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Microwave sintering of zirconia ceramics

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The potential of a microwave heating technique for the sintering of 3Y-TZP ceramics is demonstrated. High density samples were obtained by short duration firing in a domestic microwave oven. The ultrafine and monomodal size distribution of grains resulting from the process has important implications in terms of mechanical properties. The hardness and fracture toughness values compare very well with long duration, conventionally fired 3Y-TZP ceramics. © *2001 Kluwer Academic Publishers*

1. Introduction

The processing of ceramic materials using microwave heating is a relatively new and exciting technological development. Microwave heating has been used successfully to sinter a wide variety of oxide and non-oxide ceramics, composites and glasses. Beneficial effects in powder synthesis, sol-gel processing and ceramic joining have been reported [1, 2]. Rybakov and Semenov predicted an enhancement in mass transport processes under the action of such high frequency electromagnetic fields [3]. Specific benefits can be derived from this technique in terms of improved mechanical properties due to a fine grain microstructure resulting from the volumetric heating and the shorter processing times usually involved. The extent of microwave coupling is material specific in these materials, thus certain modifications such as hybrid heating configurations can be useful.

In conventional firing the radiant heat received at the surface of the ceramic component reaches the core by thermal conduction producing high temperature gradients and stresses. In contrast, in microwave heating each constituent unit of the crystal lattice is excited to a certain constant amplitude, which results in a highly uniform distribution of heat in the ceramic body. Reduced thermal stresses thus permit rapid firing rates and higher production throughput. Recent technological innovations such as microwave assisted electrical or gas fired kilns, microwave coupled continuous sintering assemblies, etc., have extended the potential of the technique [4–6].

On a microscopic scale, the mechanism of dielectric heating in ionic solids is predominantly due to impurity vacancy dipolar relaxation in the microwave frequency range. Existence of these defects in ceramics is the consequence of an aleovalent solute ion and the corresponding charge compensating vacancy forming an associated pair, a typical example being the Y'_{zr}–$V_{ö}$ dipoles in Y_2O_3 stabilized ZrO_2 ceramics [7]. When the vacancy jumps around the impurity ion to align its dipole moment with the electric field, the internal friction of the rapidly oscillating dipoles causes a considerable thermal energy dissipation. The microwave power absorption is a maximum at the frequency or temperature where the loss factor ($\tan\delta$) attains its maximum. The process is analogous to an elastic relxation resulting in the damping of mechanical vibrations in solids [8].

Zirconia doped with 3 mol% yttria system forms an important class of transformation toughened ceramics, possessing exceptionally high strength and toughness values. It has thus been studied extensively both in monophasic and composite forms [9, 10]. Relatively dense ceramics with a fine grain morphology are usually obtained by conventional sintering above about 1400°C. The impurities introduced during processing lead to a ubiquitous grain boundary liquid phase.

Doping in ZrO_2 introduces a large concentration of extrinsic O_2 vacancies. The defect reaction is expressed in terms of Kroger–Vink notation as:

$$Y_2O_3 \xrightarrow{2ZrO_2} 2Y'_{zr}V_{ö} + 3O^x_O \qquad (1)$$

The defect species are distributed in various dopant-vacancy associates. Their response to a microwave field generates heat. Zirconia ceramics thus prove to be a convenient system for microwave processing. Reports on microwave sintering of 8 mol% cubic stabilized zirconia, 3Y-TZP and magnesia partially stabilized zirconia ceramics have shown beneficial effect in terms of accelerated densification [11–15]. The additional sintering parameter investigated here is the incorporation of TiO_2 and MnO_2 additives. These sintering promoters are likely to be more effective under microwave irradiation.

2. Experimental procedure

To produce fine 3Y-TZP powders, the co-precipitation method was followed. Aqueous solutions of the component oxide precursor salts, $ZrOCl_2$ and $Y(NO)_3$, were mixed in required proportions to form a stock solution of 0.4 M concentration. For the co-precipitation reaction the reverse strike method was adopted i.e. the stock solution was added to a vigorously stirred 6 N ammonia

bath, which produced a white gelatinous precipitate. The final pH was maintained around 9.0. After washing the precipitate repeatedly with ammoniacal water, it was treated with ethanol to improve the dispersion characteristics. Oxide powders obtained by calcination treatment (600°C/3 hours) were ground in a planetary mill using TZP grinding media and characterized for particle size distribution. Additionally, two batches of calcined 3Y-TZP powders were prepared by doping with TiO_2 and MnO_2. Cylindrical samples were uniaxially pressed at 280 MPa to about 45% relative density.

The sintering assembly was constructed by modifying a domestic 1.5 kW, 2.45 GHz microwave oven (BPL India, BMC-900T). Green samples were placed inside a casket made of alumina and zirconia fiberboard. This was covered with alumina wool for heat containment. The fiber insulation, being transparent to microwaves, provides a negligible thermal load to the refractory surrounding the cavity within the chamber. To initiate heating, a hybrid mode was adopted using a thin layer of SiC powder as a susceptor. This was found to be essential in minimizing the thermal gradients within the sample. For temperature sensing a shielded R-type thermocouple was used. The cavity was operated initially at 30% power for 15 minutes and then at 80% for 30 minutes, followed by natural cooling in the oven. Under these conditions the temperature attained within the cavity was 1350 ± 10°C. For conventional sintering at 1400°C for 3 hours, a Pt-resistance furance was used.

Sintered samples were characterized for bulk density and open porosity by liquid displacement method. Flat, polished surfaces were prepared using standard metallography techniques for Vicker's indentation microhardness measurements. Fracture toughness (K_{Ic}) was estimated from the radial crack length measurements using the procedure of Anstis *et al.* [16]. Indentation loads of 100–300 N were applied for 15 s. A minimum of six perfect indentations at a given load were used to estimate average values of K_{Ic}.

For microstructural investigations, transmission electron microscopy (TEM) was used. Sintered samples were sliced to ~250 μm thickness. This was followed by disc grinding and dimpling steps. Final thinning to electron transparency was achieved in an argon ion mill (Gatan Inc. USA), operating at 4.0 kV. To prevent charge accumulation during observation a conductive carbon film was sputter coated on to the foils. A JEOL 200 FX microscope was used to image the grain size and morphological features and a JEOL 3010 microscope (with a point to point resolution of 0.21 nm) was utilized to examine the intra and inter granular fine-structure features under high resolution electron microscopy conditions.

3. Results and discussion

3.1. Microstructural evolution

Fig. 1a and b shows the typical microstructural features of the conventional and microwave sintered 3Y-TZP samples. The ceramics generally exhibit small equiaxed grains with sharp apexes and straight boundaries. These are characteristic features of high purity 3Y-TZP ceramics. This is in contrast to commercial grade, ball-milled powders which result in submicron size grains of spherical geometry (indicative of liquid phase sintering) and a large quantity of grain boundary amorphous phase [17]. The amorphous, siliceous glass phase is formed due to segregation of impurities and is a ubiquitous component of these ceramics.

Closer examination of the microstructures shows that there are differences in the microstructures in that a slightly larger grain size and a distinct bimodal size distribution is obtained in the conventionally sintered specimen. For the microwave sintered material

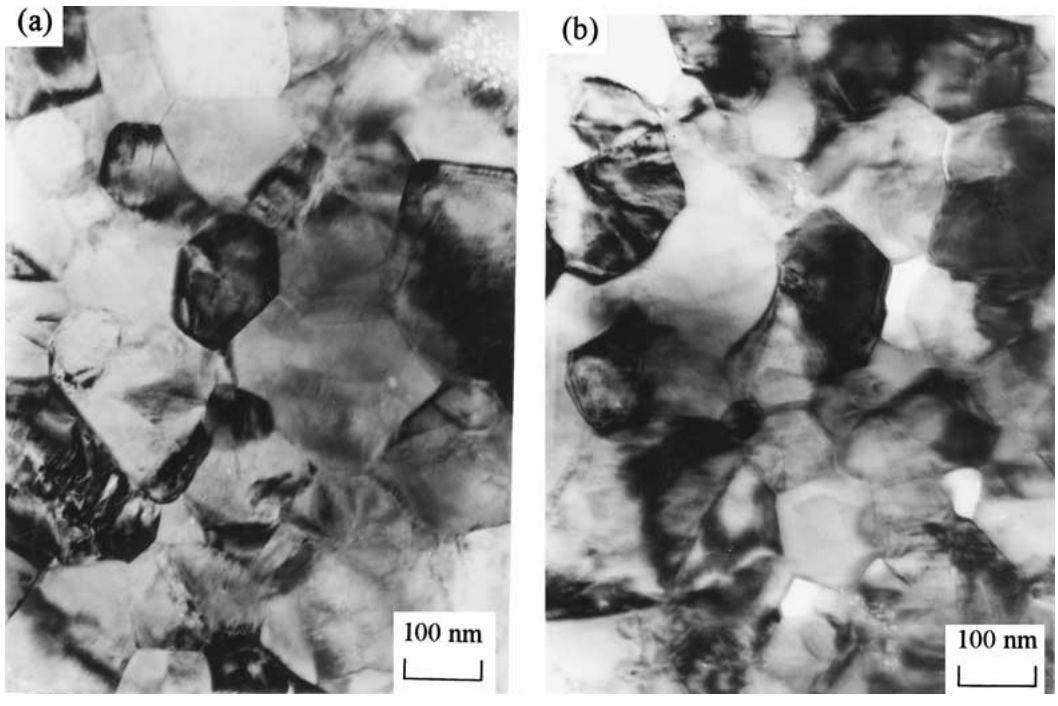

Figure 1 Bright field TEM micrographs of high purity 3Y-TZP ceramics sintered under (a) conventional and (b) microwave heating conditions.

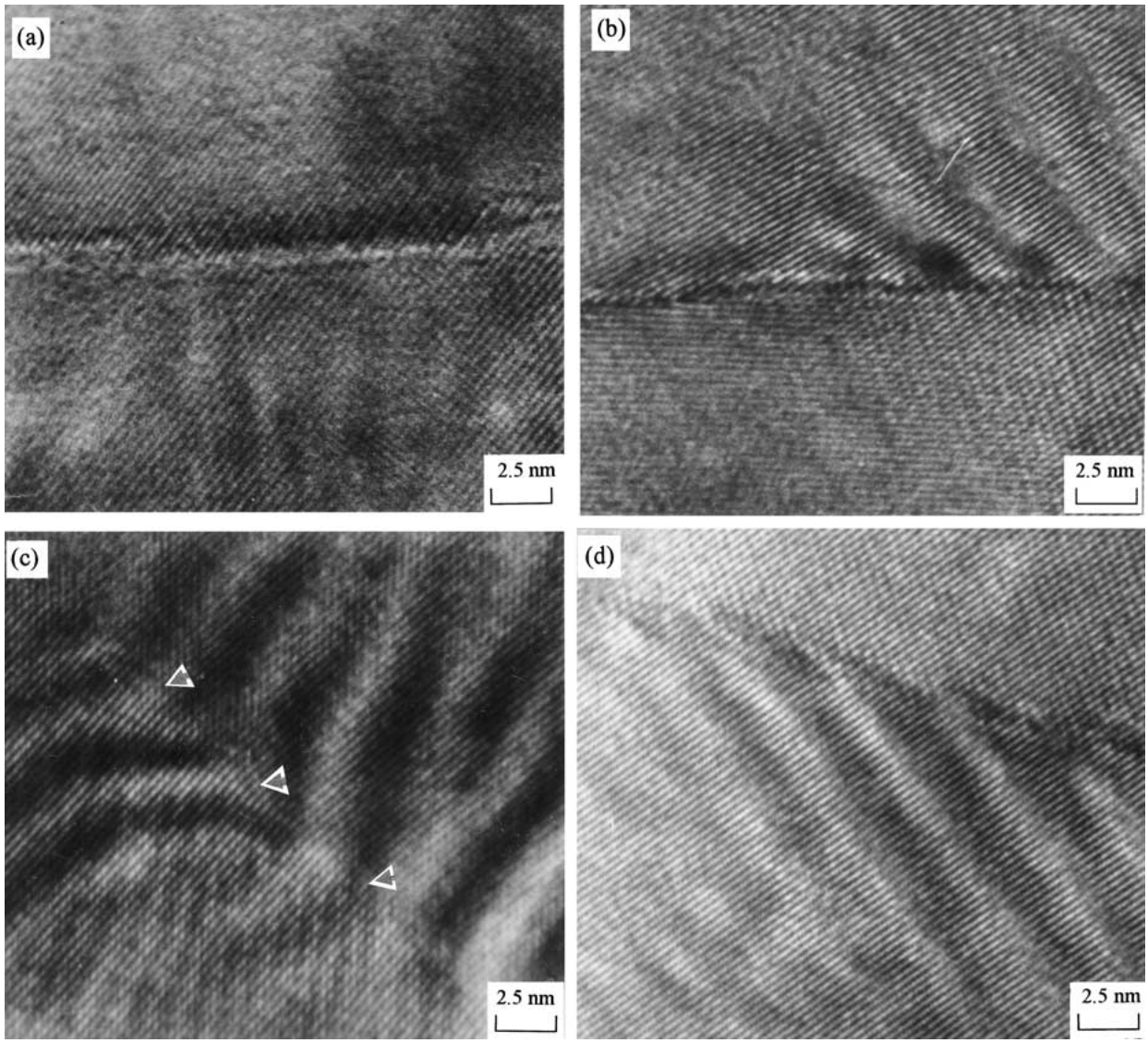

Figure 2 HRTEM images of grain boundaries in 3Y-TZP specimens sintered under (a) conventional and (b) microwave heating conditions, showing the absence of amorphous intergranular film. (c) Typical small angle boundary as marked with the arrowheads and (d) ledge type interface features of microwave processed ceramics.

the grains are relatively fine (∼100 nm), and unisized (monomodal distribution). The other important difference is the thickness of the grain boundary interface region, which is significantly thinner in the microwave sintered sample. The high resolution transmission electron microscopy (HRTEM) analysis, Fig. 2a–d shows that the grain boundaries are completely free of amorphous phase indicating that the high purity is retained even after several processing steps. A periodic strain contrast corresponding to the near grain boundary dislocation network is a very prominent feature in these ceramics. Ledge like interfaces are observed in certain orientations of the grains. No evidence of any incipient melting due to localized heating was found. The general morphology is identical to the conventional heating schedule, only a higher number of low angle grain boundaries are observed in the microwave sintered ceramics. All these observations can be considered as very significant benefits derived from microwave processing.

These results can be rationalized to some extent on the basis of the recently proposed space charge model of Rybakov and Semenov [3]. First, however, considering the thermal effect alone, in the rapid heating mode as achieved in a microwave furnace, the grain growth regime is traversed quickly on the way to the high temperature densification stage, thus a fine grain microstructure results [6]. The reported enhancement of mass transport processes in ionic solids under the action of high frequency electromagnetic fields is understood in terms of the non-linear interaction of microwaves with the space charge induced by it within the crystal near to its surface. Under the action of the tangential component of the field in the near to surface amorphised layer of fine powder particles, where the vacancy mobility is greater than in the bulk, the induction effects are likely to be of sufficient strength to promote densification. In this condition the predominant mode of transport is by near surface atoms rather than by the lattice atoms. The grain boundary diffusion is thus enhanced due to the field induced mobility of rate controlling species. There is, however, an alternative interpretation for microwave assisted sintering which is based on the faster elimination of closed pores due to

TABLE I Comparative study of conventional (con) and microwave (mw) sintered 3Y-TZP ceramics

Sl. No.	Material and sintering treatment	Bulk density ($gm \cdot cm^{-3}$)	Hardness H_v (GPa)	Toughness K_{Ic} (MPa$\sqrt{m}$)
1.	3Y-TZP (con)	5.86	6.6	8.7
2.	3Y-TZP (mw)	5.73	8.3	8.6
3.	3Y-TZP + MnO_2 (mw)	5.82	4.5	4.3
4.	3Y-TZP + TiO_2 (mw)	5.77	3.4	4.8

selective enhancement of material flux at the concave surfaces [18].

3.2. Physical and mechanical property evaluation

Table I presents comparison of conventional and microwave sintered 3Y-TZP ceramics. It reveals that reasonably high density values (∼95% theoretical density) could be obtained in a non-conventional, rapid-ramp technique of microwave heating. The reduction in processing time would provide a larger throughput rate. The effect of TiO_2 and MnO_2 as densification promoters is not very significant under microwave heating conditions. These transition elements oxides are considered as heat boosters by way of increasing the dielectric loss values of zirconia. These were added to make microwave coupling more efficient at a given temperature. In conventional sintering an enhanced sinterability of 3Y-TZP was observed in the presence of these additives [19, 20].

Under the action of an applied stress the tetragonal to monoclinic transformation occurs. The grain size and grain boundary chemistry largely control the effectiveness of this toughening mechanism. Vickers indentation results for hardness (H_v) and toughness (K_{Ic}) are presented in Table I. Although the K_{Ic} values remain unchanged the H_v increases slightly for microwave fired samples as a consequence of the finer and uniform grain size morphology. For conventionally sintered samples the K_{Ic} values are in agreement with those reported earlier [21]. For doped 3Y-TZP, the hardness and the fracture toughness values are observed to decrease considerably. This can be accounted for in terms of the segregation of MnO_2 impurities to the grain boundaries in the form of eutectic liquid. The reduction in the modulus values of TZP for TiO_2 doped samples which form a solid solution in this composition range could also have a similar effect on the mechanical behavior of zirconia. The microcracks generated across the indentation diagonals could be healed to a significant degree on repeating the microwave heating run for the test samples. This is a significant observation and such treatments could be used to remove the surface flaws of machined components.

4. Summary

Stabilized zirconia has a large concentration of point defects, which makes it an excellent susceptor of microwave energy. In the present work, the effect of microwave processing conditions on microstructural and mechanical property development has been analyzed. Comparison with conventional sintering shows that microwave sintering has a number of benefits in terms of microstructural design and mechanical properties.

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