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Effect of composition on the enhanced microwave sintering of alumina-based ceramic composites

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A series of comparative experiments were performed in which a number of alumina–zirconia compositions were sintered in both microwave and conventional furnaces, using identical heating profiles. Measurement of sample end-point densities showed an enhancement of the sintering process associated with the use of microwave heating for all compositions studied. The associated microstructures examined using scanning electron microscopy showed slightly larger grain sizes for the microwave-sintered compacts, as would be expected from their higher densities. The design of a high-temperature sintering dilatometer has allowed continuous *in situ* monitoring of the densification process in both the microwave and conventional environment. Data obtained in this way have shown that there is an effect of composition on microwave densification. This appears to be related to the increased lossiness of the composite, (increased zirconia content), rather than the effect of zirconia as a sintering aid. In addition the dilatometer results suggest that the microwave enhancement of the sintering process may be due to a reduction in the activation energy for grain-boundary diffusion.

1. Introduction

Microwave sintering is a novel electrical processing technique for ceramic materials which differs fundamentally from conventional processes by providing volumetric heating. As a result of this feature, several technical and economic advantages have been cited for the technique, including more rapid and uniform heating leading to improved microstructural properties; shorter furnace response times; and enhanced energy efficiency [1–3]. In addition, claims have been made in the literature of enhanced densification due to a reduction in the activation energy for sintering, although the micromechanisms responsible for this effect are not yet understood [4].

There are two main physical loss mechanisms by which microwaves interact with ceramics, resulting in internal heating. These are the flow of conductive currents (in particular ionic conduction), and dipolar reorientation. Mathematically both of these losses may be included in an effective dielectric loss factor

$$\varepsilon_e'' = \underbrace{\varepsilon''}_{\text{dipolar losses}} + \underbrace{\frac{\sigma}{\omega\varepsilon_0}}_{\text{conductive losses}} \qquad (1)$$

where ε'' is the dielectric loss factor; σ is the conductivity; ε_0 is the permittivity of free space; and ω is the frequency. An alternative expression of the losses which is frequently used is the effective loss tangent $\tan\delta_e$

$$\tan\delta_e = \frac{\varepsilon_e''}{\varepsilon'} = \frac{\varepsilon''}{\varepsilon'} + \frac{\sigma}{\omega\varepsilon'\varepsilon_0} \qquad (2)$$

where ε' is the relative dielectric constant. The power deposited in the ceramic dielectric is then given by

$$P = \omega\varepsilon_0\varepsilon'\tan\delta_e|E|^2 \qquad (3)$$

where E is the electric field.

Fig. 1 is a typical example of how $\tan\delta_e$ varies in a low-loss ceramic, such as alumina. At room temperature $\tan\delta_e$ is very low and the ceramic is essentially transparent to microwave radiation. Above some critical temperature (~ 1000 °C in the case of alumina) $\tan\delta_e$ rises rapidly, resulting in more effective heating. This behaviour is believed to be due primarily to the increase in ionic conductivity with temperature. Heating of alumina from low temperatures to the point where it becomes more lossy often requires some form of external preheating. This may be in the form of an external susceptor (a material with high losses at low temperatures) and/or the addition of a lossy material to the green body which may or may not be removed during processing.

The work reported is primarily concerned with determining the effect on microwave densification of adding a lossy ceramic, stabilized zirconia, to alumina. The ionic conductivity of zirconia (and hence its loss

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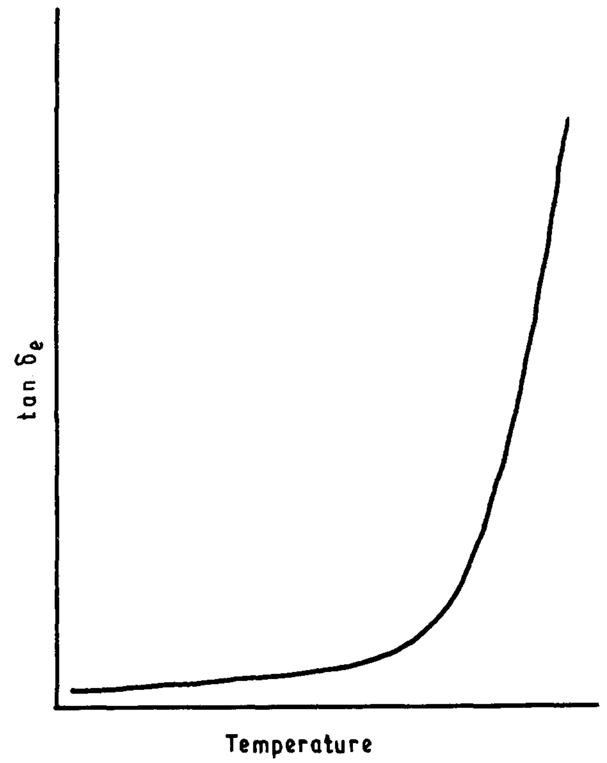

Figure 1 Typical variation of tan δ_e with temperature for a low-loss ceramic such as alumina.

factor) has been shown to increase with the addition of a cubic phase stabilizer such as magnesia, calcia or yttria. Maximum ionic conductivity is achieved with a concentration of stabilizer close to the minimum required to fully stabilize the cubic phase [5]. For this work, zirconia fully stabilized with 12 wt% yttria (YSZ) was used.

A comparative study has been made in which samples containing varying mass fractions of YSZ have been sintered in both microwave and conventional furnaces, using identical heating profiles, followed by measurement of their end-point densities. Although this work is essential to further understand the effects of microwaves, obtaining detailed sintering information in this fashion requires the preparation and testing of a large number of specimens, which is necessarily time consuming. It was decided therefore to design and construct a sintering dilatometer, capable of operating in both conventional and microwave heated furnaces, in order to monitor sintering rates continuously during firing.

2. Experimental procedure

All materials used in this study were prepared from A1000SG alumina powder supplied by Alcoa and type-ZYP (Zircar Fibrous Ceramics, Florida) yttria-stabilized zirconia (YSZ) powder supplied by Zircar Fibrous Ceramics (Alcoa, Worcester, UK). Both powders have a sub-micrometre grain size, with the zirconia having a very fine crystallite size of 0.02–0.03 µm. Four different sample compositions, detailed below, ranging from 100% alumina to 100% zirconia were studied:

(i) alumina;
(ii) alumina + 20 wt% YSZ;
(iii) alumina + 50 wt% YSZ;
(iv) YSZ.

Samples were prepared by wet-milling the powders in appropriate quantities with 1% polyethylene glycol binder. The powders were then dried, crushed and sieved, prior to uniaxial pressing using a 19-mm tool steel die at a pressure of 96 MPa. Specimens were prepared for the dilatometer using a 12-mm die and a similar pressure. The binder was then burnt out of the compacts in a muffle furnace using a slow heating cycle. The resulting compacts had a green density of approximately 55%.

Sintering trials were carried out in a modified 700W, 2.45-GHz domestic microwave oven. Fig. 2 shows the arrangement of the specimens and susceptor within the insulated fibre box. The susceptor consists of zirconia fibre loosely compacted in an alumina vessel. In order to increase its lossiness and maintain a sufficient load for the magnetron, the susceptor was preheated in a conventional furnace prior to being placed in the insulated box. Three samples were used in each of the experiments to monitor any effects resulting from temperature gradients within the hot zone. The temperature inside the hot zone was monitored during the heating cycle using an Accufiber black-body probe in contact with the top sample. This type of probe has been found to be immune to electromagnetic interference, unlike conventional thermocouples.

In each test a predetermined heating profile was followed up to the maximum sintering temperature, which ranged from 1250–1600 °C. Control of the heating rates was achieved, initially, by manual switching of the microwave power. Subsequent tests, however, used a Eurotherm 818P programmable controller linked to the Accufiber temperature-measurement system. When the samples reached the maximum desired temperature (termed the sintering temperature) the power was switched off immediately to allow natural cooling. For comparison, samples were sintered conventionally in a rapid-heating Super Kanthal furnace, using identical heating profiles. Following sintering,

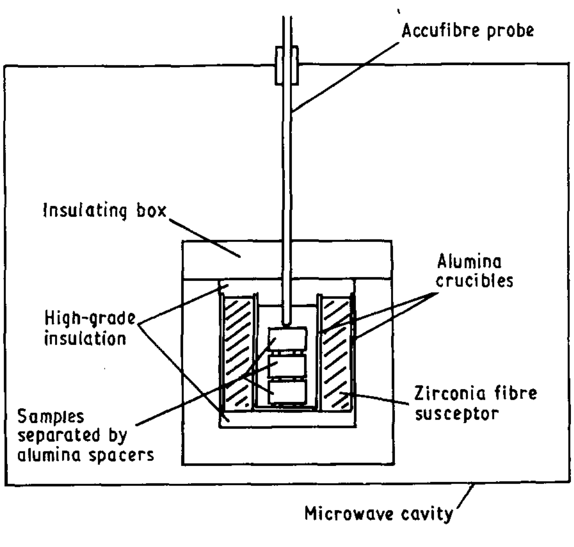

Figure 2 Sintering arrangement within the microwave furnace.

final densities were measured using the Archimedes technique, with mercury as the immersion medium. Microstructural observations were carried out using a SEM.

The dilatometer used throughout this work was constructed from recrystallized alumina tubing and utilized a linear variable differential transformer (LVDT) transducer to detect displacements with a resolution of 0.1 μm. A higher power (1.4 kW) commercial microwave oven was adapted for use as a furnace capable of reaching over 1700 °C in air. A novel susceptor design was employed, allowing repeated rapid heating from room temperature without the use of any conventional preheating. Data from the transducer and temperature-measurement system were continuously logged during the heating cycle and then processed using a spreadsheet-type programme in order to calculate both linear shrinkage and sintering rate. Measurements were made in microwave and conventional furnaces at temperatures up to 1600 and 1450 °C, respectively, with a constant heating rate of 30°C min^{-1} being used throughout.

3. Results and discussion

Fig. 3 shows the variation of final density (expressed as a percentage of theoretical density) with sintering temperature for both microwave- and conventionally sintered material for each of the four systems studied. It can be seen that, in each case, the microwave-sintered samples show enhanced densification compared to their conventional equivalents, and that this effect is most evident at low sintering temperatures/densities.

For alumina (Fig. 3a), the microwave-sintered samples reach a specified density at a temperature approximately 50 °C lower than the equivalent conventional specimen. Kimrey *et al.* [4] have also observed enhanced microwave sintering of alumina. In their system (28 GHz, 200 kW, hard vacuum) a temperature difference of 300–400 °C was measured.

The results for alumina–20 wt % YSZ and alumina–50 wt % YSZ seen in Fig. 3 b, c do not exhibit a pronounced difference from those for alumina. Although at 1400 °C no difference in densification is observed between these materials in the microwave furnace, between 1450 and 1600 °C there is a slight increase in densification. The data for specimens prepared in the conventional furnace also show a small increase in densification in this same temperature range. This feature suggests that the addition of stabilized zirconia promotes the densification of alumina in the same manner as a conventional sintering aid, and that the improvements observed in microwave-fired specimens may be a result of this process.

Surprisingly, however, no further increase in densification appears to result from the addition of 50 wt % YSZ over that of the 20 wt % addition. Finally, Fig. 3d shows the data for 100% YSZ, the

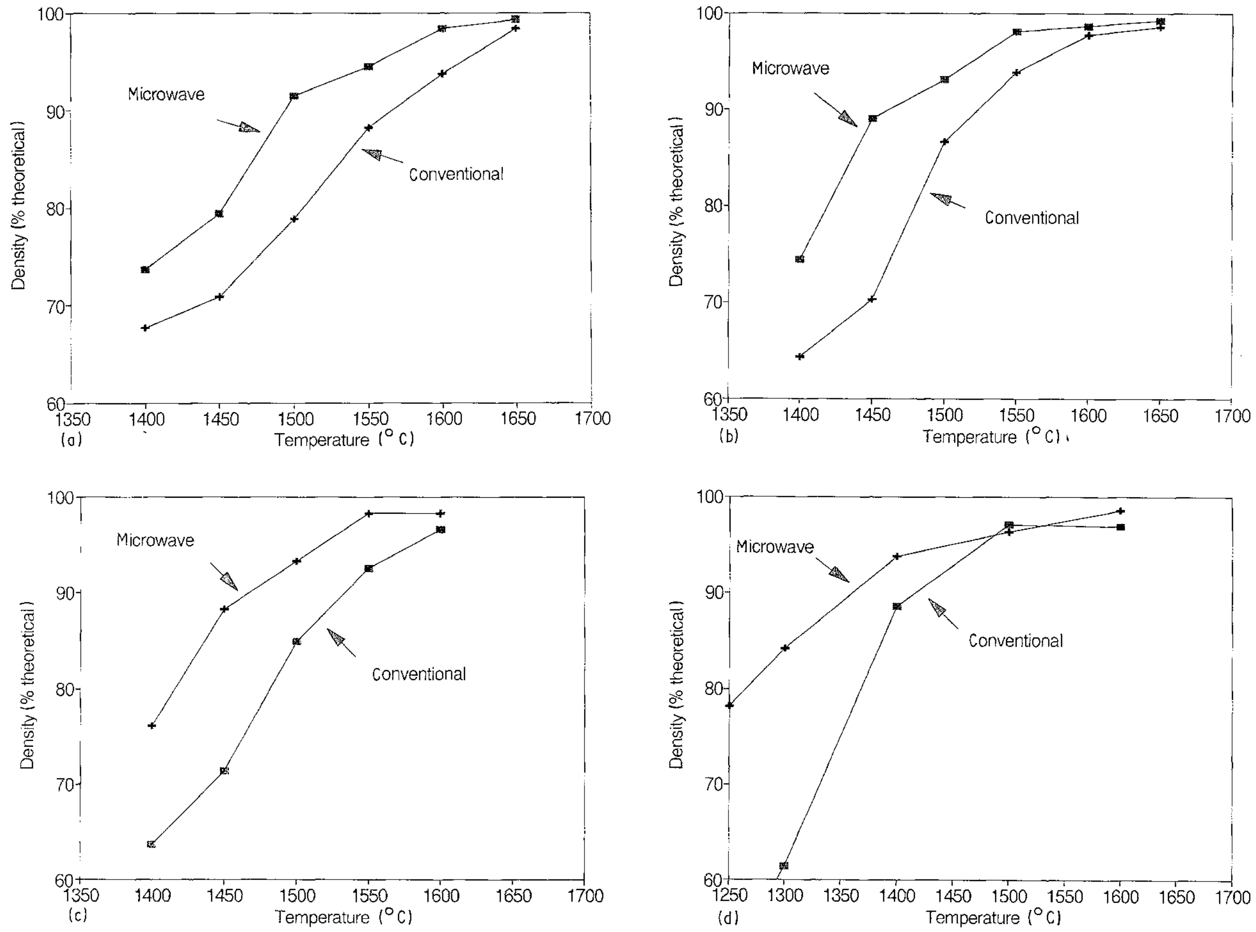

Figure 3 Variation of final density with sintering temperature for both microwave and conventional sintering, showing the microwave enhancement. (a) Alumina; (b) alumina + 20 wt % YSZ; (c) alumina + 50 wt % YSZ; (d) YSZ.

material which should be the most microwave-susceptible of all the compositions studied. The enhancement of the microwave sintering is extremely pronounced, particularly at temperatures below 1500 °C. The difference between equivalent densities of the microwave fired specimens and their conventional equivalent is as much as 100 °C in this region.

Fig. 4a–d shows the results of the equivalent sintering dilatometer tests. Each graph compares the linear shrinkage (d*l*/*l*) and the sintering rates (d*l*/*l* s) observed in both the microwave and conventional furnaces. Again a significant enhancement of sintering is evident when using microwave heating.

For alumina (Fig. 4a) both microwave and conventional specimens commence sintering at just under 1100 °C, with the sintering rate in the microwave furnace rising more rapidly to a peak value almost double that in the conventional furnace. Comparing the temperatures corresponding to an 8% shrinkage highlights a difference of approximately 170 °C between microwave and conventional furnaces.

The sintering data for the remaining three zirconia-containing compositions show a number of interesting features. In each case the temperature of the peak sintering rate is lower in the microwave furnace than in the conventional. This reflects the data obtained in the previous experiments.

For both alumina–20 wt % YSZ and alumina–50 wt % YSZ, the microwave and conventional sintering profiles have similar shapes but are displaced with respect to temperature by about 150 °C i.e. at the same shrinkage, both sintering methods resulted in similar densification rates. In a comparison with pure alumina, the dilatometry data show that alumina has a more rapid sintering rate at low temperatures, but that above about 1200 °C the zirconia-containing compositions exhibit a much higher sintering rate rising to a higher maximum. This results in overall enhanced densification above 1400 °C for the zirconia-containing compositions, as was observed in the sintering tests.

An interesting feature of the data for alumina–50 wt % YSZ and 100 wt % YSZ is the appearance of a very rapid initial rise in sintering rate, followed by a stabilization (at temperatures between 1000 and 1200 °C) before increasing more rapidly again. This effect is only slight in the alumina–50 wt % YSZ system but is extremely pronounced in microwave-heated 100% stabilized zirconia. Notably, this material also shows an extremely high peak sintering rate, in excess of 0.0005 s^{-1}. One possible explanation for the change in sintering rate may be the very reactive nature of the zirconia powder used. The initial sintering may then be due to sintering of very fine zirconia crystallites

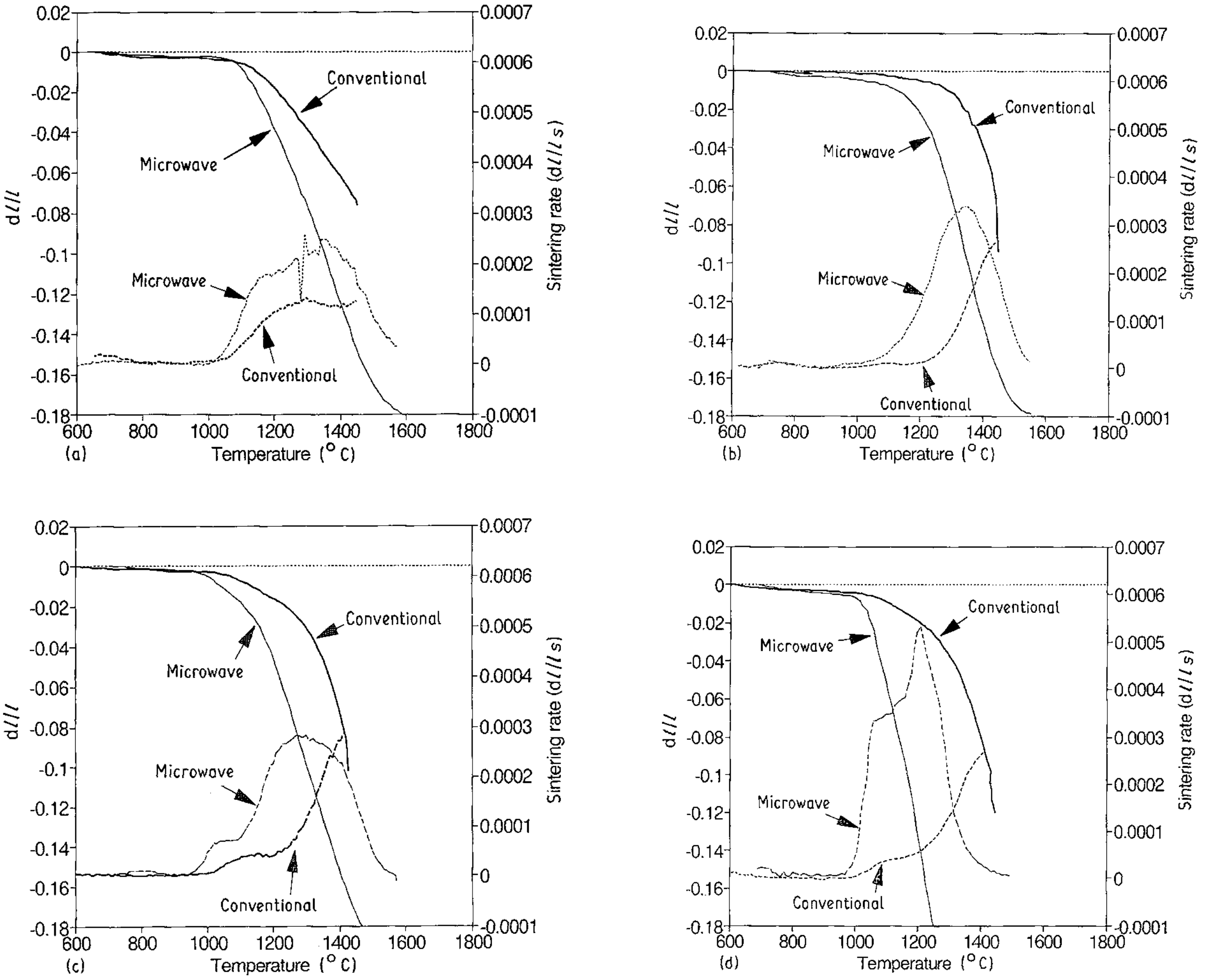

Figure 4 Sintering profiles measured in both microwave and conventional furnaces, again showing microwave enhancement. (a) Alumina; (b) alumina + 20 wt % YSZ; (c) alumina + 50 wt % YSZ; (d) YSZ. (——) d*l*/*l*; (---) rate.

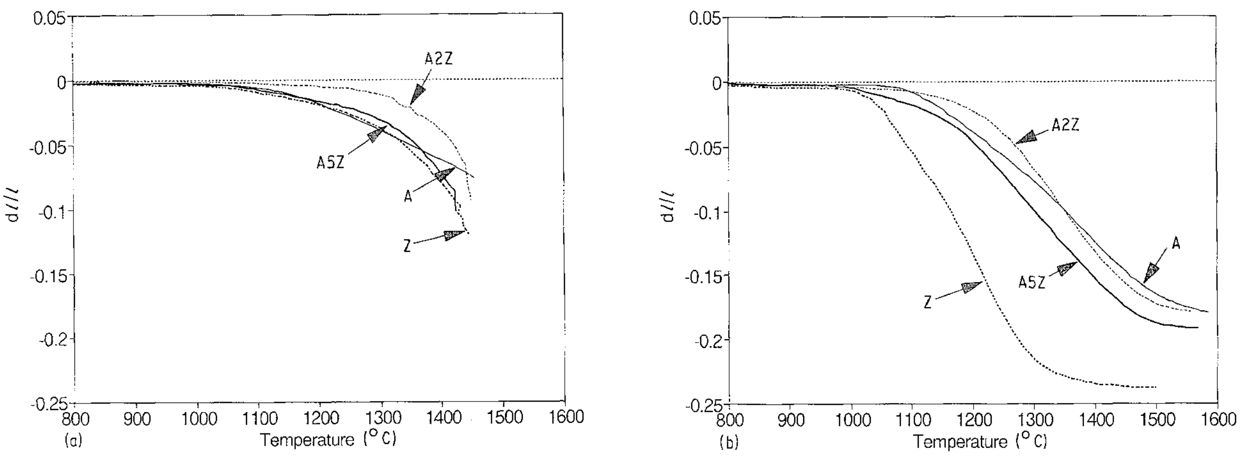

Figure 5 Comparison of the linear shrinkage curves for all four materials systems: (a) conventional; (b) microwave.

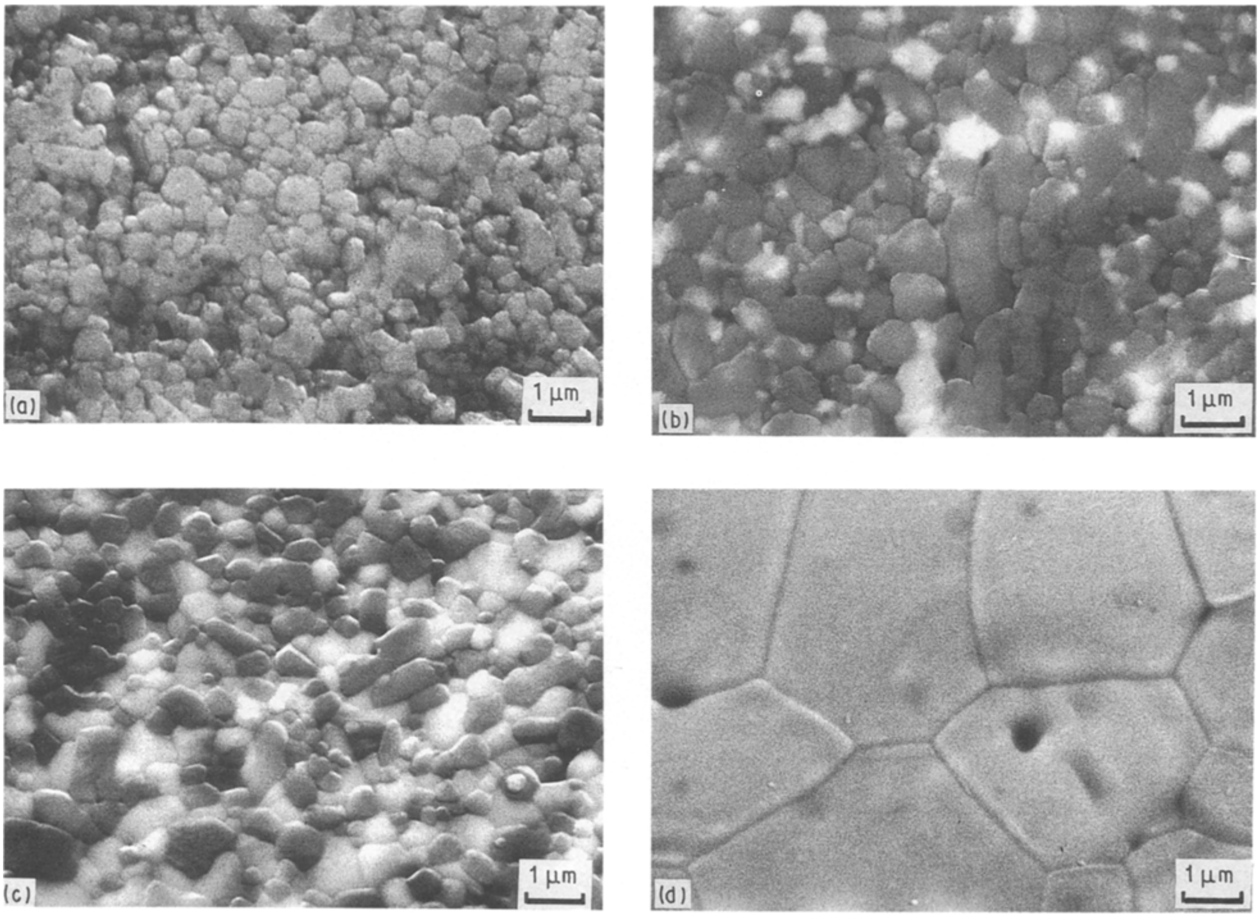

Figure 6 SEM micrographs of samples sintered at 1500 °C in the microwave furnace. (a) Alumina; (b) alumina + 20 wt % YSZ; (c) alumina + 50 wt % YSZ; (d) YSZ.

(0.02–0.03 μm) within micro-agglomerates (0.1 μm), with the second stage being due to inter-agglomerate or agglomerate/matrix sintering.

Fig. 5a shows the linear shrinkage curves for all the compositions obtained in the conventional furnace. Here, with the exception of the alumina–20 wt % composition, all the profiles follow a nearly identical pattern. This suggests that the presence of stabilized zirconia has only a limited effect as a sintering additive. Data (shown in Fig. 5b) obtained from the microwave furnace are sharply contrasting. It can be seen that, especially at relatively high shrinkages, the curves are well separated in order of increasing lossiness with decreasing temperature. The dilatometry method therefore does show an effect of composition on microwave densification, which appears to be related to the increased lossiness of the additive rather than its effect as a sintering aid.

Wang and Raj [6], using an analogy to the study of phase transformation and thermal desorption, suggested that the position and magnitude of the peak sintering rate may be used to give an insight into the

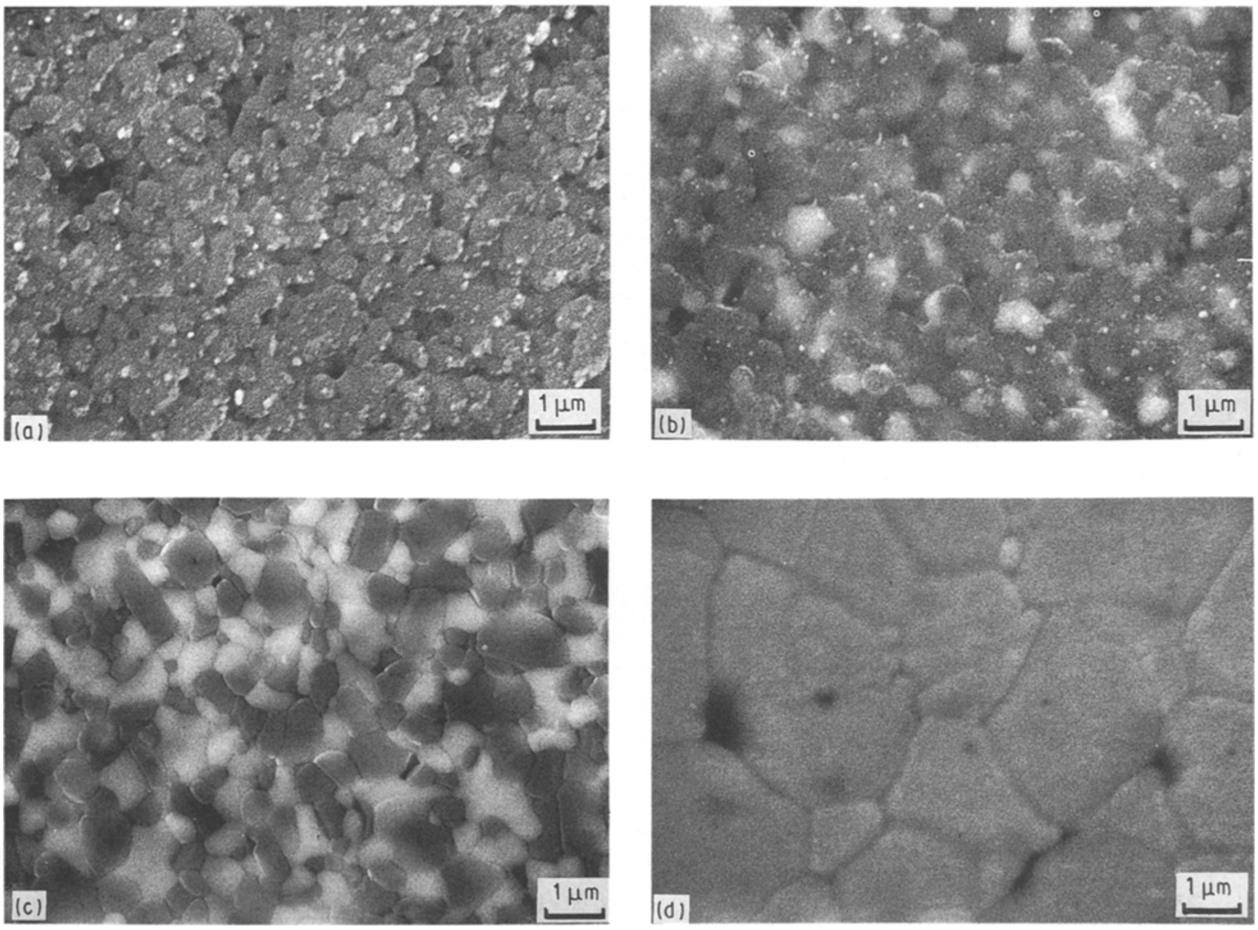

Figure 7 SEM micrographs of samples sintered at 1500 °C in the conventional furnace. (a) Alumina; (b) alumina + 20 wt % YSZ; (c) alumina + 50 wt % YSZ; (d) YSZ.

activation energy for the sintering process. Their results suggest that, for alumina, the activation energy for intermediate stage sintering is that for grain boundary self-diffusion. Their analysis, combined with their experimental results, indicates that larger peak sintering rates at higher temperatures are obtained with larger activation energies, with the temperature at which the peak occurs being the dominating factor. Following this argument, data from these tests suggest a clear reduction of the activation energy for grain boundary self-diffusion during microwave processing, as has been claimed by Kimrey *et al.* [4]. Further experiments are in progress to measure the activation energies directly using the dilatometer.

Scanning electron microscopy was used to examine the microstructures of both microwave and conventional samples. Fig. 6 shows micrographs of samples of each composition heated to 1500 °C in the microwave furnace. The alumina (Fig. 6a) shows a fairly uniform submicrometre microstructure with a large amount of porosity, consistent with its density of 92%. In the two alumina/zirconia compositions (Fig. 6b, c) in each case the zirconia appears to be fairly well distributed throughout the alumina matrix. In both of these materials, the grain size is about 1 μm. The zirconia however (Fig. 6d) has a much larger grain size (5 μm), due to the absence of small alumina grains which act as grain-boundary pinning points [7]. Fig. 7 shows the equivalent conventional micrographs which exhibit very similar features. The microwave-sintered samples have slightly larger grain sizes, as would be expected from their higher densities.

Grain-size measurements were made on samples of alumina/20 wt % zirconia sintered in both microwave and conventional furnaces for 0, 1/2, 1 and 2 h. Standard methods for a two-phase microstructure were used on SEM micrographs to obtain the results shown in Fig. 8. This showed, as expected, that the grain sizes of

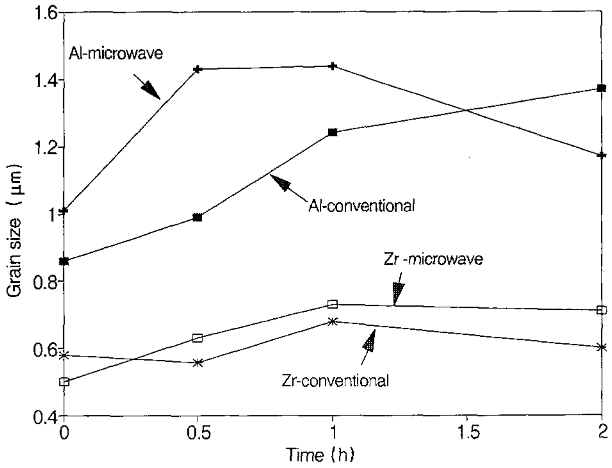

Figure 8 Variation of grain size with time at sintering temperature in alumina + 20 wt % YSZ, showing larger grain sizes in the microwave-sintered material.

microwave-sintered material tended to be larger, consistent with their higher densities.

4. Conclusions

A comparative study of microwave and conventional sintering of a series of alumina/zirconia compositions has confirmed that microwave heating enhances the densification process. Microwave-sintered materials tend to have larger grain sizes, as was expected from their greater densities.

The adaptation of high-temperature sintering dilatometry for use in the microwave environment has enabled continuous *in situ* monitoring of the sintering process. This method has shown that the microwave enhancement of the sintering process is increased for more lossy material compositions, raising the possibility of localized heating. These initial dilatometry results also suggest that the microwave enhancement may be a result of a reduction in the activation energy for grain-boundary diffusion.

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