

Prospects of microwave processing: An overview

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Abstract. Microwave processing has been emerging as an innovative sintering method for many traditional ceramics, advanced ceramics, specialty ceramics and ceramic composites as well as polymer and polymer composites. Development of functionally gradient materials, joining, melting, fibre drawing, reaction synthesis of ceramics, synthesis of ceramic powder, phosphor materials, whiskers, microtubes and nanotubes, sintering of zinc oxide varistors, glazing of coating surface and coating development have been performed using microwave heating. In addition, microwave energy is being explored for the sintering of metal powders also. Ceramic and metal nanopowders have been sintered in microwave. Furthermore, initiatives have been taken to process the amorphous materials (e.g. glass) by microwave heating. Besides this, an attempt has been made to study the heating behaviour of materials in the electric and magnetic fields at microwave frequencies. The research is now focused on the use of microwave processing for industrial applications.

Keywords. Microwave processing; ceramics; metal; polymer; composite; glass.

1. Introduction

The application of microwave energy to the processing of various materials such as ceramics, metals and composites offers several advantages over conventional heating methods. These advantages include unique microstructure and properties, improved product yield, energy savings, reduction in manufacturing cost and synthesis of new materials (Sutton 1989).

Microwave heating is fundamentally different from the conventional one in which thermal energy is delivered to the surface of the material by radiant and/or convection heating that is transferred to the bulk of the material via conduction. In contrast, microwave energy is delivered directly to the material through molecular interaction with the electromagnetic field. Microwave heating is the transfer of electromagnetic energy to thermal energy and is energy conversion rather than heat transfer. Since microwaves can penetrate the material and supply energy, heat can be generated throughout the volume of the material resulting in volumetric heating. Hence, it is possible to achieve rapid and uniform heating of thick materials. Therefore, the thermal gradient in the microwave-processed material is the reverse of that in the material processed by conventional heating. In conventional heating, slow heating rates are selected to reduce steep thermal gradient leading to process-induced stresses. Thus, there is a balance between processing time and product quality. During microwave processing, the potential exists to reduce processing

time and enhance product quality as microwaves can transfer energy throughout the whole volume of the material. In this case, energy transfer occurs at a molecular level that can have some additional advantages. When microwave energy is in contact with materials having different dielectric properties, it will selectively couple with the higher loss tangent material. Therefore, microwaves can be used for the selective heating of the materials (Thostenson and Chou 1999).

The objective of this article is to present an overview of the microwave processing of different materials. Some recent applications of microwave heating to materials processing are also described.

2. Microwaves

Microwaves are electromagnetic waves with wavelengths from 1 mm to 1 m and corresponding frequencies between 300 MHz and 300 GHz. 0.915 GHz and 2.45 GHz frequencies are commonly used for microwave heating. These frequencies are chosen for the microwave heating based on two reasons. The first is that they are in one of the industrial, scientific and medical (ISM) radio bands set aside for non-communication purposes. The second is that the penetration depth of the microwaves is greater for these low frequencies. However, heating is not necessarily increased with decreasing frequency as the internal field (E) can be low depending on the properties of the material. 2.45 GHz is mostly used for household microwave ovens and 0.915 GHz is preferred for industrial/commercial microwave ovens. Recently, microwave fur-

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naces with variable frequencies from 0.9 to 18 GHz have been developed for material processing (Sutton 1989; Thostenson *et al* 1999). Microwaves are coherent and polarized and can be transmitted, absorbed, or reflected depending on the material type (Sutton 1989).

2.1 Microwave furnace

Microwave furnace consists of three major components: the source, the transmission lines and the applicator. The source generates the electromagnetic radiation and the transmission lines deliver the electromagnetic energy from the source to the applicator while the energy is either absorbed or reflected by the material in the applicator. Generally, the processing is performed within a metallic applicator (e.g. single mode applicator, traveling wave applicator and multimode applicator). The type of applicator used depends on the materials to be processed. The single mode applicator and the traveling wave applicator are successful in processing materials of simple geometries. However, the multimode applicator has the capability to produce large and complex components. Therefore, multi-mode systems are used for industrial applications (Thostenson and Chou 1999).

2.2 Microwave-material interaction

Microwave energy is transferred to the material by interaction of the electromagnetic field at the molecular level. The dielectric properties determine the effect of the electromagnetic field on the material (Thostenson and Chou 1999). The interaction of microwaves with a dielectric material results in translational motions of free or bound charges and rotation of the dipoles. The resistance of these induced motions due to inertial, elastic, and frictional forces causes losses resulting in volumetric heating (Sutton 1989).

The power absorbed per unit volume, P (W/m^3), is expressed as (Sutton 1989):

$$P = \sigma |E|^2 = 2\pi f \epsilon_0 \epsilon_r' \tan \delta |E|^2, \quad (1)$$

where E (V/m) is the magnitude of the internal field, σ the total effective conductivity (S/m), f the frequency (GHz), ϵ_0 the permittivity of free space ($\epsilon_0 = 8.86 \times 10^{-12}$ F/m), ϵ_r' the relative dielectric constant and $\tan \delta$ is the loss tangent.

Equation (1) demonstrates that the power absorbed varies linearly with the frequency, the relative dielectric constant, loss tangent and the square of the electric field.

The penetration depth of microwaves (D) at which the incident power is reduced by one half is expressed as (Sutton 1989):

$$D = 3\lambda_0 / 8.686\pi \tan \delta (\epsilon_r' / \epsilon_0)^{1/2}, \quad (2)$$

where λ_0 is the incident or free-space wavelength.

The relative dielectric constant and the loss tangent are the parameters that describe the behaviour of a dielectric material under the influence of the microwave field. During heating, the relative dielectric constant and the loss tangent change with temperature (figures 1a–b) (Sutton 1989).

2.3 Thermal runaway

When ceramics are processed in non-uniform electromagnetic fields, the local temperature varies within the material. If a local area reaches the critical temperature before the rest of the material, it begins to get heated more rapidly. Thus, the temperature of that local region begins to increase even more resulting in localized thermal runaway leading to high enough stresses and material fracture (Thostenson and Chou 1999).

3. Applications

Excellent reviews have been provided on the general aspects of microwave processing by several experts (Sutton

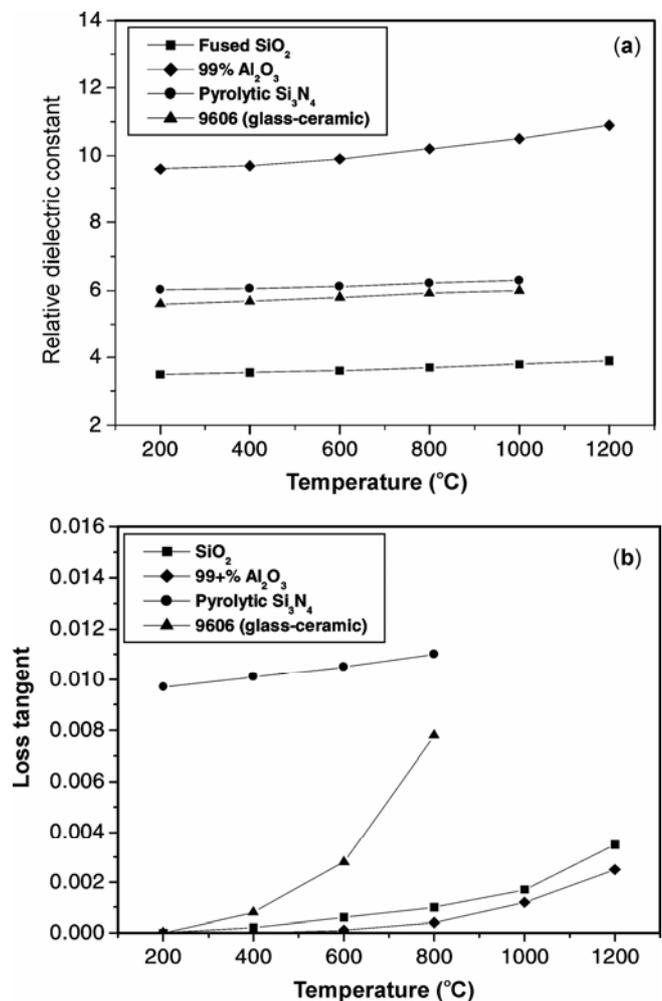


Figure 1. (a) Relative dielectric constant vs temperature and (b) loss tangent vs temperature (Sutton 1989).

1989; Clark and Sutton 1996; Agrawal 1998, 2005; Agrawal *et al* 2004; Thostenson and Chou 1999). The present review paper provides an overview of the microwave processing of a variety of conventional as well as advanced materials. Applications of microwave processing are indeed very wide. For instance, it can include processing of solution and suspension, drying, organic material burnout, clinkering, sintering of ceramics and ceramic composites, preparation of specialty ceramics, plasma processing, processing of polymers and polymer composites, fabrication of functionally graded materials, joining, fibre drawing, melting, reaction synthesis of ceramics and a host of very promising, new, advanced applications. Since application range covers a very wide spectrum, only general achievements have been highlighted leaving behind the critical issues.

3.1 Solution and suspension

In this application, the aim was to reduce the time requirement for the wet chemical analysis of minerals, ceramics and alloys by increasing their dissolution rates in acids (U.S. Bureau of Mines 1983). Also, the process of slip casting sanitary ware could be made faster by heating the slip to 65°C and then hardening the ware in the molds after casting (Guerga and Hailer 1973). Microwave assisted liquid phase deposition process was utilized to obtain nanocrystalline anatase titania from low concentration precursor solution (Zhang *et al* 2006).

3.2 Drying

Drying by this technology has been shown to be particularly effective for removing low water content from thick section. Water is driven away from the interior section due to volumetric heating (Krupa *et al* 1993; Sieke 1993; Segerer 1998; Ananthakumar *et al* 1998; Anon 2001). Hence, this technology is commercially utilized for foundry applications (Sutton 1989). This kind of heating permits efficient and faster drying of the insulating materials (Segerer 1998). Even, uniformly dispersed alumina-30 vol.% SiC particulate gel composite was prepared by this process (Ananthakumar *et al* 1998). Further, dehydration of sodium carbonate monohydrate has also been performed using this technique (Seyrankaya and Ozalp 2006).

3.3 Organic material burnout

Selective heating as well as volumetric heating has been extensively utilized for the binder burnout purposes during processing of the green ceramics (Sutton 1989; Leonelli *et al* 2004). Further applications are also upcoming.

3.4 Clinkering

The low incident power (300 W) and the short reaction time (≈ 7 min) have made this method promising for heating the refractory materials to produce clinker (Quemeneur *et al* 1983a). A microwave generator giving variable power from 0 to 3 kW at 2.45 GHz central frequency was used by Quemeneur *et al* for clinkering. Quemeneur *et al* (1983b) also studied clinkering of different clinker raw materials using microwave energy at 2.45 GHz. The properties of the microwave cement were close to those of the industrial cement. Microwave processing was utilized to prepare regular and coloured cement clinkers at 2.45 GHz at a lower clinkering temperature than that required for conventional processing (Fang *et al* 1996a). Clinkering of sulfoalumina cement was also achieved using microwave (Long *et al* 2002).

3.5 Sintering of ceramics and ceramic composites

3.5a Structural and functional ceramics: Bulk alumina, zinc oxide, silicon carbide, zirconia-toughened alumina, MgAl₂O₄, Y-PSZ, hydroxyapatite, Y-TZP/20wt%Al₂O₃ composites and glass matrix composites etc have been prepared by this technique (Fang *et al* 1993; Goldstein *et al* 1998, 1999; Lee and Case 1999; Xie *et al* 1999; Travitzky *et al* 2000; Boccaccini *et al* 2001; Mandal *et al* 2001; Mukhopadhyay *et al* 2001). Figures 2a–c show the mechanical properties of microwave sintered zinc oxide (Mandal *et al* 2001).

Similarly, for even commercial grade, less pure titania powder, high relative density ($\sim 96\%$) could be achieved while similar schedule (1300°C, 1 h) in a muffle furnace led to only $\sim 85\%$ relative density (figure 3) (Das *et al* 2005). The sintered titania had finer microstructure (average grain size $\sim 1.29 \mu\text{m}$, figure 4a) in comparison to that (average grain size $\sim 3.69 \mu\text{m}$) of the conventionally sintered titania (figure 4b). In addition, sintered 9Y-PSZ with very high relative density ($\sim 97\%$) and equiaxed grains ($\sim 15 \mu\text{m}$) was also achieved by microwave sintering for only 35 min at 1625°C (Upadhyaya *et al* 2001).

3.5b Bio-ceramics: The hydroxyapatite (HAp) ceramics were sintered in microwave with significant time and energy savings (Fang *et al* 1992, 1994). Fang *et al* (1995) showed that for transparent HAp, the total processing time from start to finish of the sintering process (5 min soaking at 1150°C) was ~ 20 min for microwave sintering while the same was about 4 h in the case of conventional sintering. Hydroxyapatite ceramics with tailored mechanical properties have also been fabricated by this technique (Rodríguez-Lorenzo *et al* 2003).

3.5c Composites: Lower sintering temperatures and times were required to microwave sinter WC/Co composites, which are widely used for cutting, drilling tools and

wear resistant applications. The sintered samples exhibited smaller WC grains and finer, more uniform distribution of cobalt binder that resulted in better resistance towards corrosion and erosion (Breval *et al* 2005). Recently, microwave assisted powder metallurgy method has been used to form nano-yttria reinforced magnesium composite (Tun and Gupta 2007).

3.6 Specialty ceramics

This technology is being increasingly employed for many specialty ceramics (Fang *et al* 1996b, 2004a, b; Xie *et al* 1998; Vaidhyanathan *et al* 2000, 2004; Cheng *et al* 2001a, 2002a; Hsu and Huang 2001; Huang *et al* 2001; Kutty *et al* 2001; Oh *et al* 2001; Rhee *et al* 2001; Lo *et al* 2002; Yadoji *et al* 2003; Agrawal 2006). Microwave sintered Ni–Zn ferrites showed lower coercivity, lower dielectric constant and higher magnetization values (Yadoji *et al* 2003). Similarly, reasonable translucency was obtained in the AlN samples at 1850°C for a much shorter time of only 30–60 min (Cheng *et al* 2002a). Fully transparent aluminium oxynitride (ALON) ceramics were prepared by microwave reactive sintering at 1800°C for 1 h in a nitrogen atmosphere (c.f. conventional sintering for 20–100 h at > 1850°C) (figure 5) (Cheng *et al* 2001a). Microwave sintering of Ni electrode multi layer ceramic capacitors (MLCCs) at 1250°C in the reducing atmosphere led to dense and uniform product without any cracks or delaminations (Fang *et al* 2004b). A strong and relatively porous glass-ceramic product was also developed by microwave sintering of flyash (Fang *et al* 1996b).

3.7 Plasma processing

Two variants of this emerging novel technique are: microwave plasma chemical vapour deposition (MPCVD) and microwave plasma induced sintering (MPIS). Diamond and diamond like films were formed by MPCVD (Kamo *et al* 1983). The MPIS method helped to sinter Al₂O₃ ceramics containing 0.25 wt.% MgO to 99.9% relative density in nitrogen plasma at 1660°C in less than 10 min (Kemer and Johnson 1985). Plasma activated sintering of AlN powders to near theoretical density was achieved within 5 min at 1730°C (Groza *et al* 1992).

3.8 Polymer and polymer matrix composites

This processing approach has reduced the processing times and improved the mechanical properties of thermo-setting and thermoplastic polymer and polymer matrix composites e.g. epoxy resin, glass fibre reinforced epoxy composite, carbon fibre reinforced epoxy composite, poly-ether-ether-ketone (PEEK) coating, SiC particle reinforced PEEK coating (Haran *et al* 1965; Lee and Springer 1984; Chen *et al* 1993; Zhang *et al* 2006). Dipole struc-

ture, frequency of processing, selective coupling, fabrication temperature, chemical nature of additives and fillers etc all influence the processing (Thostenson and Chou 1999).

3.9 Functionally graded materials (FGMs)

Compositional variations in the FGMs (e.g. steel-WC/Co) are ensured in this method due to shorter processing time (Agrawal 2005a, b). Ti–B-based FGMs were produced by microwave-activated combustion synthesis (Cirakoglu *et al* 2002). Better compositional control in calcium phosphate, titania and silver FGMs was also made possible (Katakam *et al* 2003).

3.10 Joining

Reliable joining of ceramic materials e.g. strong alumina–alumina joints (Al-Assafi *et al* 1991), other joints (Meek and Blake 1986; Palaith and Silberglitt 1989; Fukushima *et al* 1990; Cawley 1998; Cheng *et al* 1999; Zeng *et al* 2003), joints of alumina–30%zirconia composites (Aravindan and Krishnamurthy 1999) etc is an issue of significant technological importance addressed by this processing route.

3.11 Fibre drawing

Attempt was made to draw ultra pure quartz optical fibres at temperatures above 2000°C using microwave heating in a specially designed single mode applicator. The amount of material blown away by the torching during tube collapse as well as energy cost was reduced in the microwave process. The optical fibre quality was comparable with that obtained by the standard process (Hassler and Johansen 1988).

3.12 Melting

The feasibility of this emerging technique is well demonstrated for the melting of ceramics (Berteaud and Badot 1976). Melting of silica gels was also achieved by microwave heating (Roy *et al* 1985). Rapid heating and melting were observed in Na, K and Cs containing zeolites with microwave energy (Komarneni and Roy 1986). Glasses were melted using microwave radiation by Duval *et al* (1997). Microwave has been used to melt even bulk metals (Barmatz *et al* 2000).

3.13 Reaction synthesis of ceramics

In a very interesting work, Mathis *et al* (1995a) studied microwave assisted solid state reaction of alumina and

tiania to form aluminium titanate. $MgAl_2O_4$ spinel was also obtained through the solid state reaction between magnesium oxide (MgO) and aluminium oxide (Al_2O_3) along with 1 wt.% of CaO as an additive at about $1400^\circ C$ for ~ 4 min (c.f. conventional route, 96 h at $1400^\circ C$, Gómez *et al* 2004). This novel process helped to synthesize β -SiAlON within only 15 min at $1500^\circ C$ (Mathis *et al* 1995b). Even, synthesis of phase pure ALON was achievable (Cheng *et al* 1999).

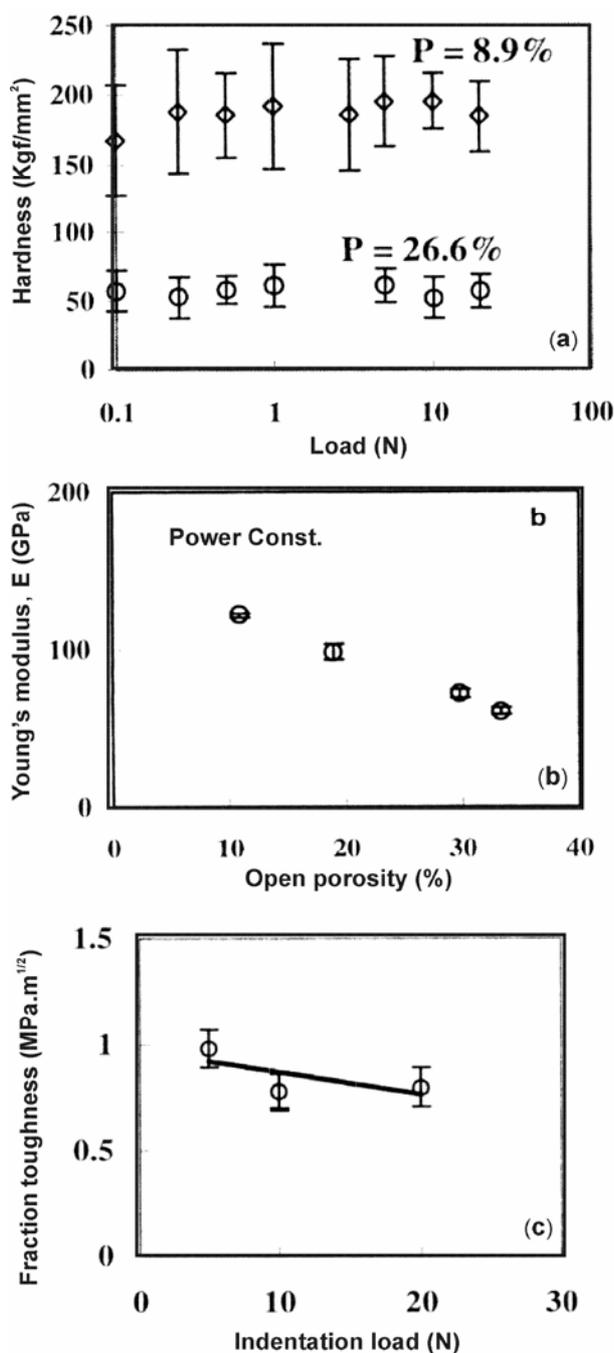


Figure 2. Mechanical properties of microwave sintered zinc oxide (a) hardness vs load, (b) Young's modulus vs volume percent open porosity and (c) fracture toughness vs load (Mandal *et al* 2001).

4. Relatively newer applications

4.1 Synthesis of ceramic powder

Cr-substituted lithium ferrite powder [$Li_{0.5}Fe_{2.5-x}Cr_xO_4$ ($0 \leq x \leq 1.0$)] with small and uniform sized particles was successfully synthesized within only a few min by microwave-induced combustion method (Fu *et al* 2006). Binner *et al* (1995) synthesized titanium carbide and tantalum carbide by carbothermal reduction of the oxides. Further, synthesis of high phase pure β -SiC powder using microwave irradiation (Ramesh *et al* 1994), $LiAl_{0.1}Mn_{1.9}O_4$ powder by microwave assisted sol-gel processing (Zhou *et al* 2006)—all demonstrate the utilities of this technique.

4.2 Synthesis of phosphor materials

ZnS based phosphor materials were prepared within a much shorter time (20 min) in a domestic microwave oven (2.45 GHz, 900 W) (Sundar Manoharan *et al* 2001). Researchers also synthesized fine particles of Sr_2CeO_4 by hydrothermal reaction at $200^\circ C$ for 30 min with a pressure of 200 psi in a microwave accelerated reaction system (2.45 GHz, 1200 W) followed by calcination of the as-prepared material at $1000^\circ C$ for 25 h in air (Khollam *et al* 2004). Synthesis of nanocrystalline $MMoO_4$ ($M = Ni, Zn$) phosphors was carried out by the modified citrate complex route using microwave irradiation (2.45 GHz, 1200 W) under ambient air for 30 min (Ryu *et al* 2006).

4.3 Synthesis of whiskers

The application of this versatile technique helped the synthesis of ultra fine silicon carbide whiskers through the reduction of ultra fine silica powders with various forms of carbon (Dai *et al* 1997) and hydroxyapatite whiskers (Yoon *et al* 2005) with high aspect ratio by the hydrolysis

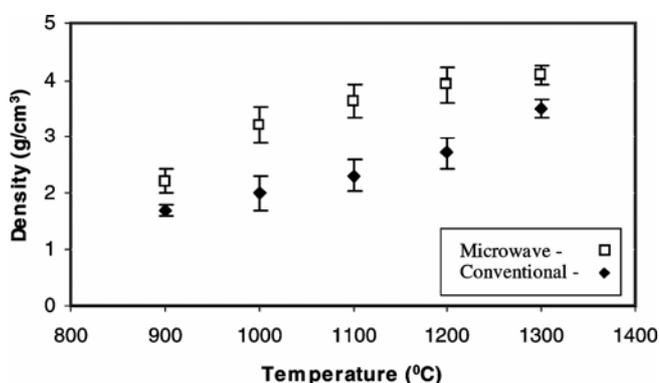


Figure 3. Density values of microwave and conventionally sintered titania samples.

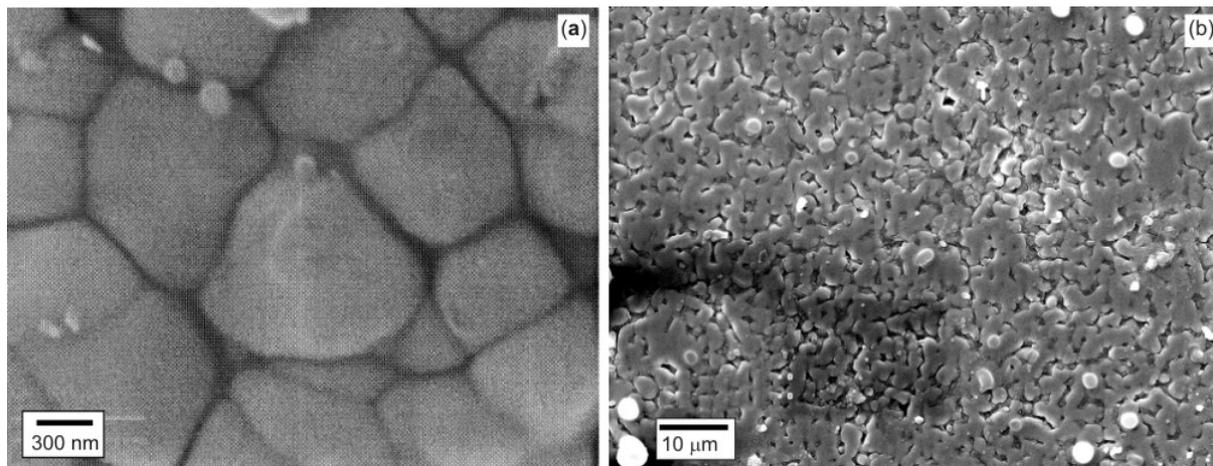


Figure 4. Microstructures of sintered titania samples (a) microwave and (b) conventional.



Figure 5. Fully transparent ALON sample (Cheng *et al* 2001a).

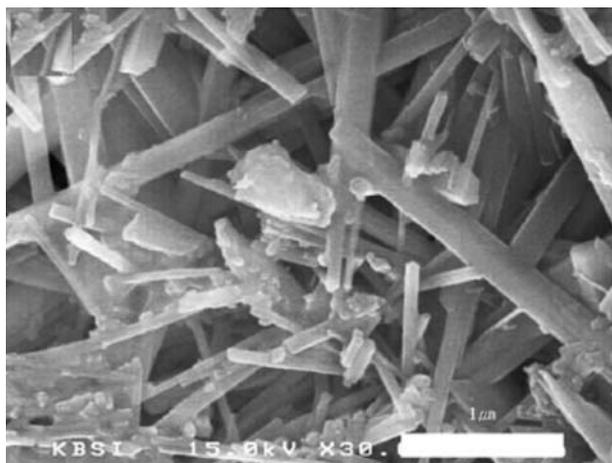


Figure 6. Hydroxyapatite whisker (Yoon *et al* 2005).

of α -tricalcium phosphate (figure 6). The hydrolysis reaction time for hydroxyapatite whiskers could be reduced by more than twice.

4.4 Synthesis of microtubes

Cheng *et al* (2004) showed that the colourless, contamination free, fully transparent, nearly perfect crystalline and hexagonal, hollow tubular shaped ZnO microtubes (wall thickness, 0.5–1 μm) could be grown by microwave heating. This prospective area should receive more attention of the researchers.

4.5 Synthesis of nanotubes

The one-dimensional nanostructured materials have potential applications in ceramics, electronics, optics, magnetic storage, catalysis and chemistry, physics and biomedical sciences. This emerging area showed promise through synthesis of ordered array of CdS nanotubes (figures 7a–c) (Ni *et al* 2004), TiO₂ nanotubes (Wu *et al* 2005) and even carbon nanotubes (Yoon *et al* 2006).

4.6 ZnO based ceramic varistors

Varma *et al* (1996) prepared doped ZnO varistors using microwave reactive precursors in a domestic microwave oven (600 W, 2.45 GHz). Such powders were further sintered to higher density (>95%) varistors having desirable microstructure and non-ohmic properties. Nan Lin *et al* (2001) used microwave energy to sinter ZnO varistors having high density and improved electrical properties in an applicator (1 kW, 2.45 GHz). Utilizing microwave processing, Agrawal *et al* (2002) sintered zinc oxide varistors with better density, finer grain size, more uniform microstructure and better electrical properties through significant reduction in the processing time.

4.7 Glazing of coating

In a singular effort, significant improvement in the microhardness (~ 1550 Hv) and the surface finish ($R_a \sim 1 \mu\text{m}$)

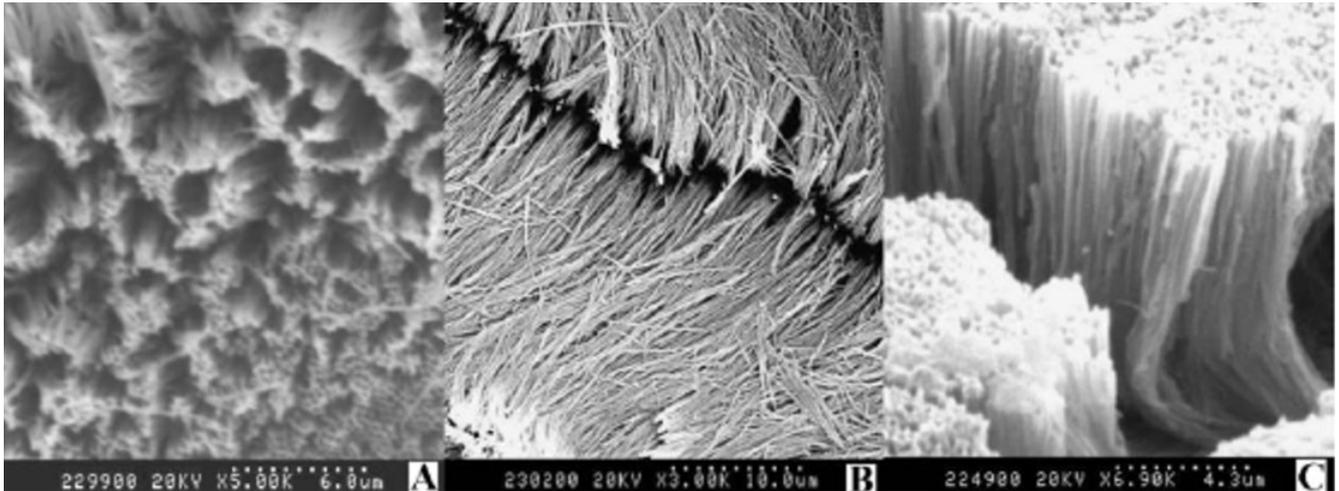


Figure 7. CdS nanotubes array (A) survey picture, (B) and (C) lateral pictures (Ni *et al* 2004).

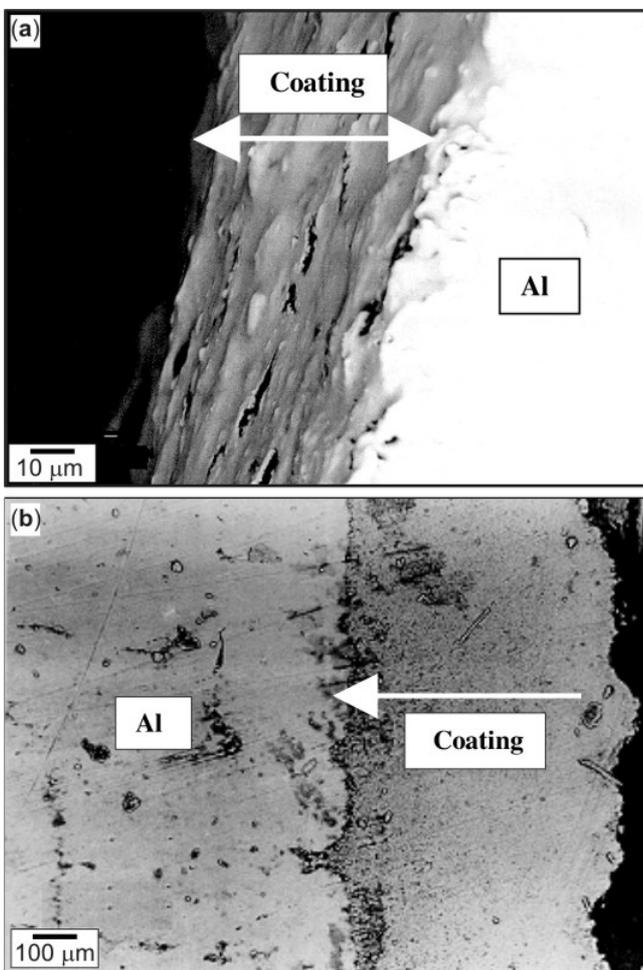


Figure 8. (a) Porous, thin coating grown by 60 min microwave heating and (b) dense, thick coating developed by 90 min microwave heating.

was observed with the microwave treated atmospheric plasma sprayed alumina–titania composite coating (Sharma *et al* 2001).

4.8 Crystallization of glass

Monoclinic celsian was obtained from 10% CuO seeded barium aluminosilicate glass using this novel technique at 1300°C for only 15 min in a 2.45 GHz microwave field (Cozzi *et al* 1993). Siligardi *et al* (1996) investigated the effect of microwave on bulk crystallization of glasses belonging to $M_2O-CaO-SiO_2-ZrO_2$ system (where $M = Li, Na, K$) in a commercial microwave oven (900 W, 2.45 GHz). The glass samples heat treated by microwave energy showed surface and bulk crystallization while only surface crystallization was observed in the glass samples heat treated by conventional method. The sintering and devitrification in the ternary $CaO-ZrO_2-SiO_2$ glass system was studied by Siligardi *et al* (2000) in the temperature range 900–1050°C using commercial microwave oven (900 W, 2.45 GHz).

4.9 Coating development

In our laboratory, this interesting method was used to develop aluminium oxide coating on commercial aluminium (Das *et al* 2003a, b). Figures 8a–b show the porous, thin coating (~42 µm) and dense, thick coating (~661 µm) developed by microwave heating of pre-oxidized aluminium samples (600°C, 200 h) for 60 and 90 min, respectively. In both of these two cases, smooth coating with crack free interface was observed. Microwave heating was also utilized to develop oxide coatings on blocks of commercial aluminium of various geometrical shapes (Das *et al* 2006). Experimental data showed that the geometrical term, i.e. the volume to surface ratio had a significant effect on the microwave induced oxidation behaviour of the samples (figures 9a–b). Coating thickness and density gradually enhanced with increasing the microwave exposure time. Protective oxide coating of varied thickness and microstructure was formed on com-

mercial aluminium using this novel technique by suitable adjustments of the processing parameters.

Crystallization of MgO–Al₂O₃–TiO₂ based glass coatings with identical composition was conducted in our laboratory by both microwave and conventional heat treatment processes. Finer crystallites were generated in the glass coating by microwave processing than the sizes of the crystallites obtained in the conventionally processed coating (figures 10a–d). Microhardness and surface finish of the microwave processed glass-ceramic coatings were improved (figures 11–12) than those of the coatings processed by conventional heating (Das et al 2008b).

4.10 Sintering of metal powder

In an unprecedented approach, sintering of fine metallic powders, intermetallic compounds and alloys was achieved by this processing wherein the sintered products showed better properties (Gerdes et al 1996; Gedevarishvili et al 1999; Roy et al 1999; Saitou et al 2006). Recently, Mg–Cu nanocomposites have been developed using micro-

wave-assisted sintering method (Wong and Gupta 2007). Unlike bulk metals that act as reflector, it is believed that in finely divided metallic powder, multiple scattering coupled with eddy current loss play a significant role in microwave absorption (Roy et al 1999).

4.11 Preparation of nanomaterials

Nanomaterials have been developed by several methods e.g. thermochemical process (Lee and Kim 2004), hydrothermal treatment (Pitescu et al 2004) and microwave-assisted synthesis method (Rao et al 1999) etc. Microwave-assisted solvothermal method was also used for the synthesis of oxide nanomaterials e.g. MgO, NiO, ZnO, Al₂O₃, Fe₂O₃, ZrO₂ etc (Rao et al 2005). Nanocrystalline anatase TiO₂ powder was synthesized utilizing microwave hydrothermal method (Vadivel Murugan et al 2006). Apte et al (2006) synthesized nanosized Mn₃O₄ powder by microwave digestion technique. Microwave induced combustion method was utilized to prepare cadmium substituted lithium ferrites (3.5–16.8 nm) with general formula, Li_{0.5-x/2}Cd_xFe_{2.5-x/2}O₄ (where $x = 0.45, 0.5, 0.55, 0.6, 0.65, 0.7$). The saturation magnetization (M_s) and the hysteresis loss per cycle of the samples were in the range of 10.45–35.23 emu/g and 25.51–65.15 erg/cc/cycle, respectively. All the samples showed the single domain behaviour. The Curie temperatures obtained using the susceptibility data were in the range of 210–300°C. The d.c. resistivity was minimum ($9 \times 10^4 \Omega \text{ cm}$) for the sample with $x = 0.55$, whereas the dielectric constant for the same composition was 1200×10^3 . The dielectric constant and d.c. resistivity showed an inverse trend with each other (Watawe et al 2006).

4.12 Sintering of nanomaterials

Recently, nanophase TiO₂, Cu metal powder and MgO have been sintered by this novel processing (figure 13) with very fine microstructures (Fang et al 2004a; Agrawal et al 2006). The nanocrystalline hydroxyapatite was sintered by microwave energy with high density (>96% T.D. at 1100°C for 30 min soaking time), fine-grained microstructure and improved mechanical properties i.e. high fracture toughness and hardness (Ramesh et al 2007). Huang et al (2007) sintered tetragonal ZrO₂ polycrystalline (TZP) composites with 2 wt.% Al₂O₃ and co-stabilized with 1 mol% Y₂O₃ and 4, 6 or 8 mol% CeO₂ at 1450°C for 20 min in a single mode 2.45 GHz microwave furnace. The microwave sintered ceramics showed finer and more uniform microstructures as compared to the conventionally sintered samples. Comparable hardness and toughness values were obtained for both the microwave and conventionally sintered samples. Nanocrystalline La_{1-x}M_xGa_{1-y}N_yO_{3±δ} (M = Sr; □ (vacancy), $x = -0.10$ to 0.15; N = Mn, Mg; $y = -0.15$ to 0.15) com-

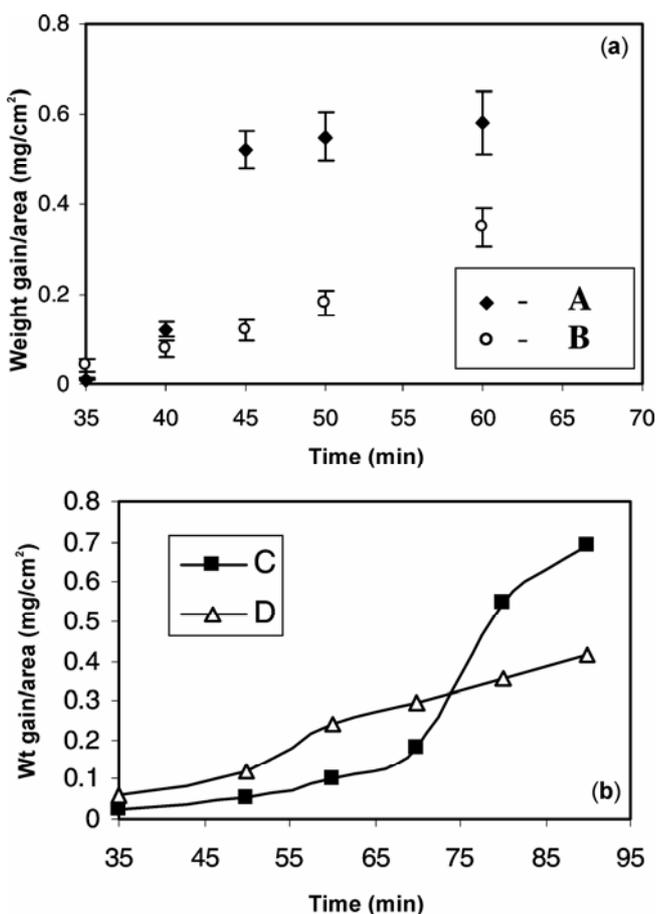


Figure 9. Weight gain data for pre-oxidized (615°C, 4 h) samples (a) sample A (hollow cylinder) and sample B (solid cylinder) and (b) sample C (solid cube) and sample D (thin rectangular block).

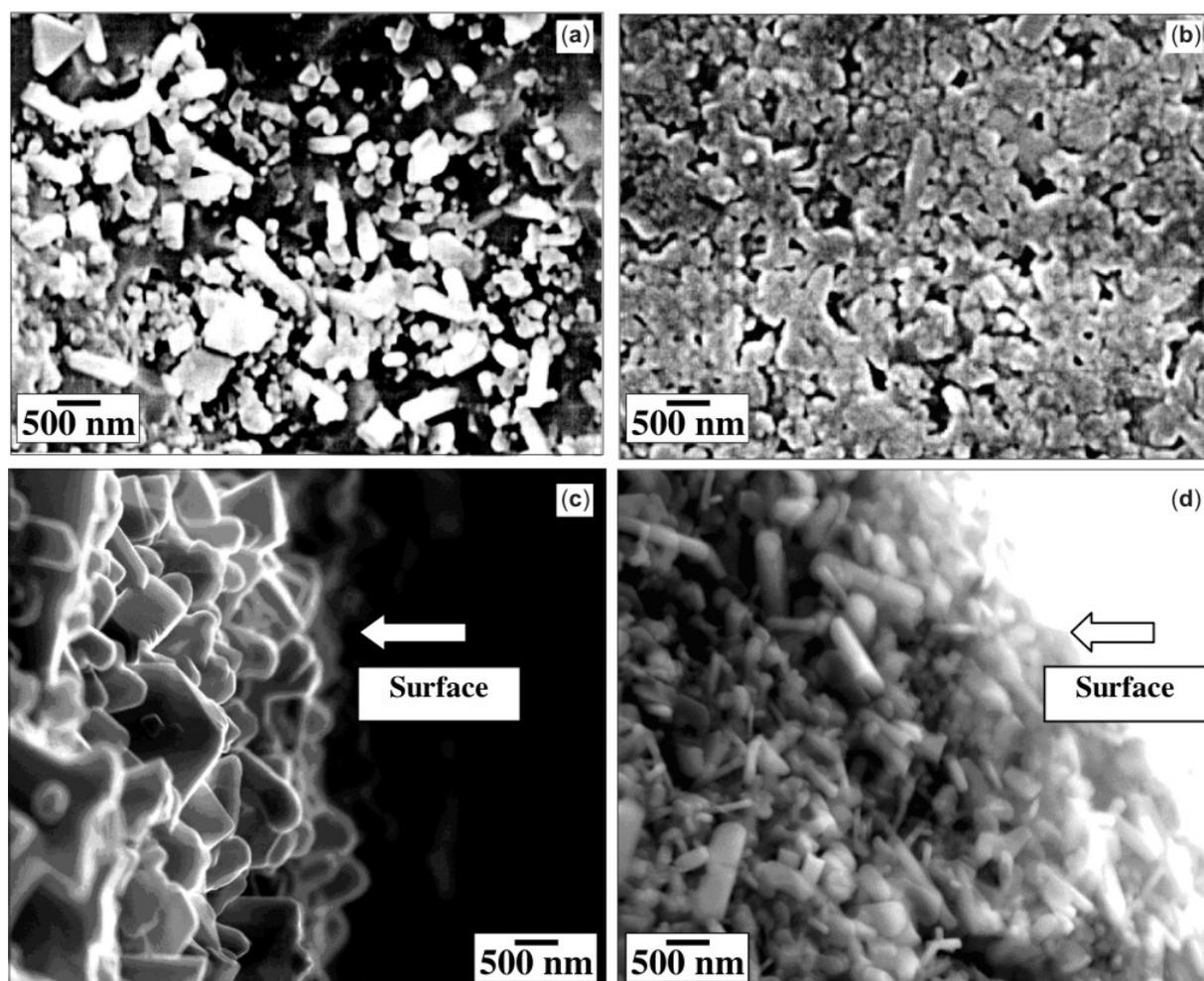


Figure 10. Surface microstructures of the glass–ceramic coatings obtained by heat treatments of the glass coatings for 90 min at 880°C followed by 90 min at 1020°C: (a) conventional, (b) microwave and cross-sectional microstructures showing surface regions of the similar coatings, (c) conventional and (d) microwave.

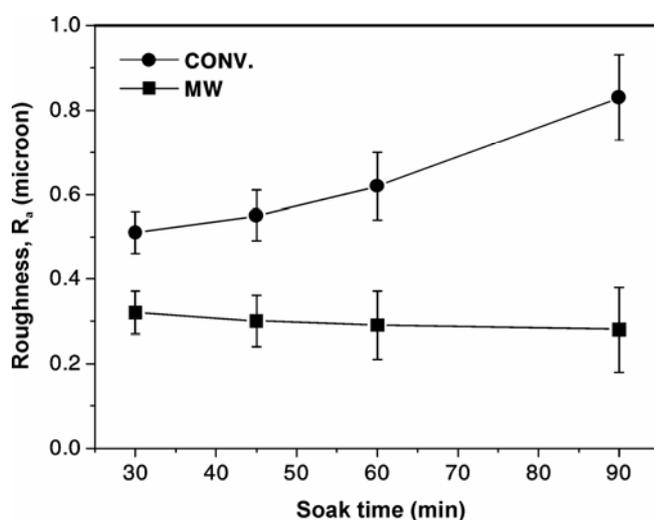


Figure 11. Typical surface roughness values of the microwave and conventionally processed glass–ceramic coatings.

positions were synthesized by various wet chemical methods. The pellets made from these powders were microwave sintered at $\sim 1200^\circ\text{C}$ in a very short interval of time (30 min). The conductivity of the sintered pellet was found to be $\sim 0.01\text{--}0.21\text{ S cm}^{-1}$ at $550\text{--}1000^\circ\text{C}$ temperature range, respectively (Jena and Rambabu 2007).

4.13 Decrystallizing solid crystalline titania

In a promising effort, the rutile structure oxides were transformed to a noncrystalline state by a very short duration treatment in the a.c. magnetic field at 2.45 GHz (Roy *et al* 2005).

4.14 Core-shell type $\text{Al}\text{--}\text{Al}_2\text{O}_3$ composite

Further work in our laboratory showed that core-shell type $\text{Al}\text{--}\text{Al}_2\text{O}_3$ composites could be developed by micro-

wave heating of the as received, commercial grade, low-purity aluminium powder and the doped aluminium powder compacts (Das *et al* 2008a). Oxidation of aluminium powder compact was remarkably enhanced by the addition of certain dopants (e.g. Mg, Mg–Si, Al_2O_3). Significant Al– Al_2O_3 composite growth was noted in the case of 5 wt.% Mg-doped aluminium powder compact. Figures 14a–d show the typical micrographs of as received and treated aluminium powders.

4.15 Heat treatment of TiO_2 films

Preliminary effort to provide crack resistant TiO_2 films on the conducting glass substrates using microwave heating showed promising results (Hart *et al* 2005). However, further research is needed to clarify many unresolved issues.

4.16 Industrial applications

This includes the curing, drying and dewaxing of ceramic moulds and shells used in the metal casting industries as well as slip casting of production shapes etc (Sutton 1989). Prospective applications encompass a much wider variety e.g. calcination, sintering, joining, plasma induced sintering, clinkering of cement materials, heating of optical fibre preforms and process control in the ceramic industry (Metaxas *et al* 1993); polymerization, composite processing, bonding, microwave-assisted chemical vapour deposition, non-destructive evaluation etc. (Fathi *et al* 1996); contaminated soil vitrification, volatile organic compounds treatment and recovery, waste sludge processing, mineral ore grinding, carbon in pulp gold recovery, minerals industry and extractive metallurgical industry (Kingman and Rowson 1998), processing of waste (Ap-

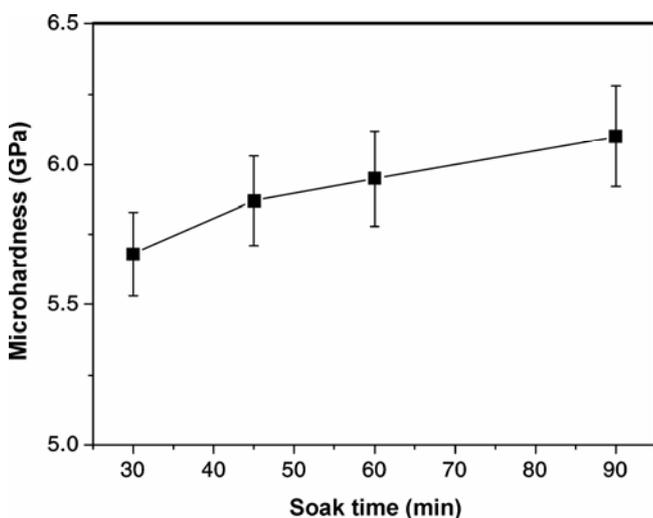


Figure 12. Typical hardness of the microwave processed glass-ceramic coatings.

leton *et al* 2005) and food industry (Zhang *et al* 2006; Biswas *et al* 2007). However, difficulties associated with the scaling up of the laboratory units to industrial capacities and lack of fundamental data on material dielectric properties are the obstacles for the widespread use of microwave processing (Jones *et al* 2002).

5. Role of electric and magnetic field components

Current research on the effects of E and H field components of the microwave field in the heating behaviour of metal, ceramic and metal–ceramic composite samples showed that powdered metal compacts were effectively heated in the H field, but not in the E field while solid metallic rod could not be heated either in the E field or in the H field at all. In contrast, ceramics and insulators could be rapidly heated in the E field but not in the H field. Furthermore, metal–ceramic composites could be heated up in both the E and H microwave fields (Cheng *et al* 2001b, 2002b). Therefore, it is no longer possible to ignore the effect of the magnetic component for the general theory of energy loss in various materials when placed in a microwave field, especially for conductor and semiconductor materials. The contributions to the magnetic loss mechanism can be hysteresis, eddy currents, magnetic resonance and domain wall oscillations. Hence, it is necessary to incorporate the effects of the magnetic field in the microwave–material interaction (Cheng *et al* 2002b).

6. Modeling of microwave heating

New and unexpected physical behaviours such as the hot spot often occur during microwave processing. Therefore,

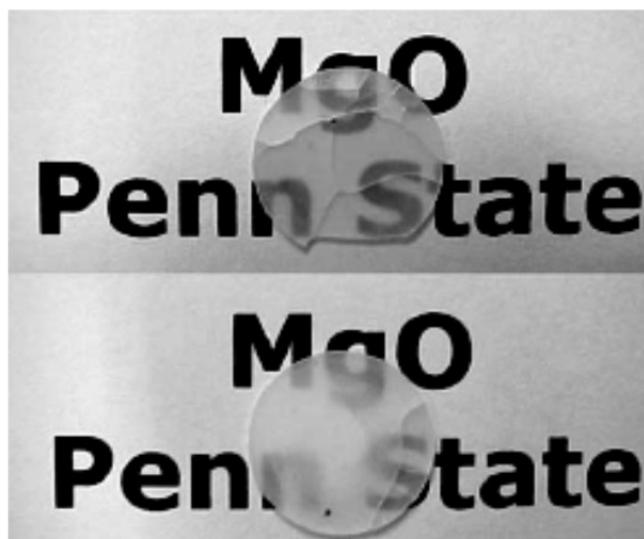


Figure 13. As-annealed translucent MgO pellet (Fang *et al* 2004a).

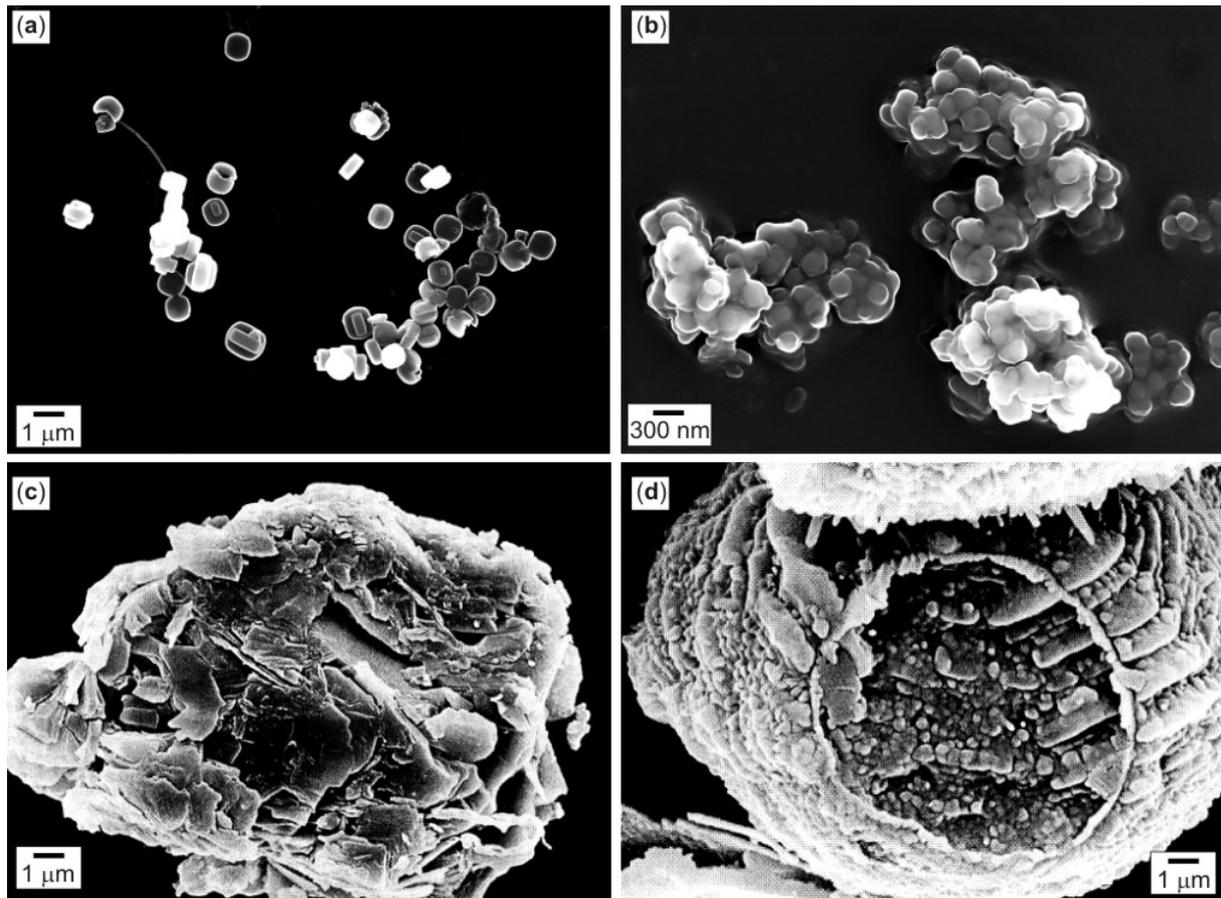


Figure 14. SEM micrographs of (a) as-received Al powder particles; (b) microwave-oxidized Al powder particles; (c) as-received Al powder agglomerate and (d) microwave-oxidized Al powder agglomerate.

it is necessary to develop the simplified mathematical models from which the occurrence of such phenomena can be predicted. Some of the recent developments in the mathematical modelling of microwave heating are: (a) models that consider isolation of the heat equation with a nonlinear source term assuming the electric-field amplitude as constant, (b) models that involve the coupling between the electric-field amplitude and temperature including both steady-state solutions and the initial heating, (c) models that control thermal runaway and (d) numerical models that elaborate on the microwave heating process (Jolly and Turner 1990; Hill and Pincombe 1991; Kriegsmann 1992; Hill and Jennings 1993; Hill and Marchant 1996; Mercado *et al* 2002; Moitsheki and Makinde 2007).

7. Future research

There is a huge scope to extend the microwave technology in broad zones including the following specific areas:

- Processing of specialty ceramics, bio-ceramics, bio-ceramic coatings;

- Synthesis of new, novel ceramic powders;
- Synthesis of whiskers, microtubes and nanotubes;
- Joining of ceramics;
- Fabrication of glass-ceramic coatings;
- Development of core-shell type composites;
- Sintering of powdered metal and understanding of the sintering mechanism;
- Analysis of the role of the H field in microwave-material interaction;
- Modelling of microwave heating.

Our laboratory based microwave technology should be successfully exploited for commercial applications overcoming the limitations and difficulties faced in scaling up the operations.

8. Conclusions

In the past decade, significant developments have taken place in the field of microwave processing of materials. However, more research must be conducted to obtain a detailed understanding about the nature and distribution of the electromagnetic field inside the microwave cavity,

microwave-material interaction, material transformations and heat transfer mechanisms for optimizing the process. Since microwave processing is a relatively new technology, considerable time may be required to implement this technology for the ceramic industry. It is hoped that significant advancements will take place in the science and technology of microwave processing so that one can envisage the introduction of batch type microwave sintering furnaces in the production units of ceramic industries.

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