Microwave sintering of ceramic materials

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Abstract. In the present study, the potential of microwave irradiation as an innovative energy-efficient alternative to conventional heating technologies in ceramic manufacturing is reviewed, addressing the advantages/disadvantages, while also commenting on future applications of possible commercial interest. Ceramic materials have been extensively studied and used due to several advantages they exhibit. Sintering ceramics using microwave radiation, a novel technology widely employed in various fields, can be an efficient, economic and environmentally-friendlier approach, to improve the consolidation efficiency and reduce the processing cycle-time, in order to attain substantial energy and cost savings. Microwave sintering provides efficient internal heating, as energy is supplied directly and penetrates the material. Since energy transfer occurs at a molecular level, heat is generated throughout the material, thus avoiding significant temperature gradients between the surface and the interior, which are frequently encountered at high heating rates upon conventional sintering. Thus, rapid, volumetric and uniform heating of various raw materials and secondary resources for ceramic production is possible, with limited grain coarsening, leading to accelerated densification, and uniform and fine-grained microstructures, with enhanced mechanical performance. This is particularly important for manufacturing large-size ceramic products of quality, and also for specialty ceramic materials such as bioceramics and electroceramics. Critical parameters for the process optimization, including the electromagnetic field distribution, microwave-material interaction, heat transfer mechanisms and material transformations, should be taken into consideration.

1. Introduction

Due to their advantages, ceramics have been extensively studied, marketed and used so far, starting from various raw materials and possessing specific characteristics for being serviceable in multiple environments. In ceramic industry as well as in powder metallurgy, sintering is one of the most important technological processes and has been developed for over 70 years. It takes places when packed particles are heated to a temperature where there is sufficient atomic motion to grow bonds between the particles. Driving force for the process is the particle surface tension leading to minimizing the surface area. Sintering mainly depends on the type of material under consideration, its melting temperature, particle size (volume, surface) and several other processing parameters. Fundamental mechanisms of the process include grain boundary diffusion, viscous flow, evaporation and recondensation. Sintering conditions determine the development of a microstructure to provide physico-mechanical and chemical properties required for the ceramic body. Solid-state sintering of clayey raw materials through conventional thermal treatment has long been considered for the

development of various ceramic materials and is traditionally a preferred manufacturing technique for industrial ceramics [1-9].

On the other side, microwave radiation is emerging as an innovative environmentally benign technology, widely employed in various fields, such as in green chemistry, biosciences, biomass processing, waste, sewage sludge and wastewater treatment (especially for oxidation/degradation of pollutants of poor biodegradability), synthesis of nanoparticles, processing of nanostructured composites (nanoconsolidation) and nanoporous materials, as well as in metallurgical processes including drying of agglomerations and reduction of ore concentrates. The goals are the reduction of processing time and equipment size to significant extent and also the increase of selectivity and product yield and purity in case of synthesis or purification reactions [10-20].

Particularly, microwave-assisted sintering can be an efficient, economic and valuable approach for eco-friendlier processing of various powdery oxide and non-oxide materials [21-24].

In the present study, an overview of the potential of microwave technology as viable and energy-efficient alternative to conventional heating procedures in ceramic manufacturing is attempted, by reviewing advances published in the scientific research literature in the field, and commenting on the advantages/disadvantages reported and also on future applications of possible commercial interest. It should be noted here that fast heating is required for sintering advanced ceramics, in order to avoid excessive grain growth that is detrimental to mechanical performance. The role of microwave processing conditions on the development of ceramic microstructures and properties is discussed and analyzed.

2. Microwave irradiation

Microwave irradiation can produce efficient internal heating, as energy is supplied directly and penetrates the material through molecular interaction with the electromagnetic field. Since energy transfer occurs at a molecular level, its interaction with a dielectric material results in translational motions of free or bound charges and rotation of the dipoles. The resistance of the induced motions causes heat losses, and thereby heat is generated throughout the material resulting in volumetric heating, thus reducing the processing time.

The power absorbed per unit volume, P (W m^{-3}), is expressed as follows (see Equation 1) [15]:

$$P = \sigma \, |E|^2 = 2 \, \pi \, f \, \varepsilon_0 \, \varepsilon'_r \, \tan\delta \, |E|^2 \tag{1}$$

where   E (V m^{-1}) is the magnitude of the internal field,
σ the total effective conductivity (S m^{-1}),
f the frequency (usually 2.45 GHz: industrial scientific and medical frequency)
ε_0 the permittivity of free space ($\varepsilon_0 = 8.86 \times 10^{-12}$ F m^{-1}),
ε'_r the relative dielectric constant and
$\tan\delta$ is the loss tangent.

The microwave field distribution within a ceramic body, and the effect on the material, is determined by the dielectric parameters (ε'_r and $\tan\delta$). Specifically, the dielectric constant measures the ability of a material to store microwave energy. The loss tangent provides an indication of how well a material can be penetrated by electric field and how it dissipates energy into heat [25].

3. Microwave sintering of ceramic materials

3.1. Bulk ceramics

Microwave processes can improve the densification efficiency and considerably reduce the processing cycle-time for rapid and uniform heating, especially of thick ceramic materials, thus resulting in substantial energy and cost savings. Hence, there is sufficient motivation to promote the use of microwaves in the sintering of various ceramics, and also glass-ceramics, nano-ceramics and bio-

ceramics, and to investigate the effect of microwave sintering conditions on the microstructure, phase composition and properties of the materials produced compared to conventionally sintered ones.

Significant developments have already been made in the use of microwaves in the sintering of ceramics. Particularly for the development of advanced ceramics, very fast sintering is required to avoid grain growth. By microwave heating, densification of ceramics can be attained in a very short time. Rapid and enhanced consolidation achieved upon microwave processing of ceramics should mainly be attributed to a microwave effect, assumed to be a non-thermal phenomenon and possibly explained by the concentration of electrical energy into the closed pores of green (non-sintered) ceramics [26]. However, other study on a microscopic scale of microwave sintering of compacted ceramic powders shows that local electric fields disproportionately intense close to grain boundaries can be generated and rough surfaces due to strong focusing can be produced, which can lead to a highly non-uniform energy deposition [27]. Therefore, in order to increase the understanding and control the sintering progress, by determining the optimal parameters of microwave irradiation for obtaining an expected microstructure, an attractive method was proposed for in-situ shrinkage measurement of a microwave irradiated sample during sintering in a specific microwave cavity appropriately designed. The sintering kinetics are found to be extraordinarily fast for achieving satisfying density, when microwave sintering of CuO was chosen as a test material [27]. Furthermore, in order to design suitable cavity and cells for both hybrid and direct microwave sintering of fine-grained pure α-Al_2O_3 powder and to allow reliable comparison with conventional sintering, finite element simulation was employed. A significant enhancement of densification under microwave irradiation during the first and intermediate stages is evidenced upon sintering the alpha alumina powder compacts along an identical thermal cycle, without use of any doping element to initiate heating [29]. On the other hand, no difference between the two heating modes during the late stages of sintering is indicated, when comparing densification and grain growth of microwave sintered Al_2O_3 ceramic materials to conventionally sintered ones, by analyzing microwave power absorption of alumina ceramics and heating profiles for both sintering modes [30]. In nanostructured Al_2O_3 ceramics in particular, with regard to the annealing of nanoporous alumina-based membranes under microwave heating, the influence of microwave processing on mass transport phenomena and phase transformations is highlighted. Actually, faster mass transport, significantly depending on the microwave field intensity, is observed upon microwave sintering of alumina powder compacts. In addition, phase transformations can be characterized quantitatively and also a preferred orientation of pores in ceramics can be predicted [31].

The sintering process of glass powder (CaO-ZrO_2-SiO_2), microwave heated to produce a glass-ceramic material, is also accelerated in comparison to conventional sintering, although the densification and microstructural evolution studied during crystallization of the glass-ceramics obtained is not affected differently when compared to conventionally-treated ones, and exhibits a negligible porosity as a result of micropores [32].

It should further be noted that, for ceramics development, several secondary resources have also been microwave processed. In particular, after rapid microwave sintering of compacts composed of highly calcareous (Class C) lignite combustion fly ash and bottom ash for 30 min (at 1000°C), dense ceramic microstructures, mainly composed of gehlenite, quartz and kyanite, are achieved [33]. Also, microwave sintered (800-1000°C) siliceous (Class F) coal fly ash samples appear to be denser, and thus stronger, than conventionally sintered ones at the same temperature and time [34]. In order to reduce the volume of municipal solid waste incineration fly ash, microwave irradiation has better sintering efficiency than traditional sintering with electro-furnace (800-1100°C) for the stabilization and transformation of washed fly ash with calcium carbonate into ceramic blocks [35,36]. Moreover, rice husk ash, SiO_2-rich material rapidly sintered (800-1200°C) by microwave energy using a multi-mode system, is shown to contain SiO_2-cristolbalite and α-SiO_2 as major ceramic phases, with amount of crystalline silica phase increased after microwave sintering, leading to enhanced mechanical performance [37].

3.2. Bioceramics
Submicrometer tricalcium phosphate (β-TCP) powder produced in-situ by wet chemical precipitation, and sintered to obtain dense β-TCP ceramics by microwave technology for 15 min at 1100°C, shows a better densified microstructure with average grain size of 3μm, and higher hardness, than samples conventionally sintered for 2h at the same temperature, leading to the conclusion of a superior mechanical performance for the microwave sintered β-TCP powder [38]. Also, porous biphasic HAP/TCP bioceramics were obtained by microwave sintering of two microspherical agglomerated HAP powders. The porous microstructures of the obtained bioceramics consist in biphasic mixtures of HAP and a-TCP crystalline phases developed during the sintering process, while spherical intra-agglomerate pores and shapeless inter-agglomerate pores are detected. The microstructure obtained appears to have only a minor effect on the indentation fracture toughness [39]. The potential of a microwave heating was further demonstrated in the sintering of bioceramics from stabilized zirconia (3Y-TZP), another excellent susceptor of microwave energy, due to its large concentration of point defects. In fact, the mechanical properties including hardness and fracture toughness of high density and ultrafine microstructures with monomodal grain size distribution resulting from short time processing in a domestic microwave oven, compare very well with 3Y-TZP ceramics conventionally sintered for a long duration [40].

3.3. Electroceramics
Microwave sintering has also widely been considered for processing electroceramics, a specific category of ceramic materials primary used for their electrical properties, including ferroelectric materials, ferrites, solid electrolytes and piezoelectrics:

In particular, microwave sintering of strontium bismuth titanate powder prepared by solid state route leads to higher densification (97% of the theoretical density), fine microstructure, and good mechanical and ferroelectric properties in much shorter duration of time, in comparison to that heated in conventional furnaces [41]. Calcium-doped barium titanate ($Ba(1-x)Ca_xTiO_3$) ferroelectric ceramics synthesized by microwave processing technique, optimized at 1100°C for 1h to form a single perovskite phase, show dense and homogeneous packing of sub-micrometer size grains [42]. Also, preparation of SiO_2 added $BaTiO_3$ ceramics was successfully attained by microwave sintering at low temperatures. A homogeneous microstructure with small grains appears for 0.5wt% SiO_2 addition, while an enhanced densification and appearance of $Ba_2TiSi_2O_8$ second phase with columnar grains for further increase of SiO_2 addition to 1and 2wt% are stated, leading to the improvement of the electrical break-down strengths [43].

Lead zirconate titanate are ceramic perovskite materials showing marked piezoelectric effect, being used in a number of practical applications in the area of electroceramics. Higher density and more uniform grain distribution are found for ceramic pellets from lanthanum-doped PZT fine powders (PLZT) processed by high energy mechanical ball milling, and then microwave sintered at 1150°C for much shorter sintering time than for conventionally sintered ones. Comparable dielectric and piezoelectric properties are obtained for microwave sintered PLZT ceramics [44].

For lanthanum gallate electrolytes, which generally present a superior ionic conductivity at intermediate temperatures than YSZ ones, especially when lanthanum is substituted by alkaline rare earths such as strontium and magnesium (LSGM), activated microwave sintering at lower temperatures makes possible to overcome problems related to grain coarsening and secondary phases formation occurring at elevated temperatures upon conventional heating. Hence, dense stable electrolyte layer for applications in intermediate temperature-solid oxide fuel cells are developed, due to heat generation in situ, leading to faster sintering kinetics [45].

Furthermore, microwave sintering can be a promising technology even for the development of materials such as MnZn-ferrites to be used in high magnetic permeability applications, as it results to higher magnetic permeability values, higher densities and coarser microstructures, in comparison to conventional firing [46-48].

4. Concluding remarks

- Microwave sintering emerges as a new field of processing and synthesis of ceramic materials, and appears to be a powerful method for sintering advanced ceramics in a short time.
- Significant progress in application and commercialization of microwave technology, particularly in specialty ceramics processing, has already been made.
- Comparison with conventional sintering reveals a number of benefits of microwave processing, in terms of microstructural design and physico-mechanical properties.
- Rapid heating with accelerated densification is enabled, while excessive grain coarsening is limited, leading to higher densities and uniform and fine-grained microstructures, with enhanced mechanical performance.
- By microwave sintering of ceramic materials, significant temperature gradients between the surface and the interior that are frequently encountered upon conventional sintering of a ceramic body at high heating rates can be avoided, which is of importance especially for manufacturing large-size ceramic products of quality.
- The distribution of the electromagnetic field, the interaction between microwaves and the material, heat transfer mechanisms and material transformations appear to be critical for the process optimization.

References

[1]   Kingery W D, Bowen H K and Uhlmann D R 1976 *Introduction to Ceramics* 2nd ed. (New York: Wiley)
[2]   Gotoh K, Masuda H and Higashitani K 1997 *Powder Technology Handbook* 2nd ed., rev. and expanded (New York: Marcel Dekker, Inc.)
[3]   Matrenin S V, Ovechkin B B, Zenin B S and Tayukin R V 2015 *IOP Conference Series: Materials Science and Engineering* **93** (1) 012040
[4]   Domopoulou A, Spiliotis X, Koukouzas N, Gudulas K, Papapolymerou G and Karayannis V 2014 Proc. IOC – 46th International October Conference, Bor Lake, Serbia
[5]   Kirchhof M J, Forster H, Schmid H-J and Peukert W 2012 *J. Aerosol Sci.* **45** 26–39
[6]   German R M 2010 *Crit. Rev. Solid State* **35** 263–305
[7]   Olevsky E A, Tikare V and Garino T 2006 *J. Am. Ceram. Soc.* **89** (6) 1914–1922
[8]   Ch'ng, H N and Pan J 2007 *Acta Mater.* **55** 813–824
[9]   Olevsky E A 1998 *Mat. Sci. Eng. R.* **23** 41–100
[10]   Motuzas J, Drobek M, Diniz da Costa J C and Julbe A 2014 *Chem. Eng. J.* **240** 155–160
[11]   Bassyouni F A, Abu-Bakr S M and Rehim M A 2012 *Res. Chem. Intermed.* **38** 283–322
[12]   Remya N and Lin J-G 2011 *Chemical Eng. J.* **166** 797–813
[13]   Budarin V L, Clark J H, Lanigan B A, Shuttleworth P and Macquarrie D J 2010 *Bioresource Technol.* **101** 3776–3779
[14]   Leonelli C and Mason T J 2010 *Chem. Eng. Process.* **49** (9) 885–900.
[15]   Das S, Mukhopadhyay A K, Datta S and Basu D 2009 *Bull. Mater. Sci.* **32** (1) 1–13
[16]   Yuen F-K and Hameed B H 2009 *Adv. Colloid Interfac.* **149** 19–27
[17]   Bai C, Ren W, Qiu G, Hu M, Chen D and Wen L 2007 *ISIJ Int.* **47** (4) 528–532
[18]   Viswanathan V, Laha T, Balani K, Agarwal A and Seal S 2006 *Mat. Sci. Eng. R.* **54** 121–285
[19]   Tompsett G A, Conner W C and Sigfrid Yngvesson K 2006 *Chem. Phys. Chem.* **7** 296 – 319
[20]   Appleton T J, Colder R I, Kingman S W, Lowndes L S and Read A G 2005 *Appl. Energ.* **81** 85–113
[21]   Zhao X, Yan L and Huang K 2011 in "Advances in Induction & Microwave Heating of Mineral & Organic Materials" 28–48
[22]   Oghbaei M and Mirzaee O 2010 *J. Alloy. Compd.* **494** (1-2) 175–189
[23]   Mascarenhas J, Marcelo T, Inverno A, Castanho J and Vieira T 2008 *Metal Powder Report* **63** (11) 12–15
[24]   Riedel H and Svoboda J 2006 in "Simulation of Microwave Sintering with Advanced Sintering

Models. Advances in Microwave and Radio Frequency Processing", edited by M. Willert-Porada (Springer, New York) 210–216

[25] Al-Harahsheh M and Kingman S W 2004 *Hydrometallurgy* **73** 189–203

[26] Agrawal D K 1998 *Curr. Opin. Solid St. M.* **3** (5) 480–486

[27] Birnboim A, Calame J P and Carmela Y 1999 *J. Appl. Phys.* **85** (1) 478–482

[28] Marinel S and Savary E 2009 *J. Mater. Process. Tech.* **209** 4784–4788

[29] Croquesel J, Bouvard D, Chaix J-M, Carry C P and Saunier S 2015 *Mater. Des.* **88** 98–105

[30] Chatterjee A, Basak T and Ayappa K G 1998 *AIChE J.* **44** (10) 2302–2311

[31] Bykov Y V, Egorov S V, Eremeev A G, Kholoptsev V V, Plotnikov I V, Rybakov K I, Semenov V E and Sorokin A A 2010 *Powder Metall. Met. C+*, **49** (1-2) 31–41

[32] D'Arrigo M C, Siligardi C, Leonelli C, So J Y and Kim H S 2002 *J. Porous Mat.* **9** 299–305

[33] Karayannis V G, Moutsatsou A K and Katsika E L 2013 *J. Ceram. Process. Res.* **14** (1) 45–50

[34] Fang Y, Chen Y, Silsbee M R and Roy D M 1996 *Mater. Lett.* **27** 155–159

[35] Chen C-L, Lo S-L, Kuan W-H and Hsieh C-H 2012 *Sustain. Environ. Res.* **20** (6) 381–385

[36] Chou S-Y, Lo S-L, Hsieh C-H and Chen C-L 2009 *J. Hazard. Mater.* **163** 357–362.

[37] Makul N and Agrawal D K 2010 *Mater. Lett.* **64** 367–370

[38] Mirhadi B 2014 *Sci. Sinter.* **46** (2) 185–193

[39] Veljovic Dj., Palcevskis E, Dindune A, Putic S, Balac I, Petrovic R and Janackovic Dj. 2009 *J. Mater. Sci.* **45** 3175–3183

[40] Upadhyaya D D, Ghosh A, Dey G K, Prasad R and Suri A K 2001 *J. Mater. Sci.* **36** 4707–4710

[41] Angalakurthi R and Raju K C J 2011 *IOP Conference Series: Materials Science and Engineering* **18** (Symposium 6) 092028

[42] Sonia, Patel R K, Prakash C and Kumar P 2011 *J. Ceram. Process. Res.* **12** (6) 634–639

[43] Yan Y, Liu L, Ning C, Yang Y, Xia C, Zou Y, Liu S, Wang X, Liu K, Liu X and Liu G 2016 *Mater. Lett.* **165** 135–138

[44] Kumar A, Reddy Emani S, Bhanu Prasad V V, James Raju KC and James A R 2016 *J. Eur. Ceram. Soc.* **36** (10) 2505–2511

[45] Kesapragada S V, Bhaduri S B, Bhaduri S and Singh P 2003 J. Power Sources **124** (2) 499–504

[46] Tsay C-Y, Liu K-S, Lin I-N 2001 *J. Eur. Ceram. Soc.* **21** (10-11) 1937–1940

[47] Thota S, Kashyap S C, Gupta H C, Nath T K 2014 *Journal of Superconductivity and Novel Magnetism* **28** (1) 131–136

[48] Tsakaloudi V, Papazoglou E and Zaspalis V T 2004 *Mat. Sci. Eng. B* **106** 289–294