MICROWAVE SINTERING OF CERAMICS, COMPOSITES AND METAL POWDERS: RECENT DEVELOPMENTS

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ABSTRACT

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. The use of microwave energy in the area of materials processing is one such new development. Microwave processing has several advantages over conventional sintering, such as the reduction in cycle time, potential for reduction in manufacturing costs, retaining fine microstructures leading to improved mechanical properties and overall performance of the product. For over 15 years a wide variety of oxide ceramics, non-oxide cermets, and transparent materials have been processed using microwave techniques. The latest surprising development in this field is the sintering of powder metals in a microwave field. It is surprising because metals are known to reflect microwaves. This paper summarizes the important developments in microwave processing of ceramics, composites and metallic materials, which have taken place at the Materials Research Lab of the Penn State University. Main areas of focus will include: hydroxyapatite, various traditional and advanced electroceramics, alumina, cemented carbide, powder metals, transparent ceramics, and designing of microwave systems, etc. In general, the research has demonstrated that in case of almost all materials processed in microwave field, near theoretical densities and better properties than conventional product, were achieved at much lower sintering temperatures and times.

INTRODUCTION

Microwave energy has been in use for over 50 years in a variety of applications such as communications, food processing, rubber vulcanization, textile and wood products, and drying of ceramic powders. Widespread use of microwave home ovens has in fact revolutionized the home-cooking. The use of microwaves in the processing of ceramics, especially the sintering of materials is relatively new. Although many potential advantages of using microwaves to process ceramics have been long recognized, it is only now that this field has finally shown to be at

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the take off stage. Recent developments and innovations made in microwave processing at the Penn State University in the last decade have attracted worldwide attention in academia and industry. Among the most prominent advances in the past few years are: sintering of tungsten carbide (WC) based composites, fabrication of transparent ceramics, sintering of powdered metals, and design of continuous microwave systems which would enable the commercialization of the technology.

Five earlier excellent reviews by Clark and Sutton [1], Schiffman [2], Katz [3], Sutton [4,5], are more than adequate to give the interested readers a broader picture of the status of microwave processing research till 1996. This article will deal primarily with the recent developments in the area of microwave processing, and will briefly touch up on general features of microwave heating and sintering.

MICROWAVE PROCESSING

Microwave processing of materials, which includes heating and sintering, is fundamentally different from conventional processing which involves radiant/resistance heating followed by transfer of thermal energy via conduction to the inside of the body under process. In case of microwave process it is the absorption of the microwave energy followed by volumetric heating involving a conversion of electromagnetic energy into thermal energy, instantaneous and a rapid process. Microwaves are a small part of the electromagnetic spectrum with wavelengths ranging from 1 mm to 1 m in free space and frequency between 300 GHz to 300 MHz, respectively. Based on the microwave matter interaction, most materials can be divided into three categories: opaque, transparent and absorbers. It is well recognized that the bulk metals are opaque to microwave and are good reflectors at room temperature, this property is used in radar detection. However, as we will see in the subsequent section of this paper that powdered metals are very good absorbers of microwaves and get heated very effectively. Most other materials either are transparent or absorb microwaves to varying degrees at ambient temperature. The degree of absorption and consequently heating changes dramatically with the rise in temperature.

In the microwave process if the material couples in microwave field, the heat is generated internally within the material instead of originating from external sources, and transmits towards outside. Hence, there is an inverse heating profile, inside out unlike in a conventional heating outside in. In general, the microwave heating is very rapid as the material is heated by energy conversion rather than energy transfer which occurs in the conventional techniques. Microwave heating is a function of the material being processed. There are major potential and real advantages using microwave energy for material processing over conventional heating [6-8]. 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,
maller product performance, environment friendly, etc.

MICROWAVE PROCESSING OF CERAMICS

Microwave energy has been in use since the late 1940s in ceramic processing
with a big push in the eighties. Ceramic processes where microwaves had 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 drying of ceramic wares there is
hardly any other area where microwave technology has been commercially
exploited. Only, recently there are reports indicating that some success has been
achieved in commercializing the microwave sintering of tungsten carbide based
cutting tools [9] using the technology developed at Penn State.

In case of most ceramics microwave heating is mainly characterized by the
dielectric loss of the material. However, there are other factors which also
significantly contribute to the microwave heating, such as ionic conductivity,
degree of porosity, particle size, electric conductivity and magnetic coupling, etc.
The exact mechanism of microwave heating and sintering has not yet been very
well explained and understood. 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 involve polarization and conduction
processes. Classically there are various absorption mechanisms identified in
microwave-matter interaction. Some of them are dipole reorientation, conduction
of space and ionic charge, etc. which are primarily found in insulators or dielectric
materials. Other losses, depending upon the material under interaction, include
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.

MICROWAVE SINTERING OF WC-Co COMPOSITES

Hard metal composites, especially the tungsten carbide (WC) based
composites due to their unique combination of hardness, toughness and strength,
are universally used for metal and rock cutting and drilling operations.
Conventional methods for sintering WC with Co as a binder phase involve high
temperature (up to 1500°C) and lengthy sintering cycles of the order of one day in
order to achieve a high degree of sintering [10]. Such conditions unfortunately
favor undesirable WC grain growth in the presence of Co liquids. Consequently,
the mechanical strength and hardness of the tools are diminished. It is generally
recognized that finer microstructures provide superior mechanical properties and
longer life 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. Since microwave heating requires very little time to obtain nearly full sintering, the grain growth is relatively suppressed and finer microstructure is generally obtained. In 1991, J. P. Cheng in a Ph.D. thesis [11] first showed that WC/Co composites could be sintered in a microwave field. Gerdes and Willert-Porada [12] also reported the sintering of similar WC objects from normal size powders, but they followed reactive sintering route using a mixture of pure W, C and Co instead of normal sintering. In another work [13], Cheng et al. at the Penn State University using a newly designed microwave apparatus (Figure 1) were able to fully sinter WC commercial green bodies containing 12% and 6% Co. They observed that microwave processed WC/Co bodies exhibited better mechanical properties than the conventional parts, fine and uniform microstructure (~1 micron size grains) with very little grain growth, and nearly full density without adding any grain-growth inhibitors when sintered at 1250-1320°C for only 10-30 minutes [9,14,15]. Table 1 provides a comparison between microwave and conventionally processed WC/Co cermets. Figure 2 shows some of the WC/Co commercial tools processed in microwave system.

Figure 1. Schematic of a continuous microwave system for sintering of WC/Co composites.
Figure 2. Microwave sintered commercial parts of WC/Co.

Table 1. Comparison of microwave and conventional processes for sintering of WC-Co composites.

<table>
<thead>
<tr>
<th></th>
<th>Microwave</th>
<th>Conventional</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sintering Temperature (°C)</td>
<td>1300</td>
<td>1450</td>
</tr>
<tr>
<td>Total Cycle Time</td>
<td>90 min</td>
<td>12-24 hrs</td>
</tr>
<tr>
<td>Sintering Time (Minutes)</td>
<td>10</td>
<td>120</td>
</tr>
<tr>
<td>Density (%)</td>
<td>99.8</td>
<td>99.7</td>
</tr>
<tr>
<td>Average Grain Size (µm)</td>
<td>0.7</td>
<td>2</td>
</tr>
<tr>
<td>Bending Strength (MPa)</td>
<td>1800</td>
<td>1700</td>
</tr>
<tr>
<td>Hardness (Rockwell A)</td>
<td>93</td>
<td>91</td>
</tr>
</tbody>
</table>

MICROWAVE SINTERING OF POWDERED METALS

Metal powders are used in industry for diversity of products and applications. Traditional powder metallurgy is a process whereby a metal or alloy powder is compacted in to a green body and then sintered to net shape at elevated temperatures. The most important metal powders in use are: iron and steel, copper, aluminum, nickel, Mo, W, WC, Sn and their alloys. It has been well recognized by the researchers that microwave heating does not work in metals and is good only to oxide ceramics and semi-metals like carbides and nitrides. But the most recent application of microwave technology has been to the sintering of powdered metals [16]. It has been found that the microwave sintering can also be applied as efficiently and effectively to powdered metals as to many ceramics.
Bulk metals are excellent reflectors in microwaves at room temperature and in general are not heated significantly. But in powdered and unsintered form virtually all metals, alloys, and intermetallics would couple/heat in a microwave field very 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 (for example: Fe-Ni-C and Fe-Cu-C systems) produced highly sintered bodies in a very short period of time [16]. Typically the total cycle time was about 90 minutes, sintering temperature ranges between 1100°C to 1300°C and soaking time 5 to 60 minutes. The mechanical properties such as the modulus of rupture (MOR) and hardness of microwave processed samples were much higher than the conventional samples (Table 2). The densities of microwave processed samples were also better than conventional samples. Figure 3 shows some of typical powder metal steel parts which have been microwave sintered at Penn State.

![Figure 3. Microwave sintered powder metal commercial parts.](image)

Table 2: Microwave and Conventionally processed Powder Metals samples

<table>
<thead>
<tr>
<th>Composition</th>
<th>Sintering Conditions, temp. ºC/time, min.</th>
<th>Sinter Density g/cc</th>
<th>Hardness</th>
<th>MOR Ksi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-Ni</td>
<td>MW 1275/10</td>
<td>7.15</td>
<td>B82</td>
<td>177</td>
</tr>
<tr>
<td></td>
<td>Conv 1121/30</td>
<td>7.10</td>
<td>B77</td>
<td>109</td>
</tr>
<tr>
<td>Fe-Cu</td>
<td>MW 1180/10</td>
<td>7.17</td>
<td>B96</td>
<td>142</td>
</tr>
<tr>
<td></td>
<td>Conv 1121/30</td>
<td>6.84</td>
<td>B80</td>
<td>118</td>
</tr>
</tbody>
</table>

MW: Microwave processed  Conv: Conventionally processed

MICROWAVE SYNTHESIS OF ELECTROCERAMICS USING

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REDUCED OXIDE PRECURSORS

Microwave energy has been used in many syntheses to either enhance the reaction kinetics or trigger new reactions at lower temperatures. However, we have used microwave energy to synthesize important ferroelectric materials and other ceramic powders by adopting a concept of pre-reduction of phases such as TiO$_2$ and Ta$_2$O$_5$ to give a highly microwave absorptive precursor material, and thereby enhancing the reaction kinetics dramatically [13,17,18]. The main idea is 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$_2$O$_5$ precursor oxides BaTiO$_3$, Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$ and Ba(Mg$_{0.33}$Ta$_{0.67}$)O$_3$ phases can 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 to 1400°C and several hours of soaking time. Pure stoichiometric metal oxides, such as Ta$_2$O$_5$ and TiO$_2$, do not couple with microwave energy very efficiently unless heated to temperatures where they become dielectrically lossy. By partially reducing these phases to oxygen defective states, such as Ta$_2$O$_{5-x}$ and TiO$_{2-x}$, their ability to absorb microwave energy at low temperatures is radically enhanced. This concept has been further reinforced by the work of Bossert and Ludwig [19] who reported rapid sintering of titania in a microwave field in nitrogen atmosphere and achieved over 98% density in 40 minutes as compared to 3 hours in a conventional method. They attributed this to the reduced titania which created oxygen vacancies and as a result enhanced the microwave coupling.

Here are some examples of specific materials prepared by this method:

**BaTiO$_3$**

In case of synthesis of BaTiO$_3$, the X-ray diffraction data for the microwave processed powders using TiO$_{2-x}$ showed most surprisingly the formation of the hexagonal BaTiO$_3$ phase (Table 3) [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 completed at 700°C. The total time necessary for BaTiO$_3$ synthesis 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 formation of Ba$_2$TiO$_4$ 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, with Ba$_2$TiO$_4$ never appearing indicates radically different reaction pathways from conventionally processed material. This reaction path difference is a convincing demonstration of some 'microwave effect'.
**Table 3: Comparison of reaction pathways for BaTiO$_3$ (BT) synthesis using microwave and conventional methods.**

<table>
<thead>
<tr>
<th>Processing Temperature</th>
<th>Microwave BaCO$<em>3$+TiO$</em>{2-x}$</th>
<th>Conventional BaCO$<em>3$+TiO$</em>{2-x}$</th>
<th>Microwave BaCO$_3$+TiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>200°C</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>300°C</td>
<td>hex-BT</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>600°C</td>
<td>tet-BT; hex-BT</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>800°C</td>
<td>tet-BT</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>900°C</td>
<td>tet-BT</td>
<td>Ba$_2$TiO$_4$ (at 950°C)</td>
<td>Ba$_2$TiO$_4$</td>
</tr>
<tr>
<td>1100°C</td>
<td>tet-BT</td>
<td>Ba$_2$TiO$_4$</td>
<td>Ba$_2$TiO$_4$; tet-BT</td>
</tr>
<tr>
<td>1300°C</td>
<td>tet-BT</td>
<td>Ba$_2$TiO$_4$</td>
<td>Ba$_2$TiO$_4$; tet-BT</td>
</tr>
</tbody>
</table>

**Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$**

One of the major problems the researchers face with the 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 [18] and Cheng et al [13] reported that stoichiometric PZT mixtures, i.e. with no excess PbO, when reacted in a microwave field using TiO$_{2-x}$ powder in the starting mixture, showed that the reaction was nearly complete at 600°C with only trace amounts of PbO and ZrO$_2$ detectable, indicating virtually complete reaction before PbO volatilization. The cubic PZT phase was formed first at 600°C, followed by the nucleation and increase of 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.

**Ba(Mg$_{1/3}$Ta$_{2/3}$)O$_3$**

Ba(Mg$_{1/3}$Ta$_{2/3}$)O$_3$ (BMT) with perovskite structure is a good dielectric material for microwave resonators because it possess high quality factor (Q) and moderate dielectric constant. In high frequency (in GHz range) 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 over 1650°C of temperature to achieve reasonable densification of BMT ceramics. Therefore, to obtain BMT ceramics with 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 Mathis [17] and Agrawal et al. [20] have synthesized and sintered BMT single phase material using reduced oxide precursors. Use of reduced Ta_{2}O_{5-x} remarkably enhanced the reaction kinetics and produced single phase material at much lower temperature (1300°C/20 min) and higher densification than normally obtained by conventional processes. Microwave processed BMT samples exhibited density as high as 97% of theoretical when heated at 1600°C for 30 minutes. The average grain size in microwave sintered BMT was about 1 μm in contrast to 3 μm in conventional sintered material.

**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. Glasses are optically isotropic and have no grain boundaries, and therefore possess excellent transparency. Most non-cubic ceramics are anisotropic and polycrystalline. The grain boundaries in the ceramic strongly scatter light. Therefore, to convert a non-cubic ceramic having grains larger than the wavelength of light, into a transparent ceramic, one must have very low grain boundary volume and no inter- or intra-granular porosity. However, if the grain size is smaller than the wavelength of the light (0.4 - 0.7 μm), the light can transmit through the ceramic. Cubic ceramic materials such as spinels and AlON can be made into transparent ceramics even if the grain size is larger than the wavelength of light. 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 often the desired properties are not achieved. However, microwave method has been successfully used to fabricate transparent ceramics due to its ability to minimize the grain growth and produce a fully dense ceramic in a very short period of time with out utilizing high pressure conditions [21,22]. Several studies were conducted on the fabrication of transparent ceramics, using hydroxyapatite as an example. This led to the first preparation by Fang et al. [23] a fully sintered transparent ceramic by microwave processing. It was shown that such useful bodies could be sintered in less than 15 minutes. The densification was shown to be critically dependent on the starting materials. Related work [24,25] also demonstrated that one could make transparent ceramics of spinel and alumina ceramics as well. Fully dense alumina and spinel ceramics

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using high purity and submicron size powders were developed with reasonable
degree of transparencies on laboratory type small samples at 1700°C sintered for
15 minutes in the microwave system. Figure 4 shows some of the microwave
processed transparent ceramics of hydroxyapatite, alumina, spinel phases and AlN
[22].

Figure 4: Microwave Processed Transparent Ceramics

SUMMARY
Recently, 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
materials. It has been demonstrated that in the case of WC/Co, microwave can
reduce the cycle time to about one-tenth the cycle time required by conventional
means, and still produces 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
defect structure causes extremely rapid reaction kinetics and new reaction paths
producing materials at much lower temperatures than normally obtained in a
conventional heating. The most significant development in the microwave
sintering has been the sintering of powdered metals and fabrication of transparent
ceramics in a single step process. It can be predicted with these significant
advances made in the field of microwave processing of ceramics, that there is a
great future of microwave technology for successful commercialization for specialty ceramics.

REFERENCES

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