

Sintering and grain growth of 3 mol% yttria zirconia in a microwave field

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A comparative study of the sintering and grain growth of 3 mol% yttria zirconia using conventional and microwave heating was performed. Extensive measurements of grain size were performed at various stages of densification, and following isothermal ageing at 1500 °C for 1, 5, 10 and 15 h. Microwave heating was found to enhance densification processes during constant rate heating. The grain size/density relationship for the microwave-sintered samples was shifted in the direction of increased density for density values less than 96% of the theoretical value when compared to conventionally heated samples. This suggests that there may be a difference in the predominant diffusion mechanisms operating during the initial and intermediate stages of sintering. Results of the ageing experiments showed that once densification was near completion, grain growth was accelerated in the microwave field, and exaggerated grain growth occurred.

1. Introduction

Microwave sintering has a number of advantages when compared to conventional heating techniques. These include the potential for rapid, volumetric heating, uniform microstructure, improved production rates and lower energy requirements. In addition, there is a growing body of evidence for the microwave enhancement of densification of a variety of ceramic materials, with higher densities being achieved at lower temperatures than is possible with conventional radiant heating [1–4].

Most of the work reported to date has focused on the relationship between density and temperature [5–9]. It has been suggested that the enhancement of densification may be due to a change in the predominant mass transfer mechanisms operating during sintering [10]. For ceramics, it is generally desirable to achieve maximum density with minimum grain growth, and a change in mass transfer mechanisms which favoured densification would be advantageous.

Yan [11] reviewed in depth the processes of densification and microstructural development during sintering. Based on a theory which incorporates simultaneous grain growth and densification, relationships between grain size and density were established for three different limiting cases. By plotting the grain size as a function of density from a number of experiments on one graph, the effects of changing process parameters on the balance between the various mass transport mechanisms operating can be shown.

In this study, the relationship between grain size and density of 3 mol% yttria zirconia sintered in a microwave field was compared to that of samples subjected to the same thermal cycle in a conventional electric furnace, in order to determine if there was any evidence for a difference in predominant mass transfer mechanisms. Isothermal ageing experiments were also performed to allow comparison of grain growth following the completion of densification.

2. Experimental procedure

Spray-dried 3 mol% yttria zirconia powder manufactured by Tosoh was used. Samples measuring 6 mm × 6 mm × 60 mm were prepared by uniaxial pressing to 200 MPa. Following binder burn-out at 600 °C, the sample density was approximately 50% theoretical density.

Conventional heating was performed in an electric furnace with SiC heating elements. A calibrated type R thermocouple was used to measure the temperature. The tip of the thermocouple was placed in direct contact with the sample surface.

The microwave system used operated at a fixed frequency of 2.45 GHz, and had a nominal power rating of 1200 W, with an infinitely variable power supply. A four-stub tuner was used to tune the field, and optimize energy absorption. The chamber had a mode stirrer fitted into the roof to improve field uniformity. A calibrated type R thermocouple encased

in a thin-walled (0.1 mm) Pt/Rh sheath was used to measure temperature. The thermocouple tip was placed in the centre of a stack of five samples. The thermocouple was linked to a computer which provided automatic control and data logging.

Zirconia is not a good absorber of microwave energy until heated to approximately 400 °C. Therefore, SiC rods were used as susceptors to initiate heating.

For the sintering studies, samples were heated at 2 °C min⁻¹ to 1300, 1400 or 1500 °C. No dwell time was included. The same heating rate was used for ageing experiments, in which the samples were heated to 1500 °C, and then held at temperature for 1, 5, 10 or 15 h.

The densities of the sintered samples were measured using the Archimedes method. Samples were prepared for electron microscopy using standard ceramographic techniques. Grain sizes were determined using the public domain NIH Image program [12]. A minimum of 200 measurements were made from each specimen, and then the results from the five specimens in each group were averaged.

3. Results

The density of the 3 mol % yttria zirconia samples as a function of temperature is shown in Fig. 1. Microwave-sintered samples were significantly denser than their conventionally sintered counterparts at the lower temperatures used, with the difference decreasing at higher temperatures.

All samples had the typical “bubble” type of microstructure usually observed for this ceramic. The residual porosity was evenly distributed, and grain size found to be very uniform throughout the sintered samples. Grain size as a function of density is shown in Fig. 2. Statistical analysis of these data indicates that there is a significant difference between the microwave and conventionally sintered samples at densities below 96% theoretical density.

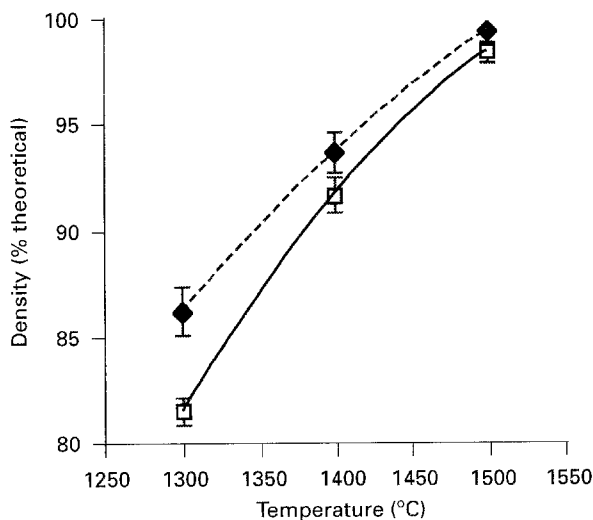


Figure 1 Average density of 3 mol % yttria zirconia as a function of temperature, with a heating rate of 2 °C min⁻¹. Error bars indicate standard deviation. (□) Conventional heating, (◆) microwave heating.

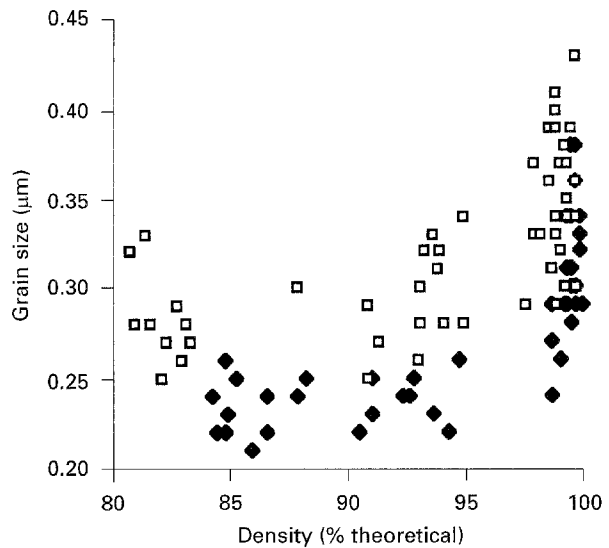


Figure 2 Grain size as a function of density for 3 mol % yttria zirconia. (□) Conventional heating, (◆) microwave heating.

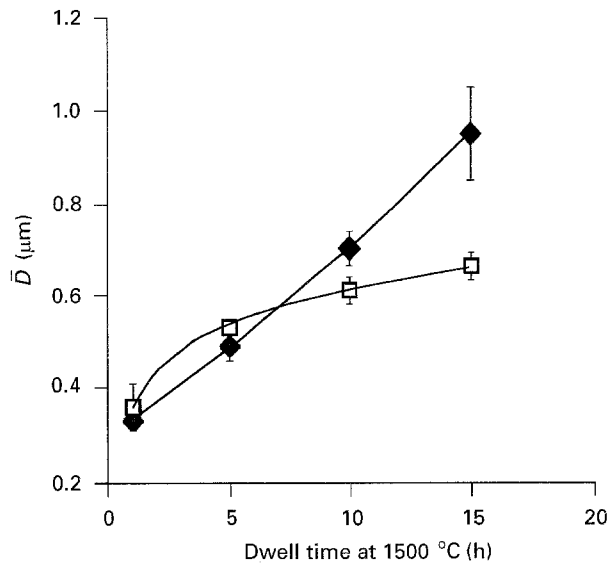


Figure 3 Grain growth in 3 mol % yttria zirconia at 1500 °C. (□) Conventional heating, (◆) microwave heating.

As densification neared completion, grain growth occurred. The average grain diameter as a function of dwell time at 1500 °C is shown in Fig. 3. Grain growth was accelerated in the microwave field, with the average grain size being approximately 50% greater than that of the conventionally heated samples after ageing for 15 h.

4. Discussion

The microwave-heated samples had significantly higher densities at lower temperatures than did the conventionally sintered samples. The density/temperature relationship shifted downwards approximately 50 °C at the lower test temperatures used, with the difference gradually decreasing as higher temperatures were reached. Janney *et al.* [13] observed a much larger shift in this relationship for 8 mol % yttria zirconia (100–150 °C). However, direct comparison

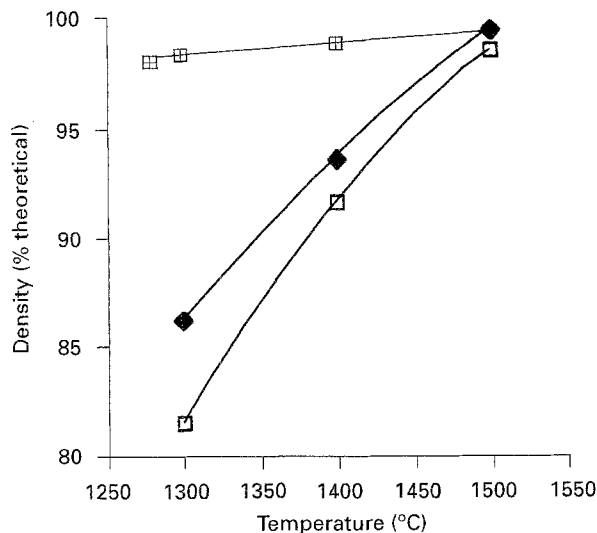


Figure 4 Comparison of data for densification of 3 mol % yttria zirconia with the data of Tian *et al.* [14] (■), (□) Conventional heating, (◆) microwave heating.

with their work is difficult as there was a number of major differences in the experimental procedures used. Most notable was their inclusion of a 1 h dwell at the maximum temperature in their experiments, which would be expected to magnify differences in time-dependent phenomena, such as diffusion. There were also differences in the temperature range studied and the atmosphere used. Details of cooling rates were not provided.

Very little research on the microwave sintering of 3 mol % yttria zirconia has been reported. Tian *et al.* [14] obtained very high densities at lower temperatures, as illustrated in Fig. 4. However, this can be explained by their use of a 1 h “pre sintering” process at 1150 °C which they introduced to combat cracking problems which occurred during sintering. This additional heating step would result in the samples having already undergone considerable densification before the microwave sintering experiments were performed.

When grain size is plotted as a function of density for the conventionally heated and microwave-heated samples, the microwave data show a significant shift in the direction of enhanced density at densities below 96% theoretical. This suggests that the microwaves tend to accelerate lattice diffusion, which contributes to densification, more than they accelerate surface and grain-boundary diffusion. The only published data available for comparison are those of Tian *et al.* [14]. Unfortunately, due to the presintering of their samples at 1150 °C, their microwave-sintered samples displayed a very small density range (98.5–99% theoretical). While the grain sizes were of a comparable range, from 0.2–0.35 μm, samples with densities between 98% and 98.5% theoretical had a smaller grain size than was found in this project. This, however, may be due to the low-temperature pre-sinter.

Differences in the activation energy for lattice diffusion and grain growth need to be considered in interpreting these results. The activation energy for grain growth in tetragonal zirconia has been found to be 105 kcal mol⁻¹, and that of cubic zirconia found to be

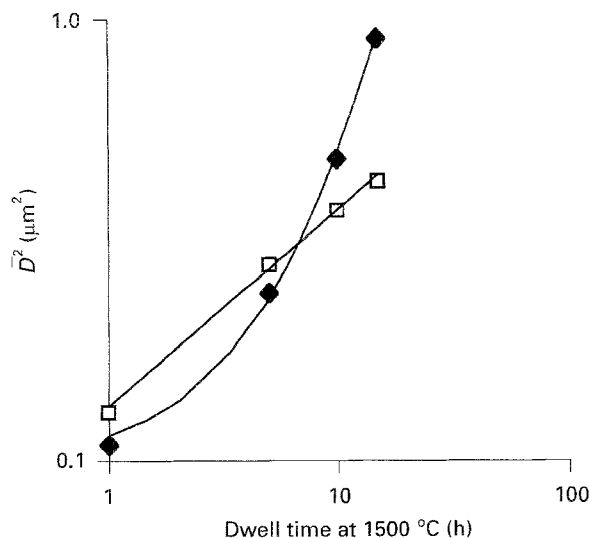


Figure 5 Grain growth during ageing of 3 mol % yttria zirconia at 1500 °C. (□) Conventional heating, (◆) microwave heating.

69 kcal mol⁻¹ [15]. The activation energies for self-diffusion of yttrium and zirconium ions in a cubic zirconia lattice have been found to be 102 and 109 kcal mol⁻¹, respectively [16, 17]. Assuming that similar values apply to tetragonal zirconia, it would be possible to enhance densification in tetragonal zirconia without increasing grain size.

During normal grain growth, the relationship between the grain diameter and time can be expressed as

$$D - D_0 = Kt^{1/2} \quad (1)$$

where D is the grain size at time t , D_0 is the grain size at time t_0 and K is a rate constant. If $D \gg D_0$, D_0 can be assumed to be equal to 0. Then, if $\log D^2$ is plotted as a function of $\log t$, a straight line is obtained. Fig. 5 shows such a plots for samples aged at 1500 °C in the conventional and microwave furnaces.

Grain growth of the 3 mol % yttria zirconia which underwent microwave heating differed markedly from the conventionally heated samples. Grain growth was significantly accelerated in the microwave field, with the average grain size being approximately 50% greater after ageing for 15 h. The relationship between average grain diameter and time indicated that exaggerated grain growth may have occurred. This was confirmed by comparison of the grain-size distributions for samples aged in the conventional and microwave furnaces for 15 h, which are shown in Figs 6 and 7. The grain-size distribution of the microwave-aged samples displays a long tail, associated with a small number of larger grains. This is reflected in the difference in the grain sizes at the 95th percentile for conventional and microwave aged samples, which were approximately 1.1 and 1.6 μm, respectively. This difference indicates that exaggerated grain growth had commenced in the microwave-aged samples.

Such grain growth is common in oxide ceramics, and is most likely to occur when minor amounts of porosity or an impurity phase inhibit normal continuous grain growth. The boundaries of some of the

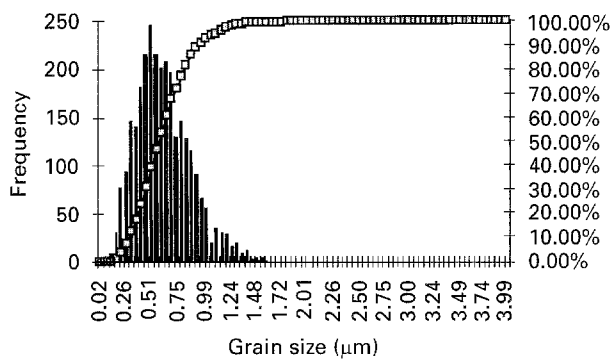


Figure 6 Grain-size distribution of 3 mol % yttria zirconia samples aged in the conventional furnace at 1500 °C for 15 h.

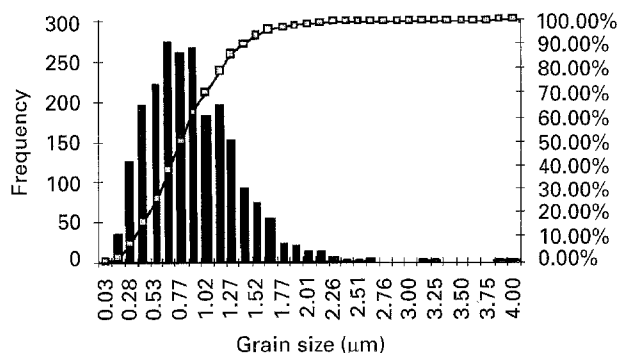


Figure 7 Grain-size distribution of 3 mol % yttria zirconia samples aged in the microwave furnace at 1500 °C for 15 h.

larger grains are unpinning when the local pores shrink, and the grain boundaries have sufficient curvature to allow selective coarsening to occur. In this case, it may be that the grains in the microwave-heated 3 mol % yttria zirconia material have reached a size where the remaining porosity impedes normal grain growth, and that if samples of conventionally heated material were aged for a long enough time to reach this same size, that they would also undergo exaggerated grain growth. Another possibility is that the mechanisms responsible for the enhancement of densification and grain growth, may also have increased the solute segregation at the grain boundaries, reducing grain-boundary mobility. Such segregation has previously been reported in yttria zirconia ceramics [18, 19]. It is also possible that localized grain-boundary heating has resulted in rapid growth of a few grains. The cause of the exaggerated grain growth remains uncertain.

These results indicate that for 3 mol % yttria zirconia, the conditions for exaggerated grain growth are achieved earlier during microwave heating than they are during conventional heating. This would be expected as a consequence of the enhanced densification. There is no evidence of any special microwave effect. Further work needs to be done on longer term ageing using conventional heating to determine if exaggerated grain growth does occur at a similar stage to that observed for microwave heating.

The data generated in this project support the existence of an enhancement of densification during

microwave heating, as has been reported by other researchers. The production of high-density components at lower temperatures offers the potential to reduce energy consumption, increase productivity, and control microstructure. Greater thermal uniformity which allows the use of rapid heating and simplifies the processing of irregular shapes would also be a significant advantage.

The way in which an electromagnetic field influences the balance between densification and grain-growth processes may not necessarily be the same for all ceramics. Chemical composition effects on the relative diffusivities, activation energies for densification and grain growth, and grain-boundary mobilities need to be considered. These results indicate that in a material with a relatively high grain-growth activation energy and low grain-boundary mobility, such as tetragonal zirconia, the use of microwave heating can cause a change in the predominant diffusion mechanisms during sintering. Such a change may facilitate the production of high-density ceramics with smaller grain size than is possible using conventional sintering techniques by allowing processing to high density to occur at lower temperatures. However, the data for 3 mol % yttria zirconia generated during the present study indicate that the difference in the grain size/density relationship disappears after densities greater than 96% theoretical are achieved. Once grain-growth processes predominate, microwave heating appears to accelerate grain growth resulting in exaggerated grain growth. Microwave sintering needs to be carefully controlled to ensure that grain growth is restricted and the desired microstructure formed.

5. Conclusion

Densification of 3 mol % yttria zirconia during constant rate heating was enhanced during microwave sintering when compared to conventional heating. A small but significant shift in the density–grain size relationship occurred for densities below 96% theoretical, indicating that microwave sintering accelerates lattice diffusion more than surface and grain-boundary diffusion during the initial and intermediate stages of sintering. However, the difference in this relationship disappeared at higher densities once grain growth began to dominate.

A change in the grain size/density relationship during microwave sintering when compared to conventional sintering was identified for 3 mol % yttria zirconia, which has a relatively high activation energy and low driving force for grain growth.

Ageing experiments conducted at 1500 °C showed that once densification was near completion, grain growth in 3 mol % yttria zirconia was accelerated in the microwave field, and exaggerated grain growth occurred.

For 3 mol % yttria zirconia, microwave sintering regimes which include a dwell time in the 1200–1350 °C range may offer some significant advantages. This would allow high densities to be achieved, while restricting grain growth.

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