



Microwave Processing of High Temperature Materials-An Overview†

SANJESH BABU^{1,*} and ANIL GOVINDAN²

¹Department of Physics, Mangalayatan University, Aligarh-202 001, India

²Department of Physics, M.M.H. (Post Graduate) College, Ghaziabad-201 001, India

*Corresponding author: Fax: +91 571 2410019, E-mail: sanjesh.babu@mangalayatan.edu.in

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Microwave processing of ceramics and composites is a relatively new technology alternative that provides new approaches for enhancing material properties as well as economic advantages through energy savings and accelerated product development. Over the last two decades, microwave energy is being increasingly applied in the area of a ceramics and composites processing for various purposes. Remarkable achievements have been made in the sintering and synthesis of ceramics and composites using microwaves. In the last decade, many significant developments and advances have taken place in the field of microwave processing of materials. Microwave technology have been used for important ceramics materials *i.e.*, Al₂O₃, ZrO₂, lead zirconate titanate, BaTiO₃, multilayer ceramic capacitors, transparent ceramics, CaCu₃Ti₄O₁₂, tungsten carbide-cobalt based ceramic-metal composites *etc.* In this article, microwave sintering technique of high temperature materials has been reviewed.

Key Words: Microwave processing, Ceramics, Composites and metallic materials.

INTRODUCTION

Microwave energy is an emerging, innovative, property improving, energy conserving, ecology-friendly, time-saving technology that can be used to process a variety of ceramic, composite and metallic materials at lower costs. Application of microwave energy is emerging as an innovative technology for the processing of a variety of products and materials at faster rates, low processing cost and, in most cases, with better properties. The first application of microwave energy was during world war II for radar. Microwave energy has been successfully applied in many low-temperature (< 500 °C) applications, such as rubber pretreatment and vulcanization, food processing, wood curing, textiles, polymers and biochemistry. In most of these areas the technology has been successfully commercialized and low-temperature industrial microwave furnaces are available worldwide. During the past two decades, many new developments have occurred worldwide in microwave research that have made it attractive for high-temperature applications (> 500 °C) that involve ceramics, composites and metals. New companies in China, the United States and Japan have been set up that provide microwave systems for high-temperature applications¹. The objective of this article is to present an overview of the microwave processing of high temperature materials.

Why use Microwave Energy?

Based on research performed by many engineers and scientists, the potential benefits as well as challenges and needs associated with microwave processing has been depicted in Table-1.

TABLE-1
BENEFITS, CHALLENGES AND NEEDS
OF MICROWAVE PROCESSING

Benefits	Challenges	Needs
Cost savings	Heating low-loss poorly absorbing materials	Availability of affordable equipment and supporting technologies
Precise and controlled heating	Controlling accelerated heating	Thermal insulation and other processing support hardware
Volumetric and uniform heating	Exploiting inverted temperature profiles	Development of compositions and processes tailored specifically for microwave processing
Short processing times	Efficient transfer of microwave energy to work piece	Better fundamental understanding and modeling of microwave-material interactions
Improved quality and properties	Timing	Smart processing
Synthesis of new materials	Economy	Better communication among equipment manufacturers, technology developers, researchers and commercial users

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Microwave sintering of ceramics

Alumina (Al_2O_3) is the most common ceramic and has been widely used in microwave-sintering research by many scientists. Because of its highly refractory nature, it is difficult to sinter to full densification unless suitable sintering aids or some special processing techniques are adopted. Almost full sintering of alumina has been achieved much faster and at lower temperature when microwave processing is used. Small disk alumina samples microwave sintered at 1400 °C, with no hold time, were 98 % of theoretical density with relatively low grain size². Conventional heating requires at least 1600 °C and 2 h of holding time to achieve the same degree of densification but with substantial grain growth. Using microwaves, nearly full density was achieved at about 200 °C less than the conventional temperature.

Zirconia (ZrO_2) is a refractory oxide ceramic that often requires high sintering temperatures and soaking time to obtain a high degree of densification. Fine-grained zirconia ceramics have been sintered using microwaves at 1360 °C for 2 min that yield 98 % of theoretical density and average grain size of 0.25 μm . The fabrication of transparent zirconia ceramics using nanopowders and microwave hybrid heating at 1600 °C have reported from the United Kingdom³.

Lead zirconate titanate (PZT) is a common ferroelectric material that belongs to the perovskite family. It is generally fabricated conventionally at temperatures >1200 °C for several hours of soaking time. Single-phase lead zirconate titanate has been obtained using a microwave-assisted process at 600 °C with non-stoichiometric titanium oxide (TiO_{2-x}).⁴ The use of TiO_{2-x} enhances microwave absorption and increases reaction kinetics substantially. The use of non-stoichiometric precursors also leads to different reaction pathways for the formation of lead zirconate titanate.

Barium titanate (BT) can be synthesized using barium carbonate (BaCO_3) (a poor microwave absorber) and TiO_{2-x} (an excellent microwave absorber) as precursors. Because microwave absorption is material dependent, it is possible to exploit this situation to enhance reaction kinetics. The reaction of the mixture of these two phases in a microwave field occurs radically different from the conventional isothermal heating situation. In the microwave case, hexagonal-barium titanate appears at 250 °C and no soak time and almost phase-pure tetragonal-barium titanate is formed at 900 °C in 5 min. The conventional process, even at 1300 °C for 1 h soak time, does not produce XRD detectable tetragonal-barium titanate phase⁵.

Zinc oxide (ZnO) varistors are electronic ceramic devices that possess highly nonlinear current-voltage characteristics. Various types of ZnO varistors produced under various processing conditions have been sintered using microwave heating in significantly shorter cycle time and with substantial improvements in electrical properties⁶.

Transparent ceramics are speciality ceramics that are fabricated conventionally using multistep processes that involve long sintering cycles and often, high-pressure methods. The microwave method has been successfully used to fabricate transparent ceramics because of its ability to produce a fully dense ceramic in a short time without using high-pressure conditions⁷. Hydroxyapatite has been fully sintered as a

transparent ceramic at 1100 °C in 10 min using microwave processing⁸. Reasonably transparent spinel and alumina ceramics have also fabricated by using highly pure and submicron-sized powders sintered at 1700 °C for 15 min^{9,10}. Fully transparent aluminum oxynitride (AlON) ceramics have been made using a multimode microwave system at 1800 °C¹¹. Translucent aluminum nitride (AlN) ceramic, which is a well-known high-thermal-conductivity material, has been developed using microwaves at 1900 °C for 1 h¹².

Single phase cubic perovskite $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) powders have been synthesized successfully by microwave heating with a relatively low energy consumption and short time, compared with conventional synthesis¹³. The ceramics from microwave synthesized powder was found to have higher dielectric constant than that from conventional synthesized powder under the same sintering conditions. In another study, $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramic phase was also synthesized by microwave heating and results indicate that the microwave processing is a promising method for preparing $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics¹⁴. For this, $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ was prepared using a domestic microwave oven operated at 2.45 GHz with 800 W. Electrical measurement was performed and shows that the dielectric permittivity of the samples is in the order of 10^6 .

Microwave sintering of composites

Tungsten carbide-cobalt (WC-Co) based cemented carbides exhibit a unique combination of properties, including high strength, hardness and Young's modulus. This makes them universally applicable for metal cutting, rock cutting and underground drilling operations in the oil industry. Conventional methods for sintering WC-Co involve high temperature and lengthy sintering cycles (*ca.* 24 h) to achieve high densification. Such conditions favour undesirable grain growth. A full sintering of WC-Co green body has been achieved using microwave processing in only 2 h¹⁵. The sintered products exhibit better mechanical properties than conventional parts. The microwave-sintering process exhibits an unprecedented improvement in abrasion resistance (15-30 %), erosion resistance (22 %) and corrosion resistance in 15 % nitric acid (20 times) without noticeable loss in hardness or fracture toughness. These improvements in the properties are believed to be caused by the fine microstructure, uniform cobalt-phase distribution and pure cobalt-phase at the grain boundaries in the microwave-sintered samples¹⁶. Commercial WC-Co parts have been fabricated successfully using microwave technology.

Multilayer ceramic capacitors (MLCCs) are used in almost all electronic devices. Microwave sintering of nickel-electrode multilayer ceramic capacitors has been conducted in an intermediate reducing atmosphere (oxygen partial pressure of *ca.* 10^{-6} atm). At a temperature of *ca.* 1250 °C, X7R multilayer ceramic capacitor chips are well sintered, which results in dense and uniform parts without cracks¹⁷.

Microwave energy has been used to melt and re-solidify oxide and non-oxide refractory ceramic eutectic compositions in yttrium aluminum garnet ($\text{Al}_2\text{O}_3 - \text{Y}_3\text{Al}_5\text{O}_{12}$; YAG) ($T_m = 1827$ °C) and boron carbide-titanium boride ($\text{B}_4\text{C}-\text{TiB}_2$) ($T_m = 2310$ °C) systems in a multimode 2.45 GHz microwave furnace¹⁸. Microwave experiments show a stability of eutectic melt temperature and the uniformity of subsequent eutectic

microstructure across the sample diameter during the re-solidification.

Microwave sintering of metallic materials

Until 2000, microwave processing of materials mostly had been confined to ceramic, semi-metallic, inorganic and polymeric materials. The main reason for this was misconception that all metals reflect microwaves and/or cause plasma formation. Hence, they could not be heated in a microwave field. It has been proved that all metallic materials in powder form do absorb microwave radiation at room temperature and can be sintered effectively. Even bulk metals, if preheated to ~400 °C, also begin coupling in a microwave field and are heated rapidly. Many recent reports have successfully demonstrated that a wide variety of metals and alloys including refractory metals, ferrous alloys and tungsten heavy alloys can be sintered to high densification with better properties using microwave energy. Recently, attempts to extract molybdenum from molybdenum sulfide (MoS₂) ore have been successfully extracted by direct use of microwave energy in an argon atmosphere in a single-step process¹⁹. The microwave process transforms the ore directly to pure metal in one-tenth of the process time. Molybdenum nanopowders also have been sintered to 99 % of theoretical density at 1400 °C in 0.5 h, whereas conventional processing requires 1400 °C for 10 h to obtain 98 % of theoretical density. The first attempt of microwave sintering of powdered metals was reported²⁰ in 1999. Many commercial powdered-metal components of various compositions including iron and steel, copper, aluminum, nickel, molybdenum, cobalt, titanium, tungsten, tungsten carbide, tin and their alloys also have been sintered using microwaves²¹⁻²³.

Future prospects

The future of microwave technology is very promising. New microwave high-temperature system manufacturers in China, Japan and the United States are expected to dominate and change the scene during the next some years. In fact, all the successes so far achieved have been with continuous microwave processing systems for specialty materials, such as cemented carbides, ferrites, varistors and metal products. The coming decade will witness more such systems to be built for many other materials and products. There are many other areas where microwave technology will be applied in the future because of its selective heating of powdered metal and highly absorbing ceramics.

Conclusion

Significant developments have been taken in the field of microwave processing of materials in the past decades. 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 product 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. Also perovskite type ceramics (CCTO) have been synthesized successfully by microwave heating with a relatively low energy consumption and short time compared with conventional synthesis.

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REFERENCES

1. D. Agrawal, J. Cheng, Hu Peng, L. Hurt and K. Cherian, *Am. Ceram. Soc. Bull.*, **87**, 3 (2009).
2. K.H. Brosnan, G.L. Messing and D.K. Agrawal, *J. Am. Ceram. Soc.*, **86**, 1307 (2003).
3. J.P. Binner, B. Vaidyanathan and T. Carney, *Adv. Sci. Technol.*, **45**, 835 (2006).
4. B. Vaidyanathan, A.P. Singh, D.K. Agrawal, T.R. Shrout and R. Roy, *J. Am. Ceram. Soc.*, **84**, 1197 (2001).
5. M.D. Mathis, Ph.D. Thesis, Pennsylvania State University, University Park, PA, USA (1997).
6. D. Agrawal, R. Raghavendra and B. Vaidyanathan, US Patent 6,399,012 (2002).
7. J. Cheng, D.K. Agrawal and R. Roy, *Am. Ceram. Soc. Bull.*, **79**, 71 (2000).
8. Y. Fang, D.K. Agrawal, D.M. Roy and R. Roy, *Mater. Lett.*, **23**, 147 (1995).
9. Y. Fang, D.K. Agrawal, D.M. Roy and R. Roy, *Mater. Lett.*, **28**, 11 (1996).
10. J. Cheng, D. Agrawal, Y. Zhang and R. Roy, *Mater. Lett.*, **56**, 587 (2002).
11. J. Cheng, D. Agrawal, Y. Zhang and R. Roy, *J. Mater. Sci. Lett.*, **20**, 77 (2001).
12. J. Cheng, D. Agrawal, Y. Zhang and R. Roy, *J. Electroceram.*, **9**, 67 (2002).
13. H.T. Yu, H.X. Liu, D.B. Luo and M.H. Cao, *J. Mater. Proces. Technol.*, **208**, 145 (2008).
14. A.F.L. Almeida, P.B.A. Fechine, M.P.F. Graca, M.A. Valente and A.S.B. Sombra, *J. Mater. Sci.: Mater. Electron.*, **20**, 163 (2009).
15. J. Cheng, D.K. Agrawal, S. Komarneni, M. Mathis and R. Roy, *Mater. Res. Innovations*, **1**, 44 (1997).
16. D. Agrawal, A.J. Papworth, J. Cheng, H. Jain and D.B. Williams, In proceedings of 15th International Plansee Seminar, 2, p. 677 (2001).
17. Y. Fang, D. Agrawal, M. Lanagan, T. Shrout, C. Randall, M. Randall and A. Henderson, *Ceram. Transact.*, **150**, 359 (2004).
18. A.V. Polotai, J. Cheng, K. Dinesh, D.K. Agrawal, E.C. Dickey and S. Cytron, *Ceram. Eng. Sci. Proc.*, **28**, 5, 127-33 (2007).
19. P. Chhillar, D. Agrawal and J.H. Adair, *Powder Metall.*, **5**, 1, (2008).
20. R. Roy, D. Agrawal, J. Cheng and S. Gedevarishvilli, **399**, 668 (1999).
21. R.M. Anklekar, K. Bauer, D.K. Agrawal and R. Roy, *Powder Metall.*, **48**, 39 (2005).
22. P. Mishra, G. Sethi and A. Upadhyaya, *Metall. Mater. Trans.*, **B37**, 839 (2006).
23. M. Gupta and W.L.E. Wong, *Scr. Mater.*, **52**, 479 (2005).