Microwave Processing of Ceramics, Composites and Metallic Materials

D. Agrawal, J. Cheng, Y. Fang, and R. Roy

Abstract
The versatility of the application of microwave energy has been long recognized in a variety of areas, such as communication, rubber vulcanization, paper/textile/wood drying, food processing, pharmaceutical and biomedical fields. Over the last two decades, microwave energy is being increasingly applied in the area of materials (ceramics, composites and metals) processing for various purposes. The increased interest in microwaves for these areas is due to its certain advantages over conventional heating, such as the reduction in cycle time, energy savings, product quality improvement and eco-friendliness. For over a decade, the Penn State's microwave research center has been working on a wide variety of materials, including oxide and non-oxide ceramics, electroceramics, hard metal composites (WC/Co), transparent ceramics, nanostructured ceramics and metallic materials. Remarkable achievements have been made in the sintering and syntheses of these materials using microwaves. Recent developments have shown that all common metals (Cu, Fe, Ni, Ti, Al, Co, Ag, Au), refractory metals (W, Re, Mo), their alloys and steel compositions have been sintered successfully using microwaves, in many cases, to full density very rapidly with improved properties. The selective heating feature of microwave heating has been utilized for metal–metal brazing and joining in a few minutes.

Introduction and Background
The application of microwave energy to process various kinds of materials in an efficient, economic and effective manner is emerging as an innovative technology with great commercial potential and many advantages. In the area of processing of ceramics and metals, it has been a kind of sintering and synthesis revolution in terms of extraordinary enhancements in materials diffusion and reaction kinetics. Though microwave energy has been in use for over 50 years in a variety of applications, including communications, food processing, rubber vulcanization, paper/textile/wood drying, pharmaceutical and biomedical fields,
it has been relatively recently that microwaves have been useful in materials processing, especially synthesis and sintering of ceramics. The very first application of microwave energy was in communications and this area still dominates microwave applications: almost all communications, in space and mobile/cordless phone technology are based on microwave frequencies.

Recent developments and innovations made in microwave processing in the last decade have attracted worldwide attention in academia and industry. The most prominent advances made in the past few years include synthesis and sintering of traditional and advanced ceramics in <30 minutes, sintering of tungsten carbide- (WC-) based composites, fabrication of transparent ceramics, processing of electroceramics, fabrication of nanostructured ceramics, sintering and melting of metals, effect of microwave E and H fields on the processing of various kinds of materials, and design of continuous microwave systems enabling the commercialization of the laboratory scale technology for various important materials. This paper will review some of these developments.

Five comprehensive reviews by Clark and Sutton [1], Schiffmann [2], Katz [3] Sutton [4,5] are more than adequate to give the interested readers a broad picture of the status of microwave processing research until 1996 and provide a historical perspective of the application of microwave energy to materials processing. The decade of 1980 to 1990 witnessed widespread interest and much research activity producing very interesting and exciting results by many researchers all over the world, but most of these results have been confined to the laboratory scale. New innovations have been reported since the early 1990s. These innovations opened up new avenues of research triggering a renewed activity all over the world by various groups, especially in Europe, Japan and China.

**Microwave Processing**

Microwave processing of materials, which includes heating and sintering, is fundamentally different from conventional processing which involves radiant/resistance and/or convection heating followed by transfer of thermal energy via conduction to the inside of the work-piece through thermal conductivity. For many applications, it is a slow process and takes considerable time to achieve thermal equilibrium. One can heat any material in a conventional furnace. In the case of microwave heating, the absorption of microwave energy is followed by volumetric heating involving a conversion of electromagnetic energy into thermal energy. In this process, the role of thermal conductivity is minimized, and heating is instantaneous and rapid and is a function of the material being processed. The heat is generated internally within the material instead of originating from external sources. In general, microwave heating provides a very rapid method for energy conversion as compared to conventional methods where energy transfer heats the material. Due to volumetric heating and the ability to heat the material uniformly from the inside-out, microwave processing offers unique advantages, especially in food and rubber processing and in drying operations.

Microwaves are a small part of the electromagnetic spectrum with wavelengths ranging from 1 mm to 1 m in free space and frequencies between 300 GHz and 300 MHz, respectively. Based on microwave–matter interaction, most materials can be divided into three categories: opaque, transparent and absorbers. It is well-recognized that bulk metals are opaque to microwaves and are good reflectors at room temperature; this property is used in radar detection. However, as will be shown in subsequent sections, metals in powder form are very good absorbers of microwaves and are heated very effectively. Further, bulk metals, if pre-heated to moderate temperatures, also become good microwave absorbers. Most other materials either are transparent or absorb microwaves to varying degrees at ambient temperature. The degree of microwave absorption and, consequently, the heating profile, changes dramatically with the rise in temperature. Microwave heating is material dependent, so only those materials that couple in with the microwave field will heat. The rate of heating will depend upon their degree of absorption, which is a function of various factors, including the dielectric loss, grain size, frequency and electrical conductivity. Selective heating of matter can be beneficial for certain applications, especially for metal–metal joining and brazing.

Microwave heating has significant advantages over conventional heating [6-9] in materials processing, such as substantial energy savings (in some cases, as much as 90% energy savings have been reported [10]), very rapid heating rates, considerably reduced cycle time, product quality improvement and eco-friendliness. It has been generally observed that microwave-sintered products possess finer microstructures and other unique features leading to considerable improvement in the mechanical properties and, hence, exhibit better overall product performance. This feature is now becoming the major driving force attracting many ceramic and metal industries to make serious efforts to commercialize the technology for their products.

**Recent Developments**

Microwave energy for ceramic processing experienced 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. Some of these areas have been commercially developed. These applications
involve the use of microwaves at low temperatures (<500°C) and, therefore, could easily be scaled-up. However, high-temperature processing successes achieved with microwaves in the laboratory could not be so easily translated to the industry due to many hurdles encountered while scaling-up. Recently, there have been reports indicating that some success has been achieved in commercializing microwave sintering of tungsten carbide-based cutting tools [11] and aluminabased products [10]. It is hoped that, in the near future, microwave processes will be successfully developed for commercialization of many specialty materials.

In the case of most ceramics, microwave heating is mainly characterized by the dielectric loss of the material. However, there are other factors that significantly contribute to microwave heating, such as ionic conductivity, degree of porosity, particle size, electrical conductivity and magnetic coupling. The exact mechanisms for microwave heating and sintering have not yet been very well explained. The interaction between microwaves and matter takes place through the electric field vector and the magnetic field vector of the electromagnetic field and involves polarization and conduction processes. Classically, there are various absorption mechanisms identified in microwave–matter interaction. Some of them are dipole reorientation and conduction of space and ionic charge, which are primarily found in insulators or dielectric materials. The vast majority of papers dealing with microwave heating of solids ascribe the heating to energy loss mechanisms of the electric vector. Very recently, experimental findings have demonstrated that magnetic losses also play an important role in microwave heating/sintering of bulk materials for a wide range of conductor (metals) and semiconductor materials [12,13].

In 1994, Cherradi et al. [14] published a paper in which they showed that the magnetic field made substantial contributions to the heating of alumina (at high temperature), semi-insulators and metallic copper. In their experiments, they had always heated the sample in both H and E fields simultaneously which caused a complicated interplay of the different absorption and conduction mechanisms. At Penn State, with very careful design of a single mode cavity, we separated E and H fields at 2.45 GHz, and then heated various materials in more or less pure electric and magnetic fields separately. In general, the conductive samples, such as metal powders and WC, could be much more efficiently heated in the magnetic field. On the contrary, the pure ceramic samples (insulators), such as Al₂O₃ and ZnO, showed much higher heating rates in the pure electric field. The structural state of the materials plays an important role in the microwave–materials interaction. For example, the powder compact copper sample absorbed a significant amount of microwave energy, but the solid bulk sample did not under the same conditions. From the data generated in this study and from the general theory of energy loss in various materials when placed in a microwave field, it is no longer possible to ignore the effect of the magnetic component, especially for conductor and semiconductor materials. The contributions to the magnetic loss mechanism can be hysteresis, eddy currents, magnetic resonance and domain wall oscillations [12].

**Microwave Sintering of Important Ceramics**

**Al₂O₃.** Alumina is the most common ceramic and has been widely used in microwave-sintering research by many scientists working in the field. Because of its highly refractory nature, it is very difficult to sinter to full densification unless suitable sintering aids or some special processing techniques are adopted. Many people have successfully sintered alumina to high densification using microwaves [4]. In general, the sintering of alumina using microwave processing can be achieved much faster and at a lower temperature than with a conventional process. Alumina samples microwave sintered at 1400°C with no hold time were 98% dense [15]. In conventional heating, it requires at least 1600°C and 2 hours of soaking time to achieve the same degree of densification and with substantial grain growth. Using microwaves, nearly full density was achieved at about 200°C less than the conventional temperature, as shown in Figure 1. This work now has been extended to fabricate some commercial alumina products with substantial improvement in the quality of the sintered product. For example, sol-gel-prepared alumina grit was sintered to full density using a continuous microwave process [16]. The alumina grit powder developed by Carborundum Universal Madras (India) is a kind of agglomerated granule with an average particle size of 0.8-1.0 mm. Microwave sintering of this material at 1500°C for 15 minutes provided a density of 3.96 g/cm³, which is very close to theoretical density. Table 1 compares the property data with conventionally prepared alumina grit. It is obvious that microwave-sintered alumina grit possesses much higher abrasion index and hardness values. The abrasion index of this grit was 94 and the Vicker's hardness 2317 kg/mm². In another study [17], large objects of alumina with diameters of 1 to 10 cm and lengths up to 2 m were also prepared using a continuous microwave system. These parts of 98% density at 1400°C were very uniformly and homogeneously produced.

**ZrO₂.** Fine-grained zirconia ceramics were microwave sintered at 1360°C for 2 min in a multimode, 2.45 GHz system. The sintered density was about 97.8% and average grain size was 0.25 μm. In another study of phase transition in Ca-stabilized ZrO₂ using microwave heating, almost complete transformation from tetragonal to cubic phase was obtained at 1600°C in 10 min: conventionally it takes several hours (~10 hours) to achieve the same degree of transformation (unpublished data).
TABLE 1. COMPARATIVE PROPERTIES OF MICROWAVE AND
CONVENTIONALLY SINTERED ALUMINA GRIT.

<table>
<thead>
<tr>
<th>Density g/cm³</th>
<th>Microwave</th>
<th>Conventional</th>
</tr>
</thead>
<tbody>
<tr>
<td>1450°C/15 min</td>
<td>3.70</td>
<td>3.92</td>
</tr>
<tr>
<td>1400°C/45 min</td>
<td>3.84</td>
<td>3.95</td>
</tr>
<tr>
<td>1500°C/15 min</td>
<td>3.90</td>
<td>3.89</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Abrasion Index</th>
<th>Microwave</th>
<th>Conventional</th>
</tr>
</thead>
<tbody>
<tr>
<td>1450°C/15 min</td>
<td>95</td>
<td>68</td>
</tr>
<tr>
<td>1400°C/45 min</td>
<td>100</td>
<td>65</td>
</tr>
<tr>
<td>1500°C/15 min</td>
<td>94</td>
<td>94</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Vickers Micro Hardness</th>
<th>Microwave</th>
<th>Conventional</th>
</tr>
</thead>
<tbody>
<tr>
<td>(kg/mm²)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1450°C/15 min</td>
<td>2205</td>
<td>732</td>
</tr>
<tr>
<td>1400°C/45 min</td>
<td>2368</td>
<td>1026</td>
</tr>
<tr>
<td>1500°C/15 min</td>
<td>2317</td>
<td>1885</td>
</tr>
</tbody>
</table>

Figure 1. Sintered density vs. temperature plots for microwave and conventionally sintered alumina with zero soak time.

PZT: PbZr₀.₅₂Ti₀.₄₈O₃: PbZr₀.₅₂Ti₀.₄₈O₃. PZT is a common ferroelectric material with the perovskite crystal structure. It is conventionally fabricated at temperatures over 1200°C for several hours. One serious problem associated with PZT fabrication is the high loss of PbO due to lengthy sintering times. This is a serious environmental issue. In the microwave-assisted process, single-phase

PZT was obtained at temperatures as low as 600°C [18] by using TiO₂. The use of non-stoichiometric TiO₂ enhances microwave absorption and increases the reaction kinetics substantially as is evidenced from the following examples. The use of nonstoichiometric precursors also leads to different reaction pathways for the formation of PZT. The rate of formation of PZT with microwave synthesis is controlled by a mechanism other than simple thermal diffusion. In another study, PZT samples were microwave sintered at temperatures 150° less than the conventional processing [19] resulting in finer grain size and minimal PbO loss. Table 2 shows a comparison of PbO loss in conventional and microwave processes for different PZT compositions.

BaTiO₃ (BT). Virtually all solid state reactions for the synthesis of materials in a conventional process are conducted under isothermal conditions; i.e., two or more phases involved are at the same temperature. However, using microwaves for materials synthesis involving two or more phases with different microwave absorptions may cause a situation known as an “anisothermal” state in which, on the microscopic level, one phase has a widely different temperature than the other phase. This may be the key to understanding the “microwave effect” that causes dramatic enhancements in reaction and material diffusion rates. In the synthesis of PZT (as shown above) and BaTiO₃, we have adopted the anisothermal approach to cause reactions to occur very quickly, producing the desired phase in a few minutes. For the synthesis of BT, we used BaCO₃ (a poor microwave absorber) and TiO₂ (an excellent microwave absorber). The reaction of the mixture of these two phases in a microwave field occurs radically different from the conventional isothermal heating situation. Table 3 lists the sequence of phases formed as a function of temperature and time in conventional and microwave settings. In the microwave case, at 250°C with no soak time, hexagonal BaTiO₃ appears; at 900°C in 5 min nearly pure tetragonal phase BaTiO₃ is formed. On the other hand, the conventional process even at 1300°C for a 1 hour soak time does not produce any XRD-detectable BaTiO₃ phase [20].

TABLE 2. PbO LOSS DATA DURING THE SINTERING
OF PZT BY VARIOUS PROCESSES.

<table>
<thead>
<tr>
<th>Open crucible method/PZT type</th>
<th>MEGAC°</th>
<th>TRS 200°</th>
<th>TRS 200B°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional firing (10°/min)</td>
<td>3%</td>
<td>5.7%</td>
<td>13.3%</td>
</tr>
<tr>
<td>Fast conventional firing (25°/min)</td>
<td>1.35%</td>
<td>&lt;0.5%</td>
<td>0.1-0.5%</td>
</tr>
<tr>
<td>MW process, 2.45 GHz (25°/min)</td>
<td>0</td>
<td>2.3%</td>
<td>0.2%</td>
</tr>
<tr>
<td>MW process, 30 GHz (30-50°/min)</td>
<td>0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

°Commercial PZTs from different vendors.
TABLE 3. SYNTHESIS OF BATO₃ USING BACO₃ AND TIO₂ AS PRECURSORS.

<table>
<thead>
<tr>
<th>Temp./soak time</th>
<th>BaCO₃ (%)</th>
<th>TiO₂ (%)</th>
<th>Ba₃TiO₄ (%)</th>
<th>Hexagonal (%)</th>
<th>Tetragonal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional heating</td>
<td>50°C/2 min</td>
<td>57</td>
<td>43</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>95°C/2 min</td>
<td>67</td>
<td>33</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>000°C/1 hour</td>
<td>62.5</td>
<td>21</td>
<td>16.5</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>1100°C/1 hour</td>
<td>36</td>
<td>38</td>
<td>26</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>1200°C/1 hour</td>
<td>29</td>
<td>37</td>
<td>34</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>1300°C/1 hour</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>Microwave heating</td>
<td>250°C/0 min</td>
<td>45</td>
<td>52</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>400°C/0 min</td>
<td>28</td>
<td>26</td>
<td>0</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>500°C/1 min</td>
<td>13</td>
<td>6</td>
<td>0</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>600°C/5 min</td>
<td>11</td>
<td>12</td>
<td>0</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>700°C/5 min</td>
<td>7</td>
<td>9</td>
<td>0</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>900°C/5 min</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Ba(Mg₁₋₁Ta₂₋₂O₆)₂/Ba(Zn₁₋₁Ta₂₋₂O₆)₂, Ba(Mg₁₋₁Ta₂₋₂O₆), and Ba(Zn₁₋₁Ta₂₋₂O₆)₂ (BMT) with perovskite crystal structure are good dielectric materials for microwave resonators because of their high quality factors (Q) and moderate dielectric constants. These remarkable materials are perhaps the most refractory oxides (melting point >3000°C). Therefore, very high temperatures (>1600°C) are required to sinter them in a conventional furnace. Often, to obtain BMT/BZT ceramics with high densities, sintering aids such as Mn and Sn are used, but the sintering aids also degrade the dielectric properties. We have synthesized and sintered BMT/BZT single-phase materials using reduced-oxide precursors and microwave processing [21, 22] without the addition of sintering aids. The use of reduced TiO₂-x enhanced the reaction kinetics and produced a single-phase material at much lower temperatures (1300°C/20 min) with higher densification than normally obtained by conventional processes. Microwave-processed BMT samples exhibited densities as high as 97% of theoretical when heated at 1600°C for 30 min. The average grain size in microwave-sintered BMT was about 1 μm, in contrast to 3 μm in the conventionally sintered material. BZT samples with an average grain size < 5 μm were sintered at 1400°C for 5 min to full densification using the microwave process.

NZP Materials. NaZr₂(PO₄)₃ is a parent composition of a very large family of materials now known as NZP and characterized by their low thermal expansion behavior [23]. NZP has a special open framework structure with corner-linked ZrO₆ octahedra and PO₄ tetrahedra. The covalent network skeleton NZP is remarkably stable with respect to temperature and chemical substitution. Compounds based on the NZP structure have found applications as superionic conductors, candidates for ceramic nuclear waste forms and catalysts for NO₃ reduction, and they are suitable for low-thermal-expansion applications. Conventional solid state reaction processes to synthesize and sinter NZP compounds require long cycle times and often do not result in high densification or single-phase materials. A novel microwave-assisted single-step procedure for the synthesis of a number of important members of the NZP family in less than 20 min has been developed [24]. This was made possible by identifying the high microwave absorption of sodium di-hydrogen phosphate monohydrate (NHMP) and using this as one of the reactants. The microwave products exhibited high phase purity and good crystallinity. The microwave-assisted synthesis was found to be simple and fast and minimized the loss of volatile species. Interestingly, the combination of microwaves and nonstoichiometric precursors (such as TiO₂-x and partially stabilized zirconia in place of regular zirconia) for the preparation of NZP was found to reduce the reaction temperatures and enhance the reaction rates even further. Specific compounds of NaZr₂(PO₄)₃, NaSn₂(PO₄)₃, and NaTi₂(PO₄)₃ were synthesized at temperatures as low as 600°C in 15 min. A microwave-assisted procedure for the rapid sintering of NZP materials has also been demonstrated, and more than 97% densification has been achieved at temperatures much lower than those required for conventional processing.

ZnO Varistor Ceramics
Zinc oxide (ZnO) varistors are electronic ceramic devices possessing highly non-linear current–voltage characteristics that enable them to be used as voltage surge suppressors. Their typical electrical behavior is controlled by their microstructure (grain size and grain boundary chemistry) and the composition. The important role of the sintering procedure in developing the microstructure necessary to obtain desired nominal voltage (V₅₀%), energy handling capability and clamping performance of the zinc oxide varistors is well-recognized. We have microwave-sintered various types of zinc oxide varistors under different processing conditions. Microwave sintering of ZnO varistor samples showed significant reduction in the cycle time and substantial improvements in the electrical properties. Microwave-sintered samples exhibited better densities, finer grain size, and more uniform microstructures relative to conventionally processed samples (Table 4 and Figure 2) [25]. Electrical characterization of microwave-sintered samples showed higher-voltage and better clamping properties as compared to conventional sintering. A
typical V–I curve obtained for V275LA4-type radials (type of varistors) is shown in Figure 3. Higher volts/mm response in microwaved samples signifies that (i) smaller devices with similar electrical properties can be used, and (ii) less material can be used to develop similar devices than those that can be obtained through conventional processes.

Multilayer varistors (MLVs) based on ZnO as the passive ceramic material and platinum as inner electrodes [25] were also processed successfully using microwave technology. Total cycle time for microwave sintering of MLVs was only 3 hours as compared to 30 hours in a conventional process where considerable time is spent during the binder burnout stage. In contrast, there is no need for a binder burnout stage in the microwave process. A typical microstructure of the multi-layer varistors sintered in a batch microwave oven is shown in Figure 4. The platinum inner electrodes were intact and continuous. This signifies that metal electrodes can be sintered (processed) using microwaves when cofired with a ceramic. Another aspect of this research is that this multilayer composite structure has much better electrical properties than the conventionally processed structure. Data presented in Table 5 indicates that the microwave process yields higher volts/mm parts and gives better clamp performance. Leakage characteristics (IR) and other electrical properties relevant to varistors (peak pulse, energy, life test) have been measured, and the data exhibited a similar trend.

**Multilayer Capacitors (MLCs)**

Multilayer ceramic capacitors (MLCCs) are used in almost all areas of electronics as an important ceramic component, comprising a large industry that produces over $10^{12}$ components per year. There is a constant increase in the demand in functionality of electronic devices and requirements for miniaturization, high capacitive volumetric efficiency, high reliability and low production cost. In designing capacitors, dopants are added to a basic BaTiO$_3$ powder to control temperature coefficient of capacitance and magnitude of dielectric permittivity and to limit dielectric loss, maximize insulation resistance and degradation resistance.

**TABLE 4. TYPICAL DENSITY and GRAIN SIZE DATA FOR ZnO RADIALS OF TYPE V275LA4.**

<table>
<thead>
<tr>
<th>Sintering condition</th>
<th>Density (g/cm$^3$ (%)TD)</th>
<th>Grain size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conv.1250°C-2h</td>
<td>5.58 (98.4)</td>
<td>10</td>
</tr>
<tr>
<td>MW1100°C-15min</td>
<td>5.56 (98.4)</td>
<td>6.0</td>
</tr>
<tr>
<td>MW1200°C-15min</td>
<td>5.59 (98.6)</td>
<td>7.5</td>
</tr>
<tr>
<td>MW1300°C-15min</td>
<td>5.60 (98.8)</td>
<td>9.5</td>
</tr>
</tbody>
</table>

![Figure 2](image1.png)  
**Figure 2.** Typical microstructures of conventional and microwave-sintered ZnO radials showing more uniform and finer microstructure of microwave-sintered part than the conventional product.

![Figure 3](image2.png)  
**Figure 3.** A comparison of V–I curves between microwaved- and conventionally sintered ZnO radials.
Over 80% of modern multilayer capacitors involve the cofiring of BaTiO$_3$ dielectric formulations with Ni inner electrodes. In order to cofire a dielectric with Ni, firings have to be conducted at a low $p_{O_2}$. Typical firings involve temperatures of ~1260–1300°C and atmospheres with $p_{O_2} = 10^{-10}$–$10^{-12}$ atm.

Microwave sintering of Ni-electrode MLCCs was conducted in an intermediate reducing atmosphere of $p_{O_2} = 10^{-6}$ atm. It was found that, in the temperature range around 1250°C, the MLCC chips were sintered well, resulting in dense and uniform parts without any delaminations or cracks [26]. Representative SEM micrographs of the fracture surface and free surface of the microwave-sintered 

![Figure 4. A typical micrograph of a microwave-sintered multilayer varistor.](image)

| TABLE 5. ELECTRICAL PROPERTIES OF MICROWAVE- AND CONVENTIONALLY SINTERED MLVS. |
|--------------------------------|-----------------|-----------------|-----------------|
| $V_{nom}$ | Variance ($V_{nom}$) | Clamp ratio | IR |
|-----------------|-----------------|-----------------|
| Microwave-sintered V5.5mla1206 | 19.22 | 2.45 | 1.539 | 0.892 |
| Conventionally sintered V5.5mla1206 | 8.23 | 2.98 | 1.027 | 0.920 |

Ni-electrode MLCC chips (cross section) are shown in Fig. 5 [27]. Highly dense microstructures were achieved by microwave sintering at about 1250°C. The internal electrodes were found to be continuous. Since the total processing time for microwave sintering was only about 10% of that for conventional sintering, the microstructures suggest that the densification kinetics of the MLCCs were substantially enhanced in the microwave sintering. The average grain size of the microwave-sintered MLCC matrix was 0.5–0.6 mm, similar to that of the conventionally sintered sample. The dielectric properties of the microwave-sintered MLCCs were comparable to the standard products sintered by the conventional process. Compared to the conventional process, microwave sintering conducted in a dry and static atmosphere, with heating rate one order of magnitude higher, heating time one order of magnitude shorter and sintering temperature 100°C lower than the conventional process, produced MLCC parts of similar quality and saved about 90% in processing time.

**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, is the main factor that influences the degree of transparency. Glasses are optically isotropic and have no grain boundaries and, therefore, possess excellent transparency. Most noncubic ceramics are anisotropic and polycrystalline. The grain boundaries in a ceramic strongly scatter light. Therefore, to convert a noncubic ceramic having grains larger than the wavelength of light into a transparent

![Figure 5. A typical microstructure of microwave-sintered MLCC showing continuity in Ni electrodes and very uniform and homogeneous sintering of BaTiO$_3$ ceramic layers. (This is how conventionally sintered electrodes look and show continuity in electrical conductivity.)](image)
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 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 complete densification. The conventional methods to fabricate fully dense and reasonably transparent ceramics involve high temperatures, lengthy sintering conditions and various complex processing steps, which make the processing of transparent ceramics very difficult and expensive. However, the 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 without utilizing high-pressure conditions [28].

Hydroxyapatite was fully sintered to form a transparent ceramic at 1100°C in 10 min by microwave processing [29]. Densification was shown to be critically dependent on the starting materials. Transparent ceramics of spinel and alumina were also fabricated [30, 31]. Fully dense alumina [32] and spinel ceramics using high purity and submicron sized powders were developed with a reasonable degree of transparencies on laboratory-typesmall samples at 1700°C sintered for 15 min in the microwave system. Fully transparent ALON ceramics were also made using a multimode microwave system at 1800°C [33]. Translucent ceramics of ALN, a well-known high-thermal-conductivity material, were also produced at 1900°C in 60 min using a microwave oven [34]. Recently, a MgO ceramic has been fabricated into a translucent form using nanometer-sized starting powders and LiF as a sintering aid [35]. Figure 6 shows some of the microwave-processed transparent and translucent ceramics of hydroxyapatite, alumina, AIN and ALON.

**Microwave Processing of Nanomaterials**

Nanostructured materials have been recognized to exhibit superior properties over standard materials due to the presence of nanometer range microstructures in the finished product. However, since the nanopowders are extremely active, and tend to agglomerate and coarsen during sintering at elevated temperatures, it has been a great challenge to sinter the nanophasic materials to high densification and still retain the nanostructure in the sintered body. Conventional sintering usually requires holding the compacted bodies at the sintering temperature for several hours. The long processing time at high temperatures often results in substantial coarsening and grain growth. Since microwave processing requires much shorter soak times for sintering, thereby minimizing grain growth, it is possible to fabricate nanostructured materials using microwaves. We have used nanophase MgO [35], TiO₂ and Cu metal powders to sinter these materials and produce very fine microstructures.

MgO was sintered at 1150–1400°C for 15 to 75 min. TiO₂ and TiO₂ₓ were sintered at 1150°C for 20 min. Nano-Cu was sintered at 868–920°C for 5–20 min. All samples were sintered in a 2.45 GHz multimode cavity. The ramp rate for these sintering experiments was 25–50°C/min. MgO ceramics were fabricated by using high-purity MgO nanopowder containing 0.2–4% LiF as a fugitive additive. LiF helped in improving the density to about 97% at 1150°C in 15 min. Figure 7(a) shows a typical microstructure of an MgO microwave-sintered nanoceramic. Dense TiO₂ ceramics were obtained by microwave sintering of nanophase TiO₂ sintered at 1150°C for 20 min. (Fig. 7(b). Nanophase Cu was microwave sintered at 920°C for 20 minutes to give about 83% density and very limited grain growth (Fig. 7(c)) with an average grain size of about 80 nm.

**WC–Co-Based Ceramic–Metal Composites**

WC-Co-based composites, due to their unique combination of hardness, toughness and strength, are universally used for cutting tools, machining of wear resistant metals, grinding, mining, geothermal as well as oil- and gas-drilling operations. Conventional methods for sintering WC with Co as a binder phase involve high temperatures (up to 1500°C) and lengthy sintering cycles (~24 hours) in order to achieve high densification. Such conditions favor undesirable
WC grain growth in the presence of Co melts. Consequently, the mechanical strength and hardness of the tools are diminished. Often, additives such as titanium carbide (TiC), vanadium carbide (VC) and tantalum carbide (TaC), are used to suppress grain growth, but unfortunately such additives, deleteriously affect the mechanical properties of the tools and add substantially to the overall cost. Since microwave heating requires very little time to obtain nearly full densification, grain growth is relatively suppressed and finer microstructures can be obtained.

In 1991, J. P. Cheng in a Ph.D. thesis [36] first showed that WC-Co composites could be sintered in a microwave field. Gerdes and Willer-Porada [37] also reported the sintering of similar WC objects from normal-sized powders. They followed a reactive sintering route using a mixture of pure W, C and Co instead of normal sintering. Using a newly designed microwave apparatus, we were able to fully sinter WC commercial green bodies containing 12% and 6% Co [38], and we observed that microwave-processed WC-Co bodies (sintered at 1250–1320°C for only 10-30 minutes) exhibited better mechanical properties than the conventional parts, fine and uniform microstructure with little grain growth, and nearly full density without adding any grain-growth inhibitors [11, 39-40]. The microstructural examination of microwave-sintered WC-Co samples, in general, exhibited smaller average grain size than the conventionally sintered sample. Microwave-sintered parts have shown significant property improvements without varying the component materials, and without the addition of grain growth inhibitors. Because of this, WC parts produced by the microwave-sintering process exhibit an unprecedented improvement in abrasion resistance (15–30% better), erosion resistance (22% better) and corrosion resistance in 15% HNO_3 (20 times better) without any noticeable loss in hardness or fracture toughness. These improvements in the properties are believed to be due to the fine microstructure, uniform Co distribution and pure Co phase at the grain boundaries in microwave-sintered samples [41]. Figure 8 illustrates some commercial WC-Co parts fabricated successfully using microwave technology. Now several companies are commercially exploiting this technology.
Microwave Processing (Sintering, Brazing and Melting) of Metallic Materials

Microwave processing of materials mostly has been confined primarily to ceramics, semi-metals, inorganic, and polymeric materials. There are few detailed reports on microwave processing of metallic materials. The main reason for this was due to the misconception that all metals reflect microwaves and/or cause plasma formation, and hence cannot be heated in a microwave field. However, the researchers did not realize that this observation is valid only for bulk metals at room temperature and not for powdered metals and/or for bulk metals at elevated temperatures. Now it has been proved that metallic materials in powder form do absorb microwaves, and if bulk metals are preheated to a temperature up to 400°C, they also start coupling with the microwave field and are heated very rapidly, so much so that they can be melted.

At 2.45 GHz, it is observed that the skin depth in the bulk metals is very low (or the order of a few microns), and, hence, very little penetration of microwaves takes place. However, in metal powders (<100 μm), rapid heating in the material as a whole can occur. Work on microwave interaction with metallic powders was performed by Nishitani [43] who reported that, by adding few percent of electrically conducting powders such as aluminum, the heating rates of the refractory ceramics are considerably enhanced. Walkiewicz et al. [43] likewise simply exposed a range of materials, including six metals to a 2.4 GHz field, and reported modest heating (but not sintering) in the range from 120°C (Mg) to 768°C (Fe). Whitaker and Mingos (44) used the high exothermic reaction rates of metal powders with sulfur for microwave-induced synthesis of metal sulfides. Shelnburg et al. [45] heated Cu powders coated with CuO to 650°C, but did not sinter them. Narasimhan et al. [46] succeeded in heating Fe alloys in a microwave oven up to 370°C in 30 minutes. However, in all these studies, no sintering of pure metal or alloy powders was reported. Our experiments [13] have shown that powdered metals are in fact very efficient microwave absorbers and as a result can be very rapidly heated to their sintering temperatures. Some powder metal steel commercial parts of FC208 and FN208 have also been sintered to near net shape. Figure 9 shows some commercial products sintered using microwaves. Many commercial powder-metal (PM) components of various alloy compositions, including Fe and steel, Cu, Al, Ni, Mo, Co, W, WC, and Sn, have also been sintered with microwaves producing essentially fully dense bodies.

Microwave sintering of PM green bodies comprising various metals, steels and metal alloys produced highly sintered bodies in a very short period of time [47]. Typically, the total cycle time was about 90 min with sintering temperature ranges of between 1100–1300°C and soak times of 5 to 60 min. The mechanical properties, such as the modulus of rupture (MOR) and hardness, of microwave-processed samples were much higher than the conventional samples. As an example, copper steel (MPIF FC-0208 composition) was successfully sintered by the microwave technique to obtain good sintered density, hardness, flexural strength and near net dimensions, thus yielding equivalent or even sometimes superior mechanical properties over those samples produced by conventional sintering [47]. In this material, a Rockwell B hardness (HRB) as high as 82 ± 2 was obtained for samples sintered at 1260°C for 5 min soaking in a flowing forming gas atmosphere. The maximum flexural strength of 1077 ± 10 MPa was obtained for microwave-sintered samples at 1140°C for 20 min.

An examination of the microstructures and porosity distributions of the conventional and microwave-sintered samples reveals that microwave-sintered samples had more uniform microstructures than the conventional samples in which the core had more pores than the surface. In some microwave-processed samples, the cores were slightly denser than the surface. This is typical of most ceramics sintered in a microwave, indicating that heat transport is from the inside out and that the interior of the material may be hotter than the surface. However, using our modified microwave-sintering system, we were able to obtain sintered samples with uniformly dense core and edges. An important distinction in the microstructures of conventional and microwave-sintered samples was that the pores in the microwave-sintered samples had more rounded edges than those of the conventional sample. It is commonly known that sintered products exhibit an increasing ductility when the pore shape is more spherical. This was proved by conducting a standard test for measuring ductility and toughness of hollow cylindrical samples.
of FC208. Figure 10 shows the result of this test. It was found that the conventional part failed at a load of 320 lbs and the microwave part at 430 lbs, indicating an increase of about 30% in the strength. But a more important feature was the manner in which the parts failed after applying the maximum load. The conventional part broke into four pieces, which is very typical of the standard PM parts. On the other hand, the microwave-processed part broke into two flat pieces, indicating a higher ductility. An explanation of this distinguishing feature was sought by analyzing the microstructures of the two samples. It was revealed that the pores in the microwave-sintered samples had rounded edges (Fig. 10(c)) in contrast to the sharp-edged porosity (Fig. 10(d)) in the conventionally sintered samples.

The implications of these findings are obvious in the field of powder-metal technology. Metal powders are used in industry for diversity of products and applications. The challenging demands for new and improved processes and materials of high integrity for advanced engineering applications require innovation and newer technologies. Finer microstructures and near theoretical densities in special PM components are still elusive and challenging. Increasing cost is also a concern of the industry. Researchers are looking for newer technologies and processes to meet these demands. The developments as reported in this paper using microwave processing may offer a new method to meet these demands of producing better microstructures and properties in powder-metal products.

As mentioned earlier, microwaves selectively heat powder metals and reflect from bulk metals at room temperature. This feature has been exploited to braze and join bulk metals using powderized-metal/alloy braze materials. We have joined steels, W bulk metals and also brazed super alloys. An example is shown in Figure 11 in which regular steel and cast-iron parts have been joined in a microwave field in 2-3 min using braze powder. The joint is almost perfect, as indicated by the microstructural examination of the sample. We have also repaired and brazed super-alloy-based turbine blades. This work can also be extended to join metal to a ceramic, and also developing ceramic coating on steels or metal coatings on ceramics.

**Summary**

In the last 5-10 years, many significant developments and advances have taken place in the field of microwave processing of materials. Traditional and advanced ceramics and composites have been fabricated using microwave technology with potential of huge savings in time and energy, with substantial improvements in the properties. It has been demonstrated that, in the case of WC-Co processing,
Microwaves can reduce the cycle time to about one-tenth the cycle time required by conventional means, and produces products with improved abrasion, erosion, and corrosion resistance. Refractory oxides, such as alumina and zirconia, have been sintered using microwaves to near full density at much lower temperatures and in dramatically shorter sintering times than normally required in a conventional method. The fabrication of Transparent ceramics, including alumina, spinel, mullite, ALN and AION, has been achieved in a single-step process at ambient pressure. The most recent significant development in microwave processing has been the sintering, brazing, joining and melting of metals.

REFERENCES


