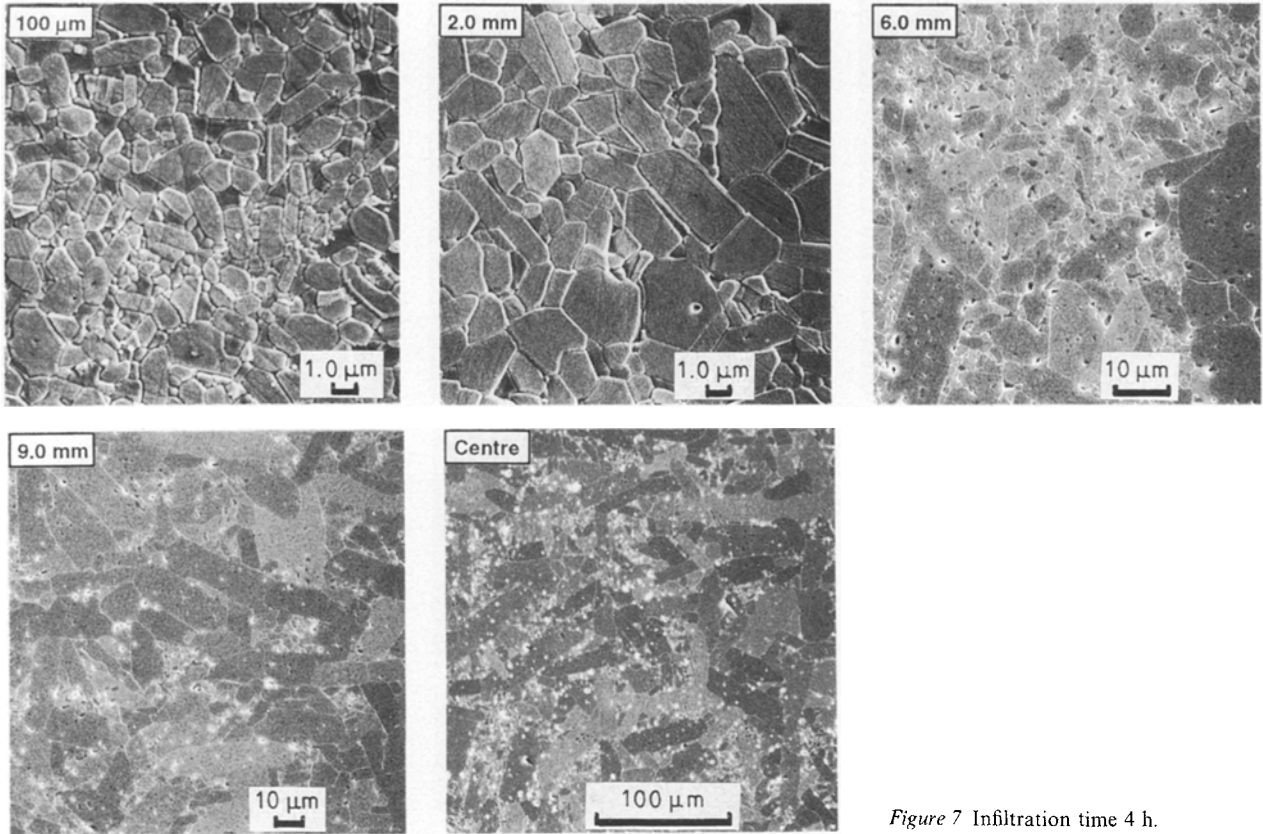


Figure 7 Infiltration time 4 h.

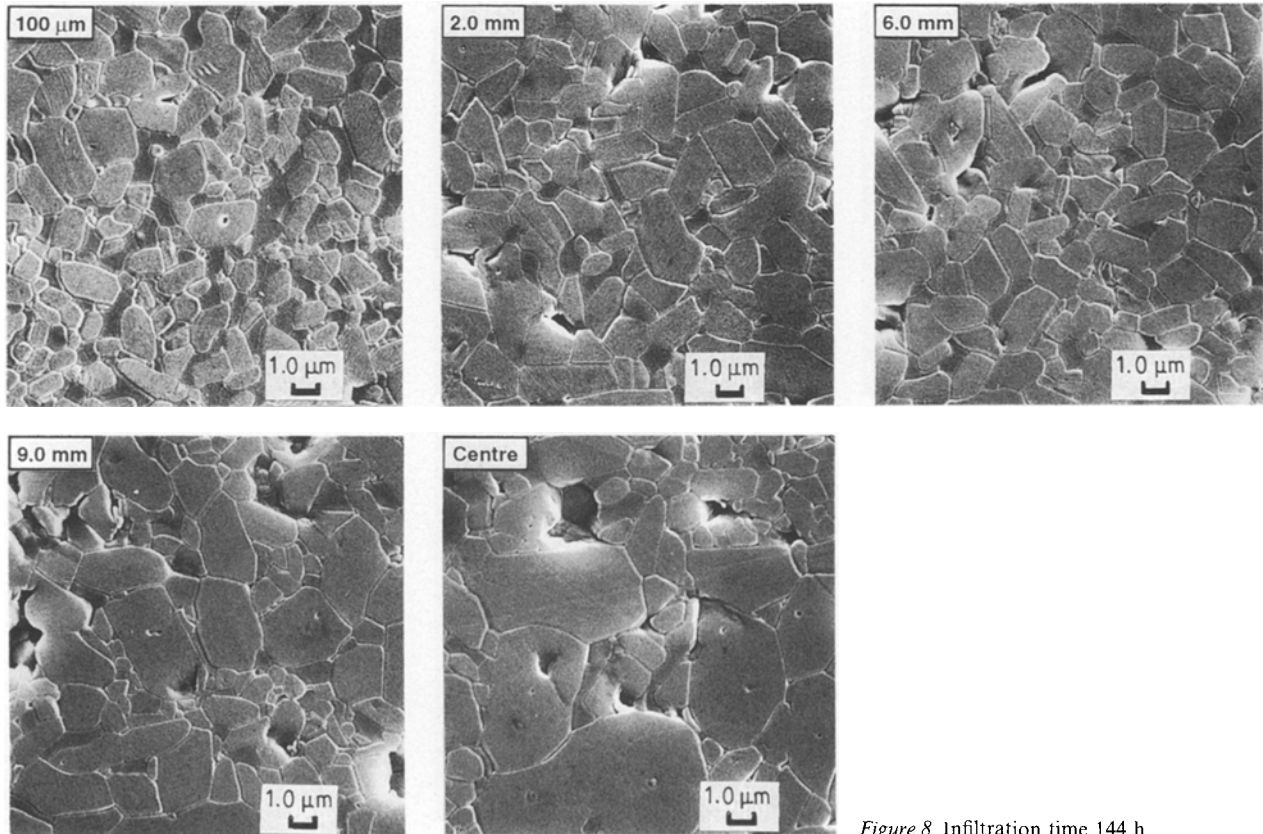


Figure 8 Infiltration time 144 h.

the surface region. Fracture toughness is determined by both composition and microstructure and using the infiltration approach to control both of these could be an attractive means of engineering materials with a gradient in fracture toughness. Indeed, it has been shown that, with some composition profiles pro-

duced using the infiltration process, very flaw-tolerant materials were fabricated [4, 7]. While these are some improvements which could result from fabricating graded materials used in structural applications, similar examples could be cited for the properties important in functional ceramics where gradients in the

microstructure and/or composition could be advantageous.

It is important to point out that the microstructural and compositional effects observed in the mullite/alumina bodies fabricated in this work were not the result of design but rather a by-product of a larger study. Further work is required to determine the extent to which the process can be controlled and applied to other systems. However, the results of the present study indicate the potential for using the infiltration approach as a means of engineering materials by controlling both the distribution of the phases and the microstructural development and thereby tailoring the properties for specific applications.

4. Conclusions

The fabrication of mullite/alumina bodies by heating alumina preforms infiltrated with an SiO₂-containing sol resulted in composite specimens having gradients in both the composition and microstructure. The mullite content decreased from the surface inwards, while at the same time the grain size tended to increase. The mullite content required in a particular region in order to control grain growth of alumina was determined to be ~5 wt %. While further work is required to determine the extent to which the infiltration approach can be applied to engineer ceramics, the results of this study indicate that there is considerable potential. The

results also indicate the importance of determining the distribution of the phases in materials fabricated by the infiltration process as there can be large differences between the bulk content of a particular constituent and its concentration in any given region.

Acknowledgements

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