Microwave processing of ceramics

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Microwave processing of ceramics is fast emerging as a new field of ceramic processing and material synthesis. The past year has witnessed significant progress in the aspect of commercialization and application of the technology to new areas. The most significant developments have been the use of microwaves in the sintering of non-oxides, such as tungsten carbide-based components and powdered metals, fabrication of transparent ceramics, and the design of continuous microwave systems.

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Abbreviations

BMT	$Ba(Mg_{0.33}Ta_{0.67})O_3$
BT	$BaTiO_3$
PZT	$Pb(Zr_{0.52}Ti_{0.48})O_3$
WC	tungsten carbide

Introduction

New developments and innovative ideas in the area of materials processing have often led to the discovery of new materials, with interesting and useful properties, and/or new technologies which are faster, better, cheaper and greener. A striking example of such innovations are recent developments in the area of microwave processing of ceramics. Although many potential advantages of utilizing microwaves to process ceramics have long been recognized, it is only now that this field has finally been shown to be at the take-off stage. Although microwave heating was conceived over 50 years ago, its use in ceramic processing is relatively new. Among the most prominent advances in the past year were those reported on tungsten carbide (WC)-based ceramic composites, fabrication of transparent ceramics, sintering of powdered metals and the design of a continuous microwave system to enable the commercialization of the technology.

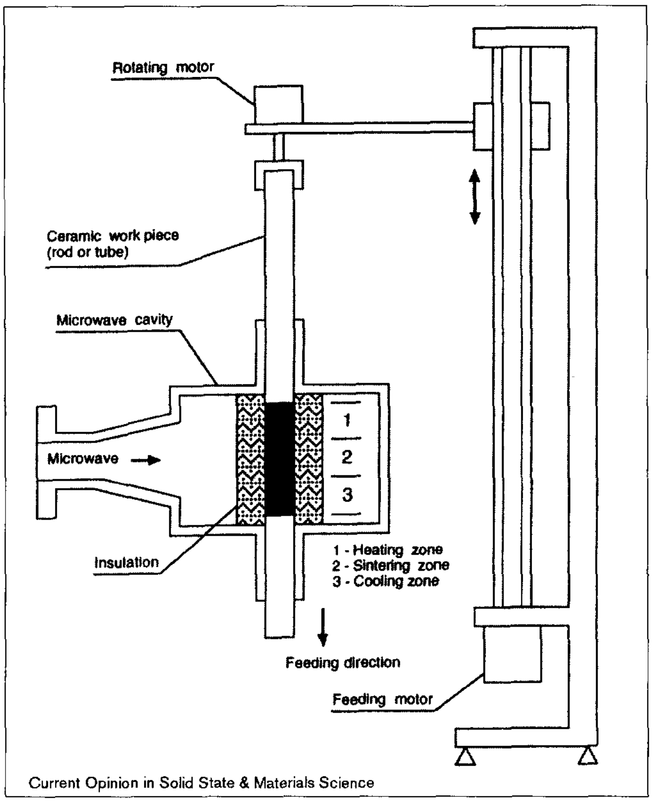
Microwave heating is fundamentally different from conventional heating. Microwaves are electromagnetic radiation with wavelengths ranging from 1 mm to 1 m in free space with a frequency between 300 GHz to 300 MHz, respectively. Today microwaves at the 2.45 GHz frequency are used almost universally for industrial and scientific applications. In the microwave process, the heat is generated internally within the material instead of originating from external sources, and hence there is an inverse heating profile. The heating is very rapid as the material is heated by energy conversion rather than by energy transfer, which occurs in conventional techniques. Microwave heating is a function of the material being processed, and there is almost 100% conversion of electromagnetic energy into heat, largely within the sample itself, unlike with conventional heating where there are significant thermal energy losses. Microwave heating has many advantages over conventional heating methods [1–5]; some of these advantages include, time and energy saving, very rapid heating rates (>400°C/min), considerably reduced processing time and temperature, fine microstructures and hence improved mechanical properties, it is environmentally friendly, and so on.

Other than radar, other communication purposes and home-cooking, microwaves are widely used in many industrial applications including, meat tempering, potato chips processing, bacon cooking, drying of pharmaceutical products and vulcanization of rubber. In the case of ceramic processing microwave energy has been in use since the late 1940s with a big push in the eighties; however, this did not result in the formation of useful products in the field of ceramics. Ceramic processes where microwaves have been applied include: process control, drying of ceramic sanitary wares, calcination, decomposition of gaseous species by microwave plasma, and sintering of oxide ceramics by microwave plasma. However, except for the drying of ceramic wares there is hardly any other area where microwave technology has been commercially exploited. Only, recently have there been reports indicating that some success has been achieved in commercializing the microwave sintering of WC-based cutting tools [6].

Many different physical phenomena are involved during the microwave processing of ceramics. The interaction between microwaves and matter takes place through the electric field vector and magnetic field vector of the electromagnetic field of the microwaves and involves polarization and conduction processes. Classically various absorption mechanisms have been identified in the interaction of microwaves with matter. Examples of these are dipole reorientation, conduction of space and ionic charge, and so on, which are primarily found in insulators or dielectric materials. Other energy losses, depending on the material under interaction, can occur through electric conduction in (semi)metals and/or magnetic resonance in magnetic materials. All these processes give rise to energy losses which manifest themselves in the form of volumetric heat in the material.

Interest and activity in microwave processing has been continuously increasing, and the use of microwave technology in industrial applications is also growing with new developments in both the engineering and design of microwave systems. This growing and renewed interest in microwave technology has been amply supported by the success of the

Figure 1



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Schematic drawing of apparatus for continuous microwave sintering.

'First World Congress on Microwave Processing', which was held in Orlando, January 5–9, 1997.

Five earlier excellent reviews by Clark and Sutton [7], Schiffman [8], Katz [9] and Sutton [10,11], are more than adequate to give interested readers a broader picture of the status of microwave processing research up until 1996. This current review presents a series of innovations and new developments in the field of microwave processing of ceramics, which occurred in the last year and half. During this period, the use of microwave sintering has been extended to new material families which contain not only white ceramics and 'semiconducting cements' but also major composite families containing substantial amounts of metals, and even pure metals and alloys. Dramatic developments have taken place in the area of material synthesis utilizing microwave energy and variable valance oxide precursors. This approach triggers very high reaction rates during the synthesis of important dielectric materials compositions. This is an unambiguous demonstration of a non-thermal 'microwave effect' in accelerating and catalyzing new reactions. The advantage of obtaining finer microstructures in microwave processed products, unattainable by conventional heating, has led to its application in the development of transparent and translucent ceramics for a variety of applications. These areas and other advances will be the focus of this review.

Table 1

Comparison of microwave and conventional processes for sintering WC–Co composites.

	Microwave	Conventional
Sintering temperature (°C)	1300	1450
Total cycle time	90 min	12–24 hrs
Sintering time (minutes)	10	60
Density (% TD)	99.8	99.7
Average grain size (μm)	0.6	2
Bending strength (MPa)	1800	1700
Hardness (Rockwell A)	93	91

TD, theoretical density.

Microwave sintering of WC + Co composites

Hard metal composites due to their unique combination of hardness, toughness and strength, especially WC-based composites, are universally used for cutting tools and drilling operations underground. Conventional methods for sintering WC with Co as a binder phase involve high temperatures and lengthy sintering cycles of the order of one day. In a conventional sintering method, the carbide specimen is subjected to high temperatures (up to 1500°C) for long periods in order to achieve a high degree of sintering. Such conditions unfortunately favor undesirable WC grain growth in the presence of Co liquids. Consequently, the mechanical strength and hardness of the tool is diminished. It is a well known fact that finer microstructures provide superior mechanical properties and a longer life-time of the product. Often, additives such as titanium carbide (TiC), vanadium carbide (VC) and tantalum carbide (TaC) are used to prevent grain growth of WC grains. Unfortunately such additives deleteriously affect the mechanical properties of the product. In 1991, JP Cheng, in a PhD thesis [12], showed for the first time that WC/Co composites could be sintered in a microwave apparatus. Gerdes and Willert-Porada [13] also reported the sintering of similar WC objects, but they followed a reactive sintering route using a mixture of pure W, C and Co instead of normal microwave sintering. In parallel work Cheng *et al.* [14], using a newly designed apparatus (Figure 1) were able to sinter WC 'commercial' green bodies containing 12% and 6% Co. It was observed that microwave processed WC/Co bodies exhibited better mechanical properties than the conventionally processed parts, a fine and uniform microstructure (~1 micron size grains) with very little grain growth, and nearly full density was achieved without adding any grain-growth inhibitors when sintered at 1250°–1320°C for only 10–30 minutes [6,15,P1]. Table 1 provides a comparison between microwave and conventionally processed WC/Co cements.

Microwave synthesis using reduced oxide precursors

Microwave energy has been used in many syntheses to either enhance the reaction kinetics or to trigger new reactions at lower temperatures. However, recently microwave

Table 2

Comparison of reaction pathways for $BaTiO_3$ synthesis using microwave and conventional methods.

Processing temperature	Microwave $BaCO_3+TiO_{2-x}$	Conventional $BaCO_3+TiO_{2-x}$	Microwave $BaCO_3+TiO_2$
200°C	–	–	–
300°C	hex-BT	–	–
600°C	tet-BT; hex-BT	–	–
800°C	tet-BT	–	–
900°C	tet-BT	Ba_2TiO_4 (at 950°C)	Ba_2TiO_4
1100°C	tet-BT	Ba_2TiO_4	Ba_2TiO_4; tet-BT
1300°C	tet-BT	Ba_2TiO_4	Ba_2TiO_4; tet-BT

hex, hexagonal; tet, tetragonal.

energy was used [12,16•,17] to synthesize important ferroelectric materials and other ceramic powders by adopting the concept of the pre-reduction of phases, such as TiO_2 and Ta_2O_5, to give a highly microwave absorptive precursor material and thereby enhancing the reaction kinetics dramatically. The main idea was to create a defect structure to make microwave coupling more efficient at room temperature. It was reported that by using pre-reduced TiO_2 and Ta_2O_5 precursor oxides, $BaTiO_3$, PZT, $Pb(Zr_{0.52}Ti_{0.48})O_3$ and BMT, $Ba(Mg_{0.33}Ta_{0.67})O_3$ could be synthesized at astonishingly low temperatures, between 300°C and 900°C in 5–12 minutes. Conventional methods for the synthesis of these phases require temperatures in the range of 900°C to 1400°C and several hours of soaking time. Pure stoichiometric metal oxides, such as Ta_2O_5 and TiO_2, do not couple with microwave energy efficiently unless heated to temperatures where they become dielectrically lossy (> 1000°C). By partially reducing these phases to oxygen defective states, such as Ta_2O_{5-x} and TiO_{2-x}, their ability to absorb microwave energy at lower temperatures is radically enhanced. This concept was further reinforced by the work of Bosssert and Ludwig [18] who reported rapid sintering of titania in a microwave field using a nitrogen atmosphere which reduced the titania creating oxygen vacancies. They achieved 98% density in 40 minutes as compared to 3 hours using a conventional heating. This they attributed to the reduced titania causing better microwave coupling leading to higher densification. Below are examples of some specific materials prepared by this method.

BT, $BaTiO_3$

In the case of the synthesis of $BaTiO_3$, X-ray diffraction data for microwave processed powders using TiO_{2-x} as one of the precursors, shows most surprisingly the formation of the hexagonal $BaTiO_3$ phase (Table 2; [18]) at 300°C with no soak time. The formation of the desired tetragonal $BaTiO_3$ phase increased with soak time and the reaction was complete by 700°C. The total time necessary for the synthesis of $BaTiO_3$ via this route was less than 12 minutes. Conventional synthesis of $BaTiO_3$ using the same reactant mixture occurs above 1300°C and always proceeds via the formation of the Ba_2TiO_4 phase first. The phase diagram for $BaTiO_3$ shows that the high temperature hexagonal phase of $BaTiO_3$ is only stable above 1400°C. The presence of this phase at 300°C and its disappearance by 700°C, without Ba_2TiO_4 ever appearing indicates that radically different reaction pathways occur compared with those observed from conventionally processed material. This reaction path difference is a convincing demonstration of a 'microwave effect'.

PZT, $Pb(Zr_{0.52}Ti_{0.48})O_3$

One of the major problems researchers face with conventional processing of PZT, $Pb(Zr_{0.52}Ti_{0.48})O_3$, is the vaporization of PbO, which starts near 750°C. Apart from the obvious environmental hazard this poses, it also results in an incomplete reaction leaving large amounts of unreacted ZrO_2. Mathis [17] and Cheng [12] reported that stoichiometric PZT mixtures, that is with no excess PbO, reacted in a microwave field using TiO_{2-x} powder in the starting mixture. Analysis of the XRD patterns of the microwave processed PZT showed that the reaction was nearly complete at 600°C with only trace amounts of PbO and ZrO_2 detectable, indicating a virtually complete reaction before PbO volatilization occurs. The cubic PZT phase was formed first (at 600°C), followed by subsequent nucleation and an increase in the tetragonal PZT phase. By 900°C a 50:50 mixture of the cubic and tetragonal phases was evident. The total time required to achieve synthesis at 600°C in the microwave field was less than 8 minutes.

BMT, $Ba(Mg_{1/3}Ta_{2/3})O_3$

$Ba(Mg_{1/3}Ta_{2/3})O_3$ with a perovskite structure is a good dielectric material for microwave resonators, because it possesses a high quality factor (Q) and moderate dielectric constant. In high frequency (gigahertz) communication systems, use of high Q materials is imperative. This remarkable material is, perhaps, the most refractory oxide (melting point > 3000°C), and therefore very high temperatures are required to sinter it in a conventional furnace. It takes several hours and a temperature of over 1650°C to achieve reasonable densification of BMT ceramics. Therefore, to obtain BMT ceramics with a high density, sintering aids such as Mn and Sn are used. But the sintering aids also influence the dielectric properties undesirably. In a recent study, Agrawal *et al.* [19] synthesized and sintered a BMT single phase material, using reduced oxide precursors. Use of reduced Ta_2O_{5-x} remarkably enhanced the reaction kinetics and produced a single phase material at a much lower temperature with higher densification than is normally obtained by conventional processes. Microwave processed BMT samples exhibited density as high as 97% of the theoretical when heated at 1600°C for 30 minutes.

Transparent ceramics

Transparency is a valuable optical property of materials. The nature of the material including grain size, density, crystal structure, porosity and the grain boundary phase are the main factors which influence the degree of transparency. To achieve transparency in a ceramic, one must control the grain growth, eliminate porosity and achieve a fully dense material. The conventional methods to fabricate fully dense and reasonably transparent ceramics involve high temperatures, lengthy sintering conditions, and various complex processing steps, which not only make the processing of transparent ceramics uneconomical, but also the desired properties are often not achieved. However, a microwave method has been successfully used to fabricate transparent ceramics due to its ability to minimize grain growth and produce a fully dense ceramic in a very short period of time without utilizing high pressure conditions [20,21]. Several studies have been conducted on the fabrication of transparent ceramics using hydroxyapatite. Such studies led to the first preparation by Fang *et al.* [22] of a fully sintered transparent ceramic by microwave processing. It was shown that useful bodies could be sintered in less than 15 minutes: the densification was shown to be critically dependent on the starting materials. Related work [23,P2] also demonstrated that one could make transparent ceramics of a spinel and alumina. Fully dense alumina and spinel ceramics using high purity and submicron size powders were developed [23,P2] with reasonable degrees of transparency on laboratory type small samples in a few minutes. Figure 2 shows microwave processed partially transparent ceramics of hydroxyapatite and spinel phases [21].

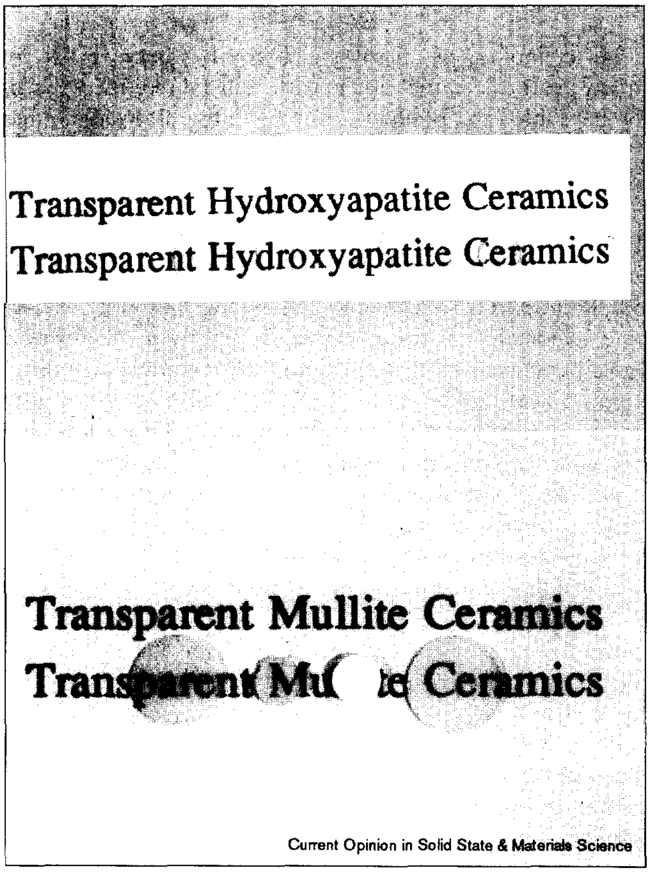
Powdered metals

As has been stated in earlier reviews the use of microwave heating and sintering has been confined mainly to oxide ceramics, and only recently has it been extended to carbide semimetals. But the most recent application of microwave technology to another completely unexpected area, yet one which encompasses a vast industry of variety of applications, namely powdered metals (PMs), has great significance [24•]. Bulk metals are excellent reflectors in microwaves and in general are not heated significantly. But in a powdered and unsintered form virtually all metals, alloys, and intermetallics will couple/heat in a microwave field both very efficiently and effectively to produce highly sintered bodies with improved mechanical properties. It is reported that the microwave sintering of PM green bodies comprising various metals and metal alloys (Fe-Ni-C and Fe-Cu-C) has produced highly sintered bodies in a very short period of time. Typically the total cycle time was ~90 minutes, the sintering temperature ranged between 1100°C–1300°C and the soaking time from 5 to 60 minutes. The mechanical properties, such as the modulus of rupture (MOR) and hardness of microwave processed samples were much higher than those of the conventionally prepared samples. The densities of the microwave processed samples were also better than those of conventional samples.

Other developments

In addition to the above mentioned recent developments in the field, there were a few minor but important areas in which microwaves were utilized and some significant progress has been made in many on-going research areas.

Figure 2



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Transparent ceramics. Top: transparent hydroxyapatite ceramics fabricated in ambient air by microwave processing for 5 minutes at 1100–1150°C. Bottom: mullite ceramics sintered by microwave processing for 10 minutes at 1300°C.

Zeolites are important materials as catalysts, adsorbents and ion-exchangers. Querol *et al.* [25] have reported a rapid method for recycling fly ash and synthesizing zeolites using a microwave assisted hydrothermal method. They used an alkaline activation experiment and synthesized various types of zeolitic material. They found that the activation time was drastically reduced from 24–48 hours (by conventional methods) to only 30 min using microwaves. In another study Kosslick *et al.* [26] prepared a series of zeolites (aluminosilicates, aluminophosphates, etc.) and found that the synthesis time decreased from the hours and days normally needed in conventional methods to a few minutes. They also claimed that in the case of an ion-exchange reaction, the isomorphous replacement was enhanced and the quality of products was considerably improved. Microwave sintering of clay ceramics is also getting attention. Shiming and McColm [27] studied clays with the addition of metal and semiconducting powders as microwave coupling aids, and achieved harder and stronger microwave sintered clay samples compared with conventional samples. Tan *et al.* [28] studied the phase transformation kinetics of four bauxite materials in a variable frequency microwave furnace, they quantitatively identified mullite, corundum and cristobalite phases in the fired extrudates.

The technology of microwave drying has been in use for many years in channel dryers with conveyor belts, especially for tableware products. But recently, at Riedhammer (Germany; [29]) large microwave dryers have been used in drying technical ceramics, such as honeycomb structures and insulators, with the advantage of energy savings and a uniform rapid drying. They claim damage-free drying of items of large volume in microwaves in hours in contrast to weeks required by conventional drying methods. This is one major area in ceramic processing where microwaves have been successfully exploited for a commercial application. Sizgek and Sizgek [30] have also reported the microwave drying characteristics of simulated high level liquid waste impregnated Synroc ceramic microspheres. They observed that at a given microwave power level, drying of water-saturated samples was quicker and produced a homogeneous distribution of the waste than with convective drying, which resulted in segregation of waste components.

Several studies of the microwave sintering and microstructural investigations of zirconia based composites [31–33] have been reported. In all of these studies an enhanced densification in the microwave processed materials was observed. Si_3N_4 ceramics, which are widely used for high temperature structural applications, were also fabricated by microwave methods and their microstructural characteristics examined [34,35]. The formation of a β-phase, which is very critical for high toughness, was enhanced in microwaves. Fiore and Clark [36] reported a microwave induced reduction/oxidation method to form ceramic–metal composites. In a pressureless microwave sintering [37] method functional gradient material (FGM) of metal–ceramic compositions have been successfully fabricated .

Researchers have been long discussing how to find out the exact nature of the so-called 'microwave-effect', which enhances the sinterability of the ceramics and other positive effects observed during microwave processing of materials. In an excellent article Willert-Porada [38•] has explained the microwave effect hypothesis by studying the microstructural changes in the ceramics sintered by both conventional and microwave methods. It was explained that in the presence of an electric field (microwave) the closed pores could be sites of enhanced material transport and therefore more efficiently removed than open pores, causing rapid and enhanced densification.

Several studies have been reported on the microwave processing of nanophase materials. The advantage of using nanopowders in microwaves is to retain the fine microstructure in the sintered ceramics. Lewis *et al.* [39] processed nanophase ceramics using 2.45 and >35 GHz microwave frequencies and found significant enhancements in the sintering properties, especially in the case of aluminum oxide. Agrawal *et al.* (DK Agrawal, J Cheng, R Roy, P Seegopaul, unpublished data) reported microwave sintering of nanophase WC/Co composites and stated that microwave sintered material exhibited higher hardness and finer grain size than the conventionally sintered material. Vollath [40] has developed a continuous process for synthesizing ceramic nanoparticles and nanocomposites of oxides, nitrides, sulfides, selenides and with certain precautions even carbides and metals. The author reported that, in general, it was difficult to obtain a uniform distribution of two or more phases when producing nanocomposites. However, in the microwave plasma process, the second phase is used to coat particles consisting of the first phase, this coating can be a second ceramic phase or a polymer.

Conclusions

In the past year and half, significant developments and advances have taken place in the field of microwave processing of ceramics. The microwave process is increasingly being exploited to develop better and cheaper products, particularly specialty ceramics. It has been demonstrated that in the case of WC/Co the use of microwaves can reduce the cycle time to about one-tenth that required by conventional means, and still obtain better properties. The advantage of using microwaves was quite dramatic when using reduced oxide precursors in synthesizing titanate and tantalate based electroceramics. The microwave coupling in the presence of a defect structure causes extremely rapid reaction kinetics and new reaction paths producing materials at much lower temperatures than normally obtained by a conventional heating method. The most significant development in microwave sintering has been the sintering of powdered metals and fabrication of transparent ceramics in a single step process. The so-called microwave effect, which is commonly assumed to be a nonthermal phenomenon and responsible for the rapid densification and enhanced sintering mechanisms has been explained by the concentration of electrical energy in the closed pores of the green ceramics. It can be predicted with these significant advances having been made in the field of microwave processing of ceramics, that there is a great future for microwave technology for the successful commercialization for specialty ceramics.

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