Microwave Sintering of Ceramics, Composites and Metallic Materials, and Melting of Glasses

Dinesh Agrawal

Microwave Processing and Engineering Center
107 Materials Research Laboratory
The Pennsylvania State University
University Park, PA 16802, USA

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Though microwaves have been in use for many applications for over 60 years, their application in ceramic processing involving synthesis, sintering, melting, joining, surface modifications, etc, has developed only in the last twenty years. Microwave materials processing is recognized for many advantages, namely, substantial reduction in cycle time resulting in large energy savings, selective and volumetric heating, providing fine microstructures, improved mechanical properties, and eco-friendliness. In the last two decades, various researchers have worked with a variety of traditional and advanced ceramics such as alumina, zirconia, hydroxyapatites, transparent ceramics, electroceramics, ceramic superconductors, glass-ceramics, non-oxide ceramics including Si₃N₄, AlN, SiC and WC/Co, etc. In all of these materials, substantial improvements in their properties over conventional products, as well as enhancements in the diffusion and reaction kinetics, were reported. Recently, microwave melting of glasses has also been achieved with many advantages over conventional melting.

It was generally believed that metals reflect microwaves, and hence cannot be processed in a microwave field like ceramics. However, recently it has been discovered that if the metals are in powder form, they will also absorb microwaves and will get heated very effectively. Almost all metals, including refractory metals (W, Re, Mo, etc), alloys, steels, have now been sintered successfully in 5–15 min. The selective heating feature of microwaves has led to effective brazing and joining of metal parts. Even bulk metals can be heated and melted in a microwave field and the melt can be cast into useful products.

Keywords: Microwave energy, Ceramics, Sintering, Powder metals, Glasses, Melting

Introduction

Innovations in material processing have always resulted in a better product and possibly a cost effective processing. Industry is always seeking new technologies which meet the growing demands of better, faster and cheaper products. The processing of ceramics and composites involves, initially powder synthesis, drying, calcination, consolidation, binder-burnout, and finally sintering of green compacted bodies into useful products. There have been many heating methods developed and used for synthesis and sintering steps in the ceramic processing. These methods can be broadly divided into two categories: contact and non-contact methods. Most traditional heating methods based on thermal conduction / radiation / convection (such as electric/resistant and fuel heating methods) are categorized as contact heating methods in which the thermal energy is in direct contact with the work-piece. Heating methods, such as induction, RF (radio frequency) or microwave heating heat the work-piece directly due to coupling of electromagnetic radiation with the matter and are thus called non-contact methods.

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 attractive advantages. In fact, it has been a kind of revolution in the area of sintering and synthesis in terms of extraordinary enhancements in the materials diffusion and reaction kinetics, as will be shown in the subsequent sections of this paper.

The very first application of microwave energy has been in the field of communication and it still dominates — almost all communications in space and mobile / cordless phone technology involve microwave frequencies. However, other than this communication, over the last 50 years microwave energy has found its use for a variety of applications including food processing, rubber industry (pre-heating and vulcanization), paper / textile / wood / ceramics drying, pharmaceutical, polymers, printing material and biomedical fields. These applications involve low temperature (<500°C) utilization of microwaves. The high temperature (>1000°C) application of microwaves is a rather recent phenomenon. Perhaps, the first reporting of microwave energy in the high temperature processing of ceramics appeared in 1968,¹ and then further reporting appeared in 1975,² but it was not until in 1980s that considerable activity was reported by many groups all over the world, and a new unconventional field of ceramic processing began to develop. Now, the field is maturing and increasingly finding its application in various aspects of materials processing, especially synthesis and sintering of ceramics, composites and metallic materials. This paper will confine itself to this aspect of microwave application.

Some earlier excellent reviews³–⁴ are more than adequate to give the interested readers a broader picture of the status of microwave processing research in the 1980s and 90s, and also provide a historical perspective of the
application of microwave energy to materials processing. The decade of 1980, when it was generally recognized that microwaves can be very effectively applied to ceramic processing, witnessed a widespread interest and enthusiasm, and plenty of research activities producing very interesting and exciting results by many scientists all over the world. However, these results were confined only to the laboratory scale. No credible and real commercial success was achieved because of the limitations encountered while attempting to scale-up the technology for large scale productions. Some of the limitations could not be overcome until recently by the design and building of continuous microwave kilns for high temperature applications by several new companies, primarily located in China (Longtech Co, Changsha, China) and Japan (Mino Yogya Co Ltd, Mizunami; Takasago Industry Co Toki-City, Japan). In the 1990s some new innovations in the composite materials area, such as WC/Co were reported, and in the last few years, The Pennsylvania State University's innovations involving metallic material processing and effect of separation of electric and magnetic fields at 2.45 GHz, and hybrid microwave processing in UK by Binner's group have opened up new avenues of research triggering a renewed activity all over the world by various groups.

In this article the application of microwave energy for high temperature material processing has been reviewed focusing mainly the developments of the last few years in the field.

**Microwave vs Conventional Heating**

Microwave processing of the materials, which includes heating and sintering, is fundamentally different from the conventional processing involving radiant resistance and/or convection heating followed by transfer of thermal energy via conduction to the inside of the work-piece through thermal conductivity mechanism. The latter is rather a slow process and takes considerable time to achieve thermal equilibrium. It is independent of the nature of the material. One can heat any material in a conventional furnace. On the other hand, in the case of microwave heating, it is the absorption coupling of the microwave field followed by the heating of the material as a whole (known as volumetric heating) by the conversion of the electromagnetic energy into thermal energy. In this process there is no thermal conductivity mechanism involved, the heating is instantaneous and rapid, and is a function of the material under process. The heat is generated internally within the material instead of originating from the 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 energy conversion rather than energy transfer heats the material. Due to the volumetric heating and ability of heating the material uniformly from inside-out, the microwave processing has a unique advantage, especially in the food and rubber processing, and drying operations for many products. Figure 1 illustrates some distinguishing features between the conventional and the microwave heating.

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 and 300 MHz. Based on the microwave-matter interaction, most materials can be divided into three categories: opaque (bulk metals), transparent (very low dielectric lossy materials) and absorbers (moderate to high dielectric loss materials). It is well recognized that the bulk metals are opaque to microwaves and are good reflectors at room temperature — this property is used in radar detection. However, as we will see in the subsequent sections, metals in powder form are very good absorbers of microwaves and get heated very effectively. Further, the bulk metals if pre-heated to moderate temperatures (−500 °C) also become good microwave absorbers. Most other materials either are transparent or absorb microwaves to varying degrees at ambient temperature. The degree of the microwave absorption and consequent heating profile changes dramatically with the rise in temperature. Microwave heating is material dependent. Therefore only those materials that couple in the microwave field will get heated and the rate of heating will depend upon their degree of absorption, which is a function of various factors including the dielectric loss, grain size, porosity, frequency, electrical conductivity, etc. The selective heating of microwave-matter interaction can be beneficial for certain applications, especially for metals/metal/ceramic joining and brazing.

Microwave heating has significant advantages over conventional heating in materials processing such as substantial energy savings (in some cases as much as 90% energy savings have been reported), 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 most importantly, overall improvement in quality and performance of the processed materials. This feature is now emerging as the major driving force to attract many ceramic and metal industries to make serious efforts to commercialize the technology for their products.
Recent Developments

Over several decades, microwave energy has been applied in the ceramic processes such as process control, drying of ceramic sanitarywares, calcination and decomposition of gaseous species by microwave plasma. Some of these areas have been commercially developed successfully. However, these applications involve use of microwaves at low temperatures (<500°C) and therefore could easily be scaled-up. However, successes achieved in high temperature materials processing with the microwaves in the laboratory could not be so easily transferred to the industry due to many hurdles encountered while scaling-up. Only recently, there are reports indicating that some success has been achieved in commercializing the microwave sintering of tungsten carbide based cutting tools and alumina based products. It is hoped that in the near future the microwave process will be successfully developed for the commercialization of many other materials where it has shown good promise.

In the case of most ceramics, the microwave heating is mainly characterized by the dielectric loss of the material. However, there are other factors that also significantly contribute to the microwave heating, such as ionic conductivity, degree of porosity, particle size, electrical conductivity, 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 involves 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. The vast majority of papers dealing with microwave heating of solids ascribe the heating to energy loss mechanisms of the electric vector. Some very recent 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. In 1999 it was experimentally established that ordinary powdered metal samples of virtually any composition could be successfully sintered in a 2.45 GHz multimode microwave cavity. Moreover, these samples exhibited physical and mechanical properties at least as good as, and usually better than those sintered in a conventional furnace.

Microwave Sintering of Important Ceramics

Many traditional and advanced ceramics have been processed in microwaves with reported enhancements in reaction and diffusion kinetics, and exhibiting better properties than the conventionally processed material. Hereunder, only a few selected ceramic materials are reported. All these materials have been processed mainly using a multimode microwave system operating at 2.45 GHz.

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 difficult to sinter it to full densification unless suitable sintering aids or some special processing techniques are adopted. Many people have successfully sintered alumina to high densification in the microwaves. High purity alumina is a low loss material and therefore is not a good microwave absorber at room temperature in a 2.45 GHz system. However, typical susceptor materials such as SiC or MoSi2 rods are used to pre-heat alumina samples. In general, full sintering of the alumina using microwave process has been achieved much faster and at lower temperature than in case of the conventional process. Small disc alumina samples microwave sintered at 1400°C, with no hold time, were 98% dense. Conventionally heating requires at least 1600°C and 2 h of soaking time to achieve the same degree of densification and substantial grain growth. In microwave nearly full density has been achieved at about 200°C less than the conventional temperature as shown in Fig. 2. This is a general observation irrespective of the quality and nature of the precursor alumina powders.

This work has been now 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. The alumina grit powder developed by Carborundum Universal, Chennai, India is a kind of agglomerated granule with an average particle size of 0.8-1.0 mm. The microwave sintering of this material at 1500°C for 15 min provided density of 3.96 g/cm3, which is very close to theoretical density. Table I compares the property data with those for conventionally prepared alumina grit. It is obvious that microwave sintered alumina grit possesses much higher abrasion index and hardness values. In another study, large objects of alumina with diameter of 1 to 10 cm and length up to 1-2 m were also prepared using continuous microwave system. These parts processed at 1400°C had a density of 98% with very uniform and homogeneous microstructure.
Table I: Comparative properties of microwave and conventionally sintered alumina grit

<table>
<thead>
<tr>
<th></th>
<th>Sintering Conditions</th>
<th>Microwave</th>
<th>Conventional</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>1450°C/15 min</td>
<td>3.70</td>
<td>3.92</td>
</tr>
<tr>
<td></td>
<td>1400°C/45 min</td>
<td>3.94</td>
<td>3.96</td>
</tr>
<tr>
<td></td>
<td>1500°C/15 min</td>
<td>3.96</td>
<td>3.89</td>
</tr>
<tr>
<td>Abrasion Index</td>
<td>1450°C/15 min</td>
<td>95</td>
<td>68</td>
</tr>
<tr>
<td></td>
<td>1400°C/45 min</td>
<td>100</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td>1500°C/15 min</td>
<td>94</td>
<td>94</td>
</tr>
<tr>
<td>Micro Vickers</td>
<td>1450°C/15 min</td>
<td>2205</td>
<td>732</td>
</tr>
<tr>
<td>Hardness (kg/mm²)</td>
<td>1400°C/45 min</td>
<td>2388</td>
<td>1026</td>
</tr>
<tr>
<td></td>
<td>1500°C/15 min</td>
<td>2317</td>
<td>1885</td>
</tr>
</tbody>
</table>

In Japan, Sato et al. have reported successful sintering of large commercial alumina products for substrate, high temperature optics and structural applications. In one example an alumina ring of 15 inch diameter was sintered to full density in microwave in only 20% of total cycle time and only 1/10th of the energy consumed when compared with the conventional process. Further, the properties such as bending strength were improved by almost 30% over the conventionally produced product; the shrinkage distortion was about 60% smaller than in the conventional process.

ZrO₂: Zirconia is a refractory oxide ceramic and often requires high sintering temperatures and soaking time to obtain a high degree of densification. Fine-grained zirconia ceramics were microwave sintered at 1360°C/2 min in a multimode, 2.45 GHz system. The sintered density was about 97.8% and average grain size was 0.25 μm (Fig. 3).

In another study of phase transition in Ca-stabilized zirconia using microwave heating, almost complete transformation from tetragonal to cubic phase was obtained at 1600°C in 10 min — conventionally it takes about 10 h to achieve the same degree of transformation. This demonstrates that microwave heating enhances kinetics of material diffusion and phase transformations.

PbZr₀.₅₂Ti₀.₄₈O₃ (PZT): PZT is a very common ferroelectric material belonging to the perovskite family of important materials. It is generally fabricated at temperatures over 1200°C for several hours of soaking time in a conventional process. One serious problem associated with PZT fabrication is the high loss of PbO due to lengthy sintering soaking time. This is a serious environmental issue. In the microwave assisted process, single phase PZT was obtained at as low as 600°C by using TiO₂-x. The use of non-stoichiometric TiO₂-x enhances the microwave absorption and increases the reaction kinetics many times. The usage of non-stoichiometric precursors also leads to different reaction pathways for the formation of PZT. It is believed that the rate of formation of PZT in microwave synthesis is controlled by a mechanism other than simple thermal diffusion. In another study, PZT samples were microwave sintered at temperatures 150°C lower than that for the conventional process, resulting in finer grain size and minimal PbO loss. Table II shows a comparison of PbO loss in conventional and microwave processes for different types of PZT sources.

BaTiO₃ (BT): It is well recognized that virtually all solid state reactions for the synthesis of materials in a conventional process occur under isothermal conditions, i.e. two or more phases involved are at the same temperature. However, the microwave processing for materials synthesis involving two or more phases may experience a situation known as ‘anisothermal’ state if the reacting phases have different microwave absorption characteristics. The anisothermal situation is associated with huge temperature differences between the phases at micro level. This is also one of the key factors to experience dramatic enhancements in reaction and material diffusion rates. In the synthesis of PZT (as shown above) and BaTiO₃, the anisothermal approach enhanced reactivity between the starting phases and produced the desired phase in a few minutes. For the synthesis of BT, BaCO₃ (a poor microwave absorber) and TiO₂-x (an excellent microwave absorber) were used as the precursors. The reaction of the mixture of these two phases in a microwave field is radically more rapid than conventional firing.

Table II: 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°C/min)</td>
<td>3%</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Fast conventional firing (25°C/min)</td>
<td>1.35%</td>
<td>5.7%</td>
<td>13.3%</td>
</tr>
<tr>
<td>Microwave process, 2.45 GHz (25°C/min)</td>
<td>0%</td>
<td>&lt;0.5%</td>
<td>0.1-0.5%</td>
</tr>
<tr>
<td>Microwave process, 30 GHz (30°-50°C/min)</td>
<td>0%</td>
<td>2.3%</td>
<td>0.2%</td>
</tr>
</tbody>
</table>

Fig. 3: Microstructure of microwave sintered ZrO₂ (2% Y₂O₃) at 1360°C for 2 min.
different from the conventional isothermal heating situation. Table III 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 BaTiO$_3$ appears and at 900°C in 5 min nearly pure tetragonal BaTiO$_3$ phase is formed. On the other hand, the conventional process — even at 1300°C for 1 h soaking time — does not produce any XRD detectable BaTiO$_3$ phase.

**Ba(Mg$_{1/3}$Ta$_{2/3}$)O$_3$/Ba(Zn$_{1/3}$Ta$_{2/3}$)O$_3$: Ba(Mg$_{1/3}$Ta$_{2/3}$)O$_3$, BMT and Ba(Zn$_{1/3}$Ta$_{2/3}$)O$_3$, BZT** 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), and therefore very high temperatures (>1600°C) and long soaking periods are required to sinter them in a conventional furnace. Often, to obtain BMT / BZT ceramics with high density, sintering aids such as Mn and Sn are used, but the sintering aids also degrade the dielectric properties. However, in the microwave process single phase materials using reduced oxide precursors were synthesized and sintered$^{24,25}$ without adding any sintering aid. Use of reduced Ta$_2$O$_{5-x}$ remarkably enhanced the reaction kinetics and produced single phase material at a much lower temperature (1300°C/20 min) with 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 20 min. The average grain size in microwave sintered BMT was about 1 μm in contrast to 3 μm in conventionally sintered material. BZT samples were sintered at 1400°C for 5 min to full density in the microwave process with an average grain size of <5 μm.

**NaZr$_2$(PO$_4$)$_3$: (NZP) Compositions**: NaZr$_2$(PO$_4$)$_3$ is a parent composition of a very large family of materials known as NZP and characterized by their low thermal expansion behaviour. NZP has a special open framework structure with corner-linked ZrO$_6$ octahedra and PO$_4$ tetrahedra. The covalent network skeleton of NZP is remarkably stable towards high temperature and chemical substitutions. Compounds based on NZP structure have found applications as superionic conductors, catalysts for ceramic nuclear waste form, for NO and CO reduction, and are suitable for many low thermal expansion applications. Conventional solid state reaction processes to synthesize and sinter NZP compounds require long cycle time and often do not result in high densification or single phase material. A novel microwave assisted single step procedure for the synthesis of a number of important members of NZP family in less than 20 min has been developed.$^{27}$ 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 processed products exhibited high phase purity and good crystallinity. The microwave assisted synthesis was found to be simple, fast, and minimizing the loss of volatile species. Interestingly, the combination of microwave and non-stoichiometric precursors (such as TiO$_{x}$ and partially stabilized zirconia in place of regular zirconia) for the synthesis of NZP was found to reduce the reaction temperatures and enhance the reaction rates even further. Specific compounds — NaZr$_2$(PO$_4$)$_3$, NaSn$_2$(PO$_4$)$_3$ and NaTi$_2$(PO$_4$)$_3$ — were synthesized at 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 that required for conventional process.

**Table III: Synthesis of BaTiO$_3$ using BaCO$_3$ and TiO$_2$ as precursors**

<table>
<thead>
<tr>
<th>Temperature/Soak time</th>
<th>BaCO$_3$ (%)</th>
<th>TiO$_2$ (%)</th>
<th>Ba$_5$Ti$<em>4$O$</em>{12}$ (%)</th>
<th>BaTiO$_3$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Hexagonal</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>Conventional heating</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>900°C/2 min</td>
<td>57</td>
<td>43</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>950°C/2 min</td>
<td>67</td>
<td>33</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>900°C/1 h</td>
<td>62.5</td>
<td>21</td>
<td>16.5</td>
<td>0</td>
</tr>
<tr>
<td>1100°C/1 h</td>
<td>36</td>
<td>38</td>
<td>26</td>
<td>0</td>
</tr>
<tr>
<td>1200°C/1 h</td>
<td>29</td>
<td>37</td>
<td>34</td>
<td>0</td>
</tr>
<tr>
<td>1300°C/1 h</td>
<td>0</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Microwave heating</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>250°C/0 min</td>
<td>45</td>
<td>52</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>400°C/0 min</td>
<td>28</td>
<td>26</td>
<td>0</td>
<td>42</td>
</tr>
<tr>
<td>500°C/1 min</td>
<td>13</td>
<td>8</td>
<td>0</td>
<td>54</td>
</tr>
<tr>
<td>600°C/5 min</td>
<td>11</td>
<td>12</td>
<td>0</td>
<td>30</td>
</tr>
<tr>
<td>700°C/5 min</td>
<td>7</td>
<td>9</td>
<td>0</td>
<td>14</td>
</tr>
<tr>
<td>900°C/5 min</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

**ZnO Based Ceramic Varistors**

Zinc oxide (ZnO) varistors are electronic ceramic devices possessing highly non-linear current-voltage characteristics, which enable them to be used as voltage surge suppressors. Their typical electrical behaviour 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 ($V_{nom}$), energy handling capability and clamping performance of the zinc oxide varistors is well recognized. Various types of zinc oxide varistors under different processing conditions have been sintered using microwave heating.$^{28}$ Microwave sintering of ZnO varistor samples indicates significant reduction in the cycle time and substantial improvements in the electrical properties. Microwave sintered samples exhibit better densities, finer grain size, and more uniform microstructure relative to conventional process (Table IV and Fig. 4).

Electrical characterization of the microwave sintered samples showed higher volts and better clamping properties than those of the conventionally sintered ones. A
CONVENTIONAL SINTERING

V-I CURVE COMPOSITION

Fig. 5 – A comparison of V-I curves between microwave and conventionally sintered ZnO varistor samples.

MICROWAVE SINTERING

Fig. 4 – Typical microstructures of conventional and microwave sintered ZnO varistor samples showing more uniform and finer microstructure of microwave sintered part than the conventional product.

typical V-I curve obtained for V275LA4 type radials is shown in Fig. 5. Higher volts/mm response in the microwave samples signifies that (i) smaller devices with similar electrical properties can be used, and (ii) it enables to use less material to develop similar devices obtained through conventional processes.

Multilayer Ceramic Capacitors (MLCCs)

Multilayer ceramic capacitors are used in almost all areas of electronics as important ceramic components. Their manufacturing is a large industry, producing over $10^{12}$ components per year. There is a constant increase in their demand in functionality of electronic devices and requirements for miniaturization, high capacitive volumetric efficiency, high reliability and low production cost. Over 80% of modern multilayer capacitors involve co-firing of the BaTiO$_3$ dielectric formulations with nickel inner electrodes. In order to co-fire a dielectric with nickel, firings have to be conducted at a low $pO_2$; typical firings involve temperatures ~1260$^\circ$C to 1300$^\circ$C and atmospheres with $pO_2$ = $10^{-13}$ to $10^{-12}$ atm.

Microwave sintering of Ni electrode MLCCs was conducted in an intermediate reducing atmosphere ~$pO_2$ x $10^{-6}$ atm. It was found that at the temperature around 1250$^\circ$C, the X7R MLCC chips were sintered well, resulting in dense and uniform parts without any delaminations or cracks. Representative SEM images of the fracture surface and free surface of the microwave sintered Ni electrode MLCC chips (cross section) are shown in Fig. 6. Highly dense microstructures were achieved by microwave sintering at about 1250$^\circ$C. The internal electrodes were found to be continuous. Since the total processing time in the microwave sintering was only about 10% of that in the conventional sintering, the dense microstructures suggest that the densification kinetics of the MLCCs was substantially enhanced in the microwave sintering. The average grain size of the microwave sintered X7R matrix was ~0.5-0.6 mm — similar to that of the conventionally sintered sample. The dielectric properties were comparable to those of the standard products sintered by conventional process.

A selected batch of microwave sintered MLCCs passed HALT. Compared to the conventional process, the 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$^\circ$C lower than the former, produced MLCC parts of similar quality and saved about 90% in processing time.

Table IV: Typical density and grain size data for ZnO radials of type V275LA4

<table>
<thead>
<tr>
<th>Sintering condition</th>
<th>Density (g.cm$^{-3}$)/% theoretical density</th>
<th>Grain size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional: 1250$^\circ$C/2 h</td>
<td>5.58 / 98.4</td>
<td>10</td>
</tr>
<tr>
<td>Microwave: 1100$^\circ$C/15 min</td>
<td>5.58 / 98.4</td>
<td>6</td>
</tr>
<tr>
<td>Microwave: 1200$^\circ$C/15 min</td>
<td>5.59 / 98.6</td>
<td>7.5</td>
</tr>
<tr>
<td>Microwave: 1300$^\circ$C/15 min</td>
<td>5.60 / 98.8</td>
<td>9.5</td>
</tr>
</tbody>
</table>

Transparent Ceramics

Transparency is an important optical property of many materials. The nature of the material including grain size, density, crystal structure, porosity and the grain boundary phase are the main factors that influence the degree of
transparency. Glasses are optically isotropic and have no
grain boundaries, and therefore possess excellent trans-
parency. Most non-cubic ceramics are anisotropic and poly-
crystalline. The grain boundaries in a 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 spinel 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 trans-
parent ceramics involve high temperatures, lengthy sinter-
ing conditions, and various complex processing steps,
which make the processing of transparent ceramics very
difficult and uneconomical. However, the microwave method
has been successfully used to fabricate transparent ce-
ramics 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.31

Hydroxyapatite was fully sintered into a transparent ceramic at 1100°C in 10 min by microwave processing.32
The densification was shown to be critically dependent on
the starting materials. Transparent ceramics of spinel and
alumina were also fabricated.33, 34 Fully dense alumina35
and spinel ceramics using high purity and submicron size
powders were developed with reasonable degrees of trans-
parency on laboratory size small samples at 1700°C sinter-
der for 15 min in the microwave system. Fully transpar-
ent ALON ceramics were also made using multimode mi-
crowave system at 1800°C.36 Translucent ceramics of AlN,
which is a well-known high thermal conductivity material,
were also developed in microwave at 1900°C in 60 min.37
Recently, MgO ceramic has been fabricated into trans-
lucence form using nano starting powder and LiF as a sinter-
ing aid.38 Figure 7 shows some of the microwave processed
transparent and translucent ceramics of hydroxyapatite,
alumina, AlN and ALON. Yttrium aluminium garnet (YAG),
Y₃Al₅O₁₂ is a host material for lasers and phosphors; how-
ever, its synthesis and subsequent sintering into a trans-
parent product is very complex and requires high tempera-
tures and long sintering cycle. Panneerselvam et al.39 re-
ported the successful application of microwave processing

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Fig. 6 – A typical microstructure of microwave sintered MLCC showing continuity in Ni electrodes and very uniform and homogenous sintering of BaTiO₃ ceramic layers.

Fig. 7 – Various kinds of transparent and translucent ceramics fabricated in microwave:
(a) pure alumina, (b) doped alumina, (c) AlN, (d) ALON and (e) hydroxyapatite. 

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to produce translucent YAG ceramics at 1350°C in 20 min. However, problems in making large samples of commercial products of transparent ceramics in microwave still persist.

**Microwave Processing of Nanomaterials**

Nanostructured materials have been recognized to exhibit superior properties over standard materials due to the presence of nano 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 nanopowders to high densification and still retain the nanostructure in the sintered body. Conventional sintering usually requires holding the compacted green 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 requires much shorter soaking time for sintering, thereby minimizing the grain growth, it is possible to fabricate nanostructured materials using microwave. Nanophase MgO, TiO$_2$, and Cu metal powders have been used to sinter them in the microwave and produce very fine microstructures.

MgO was sintered at 1150°C to 1400°C for 15 to 75 min. TiO$_2$ and TiO$_{2-x}$ were sintered at 1150°C for 20 min. Nano-Cu was sintered at 868°C to 920°C for 5 to 20 min. All the samples were sintered in a 2.45 GHz multimode cavity. MgO ceramics were fabricated by using high purity MgO nanopowder containing 0.2 to 4% LiF as a fugitive additive. LiF helped in improving the density to about 97% at 1150°C in 15 min. Figure 8a shows a typical microstructure of microwave sintered nanophase MgO. Dense TiO$_2$ ceramics were obtained by microwave sintering of nanophase TiO$_2$, sintered at 1150°C for 20 min giving high densification (Fig. 8b) Nanophase Cu was microwave sintered at 920°C for 20 min to give about 83% density and very limited grain growth (Fig. 8c) with the average grain size of about 80 nm.

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

WC-Co composites (also known as cemented carbides) due to their unique combination of hardness, toughness and strength are universally used for cutting tools, machining of wear resistant metals, grinding, mining, and geothermal, oil and gas drilling operations. Conventional methods for sintering WC with Co as a binder phase involve high temperature (up to 1500°C) and lengthy sintering cycles (~24 h) in order to achieve high densification. Such conditions favour undesirable WC grain growth in the presence of Co melts. Consequently, the mechanical strength and hardness of the tools are diminished. The 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 suppress the 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, the grain growth is relatively suppressed and finer microstructure is generally obtained without using any grain growth inhibitors.

In 1991, J. Cheng in a Ph.D. thesis first showed that WC/Co composites could be sintered in a microwave field. Gerdes and Willert-Porada also reported the sintering of similar WC objects from normal size powders, but they followed the reactive sintering route using a mixture of pure W, C and Co instead of normal sintering. At Penn State, using a newly designed microwave apparatus, fully sintered WC commercial green bodies containing 12% and 6% Co were achieved, and it was observed that microwave processed WC/Co bodies 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 when sintered at 1250°C-1320°C for only 10-30 min. The microstructural examination of the microwave sintered
WC/Co samples, in general, exhibited smaller average grain size than the conventionally sintered samples. Microwave sintered parts also showed significant property improvements without varying the component materials, and without the addition of grain growth inhibitors. The WC/Co part produced by the microwave sintering process exhibited an unprecedented improvement in abrasion resistance (15-30% better), erosion resistance (22% better), and corrosion resistance in 15% HNO3 (20X 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 cobalt phase distribution and pure Co phase at the grain boundaries in microwave sintered samples.45 Figure 9 illustrates some commercial WC/Co parts which have been fabricated very successfully using microwave technology. Now several companies are commercially exploiting this technology for specialty carbide products.

Microwave Processing of Metallic Materials

Until recently, microwave processing of materials mostly has been confined to ceramics, semi-metals, inorganic and polymeric materials. There have been very few detailed reports on microwave processing of metallic materials. The main reason for little work in microwave heating/sintering of metals was due to the misconception that all metals reflect microwave and/or cause plasma formation, and hence, cannot be heated in a microwave field. This observation is evident from the conventional view shown in Fig. 10 depicting a plot of microwave absorption in the solid materials of varying electrical conductivity.46 It is evident from this that only semiconductors will be good microwave absorbers, ceramics/insulators will be transparent in microwave, and the metals will reflect microwaves. However, this relation is valid only for sintered or bulk materials at room temperature, and not for powdered materials and/or at elevated temperatures. Now, it has been proved that all metallic materials in powder form do absorb microwaves at room temperature, and if even bulk metals are pre-heated to a temperature of at least 400°C, they also start coupling in microwave field and get heated rapidly, so much so that they can be melted.

![Diagram of Effective Conductivity](image_url)

Fig. 10 - Microwave energy absorption as a function of electrical conductivity

The earliest work of microwave interaction with metallic powders was reported by Nishitani47 who observed that by adding a few per cent of electrically conducting powders such as aluminium, the heating rates of the refractory ceramics are considerably enhanced. Walkiewicz et al.48 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° (Mg) to 768°C (Fe). Whittaker and Mingos49 used the high exothermic reaction rates of metal powders with sulphur for the microwave induced synthesis of metal sulphides. Sheinberg et al.50 heated Cu powders coated with CuO to 650°C but did not report any sintering of them. Narasimhan et al.51 succeeded in heating Fe alloys in a microwave oven only up to 370°C in 30 min. However, in all these studies no sintering of pure metal or alloy powders was reported. It was only in 1998 that the first attempt of microwave sintering of the powder metals52 was reported and since then many other researchers have reported successful sintering of many metallic materials.52,53

It has been observed that microwave sintering of metal powders produces a superior product. The steel commercial parts of FC-208 and FN-208 have been sintered to near net shape. Figure 11 shows some commercial products sintered in microwave. Many commercial powder metal (PM) components of various alloy compositions including iron and steel, Cu, Al, Ni, Mo, Co, Ti, W, WC, Sn, etc and their alloys have also been sintered in microwaves, producing essentially nearly full-dense bodies.

The microwave sintering of PM green bodies comprising various metals, steels and metal alloys produced highly sintered bodies in a very short period of time.54 Typically the total cycle time was about 90 min, sintering temperature ranged between 1100° and 1300°C, and soaking time between 5 and 60 min. The mechanical properties such as the modulus of rupture (MOR) and hardness of microwave
processed samples were much higher than those of the conventional samples. As an example, copper steel (MPIF FC-0208 composition) was successfully sintered by the microwave technique to produce good sintered density, hardness, flexural strength and near net dimensions, thus yielding equivalent or even sometimes superior mechanical properties compared to those obtained via conventional sintering. In this material the Rockwell B hardness (HRB) as high as 82 ± 2 was obtained for microwave processed samples sintered at 1260°C for 5 min soaking in 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 samples have more uniform microstructure than the conventional samples in which the core has more pores than the surface, though some microwave processed samples exhibit slightly denser core than the surface. This is typical of most ceramics sintered in a microwave, indicating that heat transport is from inside out, and the interior of the material may be hotter than the surface. However, using a modified microwave sintering system, the sintered samples with both uniformly dense core and edges can be obtained. An important distinction in the microstructures of conventional and microwave sintered samples has been noticed — the pores in the microwave sintered samples have more rounded edges than the conventional samples. It is commonly known that the sintered product exhibits a higher ductility and strength when the pore shape is more spherical. This has been proven by conducting a standard test for measuring ductility and toughness of hollow cylindrical samples of FC-208. Figure 12 shows the result of this test. It was found that conventional parts failed at a load of 320 lbs and microwave part at 430 lbs, indicating an increase of about 30% in the strength. However, a more important feature was the manner in which the parts failed after applying the maximum load. The conventional part broke into four curved 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 did have rounded edges (Fig. 12c) in contrast to the sharp edged porosity (Fig. 12d) in the conventionally sintered samples. Takayama et al. used green sample compacts of C, V, Ti and Mg metal powders surrounded by BN powder and successfully sintered them in the microwave. They reported obtaining higher tensile strength in the microwave sintered products than the conventional sintering. A comparative study of the sintering behaviour of Cu-12Sn bronze system reported that bronze was microwave sintered in significantly less time, resulting in higher density and more uniform microstructure. Also, hardness of the microwave
sintered samples compacted at 300 MPa was 50% higher than the conventionally sintered samples.

The application of microwaves to metallic materials has been now further extended from the sintering area to melting, brazing and joining of bulk metals.\textsuperscript{56-58} Figure 13 shows some bulk metals which have been melted in a microwave field using a special insulation package with susceptors.

As mentioned earlier, microwave selectively heats powder metals and reflects bulk metals at room temperature. This feature has been exploited to braze and join bulk metals using powdered metal / alloy braze materials. We have joined steels, W bulk metals, and also brazed super alloy components. An example is shown in Fig. 14 in which regular steel and cast iron parts have been joined in the microwave field in 2-3 min using a braze powder. The joint is almost perfect as indicated by the microstructural examination of the sample. This work can be extended to join metal to a ceramic, and also to develop ceramic coatings on steels or metal coatings on ceramics.

Carbon Nanotubes

Carbon nanotubes (CNTs) are hollow cylindrical molecular species that can be conceptually constructed by rolling up a graphene sheet. Due to CNTs' unique one-dimensional structure and outstanding electronic and mechanical properties, they are considered as excellent materials for nanoelectronic devices, nanoelectromechanical (NEMS), microelectromechanical (MEMS) systems and for the next generation composite materials that can offer high strength and stiffness. Since the first observation of carbon nanotubes in arc-discharge soot materials,\textsuperscript{59} numerous methods have been developed for synthesis of well graphitized nanotubes, such as arc-discharge and laser vaporization of a graphite electrode in the presence of metal catalysts,\textsuperscript{60, 61} plasma enhanced hot filament chemical deposition,\textsuperscript{62} thermal catalytic decomposition,\textsuperscript{63} and microwave enhanced chemical vapour deposition.\textsuperscript{64-67}

Recently at Penn State, using a TE\textsubscript{103} single mode cavity at 2.45 GHz and E (electric) and H (magnetic) field separation approach, multiwell carbon nanotubes were synthesized on Fe-coated Si wafers in the H field using acetylene or ethylene as the gaseous carbon source at temperature of 700°C in 10 min (Fig. 15). The diameter of microwave synthesized CNTs could be tailored from 30 to 150 nm by adjusting the acetylene / hydrogen ratio. By using thermal oxide on B-doped Si wafer as the substrates, well aligned CNTs were fabricated with an average diameter of ~30 nm and the length of ~10 microns. The morphology and diameter of the CNTs synthesized in microwave H field on Fe-coated Si wafer vary with the
concentration of the gaseous carbon source and the temperature.

**ZnO Single Crystal Microtubes**

ZnO is a promising material for UV and blue light emitting devices because it offers several advantages over its chief competitor, GaN. Single crystal microtube of ZnO has a band gap of 3.37 eV, with a 60 meV binding energy of the free exciton, and permits excitonic emission at room temperature. To date, most ZnO single crystals have been fabricated in the form of bulk crystals or thin films or nanowires / nanorods. The ZnO single crystal microtubes exhibit strong near band-edge emission, highly selective UV light response, excellent electron field emission, and...
interesting piezoelectric properties. Recently, ZnO microtubes have been grown by microwave heating and found to be colourless, fully transparent, contamination free, and of near perfect crystallinity. The morphology of the ZnO microtubes observed by optical microscope and SEM is shown in Fig. 16. The ZnO crystals are grown in a hexagonal hollow tubular form with a well faceted end and side surfaces. The wall thickness of the ZnO microtubes is less than 2 μm, typically between 0.5 and 1 μm. By adjusting microwave growth conditions such as the temperature and time, the ZnO tubes have been fabricated into different cross-sectional dimensions ranging from 100 to 250 μm, and different lengths up to 5 mm. ZnO has a high melting point of 1975°C, and sublimes or thermally decomposes rapidly at temperatures above 1400°C, which makes it very difficult to achieve high temperature crystal growth. In a carefully designed microwave cavity and insulation package, ZnO sublimation and selective nucleation and growth into microtubes have been achieved. The self contained vapour phase growth is a unique feature of the encapsulated microwave heating process critical for the growth of high quality ZnO single crystals, which is not achieved by conventional heating methods.

Microwave Melting of Glasses

Glasses generally are considered as microwave transparent and therefore cannot be effectively processed in a microwave field. However, depending upon their composition and use of susceptors they can be made to be heated very rapidly and selectively in the microwaves. Prof. Milan Hájek (GLASS vol. 79, No. 9, October 2002, www.microwaveglass.com) has developed a new glass melting system using microwave technology. It is claimed that it uses significantly less energy and offers better quality glass than in the conventional process.

An ordinary glass is an amorphous substance often consisting of silicates, possessing high resistivity and dielectric strength at room temperature. At higher temperatures (500°-600°C) glass becomes conductive and eventually, when melted, presents very high conductivity. Hájek’s innovation is based on the generation of a high intensity microwave field focused to a minimum space to start the melting locally inside out. He has also successfully designed and built a prototype microwave furnace with glass capacity up to 350 kg (Fig. 17).

Microwave-Matter Interaction

In the case of microwave sintering, there are two issues: rapid heating, and rapid material diffusion and/or enhancement in reaction kinetics. The heating part more or less has been studied and explained to a certain degree of satisfaction, but the rapid material diffusion and enhancements in the reaction kinetics have not yet been fully understood and explained as there are reportedly some ‘non-thermal’ (microwave) effects responsible for material diffusion.

Many different physical phenomena are involved in the microwave processing of materials. Classically, there are various absorption mechanisms identified in microwave-matter interaction, almost always connected to the E field. Some of them are dipole reorientation, space and ionic charge, etc. that are primarily found in insulators or dielectric materials. When microwaves penetrate and propagate through a dielectric material, the internal electric field generated within the affected volume induces translational motions of the free or bound charges (e.g., electrons or ions) and rotates charged complexes such as dipoles. The resistance of these induced motions due to inertial, elastic, and frictional forces causes energy losses and attenuates the electric field. As a consequence of these losses, volumetric
heating inside the solid material occurs. Due to this volumetric heating, the thermal gradients and the flow of heat in microwave processed materials are the reverse of those in conventional heating. Other losses, depending on the material, include the electric conductivity and/or magnetic resonance and eddy currents. In the case of metal powders, the interaction will be mainly based on the electric conduction, scattering, and/or probably also magnetic resonance. Rapid heating of the materials in a microwave field can be explained to a certain extent, but the rapid material diffusion aspect has not yet been very well explained. The classical sintering equations based on thermal mechanisms cannot fully explain the material diffusion in a microwave field.

The microwave power absorbed per unit volume \( P \) in W m\(^{-3} \) is expressed by the equation:

\[
P = 2\pi f_0 \left( \varepsilon_\infty \varepsilon' - \mu_0 \mu' H^2 \right)
\]

where \( E \) and \( H \) are the electric and magnetic fields respectively, \( f_0 \) is the frequency, \( \varepsilon' \) and \( \mu' \) are dielectric and magnetic loss factors respectively.

So it can easily be explained that the microwave power absorbed (the resultant heat) is directly proportional to the dielectric and magnetic losses, and of course, field intensity and frequency. There is another factor responsible for providing uniform and volumetric heating: penetration depth, \( D \), which is the distance in the direction of penetration at which the incident power is reduced to half of its initial value, and is a strong function of the loss and frequency of the field:

\[
D = 3\lambda_0 / 8.686\pi \tan(\varepsilon \gamma)^{1/2}
\]

where \( \lambda_0 \) is the wavelength of the microwaves. The equation suggests that there is a slight advantage in working at lower frequencies, however, large samples are involved, but is associated with a payoff in terms of power absorbed per unit volume. In bulk metallic materials, the microwave penetration is rather low at room temperature, and it is commonly described by a quantity known as skin depth \( \delta \), given by:

\[
\delta = 1 / (\pi \nu \mu \sigma)^{1/2}
\]

where \( \nu \) is microwave frequency, \( \mu \) is the permeability, and \( \sigma \) is the electrical conductivity. From this equation it is noted that a bulk metallic material at room temperature would have only a few microns of skin depth and would reflect most of the incident power. However, the situation in the case of powdered metallic materials is entirely different. They would easily get heated more effectively; smaller metallic particles, especially the nanosize powders would be most effective in 2.45 GHz frequency.

As it turned out, results from experimental investigations of microwave processing of materials have periodically suggested the existence of a controversial unexplained non-thermal interaction between high strength microwave fields and ceramic materials. This non-thermal interaction was unanticipated, lacked a credible or verifiable explanation, and was broadly termed as a 'microwave effect'. For high temperature reaction experiments, involving thermally activated chemical diffusion, the common manifestation of the microwave effect was (is) to enhance the process kinetics either by reducing the temperature or the time necessary to complete the reaction.

As far as the mechanisms for enhanced kinetics and sinterability are concerned, there are several hypotheses proposed by some researchers. These are associated with the so-called 'microwave effect' or non-thermal factors responsible for such enhancements in reaction and sintering kinetics. The most common theories are:

1. Ponderomotive force interaction: Booske and Rybakov proposed that microwave excited ionic currents become locally rectified (near the interface), giving rise to an additional driving force for mass transport. Their model and experiments with ionic crystals such as NaCl do show some validity of enhanced material diffusion. However, whether the model can be applied to non-ionic solids, even to metals, is doubtful.

2. In the case of materials with substantial amount of porosity (green samples of ceramics), there is an enhancement in the electric field at the convex surfaces of the pores. This enhancement in the electrical fields would provide a non-ohmic and a localized plasma contribution to the driving force for pore removal and thereby accelerate material diffusion as proposed by Willert-Porada. However, no experimental verification for such hypothesis has yet been demonstrated.

3. Anisothermal heating caused in two different phases of widely varying microwave absorption characteristics, can provide a strong driving force to cause enhancement in the reaction kinetics followed by sintering as has been observed by Roy and Agrawal. Several systems have been...
shown to prove this theory experimentally. However, this is applicable only to multi phase systems with selective heating. Single phase materials cannot be explained by this theory.

Summary

In the last 5-10 years, many significant developments and advances have taken place in the field of high temperature microwave processing of materials. Many traditional and advanced ceramics and composites have been fabricated using microwave technology with potential of huge savings in time and energy, and overall quality improvement. Recent developments, especially in processing of metallic materials, have opened up new avenues of research and application of microwave energy. It is expected that in the next few years the microwave technology could be developed for new products and new fields, and commercialization will be successfully accomplished for many niche applications.

References

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