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Characterization of ZrO_2–Al_2O_3 composites sintered in a 2.45 GHz electromagnetic field

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The microwave heating process has shown potential for uniform material heating with rapid heating rates possible. The ceramic composite 80 wt% ZrO_2 (+ 3 mol% Y_2O_3) 20 wt% Al_2O_3 was sintered in a Cober S6F microwave oven operating at 2.45 GHz even though it was considered to be microwave transparent at room temperature. The microwave-sintered sample was densified more rapidly and in a short time and lower temperature than the conventionally sintered sample. The fracture of the conventionally sintered sample was intergranular, but one of the microwave-sintered samples was transgranular. The fraction of the monoclinic-phase zirconia was different in the conventionally and microwave-sintered samples. The unusual microstructure of microwave-processed materials is explained by a microwave heating theory.

1. Introduction

Microwave processing of ceramic materials has been investigated over the last 30 years by various researchers. In the 1940s, Von Hippel began investigating how oxide materials interact with microwave radiation and how the loss characteristics of these materials vary as a function of microwave frequency. In the 1960s, Tinga investigated how certain oxides heat in a microwave field and developed reaction cavities. During the last 7 years, Meek and his co-workers [1–5] showed significant differences between conventional thermal processing and microwave processing of ceramics, glasses and composites. They have observed what appears to be enhanced material transport, rapid sintering, and different microstructure for various ceramic materials heated at 2.45 and 6 GHz. To sinter the low-loss ceramics at 2.45 GHz, they suggested the use of various materials to act as both a microwave susceptor material and a second or primary phase material which act as a crack inhibitor upon sintering.

Firstly, microwave processing is generally characterized by uniform heating on a macroscopic scale and rapid heating rates, as compared to conventional thermal processing. The applicability of high heating rates in conventional sintering is limited because of heat transfer and thermal shock limitations. However, it is quite possible that microwave-processed ceramics will exhibit finer and more uniform microstructures due to rapid heating rates because the heat is generated within the material. Because the sintering time can be lowered in microwave processing, the possibility for exaggerated grain growth may be reduced. Also, Brook and co-workers [6–8] showed that rapid sintering led to improved ceramic microstructures and high density with the development of finer and more uniform grain structures. Secondly, microwave processing [9, 10] has demonstrated the ability to sinter large and complex-shaped ceramic components because heating occurs within the material volume by the microwave energy causing the molecules throughout the volume to vibrate. As a result of this internal and volumetric heating, thermal stresses may be significantly reduced due to a reduced intergranular temperature gradient from that seen in materials processed by conventional heating. Thus, microwave processing makes it possible to reduce cracking during the processing of large and irregular-shaped ceramics, which would normally occur in conventional processing. Thirdly, microwave processing [5, 11] has the potential for selective heating of microstructural constituents and phases. This occurs due to different microwave absorption characteristics in different phases. This has important implications for the microwave processing of ceramic composites with improved properties. Finally, microwave processing [12, 13] has great potential for saving energy when compared with conventional heating. Because the energy couples directly to the ceramics to be heated, the ceramics may be brought to high temperature in relatively cool surroundings. Owing to its selectivity, microwave processing may require significantly lower power consumption.

The results of the present study demonstrate that ceramic materials may be fabricated using 2.45 GHz microwave radiation in a 6 kW Cober S6F microwave facility. The material system discussed in this study is 80 wt % ZrO_2 (+ 3 mol % Y_2O_3) 20 wt % Al_2O_3 composite. This paper discusses the feasibility of using microwave energy to process this material. Also, it discusses microstructure, phase analysis, and other data such as sintering data which have been obtained on samples of this material heated using 2.45 GHz electromagnetic radiation.

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2. Experimental procedure

The composite powder Super-Z was fabricated from 75.7 wt % ZrO_2 which contained 4.2 wt % Y_2O_3 in solid solution and 20 wt % Al_2O_3. Green samples, weighing 2.4–2.5 g, of approximate diameter 1.283 cm and height 0.710 cm, were prepared by pressing uniaxially into a right circular cylinder at 230 MPa; green density was approximately 50% theoretical. Small samples were used for experiments to reduce density variations caused by thermal gradients.

Conventional sintering was done where the cold-pressed pellets were heated for 108 h at 1350 °C in a conventional electric furnace at a heating rate of $50\,°C\,h^{-1}$. Microwave sintering was done in a Cober model S6F microwave oven with a heating rate of $100\,°C\,min^{-1}$. Power was supplied to the waveguide by a 6 kW variable-power microwave generator operating at 2.45 GHz. Typically, the power level was 500 W initially, which was gradually increased up to 3 kW at the onset of sintering. The green samples were located in the region of highest electric field intensity which is the central area of the cavity which is surrounded by insulation. This means that the expected temperature profile is symmetrical across the width of the cavity. To measure the sintering temperature, the infrared thermometer was focused on the front edge of the specimen with a small hole in the front part of the reaction cavity. All the experiments and data recordings were performed manually with a conventional time clock.

Microstructure analysis was done by direct examination of the samples with the AMR 900 scanning electron microscope. The composition of the sample contents was determined by energy dispersive X-ray analysis (EDAX). The average grain size of the polished and thermally etched surface was determined by a linear intercept method [14]. A Rigaku X-ray diffractometer in reflection mode was used for analysing the phases present with CuK_α radiation using the method of Garvie *et al.* [15].

3. Results and discussion

A constant power input of 0.5 kW was applied for the first several minutes until the samples were coupled. After coupling, the input power was gradually increased to reach the sintering temperature. Just below the sintering temperature, the input power was rapidly decreased 1.0–1.5 kW to prevent thermal runaway, and then controlled to reach the sintering temperature. All specimens tested showed an increase in heating rates as input power increased. This means that the surface temperature increase is due to the increase in the specimen power density and the dielectric loss of the specimen. The specimen in microwave heating with a susceptor coupled more easily at lower input power than one with no susceptor. During microwave heating with no susceptor, a significant fraction of the total heat generated in the cavity is actually generated in the cavity wall. While the samples were able to achieve a high enough temperature, the external portions of the cavity were hot to the touch. However, during microwave heating with the susceptor, all of the heat generated was generated in the samples. When the temperature of the samples was already up to 1400 °C, the cavity wall was relatively cooler to the touch than in the former case.

The green-state of a zirconia–alumina composite, even though it was an electrically low-loss material, could be heated to its sintering temperature in a microwave cavity. Bulk density of the sintered samples was measured by the water immersion method [16]. Tables I and II show the bulk densities of the microwave-sintered and the conventionally sintered samples. The maximum density of the conventionally sintered sample was 92.59% theoretical at 1350 °C for 108 h. However, the minimum microwave-sintered density observed was over 95% theoretical at any sintering temperature and time. Clearly, densification rates for the microwave-sintered samples are much higher than for the conventionally sintered samples at a comparable temperature. In addition, the real sintering temperature is thought to be much higher than the measured surface temperature. This assumption will be explained in more detail in the microstructure analysis.

As shown in Fig. 1 plotted as a function of the sintering time and the surface temperature, the enhanced sintering characteristics were most likely the result of the extremely fast heating rates achievable by

TABLE I Density of microwave-sintered samples

Sintering temperature (°C)	Sintering time (min)	Initial density (%)	Final sintered (%)
1200	5	50	94.99
	10	50	95.25
	30	50	95.92
	60	50	98.54
1300	5	50	94.72
	10	50	95.38
	30	50	96.88
	60	50	98.88
1400	2.5	50	98.5
	5	50	98.29
	10	50	98.63
	30	50	99.33
1500	2.5	50	97.94
	5	50	98.35
	10	50	100
	30	50	100

TABLE II Density of conventionally sintered samples

Sintering temperature (°C)	Sintering time (h)	Initial density (%)	Final sintered density (%)
1350	14	50	80.98
	24	50	86.3
	38	50	88.08
	48	50	90.17
	60	50	90.49
	72	50	91.1
	84	50	92.56
	108	50	92.59

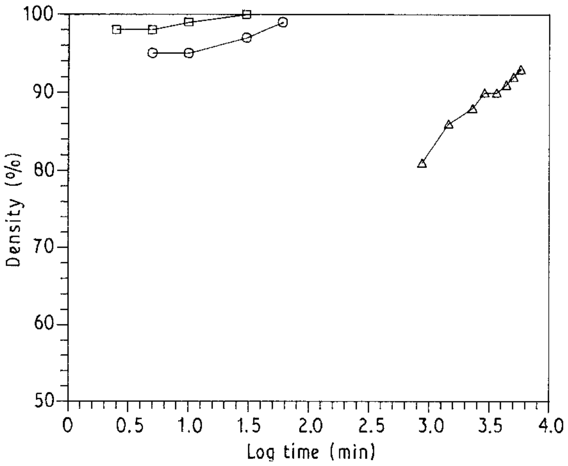

Figure 1 Densification rates for (○, □) microwave-sintered samples and (△) conventionally sintered samples at a comparable temperature: (○) 1300° C, (□) 1400° C, (△) 1350° C.

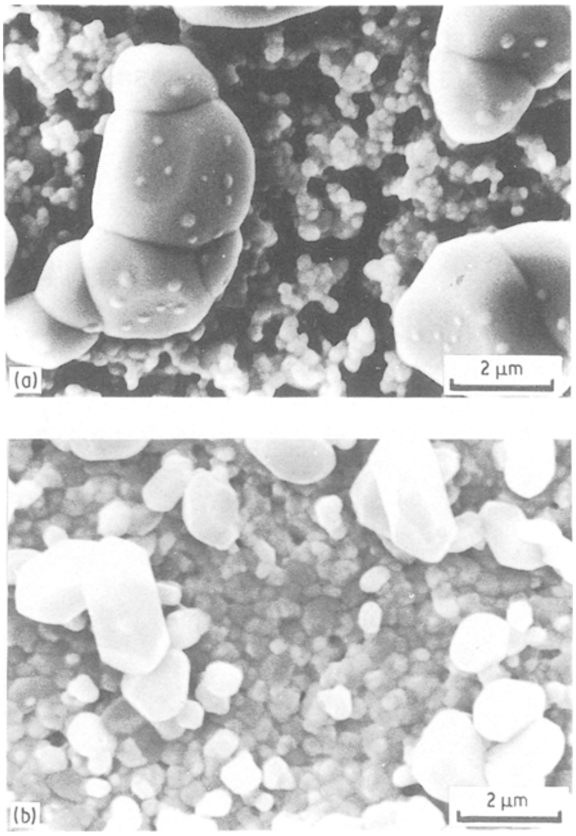

Figure 2 Scanning electron micrographs of polished and thermally etched surfaces of (a) conventionally sintered sample, (b) microwave-sintered sample.

the unique direct-heating mechanism. It meant that microwave-sintered samples were densified much more rapidly and at much shorter time and lower temperature than the conventionally sintered samples. However, it should be noted that the temperature measured is an average temperature and not the intergranular temperature which is thought to be much higher. Fig. 1 leads to an apparent activation energy for sintering that is lower in the microwave case. However, it is believed that there is no change in the real activation energy for sintering if the true intergranular temperature is measured. As a result, the electromagnetic radiation is responsible for the observed phenomenon of a tremendous increase in the densification rates. Also, enhanced diffusion appears to be responsible for the accelerated densification rates in the microwave heating. Independence of density with the sintering temperature over such a large range for microwave sintering is certainly unusual but could be readily explained by examination of a microstructure as shown by Katz *et al.* [17]. Therefore, microwave sintering has the potential of enhanced densification and suppressed grain growth due to a fast heating rate and an apparent low-temperature firing.

Scanning electron micrographs of samples polished and thermally etched at 1050 °C for 8 h are given in Fig. 2. By using EDAX, the large grains were found to be zirconia and small grains were zirconia and alumina in both processes. In the conventionally sintered sample, little densification occurred with the morphology of the initial powder particles even after a relatively long processing time. However, in the microwave-sintered sample, a uniform and improved microstructure was seen, even though a short sintering time and lower sintering temperature were used. The ability for the fast firing to produce high-quality microstructures has been demonstrated. Also, there was no evidence of exaggerated grain growth, probably because of the zirconia phase impeding the growth of the alumina phase, the alumina phase impeding the growth of the zirconia phase, and the short sintering time. The average grain size of the microwave-sintered sample was found to be 0.41 μm using a linear intercept method. In comparison with the average grain size of a hot isostatically pressed sample reported by Rajendran *et al.* [18], the grain size of the microwave-sintered sample was smaller than of the conventionally sintered sample because the penetration action of the microwave energy into the material resulted in the internal heating of cross-sections uniformly in the shortest sintering time and fastest heating rate. It was reasonable to adopt Brook and co-workers theory [6–8] to give a general explanation for the results of the smaller grain size for the microwave sintering.

Fracture microstructures of the samples were analysed as shown in Fig. 3, in order to understand the different fracture behaviour between the microwave-sintered and the conventionally sintered samples. The fracture of the conventionally sintered sample was intergranular fracture, indicating grain-to-grain separation. Intergranular fracture is typical of a highly monoclinic material, suggesting that the crack path follows the intergranular microcracks produced during fabrication as a result of the phase transformation. This material is quite friable. The fracture behaviour of the microwave-sintered sample was unusual in that very little intergranular fracture was seen. Transgranular fracture is common with obvious cleavage steps, indicating grain-to-grain bonding. The irregular fracture topography of individual grains might be a result of the crack interacting with the complex internal structure of the twinned monoclinic grains which transformed ahead of the propagating crack as reported by Lange [19], or it may be the result of the

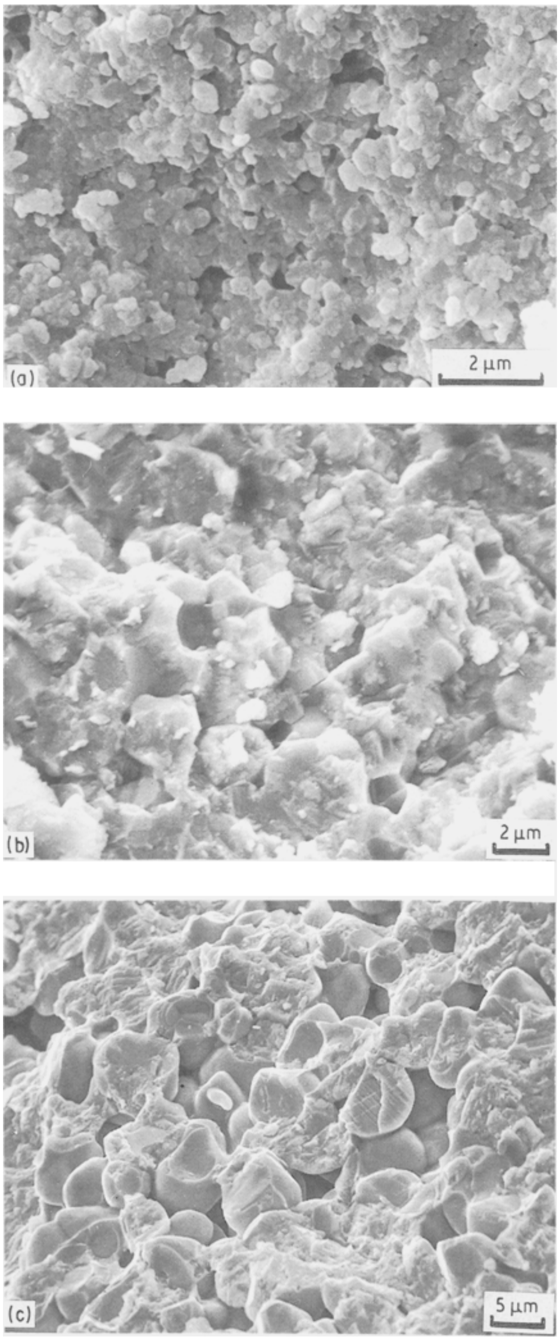

Figure 3 Scanning electron micrographs of the fracture surfaces of (a) conventionally sintered sample, (b, c) microwave-sintered samples.

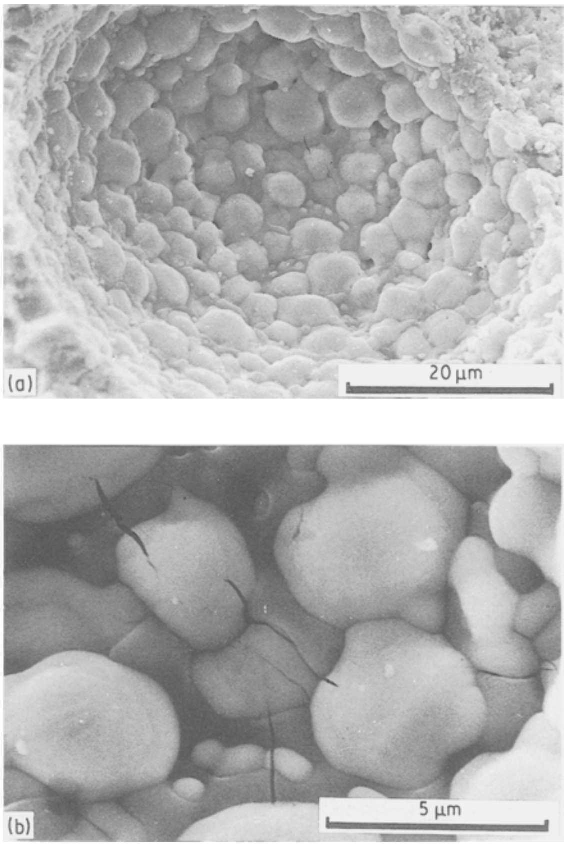

Figure 4 Scanning electron micrographs of the fracture surface of a microwave-sintered sample.

crack being inhibited by the melted pore surface, and of the wetting of melted alumina. A pore region of the microwave sintered sample is shown in Fig. 4. EDAX revealed that the wetted regions were alumina and the grains were zirconia. Wetting was believed to be caused by the formation of a liquid-phase alumina when the real temperature exceeded the melting temperature of an alumina, due to thermal runaway. These results indicated that the real microwave sintering temperature was higher than the measured surface temperature because the melting point of alumina is 2045 °C and the measured surface temperature was 1400 °C. Typically, the melted pore surface and strongly bonded grain boundaries by wetting could act as a crack inhibitor during the fracture thus causing the transgranular fracture observed, rather than intergranular fracture.

X-ray diffraction (XRD) analysis of the polished microwave-sintered samples showed the presence of tetragonal-phase zirconia and α-alumina only. The peak patterns for the conventionally sintered samples were similar to the microwave-sintered samples except for the traces of the monoclinic-phase zirconia. The fraction of the monoclinic-phase zirconia could be determined by measuring the relative intensity of the $(1\,1\,1)$ and $(1\,1\,\bar{1})$ monoclinic and $(1\,1\,1)$ tetragonal reflections. The fraction of the monoclinic-phase zirconia was found to be approximately 28% in the conventionally sintered samples and almost zero per cent in the microwave-sintered samples. Thus, the microwave-sintered samples retained the metastable tetragonal grains better than the conventionally sintered samples. Wilson and Kunz [20] also reported that the XRD scans showed a mixture of tetragonal and cubic phases, but essentially no conversion to the monoclinic phase in the microwave-sintered zirconia. This effect was assumed to be responsible for the high degree of retained strength in the microwave-sintered sample after the thermal shock, as suggested by Becher *et al.* [21].

In conventional heating, energy is absorbed only at the surface of the material and must be transferred into the bulk of the material by thermal conduction. Thermal conduction takes a finite amount of time, and gradients in temperature within the material must exist until the material achieves thermal equilibrium. It was assumed that the monoclinic phase existed in the conventional sintered sample due to thermal stresses. However, in microwave heating, energy is absorbed throughout the volume by the electromagnetic energy causing the molecules throughout the volume to vibrate. It was assumed that material is heated uniformly without gradients in temperature during microwave heating on a macroscopic scale. Thus, the monoclinic phase did not exist in the microwave sintered samples due to the absence of a thermal gradient. Also, there was no time for the nucleation of the monoclinic phase to occur during the very rapid heating and cooling. As a result, microwave sintering has the ability to sinter brittle ceramic materials toughened and strengthened by utilizing the phase transformation of zirconia particles dispersed in a ceramic matrix.

4. Conclusions

The enhanced densification was most likely the result of the extremely fast heating rate achievable by microwave heating. It was clear that the electromagnetic radiation was responsible for the observed phenomenon of a tremendous increase in densification rates. Also, the average grain size of the microwave-sintered sample was smaller than of the conventionally sintered sample because of the rapid sintering time for the microwave-sintered sample. The microwave-sintered samples retained the metastable tetragonal grains better than the conventionally sintered one due to the absence of a thermal gradient, no time for the nucleation of monoclinic phase, or lower sintering temperature. Wetting caused by the formation of a liquid-phase alumina indicated that the real microwave sintering temperature was higher than the measured surface temperature. The melted pore surface and strongly bonded grain boundaries could, by wetting, act as a crack inhibitor during fracture thus causing the transgranular fracture. These results indicate that the electric field intensity is greatly intensified in the porous regions, and the microwave radiation is linked more strongly to the regions of low density and low dielectric constant.

References

1. T. T. MEEK and R. D. BLAKE, *J. Mater. Sci. Lett.* **5** (1986) 270.
2. T. T. MEEK, C. E. HOLCOMBE and N. DYKES, *ibid.* **6** (1987) 1060.
3. T. T. MEEK, R. D. BLAKE and J. J. PETROVIC, *Ceram. Engng Sci. Proc.* **8** (1987) 861.
4. T. T. MEEK, *J. Mater. Sci. Lett.* **6** (1987) 638.
5. R. D. BLAKE and T. T. MEEK, *ibid.* **5** (1986) 1097.
6. M. P. HAMER, E. W. ROBERTS and R. J. BROOK, *Trans. J. Br. Ceram. Soc.* **78** (1979) 22.
7. M. P. HAMER and R. J. BROOK, *ibid.* **80** (1981) 147.
8. H. MOSTAGHACI and R. J. BROOK, *ibid.* **82** (1983) 167.
9. W. R. TINGA, in "Proceedings of IMPI, Short Course for Users of Microwave Power" (1970) 19.
10. H. D. KIMREY, T. L. WHITE, T. S. BIGELOW and P. F. BECHER, *J. Microwave Power* **21** (1986) 1161.
11. W. R. TINGA and S. O. NELSON, *ibid* **3** (1975) 144.
12. S. DAS and T. R. CURLEE, *Ceram. Bull.* **66** (1987) 1093.
13. L. M. SHEPPARD, *ibid.* **67** (1988) 1656.
14. M. I. MENDESON, *J. Amer. Ceram. Soc.* **52** (1969) 443.
15. R. C. GARVIE, R. H. J. HANNICK and M. V. SWAIN, *J. Mater. Sci. Lett.* **1** (1982) 437.
16. W. D. KINGERY, H. K. BOWEN and D. R. UHLMANN, in "Introduction to Ceramics", 2nd Edn (Wiley, New York, 1976) p. 530.
17. J. D. KATZ, R. D. BLAKE and J. J. PETROVIC, *Ceram. Engng Sci. Proc.* **9** (1988) 725.
18. S. RAJENDRAN, M. V. SWAIN and H. J. ROSSELL, *J. Mater. Sci.* **23** (1988) 1805.
19. F. F. LANGE, *ibid.* **17** (1982) 240.
20. J. WILSON and S. M. KUNZ, *J. Amer. Ceram. Soc.* **71** (1988) C-40.
21. P. F. BECHER, C. Cm. WU and B. A. MacFARLANE, *Ceram. Bull.* **59** (1980) 357.

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