JOURNAL OF MATERIALS SCIENCE **32** (1997) 4925–4930

Enhancing densification of zirconia-containing ceramic-matrix composites by microwave processing

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Various ceramic-matrix composites containing zirconia were sintered using a 2.45 GHz microwave field. The effects of the addition of zirconia and the processing parameters on the sintering and microstructure development were investigated. The results showed that microwave processing enhanced the densification of these composites considerably. The enhancement in sintered density was up to 46% over conventional sintering, depending on the systems.

1. Introduction

Ceramics are usually brittle and transformation toughening is adopted to improve fracture toughness of various ceramics. Partially stabilized tetragonal zirconia is a toughening agent popularly used. Since any toughening effect in such a composite through transformation of zirconia directly depends on the density of the composite, a high density is critically important in achieving the desired transformation toughening. The addition of zirconia, however, may reduce sinterability of the ceramic and thus high densities become difficult to achieve under conventional sintering conditions. For example, about 95% relative density is easy to achieve in conventional sintering of hydroxyapatite (HAp), $Ca_5(PO_4)_3OH$, a common biomaterial; but, once zirconia is added to HAp, the sinterability of the composite becomes very poor. In conventional sintering of HAp/ZrO_2, earlier researchers achieved a relative density of only about 50–78% at 1100–1400 °C for 3 h [1]. However, by microwave processing, we have reported relative densities of 93% in HAp/10%ZrO_2 composites [2] at 1200 °C for only 30 min.

Microwave heating of ceramics goes back to the post WW II era when old radar equipment was used for drying large whiteware. Early work on the use of microwave sintering was concentrated on dark ceramics, especially magnetic materials as discussed in the review by Sutton [3]. Extraordinarily rapid heating and high temperatures were reported by Haas [4] in urania gels. The first report on the same effects, including thermal runaway, in white ceramics (specially Al_2O_3 and silica) was given by Roy *et al.* [5]. Subsequent to this, starting in about 1990, a wide range of symposia have brought together an enormous variety of papers on the practice and theory of microwave sintering of white ceramics. These are reported in several proceeding volumes starting in 1988 [6]. So far the value of microwave sintering of white ceramics in these papers has principally been demonstrated in speed (by one to two orders of magnitude) and to a lesser extent in microstructure control and in total energy consumption (e.g. for Al_2O_3 by Cheng *et al.* [7]). Yet no major innovation has demonstrated the use of microwave heating. While transparent Lucalox has been known for decades, only our own work on hydroxyapatite [8] has led to transparent ceramics by microwave sintering. It has been shown that the densification of the diphasic aluminosilicate gels under microwave conditions is substantially enhanced [9, 10], lowering the apparent activation energy for densification by about 50%.

Microwave sintering of ceramic materials is different from conventional sintering in its heating mechanism [3]. In microwave sintering, the work piece is directly heated as a whole by heat generated through microwave–material interaction. The wave–material interaction, or microwave absorption, of a material depends on the total dielectric loss factor of the material, so that microwave processing will have a selective heating effect in some ceramic composites.

Stabilized tetragonal zirconia is a transformation toughening agent and also a highly efficient microwave absorber. It can be preferentially heated in a microwave field. It was the objective of this study to determine if the presence of zirconia in the selected ceramic matrices can improve the microwave absorption of these systems and thus enhance their sinterability.

For this purpose, microwave sintering of ceramic composites of zirconia and four matrices, including alumina, mullite, calcium strontium zirconium phosphate (CSZP, $Ca_{0.5}Sr_{0.5}Zr_4P_6O_{24}$), and barium zirconium phosphosilicate (BS25, $Ba_{1.25}Zr_4P_{5.5}Si_{0.5}O_{24}$) was carried out in the current study. Among them, alumina and mullite are the most important ceramic materials commonly used, CSZP and BS25 belong to a very large new family known as [NZP] and characterized for their low thermal expansion behaviour [11, 12].

For comparison, conventional sintering of the duplicate samples was also carried out in a high capacity, low thermal inertia furnace at heating rates comparable to those in the microwave processing. In this way, any differences in the sintering behaviour mainly attributable to the effect of microwave irradiation can be separated out.

2. Experimental details

2.1. Materials

The starting material of alumina was an amorphous alumina powder from a commercial source (Rhone-Poulenc, France). The powder was sieved to 325 mesh (45 μm opening) before compaction. The mullite precursor was prepared by a diphasic xerogel method by mixing sols of boehmite (AlOOH) and silica (Ludox) at a molar ratio of 3:2. The CSZP powder was also prepared by a sol-gel method [11]. The BS25 powder was synthesized by a solid-state reaction method using dry oxide precursors [12]. The zirconia powder (HSY-3.0, Zirconia Sales, Inc., Atlanta, GA) used in this study was tetragonal phase partially stabilized by Y_2O_3 (5.4%), with a minor monoclinic phase. The average particle size of this zirconia powder was about 0.1 μm.

Each matrix powder was mixed with zirconia in various proportions. An appropriate amount of 2% PVA solution was used as a binder during mixing. The mixture was homogenized by hand mixing with an agate mortar. The alumina/zirconia and BS25/zirconia mixtures were compacted into pellets of 12.7 mm diameter, and the mixtures of mullite/zirconia and CSZP were compacted into pellets of 6.35 mm diameter. The compaction was uniaxially carried out at 350 MPa. The relative green densities of the as-compacted pellets of various systems were in the range of 39–53% for alumina/zirconia, 46–51% for mullite/zirconia, 53–58% for CSZP/zirconia, and 60–67% for BS25/zirconia, respectively. No sintering additive was used in this study.

2.2. Sintering

Microwave sintering was carried out in a 900 W, 2.45 GHz microwave oven (Panasonic). The sintering packet is schematically illustrated in Fig. 1. Multi-pellet runs were adopted in the sintering. The pellets, usually in two (6.35 mm pellets) to three (12.7 mm pellets) layers, were placed in the centre of the packet. Each layer containing 6–7 pellets of the 6.35 mm samples, but only one pellet of the 12.7 mm samples. The sample pile was vertically surrounded by a porous zirconia cylinder which worked as a microwave absorber to preheat the specimens as well as a thermal insulator to keep heat from dissipating. Around the zirconia cylinder, eight thin rods of molybdenum disilicide were arranged in parallel. These rods also worked as heating elements during microwave irradiation. The sintering packet was placed on a rotating plate. The rotation keeps all the samples under the same irradiation conditions and provides uniform heating.

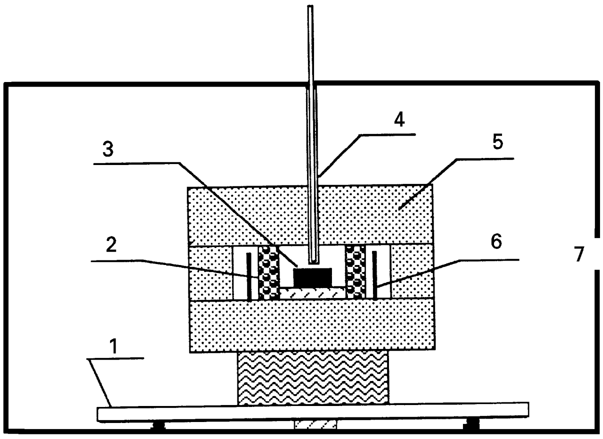

Figure 1 Schematic display of the microwave sintering packet composed of (1) turntable, (2) porous zirconia cylinder, (3) samples, (4) thermocouple, (5) Fibermax insulator, (6) $MoSi_2$ rods, and (7) microwave port.

Temperature was measured using a platinum-sheathed S-type (Pt–Pt/10Rh) thermocouple inserted from the top of the microwave cavity. The platinum sheath was grounded to the cavity, so that microwave interference to the temperature measurement was completely avoided during processing. A small piece of alumina was fixed on the tip of the thermocouple (to obtain better reliability of the temperature measurement), which was located directly above the samples (Fig. 1). The heating rates and the soaking temperatures were controlled by adjusting the power input with a variac.

Conventional sintering was carried out in a high capacity, low thermal inertia, high temperature furnace built in-house. The heating rates were comparable to these of microwave sintering. With molybdenum disilicide as a heating element, the furnace has the capacity of providing heating rates up to 300 °C min^{-1} below 1000 °C and can attain a temperature of 1500 °C in 13 min. The temperature in the conventional sintering was measured with the same type-S thermocouple as in the microwave sintering, but without a platinum sheath. The samples were placed in a platinum crucible which was in contact with the tip of the thermocouple. The heating rates and soaking temperatures were also controlled by adjusting the power input with a variac.

The sintering of the composites based on alumina, mullite, and CSZP, was conducted at 1500 °C. Composites of BS25 were sintered at 1550 °C. All samples were soaked at the peak temperature for 20 min. The sintering of the diphasic mullite gel is a reaction sintering process. Our earlier experiments showed that the diphasic mullite gel used in this study starts crystallizing (mullitization) at about 1330 °C [13]. Since the densification of gels through viscous flow is far more efficient than that of the related crystalline materials through ordinary solid diffusion, step sintering was adopted for the composites based on the mullite gel, in which the samples were first heated to 1200 °C, then soaked for 30 min for densification by viscous flow, and finally heated to 1500 °C for mullitization.

2.3. Characterization

Sintered density was measured by weighing and dimensional measurement of the pellets. Powder X-ray diffraction (CuK_α) was carried out with a Scintag diffractometer (Scintag, Sunnyvale, CA) on the starting powders and on some selected sintered samples for phase identification. The microstructure of the sintered specimens was examined with a scanning electron microscope (SEM) (ISI DS-130, Akashi Beam Tech. Corp.).

3. Results and discussion

3.1. Sintering behaviour

The heating curves and the sintered densities of various composites are shown in Fig. 2. It can be seen that the heating rates in the microwave and conventional

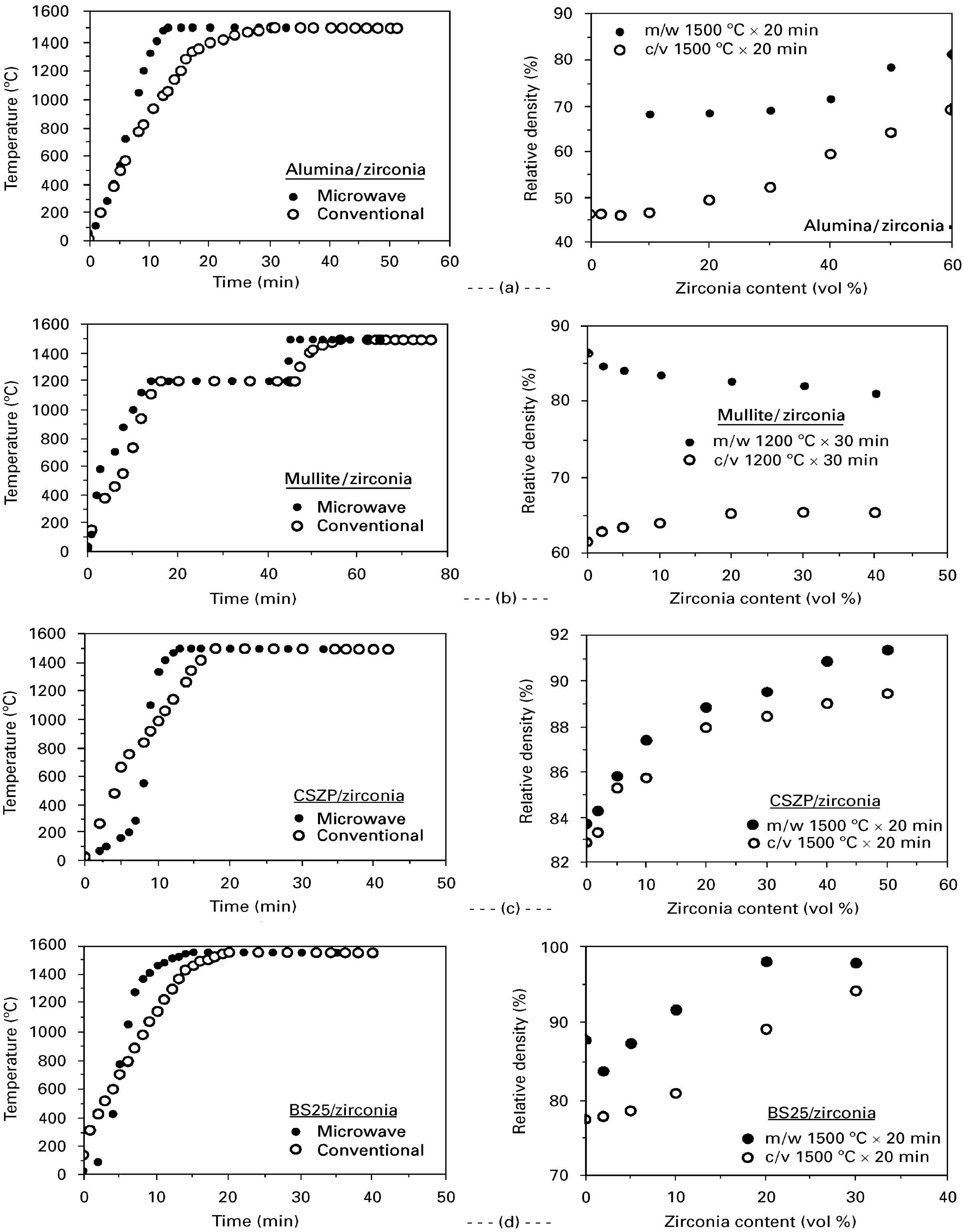

Figure 2 Heating curves and sintered densities of zirconia-containing composites based on (a) alumina, (b) mullite, (c) CSZP, and (d) BS25.

processes are essentially the same. In all the materials studied, density increases with increasing zirconia content in both microwave and conventional sintering, with the mullite system before crystallization as an exception. Higher densities have been achieved in microwave sintering in all cases.

3.1.1. Al_2O_3/ZrO_2 system

Significantly higher sintered density was produced in the microwave sintered specimens of alumina/zirconia system. The difference between microwave and conventional sintering in the low zirconia content side is more significant. As zirconia content increased, the difference diminished, indicating that the microwave enhancement in sintering to alumina is more effective than to zirconia, which is due to the better sinterability of zirconia, even under conventional conditions. The relatively low density was due to the agglomeration of the alumina powder, the micro-porous structure of which was retained during sintering thus hindering the densification of the composites. The low green density, low processing temperature, and short processing time were other factors related to the low sintered density. Also, no sintering additive was used. Kimrey *et al.* [14] have shown that alumina/zirconia system couples better with microwaves at 28 GHz than at 2.45 GHz, so that better densification could be achieved with a specific frequency which couples best with the material system specified. However, the relatively low density does not affect the analysis of the results, since we used the same material for both microwave and conventional processings.

3.1.2. Mullite/ZrO_2 system

In the mullite/zirconia system, no significant difference in sintered density was found after sintering at 1500 °C. A comparison of the density after the first-stage sintering (1200 °C for 30 min), however, clearly showed the difference (Fig. 2b). The densities after the 30 min microwave heating at 1200 °C were much higher than the conventionally heated samples. Obviously, microwave irradiation is more efficient in the densification of the diphasic mullite gels before mullitization. This is in good agreement with the earlier observation of Roy *et al.* [15, 16] that the alumina and silica gels absorb microwave energy and are heated very quickly. Once the crystalline mullite is formed, the sintering mechanism changes and there is no more viscous flow. Further densification can only rely on the boundary diffusion and related factors as in ordinary solid state sintering. Since the solid state diffusion of ions in mullite is very low, conventional sintering of mullite is usually carried out at 1600–1700 °C [17] for many hours. Due to the limit in processing temperature and time, and, more importantly, the transparency of the crystalline mullite to microwaves, the microwave sintering of the mullite system after mullitization, under the current experimental conditions, did not show much advantage over the conventional method.

3.1.3. [NZP]/ZrO_2 systems

In the BS25/zirconia system containing up to 30% zirconia, the microwave enhancement was also obvious. The increase in density of the CSZP/zirconia system, although obvious, was not as significant. This is probably due to the high processing temperature. When the processing temperature is sufficiently high, the solid state diffusion of ions under the conventional conditions might also have been substantially accelerated to allow the microwaves to lose their effectiveness. The results of the previous study [18] showed that pure CSZP could be sintered to a relative density of 94% by microwave processing at 1300 °C for 30 min which was about 24% higher than that achieved in conventional sintering under the same temperature and same duration. This may explain why the CSZP/zirconia system sintered at 1500 °C did not show an obvious microwave enhancement.

3.1.4. Microwave effect

Table I summarizes the enhancement of sintered density of the composites through microwave sintering. The values were obtained from the difference of sintered densities (microwave sintered density minus conventionally sintered density) divided by the conventionally sintered density, and they can be considered as the microwave effect in densification. It can be seen that with increasing zirconia content up to 40 vol %, microwave enhancement in densification consistently decreases in alumina and mullite systems, but irregularly in the systems of CSZP and BS25. An optimum zirconia content may exist in a composite system for the best densification. The microwave enhancement in the composites of alumina, mullite,

TABLE I Microwave enhancement in densities over the conventionally sintered samples, %

No.	ZrO_2 (vol %)	Alumina (1500 °C/20 min)	Mullite (gel) (1200 °C/30 min)	CSZP (1500 °C/20 min)	BS25 (1550 °C/20 min)
1	0	48.69	40.29	1.00	13.36
2	2	—	34.46	1.12	7.68
3	5	—	32.45	0.64	11.16
4	10	46.40	30.52	1.97	13.40
5	20	38.55	26.85	1.00	9.91
6	30	32.41	25.61	1.23	3.86
7	40	19.82	23.75	2.04	—

CSZP, and BS25 are 20–46%, 24–34%, 1–2%, and 4–13%, respectively. The ceramics without addition of zirconia showed even greater enhancement, with CSZP an exception.

In both microwave and conventional sintering, there is a general trend that the sintered density increases with increasing zirconia content for all the systems studied, with the mullite/zirconia before mullitization an exception. This is because all the matrix materials used in this study are harder to sinter than zirconia, so that the addition of zirconia improves the sinterability of the resultant composites. This was also observed by other investigators under both microwave and conventional conditions [14, 19]. In the mullite/zirconia system, the sintering before mullitization is caused by the viscous deformation of silica gel, which starts at temperatures as low as 700 °C [20]. The addition of zirconia powder separates the gel and thus reduces the viscous deformation, so that before mullitization, the density of the composites decreases with increasing zirconia content. The trend is reversed after mullitization since at higher temperatures, the sintering mechanism changes to solid state diffusion, so that the presence of the easier-to-sinter zirconia will improve the sinterability of the crystalline mullite/zirconia composites.

3.2. Phase composition

Powder XRD studies showed that the sintered alumina was pure α-Al_2O_3 phase when there was no zirconia addition, and was a mixture of the alumina (matrix) and tetragonal zirconia in the composites, with monoclinic zirconia in trace amounts. The same is true for the mullite and BS25 systems. In the CSZP system, zirconia had completely transformed to the monoclinic phase. Further study is needed to explain this phenomenon. The pure mullite gel remained amorphous after sintering at 1200 °C for 30 min, while after processing at 1500 °C, the material was found to be highly crystalline single phase mullite. No decomposition was found in any of these systems.

3.3. Microstructure

Fig. 3 shows the surface microstructures of the microwave-sintered composites. It is seen that the microstructures of the composites were fairly homogeneous, and the bonding between the matrices and zirconia (white particles) was reasonably good. Better homogeneity and further densification may be achieved by optimizing the mixing procedure and sintering conditions. For example, mixing the components in the wet state, especially during the synthesis of the matrix materials, is obviously superior to dry mixing.

As duplicate green samples were used, the heating rates in the microwave and conventional sintering were comparable, the temperature measuring technique was the same and microwave interference was avoided, and sintering times and temperatures were identical, the enhanced densification in the microwave processed samples can be attributed with certainty to

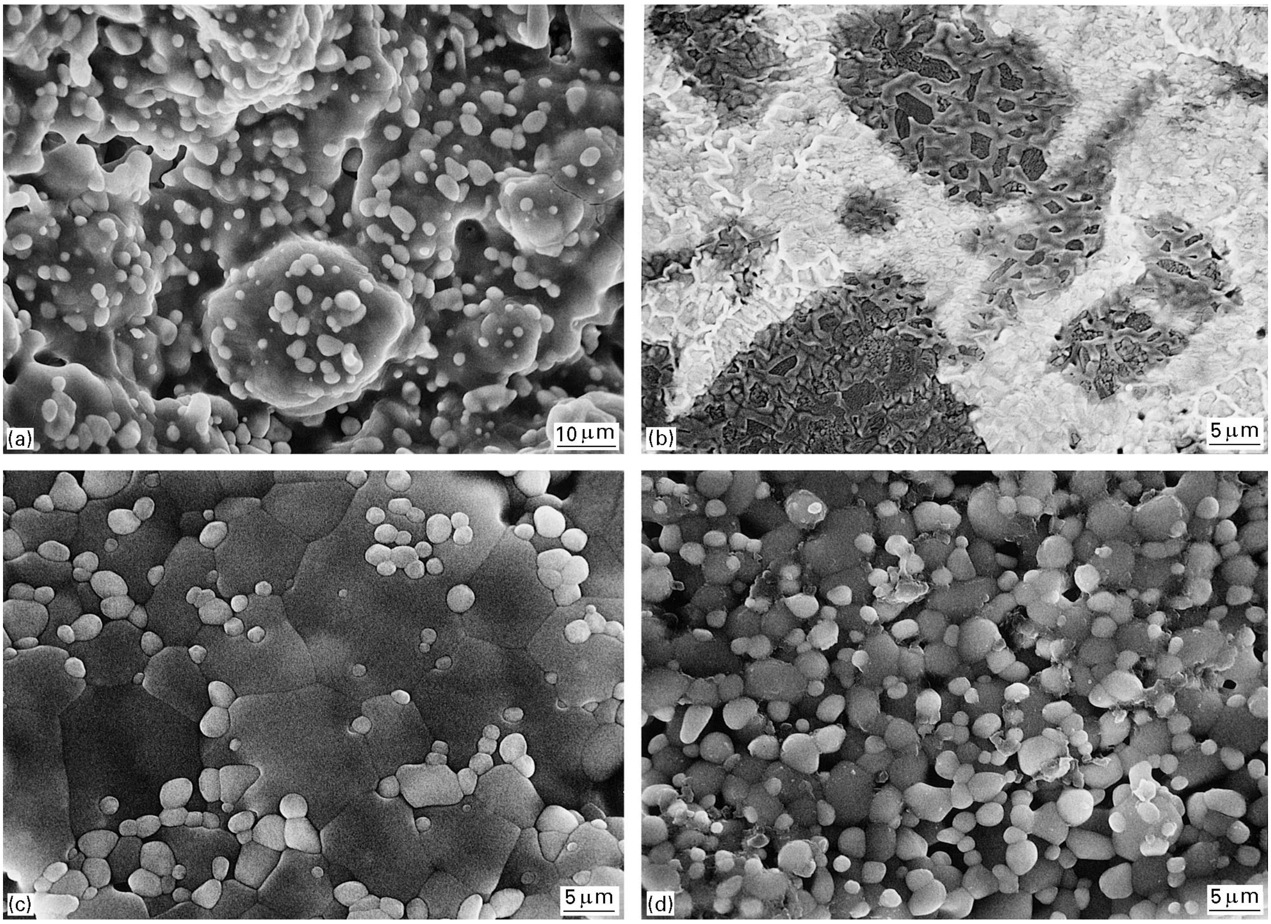

Figure 3 Microstructures of microwave-sintered zirconia-containing composites based on (a) alumina, (b) mullite, (c) CSZP, and (d) BS25.

the microwave effect. Although some of the composites were not very dense, we believe that it is only a problem of optimization of processing parameters.

4. Conclusions

Microwave sintering studies of various ceramic composites containing zirconia were carried out along with parallel conventional sintering studies. The results show that microwave processing significantly enhanced the densification in most cases, but the enhancement decreased with increasing zirconia content. This is due to the relatively higher sinterability of zirconia over the matrix materials. The maximum enhancement was up to 46%, varying with the system and zirconia content. The influence of zirconia addition on the densification of the composites is determined by the sinterability difference of the components. The addition of zirconia to a harder-to-sinter matrix enhances densification, under both microwave and conventional conditions.

Acknowledgement

This research was financially supported by the NSF under research contract DMR 8812824.

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Received 6 February 1996
and accepted 11 February 1997