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Microwave sintering of cubic zirconia

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Abstract

Microwave processing is of considerable interest because of its potential applications in the ceramic industry. The present investigation describes the technique for the sintering of yttria stabilised cubic zirconia. Significant advantage in terms of higher density of the ceramics at lower heat work is noted compared to the conventional radiant heat fired products. Its effectiveness for thin foil samples is more pronounced for generating the desired microstructural refinement. © 2001 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

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1. Introduction

There has been considerable interest in recent years in harnessing the phenomenon of microwave heating for the synthesis and processing of ceramic materials. In conventional firing, heat is applied to the surface of the ceramic component and it reaches to the core by thermal conduction, producing high temperature gradients and stresses. In contrast the important characteristics of microwave heating is its volumetric effect which results in a much more uniform distribution of heat in the ceramic body [1,2]. Reduced thermal stresses thus permit rapid firing rates, to speed up production. A recent technological breakthrough with microwave assisted gas fired kilns developed by EA Technology, UK, claims a considerable reduction in energy consumption in the ceramic industry [3]. It uses microwaves in combination with gas firing to produce tiles, pottery and other ceramics more efficiently. On the laboratory scale similar dual mode of energy transfer like combined microwave and hydrothermal crystallization technique is a novel feature for synthesis of reactive ceramic grade powders [4,5]. Although the magnitude of interaction is material specific, considerable enhancement in the densification process has been observed for ceramics under the action of high frequency e.m. fields. Specific to ZrO_2, its potential has been demonstrated in different variants of zirconia ceramics as well as in ZrO_2 dispersed alumina ceramic composites [6–10]. This paper describes the techniques as adopted for sintering of 9.0 mol% yttria cubic stabilized zirconia (9Y-CSZ) ceramics.

1.1. Microwave interaction with ceramics

The electromagnetic radiations in the frequency band of 0.3–300 GHz (corresponding wavelength of 1.0 m to 1.0 mm) belong to microwave range. A major portion of it is used in the communication sector and only certain frequencies, viz. 915 MHz, 2.45, 5.85 and 21.2 GHz are allotted for industrial and medical applications. The interaction and heating of ceramics under microwave field is dependent on the dielectric properties, viz., the relative dielectric constant (ϵ') and the loss factor (ϵ'') which are frequency and temperature dependent parameters [1]. These are related as:

$$\tan\delta = \varepsilon''/\varepsilon' \tag{1}$$

Where δ is the change in phase angle between the electric field and the current due to the presence of the material. Value of δ accounts for whether a given material will be transparent (low loss), good absorber (medium value) or a reflector (very high loss) of microwave

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radiations. The power dissipated per unit volume in a dielectric medium is expressed as :

$$P = \omega\varepsilon' E^2 . \tan\delta \qquad (2)$$

Where, $\omega = 2\pi f$ and f is the frequency (2.45 GHz commonly used) and E (Vm^{-1}) is the magnitude of electric field inside the material. The rate of power dissipation and the heat capacity of the material determine the rate of temperature rise. The penetration of electromagnetic power into the absorber is characterized by the depth of penetration (D_p) or skin depth parameter expressed as:

$$D_p = (\pi f \mu \sigma)^{-1/2} \qquad (3)$$

Where, μ and σ are the magnetic permeability and conductivity, respectively. D_p is the measure of depth from the surface at which power drops to e^{-1} of the original value. The effective attenuation depth decreases with increasing frequency, which in turn causes less heating. Thus a suitable combination of parameters in Eqs. (2) and (3) is required for achieving optimum coupling. The multifrequency processing equipment with provision for independent dynamic control of the power at each frequency overcomes these limitations.

2. Experimental

To produce fine reactive ZrO_2-9.0 mol% Y_2O_3 powders, co-precipitation method was followed. Aqueous solutions of the component oxide precursor salts, viz; $ZrOCl_2$ and $Y(NO)_3$ were mixed in required proportions to form a stock solution of 0.4 M concentration. For co-precipitation reaction the reverse strike method was adopted by adding the stock solution to a vigorously stirred 6 N ammonia bath, which produced a white gelatinous precipitate. The pH was maintained at around 9.0. After washing the precipitate repeatedly with distilled water to make it chloride free, it was treated with ethanol to improve the dispersion characteristics. Oxide powders obtained by calcination treatment (600°C/3 h) were ground in a planetary mill using TZP grinding medium and characterised for particle size distribution (Horiba-2000). Green samples were fabricated using both cold compaction and slip casting methods.

The sintering assembly was constructed by modifying a domestic 1.5 kW, 2.45 GHz microwave oven (BPL India). Green samples were placed inside a casket made of zirconia fibre board. This was covered with alumina wool for heat containment. This refractory material surrounding the cavity within the chamber, being transparent to microwaves provides a negligible thermal load to the furnace. To initiate heating a hybrid mode was adopted by the use of a thin layer of SiC susceptor powder. For temperature sensing a shielded R-type thermocouple was used. The cavity was operated initially at full power for 35 min and then at 90% for 35 min hold period, followed by natural cooling in the oven. Heating profile generated inside the cavity is presented in Fig. 1. Sintered samples were characterised for bulk density and open porosity by liquid displacement method. Microstructural evolution was studied by SEM technique.

3. Results and discussions

The yttria stabilised cubic zirconia has a wide range of applications both in the mono- and poly-crystalline forms. While for the former the superior optical quality is the hallmark of its dominance in diamond imitation segment, the latter finds many important technological applications like solid electrolytes, thermal barrier coatings etc. in new generation energy conversion devices. Powder synthesis is an important step to realise its optimum functional properties. In an ideal situation the requirement is for a ultrafine, unagglomerated and unisized powder source. These are essential features required for obtaining impervious products with a high degree of chemical and microstructural homogeneity.

Fig. 2 presents the particle size distribution of 600°C calcined powder prepared by coprecipitation rout. The XRD patterns presented in Fig. 3 indicate the powders to have evolved in desired monophasic, cubic solid-solution form (fluorite phase). Particle size distribution

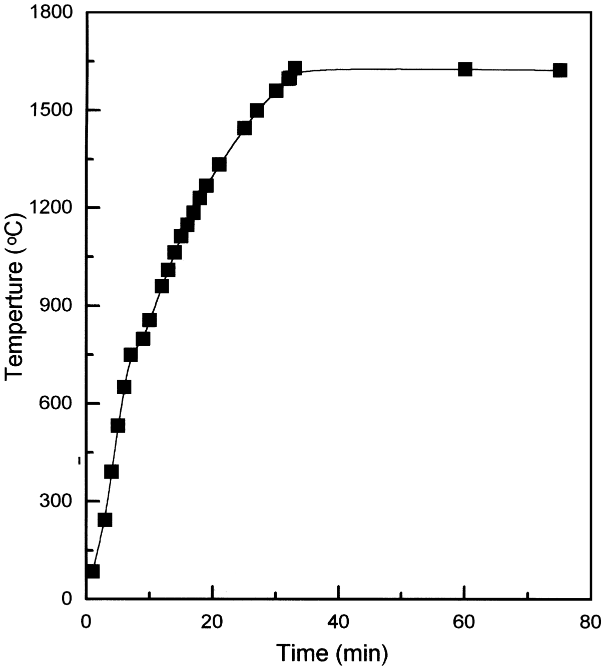


Fig. 1. Temperature profile recorded inside the sintering zone of microwave furnace. A comparatively short heat up and hold period is employed.

study shows a distinct bimodal distribution with median value of 0.69 µm. Such powder characteristics could yield about 50% green density for cylindrical samples (12 mm dia × 10 mm ht) at a uniaxial compaction pressure of 280 MPa. For preparation of aqueous slip a solid loading of 70 wt.% was achieved in the presence of 0.75 wt.% polyacrylic acid (PAA, M.W. 5000) at pH~9.0. The organic additive acted as a dispersant. The higher solid content of the slip enabled the thin wafers to be produced with minimum warpage (thickness ~0.5 mm).

On subjecting the green samples of different thickness to microwave heating treatment of Fig. 1 the bulk density of more than 97% of theoretical density (TD) was recorded consistently. By conventional sintering such high densities are obtained only by giving a long soaking period at 1700°C. A higher density is achieved here in microwave firing even at 1625°C for a very short (35 min) soaking time. The thin wafers could attain a higher density value of 98.5% TD but the cold pressed thick samples could reach to a slightly lower 97.2% TD level, under identical conditions. Component thickness dependence is thus exhibited (under a rapid rate of sintering) in microwave firing. This variation can be attributed to the temperature gradient, which usually develops in the thick section of the ceramic samples as a result of the inverted temperature profile, inherently produced in microwave heating [11]. The densification of these samples is likely to be hindered due to inhomogeneous temperature distribution, at a given power dissipation level.

Microstructural features of above two types of samples were studied by SEM technique. Representative micrographs are shown in Fig. 4. The fractograph of thick sample shows the characteristic transgranular fracture mode of c-ZrO_2 ceramics. The microstructure is composed of large, ~ 15 µm grains with a finely dispersed residual porosity. The thin foil as-fired surface

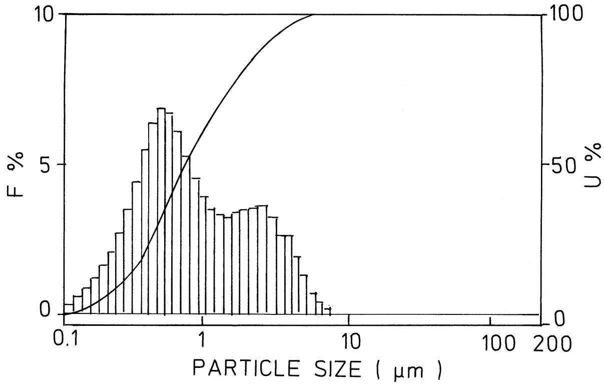


Fig. 2. Particle size spectrum for 9Y-CSZ powder calcined at 600°C for 3 h. The bimodal agglomerate size distribution is characteristic for the co-precipitated powders.

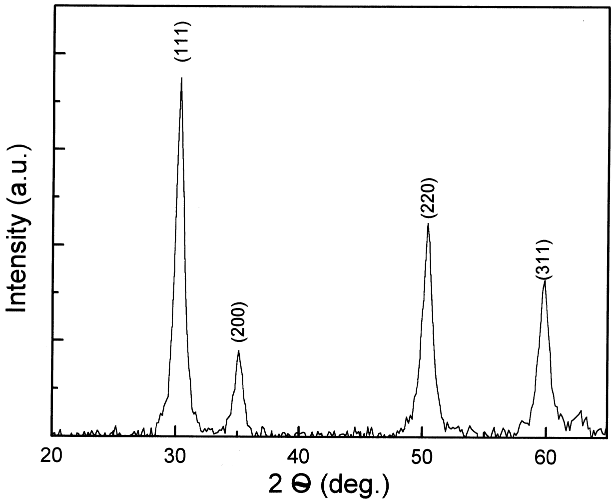
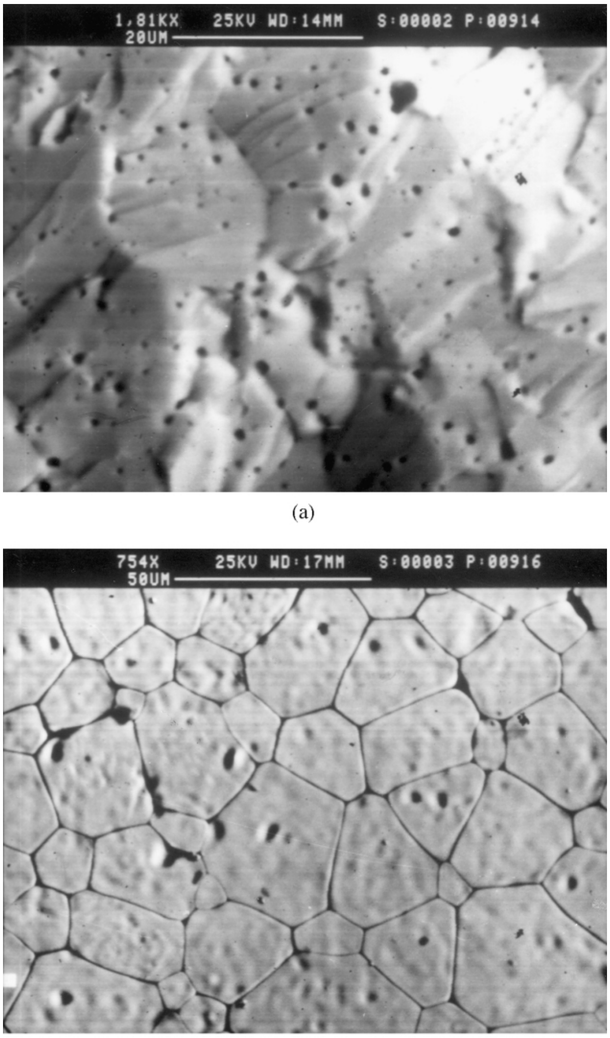


Fig. 3. X-diffraction pattern of 9Y-CSZ powder showing a monophasic cubic phase of ZrO_2.



(a)

(b)

Fig. 4. SEM micrographs of microwave field sintered 9Y-CSZ ceramics; (a) fracture surface features of a thick sample, (b) as fired surface features of a thin foil sample.

micrograph (Fig. 4b) gives a model equilibrium microstructure consisting of reasonably equiaxed grains. For Y-TZP ceramics, in microwave sintering a very fine grain (~0.1 μm) structure is obtained [8,9]. This is accounted for the activation energy for grain growth in the cubic matrix being much smaller (69 kcal mol^{-1}) than in the TZP phase (105 kcal mol^{-1}). Moreover, for a given system, in rapid heating mode of microwave processing the grain growth regime is traversed quickly to the high temperature densification stage, thus resulting in a fine grain microstructure [2].

The mechanism of dielectric heating in zirconia and other ionic solids is understood as a result of impurity-vacancy dipolar relaxation in the microwave frequency range. Doped ZrO_2 contains a large concentration of such lattice defect species. The defect reaction is expressed in Kroger-Vink notation as :

$$Y_2O_3 \xrightarrow{2ZrO_2} 2Y'_{zr} + V_o^{\bullet\bullet} + 3O_o^x \tag{4}$$

These point defects are distributed in various dopant-vacancy associates, forming elastic and electric dipole [12]. Under the action of high frequency electric field the vacancy jumps around the dopant ion to align its dipole moment in the direction of the field. The internal friction of the rapidly oscillating dipoles cause considerable thermal energy dissipation. The microwave power absorption is maximum at the frequency or temperature where the loss factor (tan δ) of the material attains its maximum. Zirconia ceramics thus turn out to be excellent susceptor in microwave field. The phenomenon is analogous to anelastic relaxation resulting in damping of mechanical vibrations in these ceramics [13].

The mechanism of microwave assisted densification is rather complex and can only be rationalized by way of assigning a non-thermal component (due to high frequency electric field) to the ionic mobility. The driving force for material transport is the vacancy concentration gradient in normal Jule heating conditions. The observed enhancement of densification kinetics can be understood to be due to the field induced dipolar ionic mobility component superimposed over the intrinsic value, in Fick's diffusion reaction relationship. The effective diffusion coefficient (D_{eff}) will thus have the intrinsic (D_i) and a charge or field sensitive component (D_f) as:

$$D_{eff} = D_i + D_f \tag{5}$$

Previous authors have visualized this effect in similar diffusion related terms, such as faster elimination of closed porosity due to selective enhancement of material flux at the concave surfaces [14] and formation of a space-charge layer in near-surface amorphised regions of the ceramic particles leading to enhanced grain boundary diffusion process [15]. However, a comprehensive model for ceramic material interaction with the microwave field is yet to be evolved.

4. Summary

Zirconia ceramics of cubic variant are playing important role in many energy conversion devices. Conventional processing requires its sintering at elevated temperatures for extended periods. Present work have shown the beneficial effects on microwave field processing of these ceramics. This is ascribed to the presence of a large concentration of lattice imperfections in its structure and their response to the high frequency field. A combined effect of dielectric heating and the field-enhanced mobility during diffusion is manifested in observed rapid kinetics. It is, therefore, considered to make the processing cost effective for zirconia ceramics.

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