Making the Case for Scaling up Microwave Sintering of Ceramics

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The densification and sintering of ceramics using microwaves was first reported in the mid-1960s. Today, the reduced carbon footprint of this process has renewed interest as it uses less energy overall compared to conventional process heating/furnaces. However, scaling-up and commercializing the microwave sintering process of ceramics remains a formidable challenge. As a contactless method, microwave sintering offers geometric flexibility over other field-assisted sintering processes. Yet, the inability to address multi-scale, multi-physics-driven heterogeneities arising during microwave coupling limits discussions about a future scale-up process. We make the case here that unlike 60 years ago, new advances in multiscale computational modeling, materials characterization, control systems and software open up new avenues for addressing these challenges. More importantly, the rise of additive manufacturing techniques demands the innovation of sintering processes in the ceramics community for realizing near-net-shaped and complex parts for applications ranging from medical implants to automotive and aerospace parts.

1. Introduction

Ceramic materials possess specific characteristics that make them well-suited to be used in multiple settings.[1-2] Ceramics have been processed and used for various cutting-edge applications in automotive, aerospace, biomedical industry and many other sectors.[3-6] Traditionally, ceramic parts were sintered using high-temperature furnaces and this consumed a lot of resources in terms of time and energy. To overcome this issue, various field-assisted sintering techniques like spark plasma, flash and microwave sintering were developed as a green alternative to conventional sintering processes.[7]

In particular, microwave-assisted sintering has come forward as an economic, energy-efficient and rapid processing technique to sinter various ceramic parts.[8] However, the challenges associated with scaling up of microwave-assisted sintering of solid ceramic structures and the recent advancements in the state-of-the-art technologies that can address the challenges, is not comprehensively discussed in existing review articles. Our article addresses this gap by reviewing the various challenges associated with scaling up the ceramic microwave sintering process and the advancements in various fields that can help in potentially addressing these challenges (**Figure 1**).

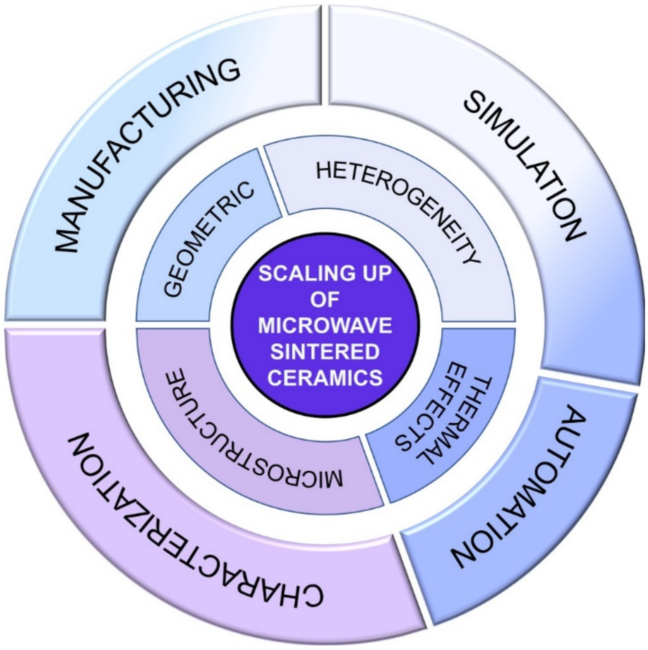

Figure 1. Overview of challenges associated with scaling up microwave sintered ceramics (inner ring) and advancements in various fields that can help address these challenges (outer ring).

In this review, we discuss the background of microwave sintering and its development. We then explore the challenges associated with sintering of ceramics using microwaves, particularly in regard to scaling up the samples. We expound the challenges corresponding to the sample geometry and microstructure, heterogeneity in material properties, and thermal effects arising during microwave sintering. To address these challenges, we discuss about the advancements in simulation of microwave-assisted sintering process along with advancements in manufacturing, material characterization and automation of the microwave sintering process in order to realize the possibility of scaling up of ceramic parts (**Figure 1**). These advancements help in understanding the current capabilties of the state-of-the-art technologies.

In particular, coupled electromagnetic-thermal modeling tools can now predict heterogeneities as a function of field intensity distribution inside the microwave reactor by simulating the microwave sintering process.[9] Frequency and temperature-dependent measurements of dielectric permittivity are now available and can be leveraged to understand the simulated temperature gradients over the scaled-up ceramic thereby building a new foundation for tackling the all-important hot-spot formation problem.[10] Results from such simulations can guide experimental optimization of sintering parameters,

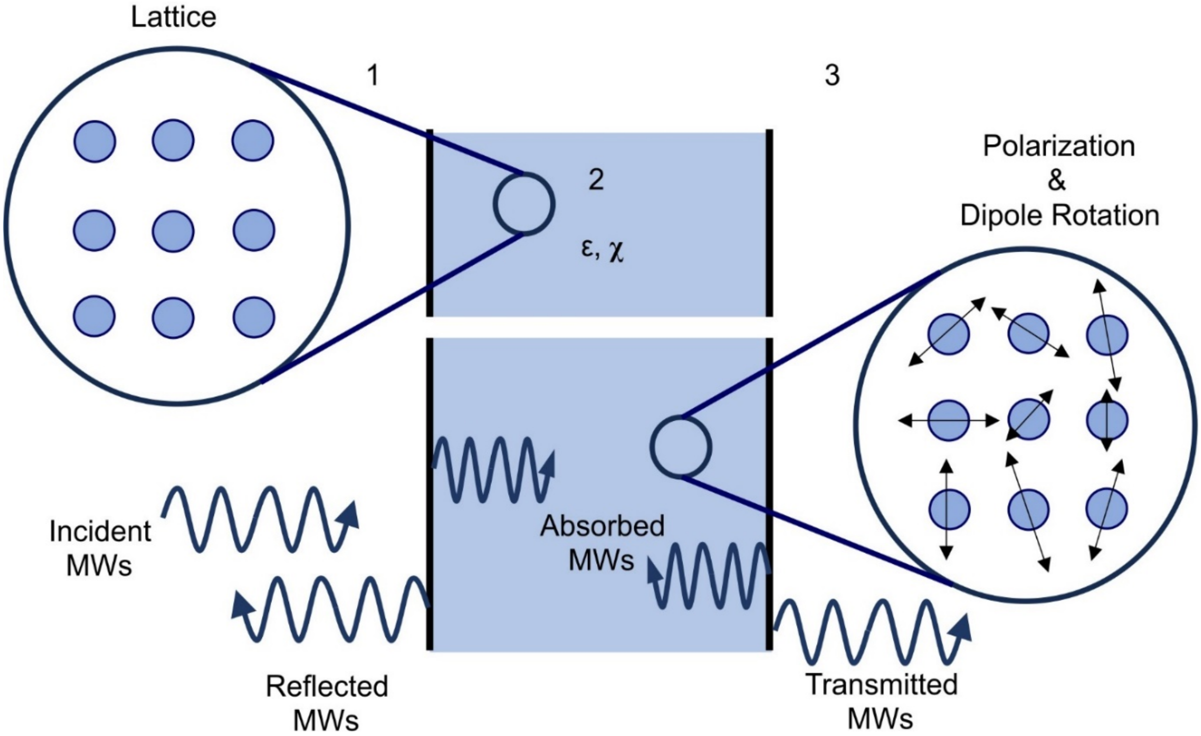

Figure 2. Underlying heating mechanism of ceramic dielectrics due to microwaves (MWs) – ceramic interaction when MWs are (1) incident on the ceramics with a fraction getting reflected, (2) absorbed, and (3) the rest transmitted.

such as microwave power, temperature, frequency, polarization as well as waveguide geometry and susceptor material. These combinatorial studies will eventually arrive at homogeneous heating environments around the large ceramic parts. Metallurgical techniques like x-ray diffraction and scanning electron microscopy can investigate the phase transformations and microstructural changes in the ceramic samples during sintering. These characterization tools can showcase the benefits of microwave heating, in terms of, achieving the desired chemical compositions and reducing the phase transition temperatures.[11-12] Moreover, recent spectacular advancements in material characterization techniques such as high energy (>80 keV) synchrotron x-rays for in-situ monitoring and 3D computed tomography can simultaneously map the multiscale structure of large ceramic samples during these sintering studies.[13-14] Automation tools and control software can monitor, adjust and track process parameters for reliable thermal management in a closed power loop.[15] Furthermore, advancements in additive manufacturing techniques allow to create ceramic samples with complex morphologies and multiple materials that are typically difficult and time-consuming to make.[16] Together, our review article will make the case that the time is now for scaling up the ceramic microwave sintering process if we can leverage and invest in these new research directions. The growing industrial microwave heating market of USD 970.27 million in 2022 also supports the scaling up case with a promising future.[17]

2. Background of microwaves & microwave sintering

2.1. Microwave-assisted heating

Microwaves are electromagnetic radiation, comprised of electric ($\vec{E}$) and magnetic ($\vec{B}$) fields, having wavelengths in the range of 1 mm to 1 m.[18] The possibility of using microwaves for heating applications was discovered in the 1940s when experiments were being conducted with magnetrons.[19] Due to the interaction of the microwave radiation with the ceramic material, energy transfer takes place at a molecular level. The electric field interaction results in polarization and dipole rotation of the molecules of the ceramic material subjected to microwaves, causing volumetric heat generation in the ceramic material and resulting in drastically reduced heating time.[18] The heating effect of the microwaves on the ceramic material due to its electric field component is determined by the material's dielectric properties such as complex dielectric permittivity (ϵ) and susceptibility (χ) (**Figure 2**).[20] The heating effect of the microwaves on the ceramic material due to its magnetic field component in the form of hysteresis loss, eddy current loss and residual loss is negligible as ceramics are typically non-magnetic.[21]

The complex dielectric permittivity of the ceramic material has a real component (ϵ') and an imaginary component (ϵ'') as shown in **Equation 1**.[20]

$$\epsilon = \epsilon' - i\epsilon'' = \epsilon_0(\epsilon_r{}' - i\epsilon_r{}'') \quad \textbf{(1)}$$

where ϵ_0 is the dielectric permittivity of free space, $\epsilon_r{}'$ is the real part and $\epsilon_r{}''$ is the imaginary part of the complex relative permittivity. The real component is a measure of electric charge stored in the material and the imaginary component is a measure of the dielectric loss.

The susceptibility determines the polarizability of the ceramic material when subjected to an electric field as shown in **Equation 2**.[20]

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$$\vec{P} = \epsilon_0 \chi \vec{E} \quad \textbf{(2)}$$

where $\vec{P}$ is the polarization of the ceramic material.

Therefore, the constitutive relation for the microwave-ceramic interaction is as shown in **Equation 3**.

$$\vec{D} = \epsilon_0 \vec{E} + \vec{P} = \epsilon_0 (1 + \chi) \vec{E} \quad \textbf{(3)}$$

where $\vec{D}$ is the electric displacement field induced in the material.

The amount of heating produced due to microwave-ceramic interaction is determined by the dielectric loss tangent (tan δ) of the ceramic material which comprises of dielectric heating and ohmic heating respectively as shown in **Equation 4**,[20]

$$\tan \delta = (\epsilon''/\epsilon') + (\sigma/2\pi f \epsilon') \quad \textbf{(4)}$$

where σ is the electrical conductivity of the ceramic material and f is the operating frequency of the microwave. Ohmic heating within the ceramic material is possible as a result of electric current density $\vec{J}$, where

$$\vec{J} = \sigma \vec{E} \quad \textbf{(5)}$$

2.2. Microwave Sintering

Sintering is a thermal process comprising of two aspects, densification and coarsening, each of which is driven by the reduction of the total interfacial surface energy. Densification occurs due to mass transport mainly during grain boundary diffusion and lattice diffusion whereas coarsening happens primarily due to mass transport during surface diffusion. Microwave sintering of ceramics is a thermal dielectric heating process developed as a potential alternative to conventional ceramic sintering. In this process, ceramics are heated by means of microwave irradiation as discussed in section 2.1 to sinter the ceramic green parts. The effects of microwave irradiation on the sintering of ceramics can be broadly categorized into two effects, thermal and non-thermal. Microwave irradiation heats the ceramic sample volumetrically up to a penetration or skin depth (δ) which depends on the wavelength of the microwave radiation (λ) and the real (ϵ_r') and imaginary (ϵ_r'') part of the complex relative permittivity of the ceramic material according to the relation,

$$\delta = \frac{\lambda}{2\pi (2\epsilon_r')^{1/2}} \left\{ \left[1 + \left(\frac{\epsilon_r''}{\epsilon_r'} \right)^2 \right]^{1/2} - 1 \right\}^{-1/2} \quad \textbf{(6)}$$

This volumetric heating causes thermal effects such as thermal gradients and hotspots, resulting in uneven and localized heating of the ceramic sample. Additionally, microwave irradiation is hypothesized to trigger non-thermal effects that include changes in the diffusion activation energy, anisotropy and phase transformation temperatures.[20]

High temperature processing of ceramics started in the mid-1960s and advanced microwave sintering techniques were introduced for refractory materials.[22] The feasibility of microwave sintering of oxide ceramics such as alumina, zirconia, yttria was first experimentally demonstrated in 1980s.[20] In 1987, the microwave heating mechanism of porous ceramics was qualitatively modeled by studying the effects of electric field at a lossless dielectric interface.[20] By 1996, it was shown that a higher densification could be achieved in ceramics using microwave sintering as compared to conventional sintering.[23-25] Since then, the viability of microwave sintering of various functionally and structurally enhanced ceramic composites and cemented carbides was successfully demonstrated along with the development of advanced modeling of microwave sintering process.[20][22]

At present, a hybrid microwave sintering technique is commonly employed wherein a specific proportion of conventional heating elements-based resistive heating and microwave heating are coupled.[26] In addition, a hybrid microwave sintering approach is also carried out for the fabrication of electro-ceramics such as TiO_2 and ZnO. In this approach, microwave sintering at lower temperatures results in the densification of ceramic samples prepared after mixing the ceramic powder with a transient liquid phase such as deionized water, acidic or basic aqueous solutions.[27] An alternate hybrid microwave sintering is also carried out using a combination of microwave heating and infrared heating from susceptors surrounding the ceramic sample. This technique helps in sintering ceramics with low dielectric loss by means of infrared radiation-based heating at lower temperatures using susceptors made of materials having high dielectric loss. This technique also ensures a finer microstructure post-sintering as compared to conventional as well as microwave sintering individually. The grain growth or coarsening of the ceramic grains is restricted when using the hybrid microwave sintering technique at lower temperatures due to a faster ramping rate.

2.3. Comparison with other Field-Assisted and Conventional Sintering Techniques

The current ceramic industry depends on conventional sintering processes for densifying scaled up ceramic parts. Multiple batches of complex shaped ceramic parts can be simultaneously heated in the high temperature conventional furnaces. However, a higher energy consumption due to a longer heating time at a higher temperature in the conventional furnace increases the total production cost. Hence, the need for a more eco-friendly, fast and energy efficient ceramic sintering process arises. Field-assisted sintering techniques, that use electric and/or electromagnetic fields to sinter ceramic parts at high temperatures, have been developed which can be commercialized to address the conventional sintering limitations. Techniques such as spark plasma, flash and microwave sintering can densify the ceramic parts at high temperatures in lesser time (~10 seconds to 20 minutes) with a reduced energy consumption resulting in a reduced total production cost. Contact sintering methods such as spark plasma and flash sintering use graphite dies and electrodes respectively to sinter the ceramic parts. The small dies, which are a major cause in reducing the bulk material production, limit the geometric flexibility of these two electric field-assisted sintering techniques. Microwave sintering, being a contactless sintering technique, can volumetrically heat and sinter larger complex shapes efficiently through selective and rapid heating after microwave-ceramic coupling. The scaling

Table 1. Factors deciding the current potential of scaling up different field-assisted and conventional sintering techniques.

Technique	Commercialization	Geometry	Time	Cost	Productivity	Reference
Spark Plasma (SPS)	Rotary spark plasma sintering inspired on the high throughput rotary presses proposed	Complex shapes hard to produce due to the usage of die	Less sintering time (order of seconds)	Higher cost due to more power consumption (e.g., ~1050 kJ g^{-1} energy required to sinter $BaTiO_3$)	Limited bulk material sintering due to small dies (~120 SPS plates/day with multiple interchangeable die-sets)	[29-30][32]
Flash	A British company, Lucideon, prototyped a continuous furnace design for mass production	Complex shapes hard to sinter in this contact method requiring die and electrodes	Less sintering time (order of seconds)	Higher cost in field-assisted sintering (e.g., ~1050 kJ g^{-1} energy required to sinter $BaTiO_3$)	Limited bulk material sintering due to small dies (Like SPS, small number of samples in each run)	[28-29][33]
Microwave	28-30 GHz high power gyrotrons integrated into a complete self-contained system used for sintering	Altered complex shapes produced through selective and superheating	Less sintering time (order of minutes)	Less expensive due to less energy usage (e.g., ~540 kJ g^{-1} energy required to sinter $BaTiO_3$)	Reduced processing time due to volumetric heating (up to 27 whiteware ceramic pieces per worker/day)	[20][31]
Conventional	Commonly used scaled up sintering process around the world	Complex shapes sintering and production possible	Long sintering time (order of hours) due to a lower heating rate	Higher cost due to huge amount of energy consumption (e.g., ~2800 kJ g^{-1} energy required to sinter $BaTiO_3$)	Simultaneous heating of multiple batches (~40k kg/h average ceramic output in industrial ovens)	[31-32]

up potential of these field-assisted sintering techniques is explored in **Table 1**, along with a summary of the current commercialization milestones and the determinant factors that can present microwave sintering as an alternative to conventional sintering of ceramics.[20][28-34]

3. Challenges associated with scaling-up

With a growing industrial microwave heating market of USD 970.27 million in 2022,[17] microwave sintering promises a more efficient (as high as ~80-90% volumetric heat generation efficiency) and economic densification approach (with energy saving of ~90% over conventional sintering) for the ceramic industries.[35] Different ceramic oxides (such as SiO_2, Al_2O_3, $KAlSi_3O_8$, $CaCO_3$), carbides (such as SiC, B_4C) and nitrides (such as SiN, BN) can be sintered using microwaves at a faster dielectric heating rate that shows its scaling up potential,[36-40] and nominates microwave sintering as an alternative to conventional sintering. However, challenges associated with heterogeneous ceramic material properties, sample geometry, microstructure and thermal effects arising during microwave sintering limit the adoption of microwave sintering for manufacturing ceramics at the industrial scale and are discussed in detail below (**Figure 3**).

3.1. Challenges Associated with Heterogeneous Material Properties

In general, ceramics are dielectric materials with low electrical conductivity that are heated as a result of dipole rotation and ionic conduction when subjected to microwaves. Polar ceramics are characterized by a net non-zero dipole moment, due to first, the electronegativity difference between the bonding atoms and second, the orientation of the atomic bonds in the molecule. Under the microwave influence, they rapidly oscillate due to the changing direction of the electric field, resulting in thermal vibration and dipole rotation. As the molecular dipoles polarize and rotate, friction is experienced between the adjacent rotating molecules, thereby generating enough heat as dielectric loss that helps in sintering the polar ceramics beyond their necking temperature. Some of the non-polar ceramics such as SiC possess a higher electrical conductivity, thereby gets heated mainly due to ohmic heating as the dissolved charges in the ceramic sample (electron and ions) oscillate under the microwave influence and collide with the adjacent atoms or molecules generating heat.[41]

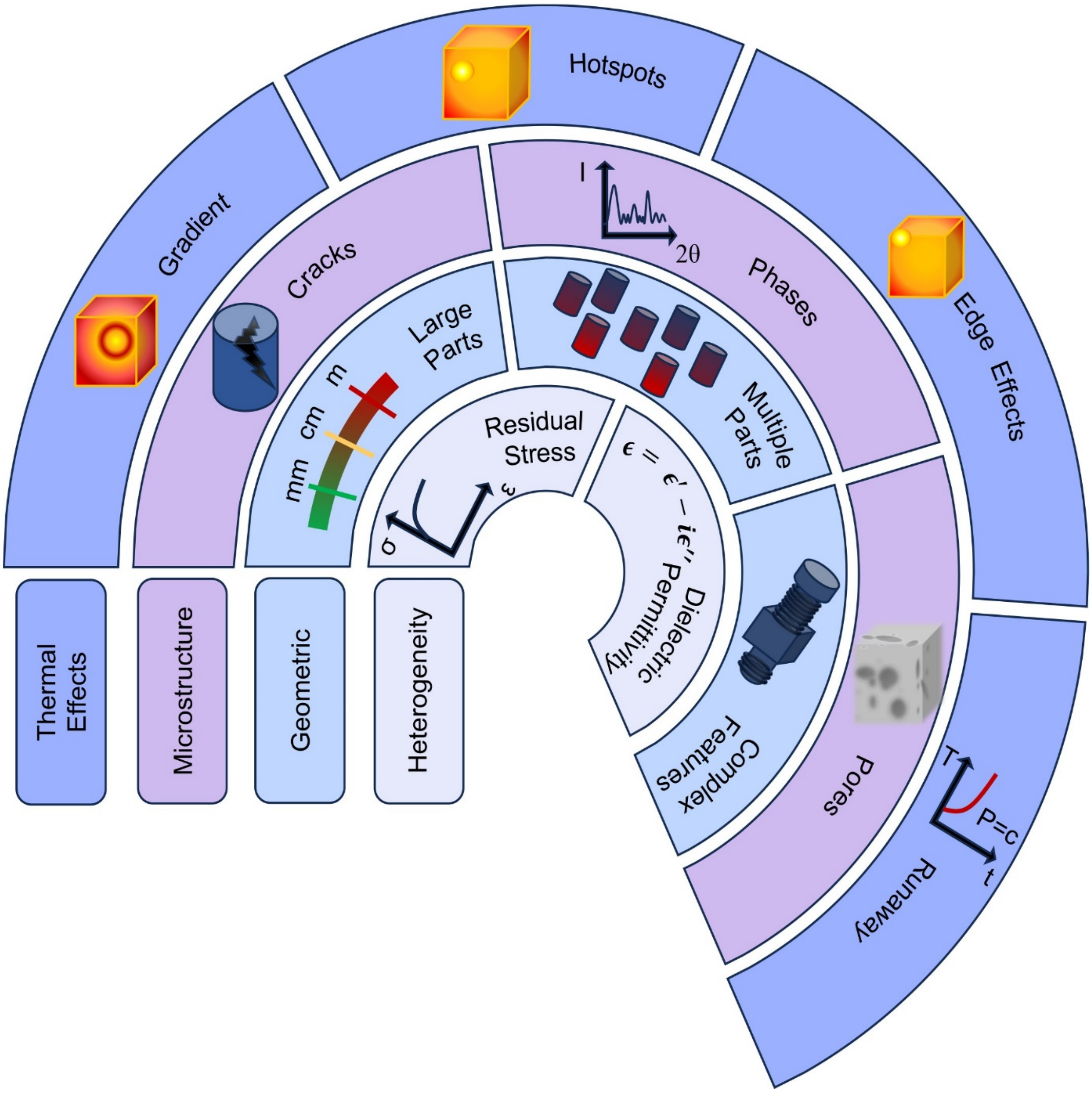

Figure 3. Challenges associated with scaling up of microwave sintering of ceramics. There are four main types of challenges associated with the ceramic sample being microwave sintered - heterogeneity of the ceramic material properties, complexity in the ceramic sample geometry, defects in the microstructure of the ceramic sample caused due to microwave sintering and thermal effects produced within the ceramic sample as a result of dielectric heating due to microwave radiation.

The polarization characteristics of the ceramic dielectrics are non-linear due to a wider particle size distribution and presence of impurities, arising as a result of heterogeneous mixing during ceramic powder synthesis.[42-43] As a result of this non-linearity, ceramic dielectric permittivity, a material property that determines the extent of polarization of the ceramic molecules under the influence of electric field, eventually turns non-homogeneous.

Furthermore, due to the variation in thermal expansion inside the ceramic part, residual stresses arise within the ceramic sample that affects the thermal vibration of the dipoles and dissolved charges inside the ceramic sample, resulting in a non-uniform dielectric loss from the ceramic sample.[44-46] In addition, ceramic material properties such as dielectric permittivity and dielectric loss are also non-linear function of sample temperature and microwave sintering frequency.[47-48] As a result, understanding the heterogeneous ceramic material properties such as dielectric permittivity and dielectric loss at different temperatures and microwave frequencies remains challenging.

3.2. Challenges Associated with Sample Geometry

Attempts have been made to microwave sinter a wide range of ceramic geometries at various length scales. However, exposing microwave energy to larger ceramic parts (order of 10 cm) will increase the sample dimension to penetration depth scale factor, mainly for low penetration depth ceramics such as graphite (~38 µm at 2.45 GHz microwave irradiation), resulting in uneven heating of the sample.[36] As described in section 2.1 and 2.2, the amount of microwave energy absorbed by the ceramic sample during volumetric heating depends on its volume, while the surface area of the ceramic part affects the total heat loss from the ceramic sample.[49] Larger ceramic parts with a higher volume to surface area ratio will exhibit higher temperature gradient during microwave sintering. Hence, for large and complex ceramic samples, localized and non-uniform microwave heating is a common problem resulting in early cracks and refractory losses.[50]

The inability to successfully microwave sinter multiple ceramic parts simultaneously is also a major factor limiting the scaling up of microwave sintering. Continuous microwave sintering of multiple ceramic samples in tunnel kilns needs synchronization of microwave power and samples' translational speed in order to reduce the difference between the work piece and tunnel inner wall temperature.[51]

3.3. Challenges Associated with Microstructure

Microwave sintering achieves ceramic sample densification at a significantly faster rate compared to conventional sintering.[52] The faster heating rapidly surpasses the dominant grain growth region which occurs at low temperatures and thus, microwave sintering typically results in finer grains within the sample microstructure, post-sintering.[53] However, due to the rapid heating and heterogeneity within the sample, thermal stresses can be induced leading to crack formation and propagation within the ceramic parts. As a result of the crack growth, ceramic part breaks during (or immediately after) the microwave sintering process. In addition, presence of solvents in the green samples that bind the ceramic particles, ceramic powder morphology, and the green part fabrication process parameters affect the ceramic sample porosity, which may lead to formation of stress concentration zones during the microwave sintering process.[54] This may eventually increase the brittleness of the final sintered ceramic sample, leading to its mechanical failure. Furthermore, localized heating may cause formation of thermal gradients and hotspots, resulting in a non-uniform temperature profile within the ceramic sample, thereby making pathways for formation of new material phases within the ceramic sample.

3.4. Challenges Associated with Thermal Effects

The sintering of ceramics using microwaves occurs as a result of volumetric heating of the ceramics as discussed in section 2.2. This heating of ceramic samples takes place at an extremely rapid rate (on the order of minutes) and depends on the penetration depth of the microwaves.[52] If the sample is larger in size or has complex features; if the sample or the microwave field is not homogeneous; or if the sample has a highly microwave absorbing material in a matrix of low microwave absorbing material, the penetration depth of the microwaves is limited. In general, a temperature gradient occurs within the sample because of the dynamic imbalance between the electromagnetic energy absorbed throughout the sample's volume and the energy loss from its surface. All these factors result in a non-uniform absorption of the microwave energy which causes non-uniform heating of the ceramic sample, thereby creating a thermal gradient within the sample. This non-uniform heating can also lead to localized heating within the sample creating areas of hotspots on the surface or within the bulk of the ceramic sample.

Another common problem in microwave sintering is “thermal runaway”, which is when the temperature of the sample increases rapidly with time. Here, under a fixed power of microwave irradiation, there is a sharp increase in the rate of heating of the sample. The temperature of the sample abruptly rises to extremely high values, leading to the melting and/or destruction of the sample. The development of thermal runaway is driven by the inverse relationship between the temperature and thermal conductivity of the sample. As the temperature of sample with lower thermal conductivity increases, heat inside the core is not easily lost due to conduction, unlike the sample’s surface where heat losses due to radiation can occur. As a result, enhanced heating of the core occurs, leading to more reduction of the sample’s thermal conductivity. Hence, the temperature of the sample increases at a faster rate due to this recursive loop of the temperature and thermal conductivity of the sample.[55] Furthermore, uneven heat generation and heat loss also drives thermal runaway, that depends on the material’s dielectric permittivity,[56] properties of thermal insulation package, and phase transformations during microwave sintering. Thermal runaway occurs concurrently with a rapid increase in material transport rates, leading to extremely fast sintering (within a minute). The underlying physical mechanism that triggers this phenomenon could involve the softening of grain boundaries or the formation of a transient liquid phase. This, in turn, enhances both mass transport within the sample and the absorption of microwaves by the sample.

4. State-of-the-art/ Advancements

Unlike 60 years ago, the recent advancements in the state-of-the-art technologies have increased their capabilities to address the different challenges associated with microwave sintering of ceramic parts. These advancements can be categorized into advancements in simulation of the microwave-assisted sintering, material characterization and automation of the microwave sintering process as discussed in sections 4.1, 4.2 and 4.3. Furthermore, the growing popularity of additive manufacturing has shown the potential to rapidly prototype complex ceramic parts. Capabilities of additive manufacturing of ceramics is discussed in section 4.4 which offers geometric flexibility to microwave sintering process.

4.1. Simulation

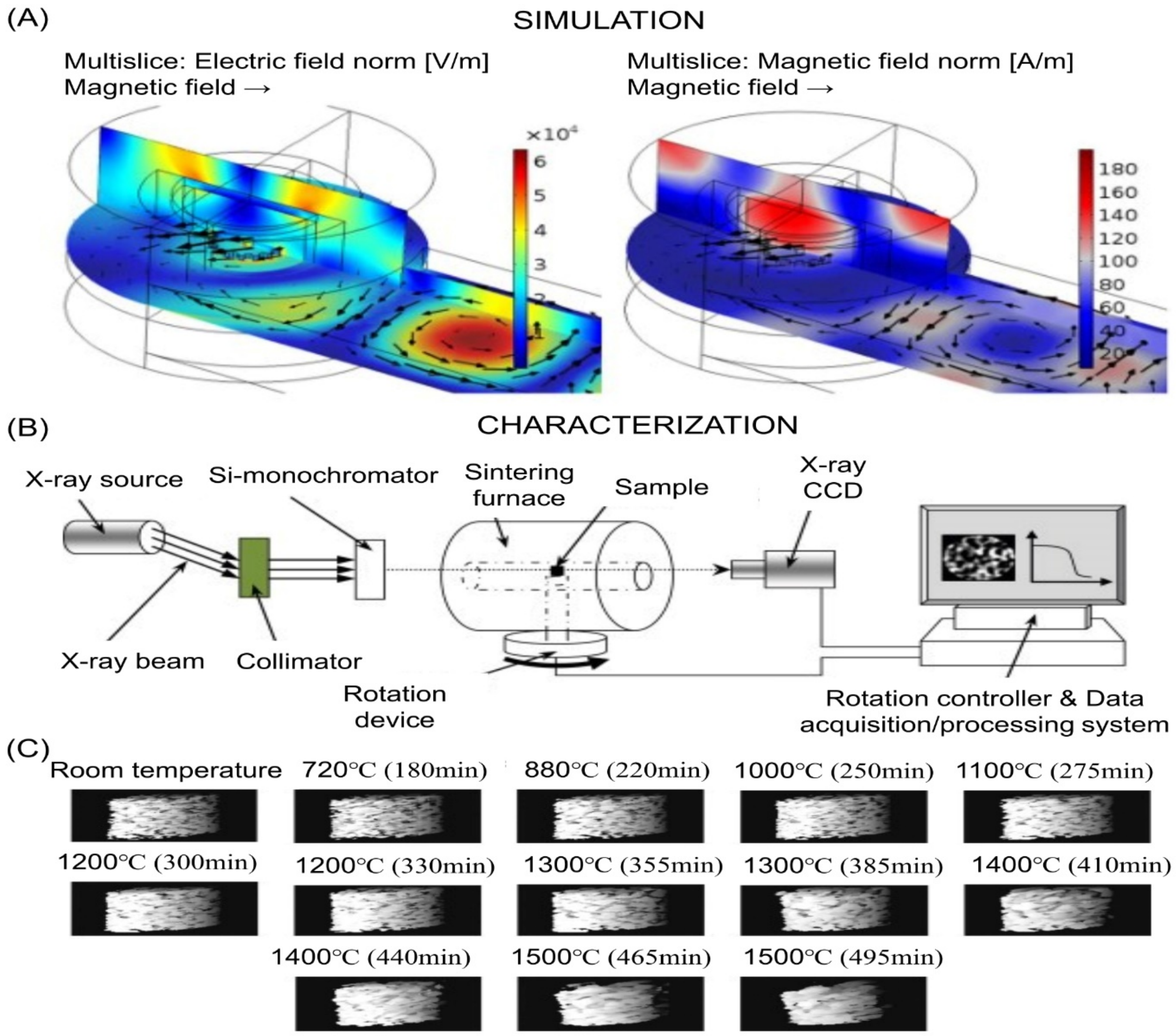

Figure 4. (A) Advancements in simulation of microwave sintering of ceramics. (Reproduced with permission conveyed through Copyright Clearance Center, Inc.[57] 2019, Journal of the American Ceramic Society.) (B) Advancements in characterization of ceramics during sintering. (C) In-situ micro-CT imaging of ceramic samples at different sintering temperatures and sintering times. (Reproduced with permission conveyed through Copyright Clearance Center, Inc.[58] 2010, Optics and lasers in engineering.)

The various challenges associated with microwave sintering of ceramic parts were discussed in sections 3.1, 3.2, 3.3 and 3.4. Overall, microwave sintering of ceramics is a developing field and as such, there are many variables that need to be understood thoroughly in order to optimize the microwave sintering process.[59] Simulations have been able to shed light on the physics of microwave sintering and have been able to develop theoretical and numerical models of the microwave sintering process.[60-61] Primarily, simulating the interaction of ceramic particles with microwaves, along with inter-particle interaction in the presence of microwaves have enabled us in understanding the temperature gradients and hotspot formation regions within the ceramic sample. The simulation of the microwave energy distribution in the reactor chamber provides us the flexibility of exploring the probable hotspot zones inside the reactor. Furthermore, the simulation results help us analyze what the microstructure of the ceramic sample may look like post-sintering and how the sample may densify.[62] These electromagnetic, thermal and multiphysics models and simulations are also capable of envisioning the temperature distribution within the microwave reactor chamber to predict the occurrence of thermal runaways (**Figure 4**A). Understanding results from these models and simulations will help in improving the processing capabilities of microwave sintering and may soon facilitate microwave sintering of large samples, samples with complex geometries, multi-material samples and multiple samples.

4.2. Characterization

Sintered ceramic samples are usually characterized to ensure the attainment of the predicted density, appropriate microstructure and phase of the sintered ceramic material. Furthermore, the sintered ceramic samples are also functionally tested to confirm if the desired mechanical properties like hardness and flexural strength are achieved. Various mechanical and metallurgical techniques like X-ray diffraction, scanning electron microscopy, energy-dispersive spectroscopy,[63-64] Vicker's micro-hardness, porosity measurement, Archimedes density measurement and flexural study are utilized in order to characterize the sintered ceramic samples.[65] However, these techniques analyze the samples after they have been sintered. In order to perform in-situ characterizations, techniques like x-ray diffraction, micro-CT and pair distribution function analysis have been utilized to collect data while the sample is being sintered (**Figure 4**B).[13-14][66-67] These characterizations give detailed information about how the ceramic material interacts with microwaves and the changes that take place in the microstructure of the ceramic samples as they sinter. Microstructural evolution and sintering phenomena can also be visualized using in-situ micro-computed tomography (micro-CT) imaging of ceramics undergoing sintering. As a result, formation of any defects such as pores, cracks and unexpected material phases due to thermal gradients, hotspots and runaways can be tracked at different sintering temperatures and sintering times (**Figure 4**C). Moreover, in-situ monitoring using pair distribution function provides information about atomic-scale defect generation by tracking atomic displacement during the field-assisted sintering processes such as flash sintering.[66] These techniques will be substantially useful in creating improved microwave sintering setups that are capable of uniformly sintering complex geometries at various length scales and in higher quantities.

4.3. Automation

Over the last 15 years, attempts have been made to automate the microwave sintering process for controlling the microwave-ceramic interaction in a better way.[20] Challenges associated with thermal effects as discussed in section 3.4 can be avoided using a feedback loop-based microwave power controller. Traditionally, magnetron-based microwave reactors have been automated to address these challenges. Multimode frequencies-based microwave reactors are also used to ensure resonant conditions inside the reactor chamber resulting in maximum microwave power absorption inside the ceramic material. Recently, 24 GHz microwaves produced using high power gyrotron systems are being used to irradiate the ceramic samples as a focused wave beam for localized rapid densification.[15] Temperatures at the different locations on the ceramic sample surface and core are measured using fiber optic thermocouple sensors.[68] Unlike conductive metal thermocouples which can experience arcs or otherwise perturb the microwave field under microwave-metal coupling,[69-70] fiber optic temperature sensors provide an added benefit of not exposing ceramic samples to external arcs. The measured localized temperatures are fed as an input to the feedback loop-based control system which work within a maximum allowable sample temperature. The control system in the feedback loop decides control lines commands and the cooling system determines cooling lines commands that change the microwave power and temperature boundary conditions of the microwave reactor and ceramic sample (**Figure 5**A).[15] The rotating mode stirrer helps in homogenizing the microwave field distribution inside the microwave reactor, thereby ensuring uniform heating of the ceramic sample with a higher heating efficiency. The microwave power control flow chart can be used to automate the microwave sintering process thereby avoiding sudden temperature rise, thermal runaway, hotspot formation due to localized heating and thermal gradients, resulting in a more uniformly sintered ceramic part (**Figure 5**B).

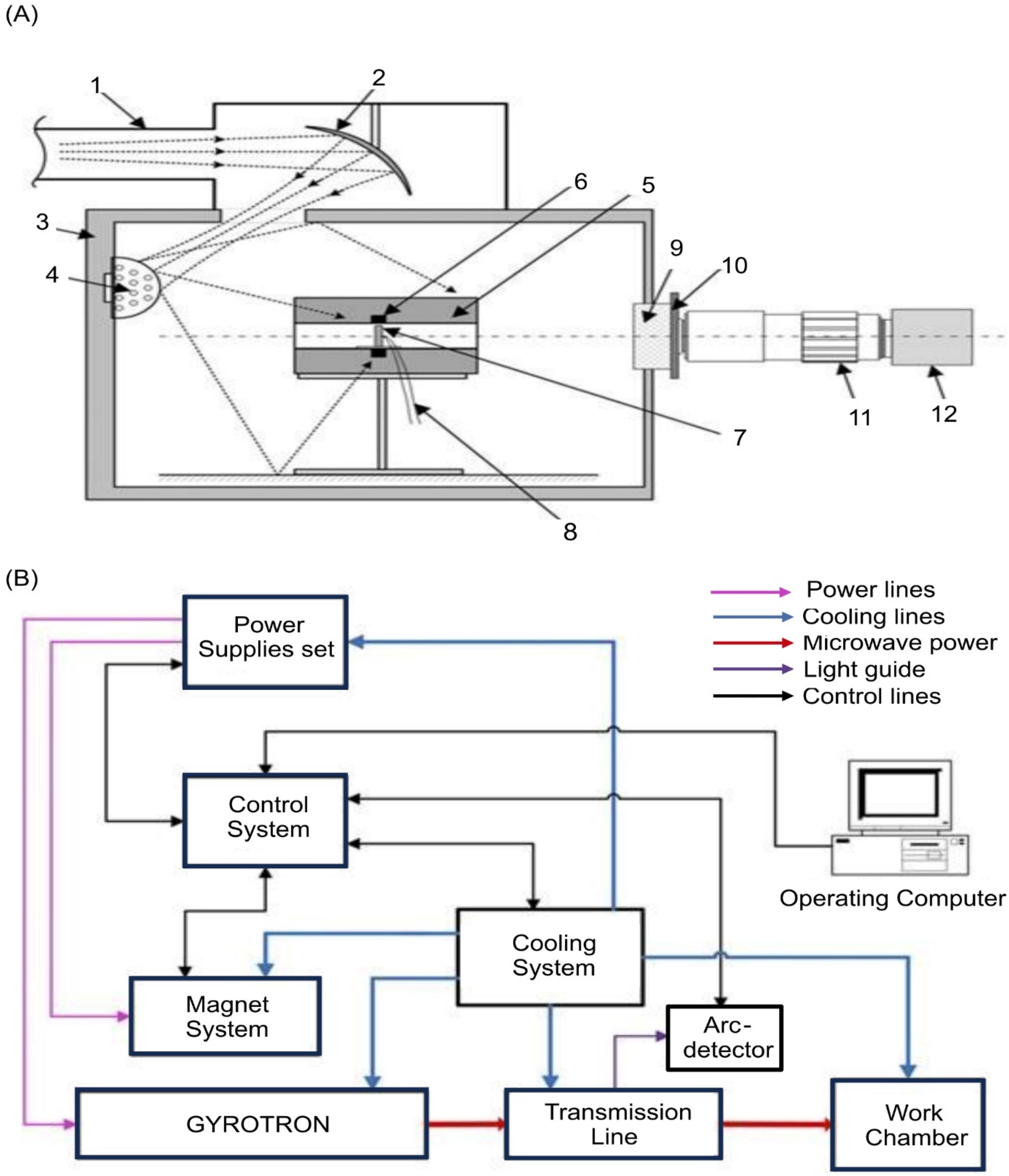

Figure 5. (A) Schematic diagram of the reactor used for microwave sintering process automation. 1: transmission line, 2: mirror, 3: work chamber, 4: rotating mode stirrer, 5: thermal insulation assembly with a through channel, 6: susceptor ring (optional), 7: sample, 8: thermocouple(s), 9: optical output window, 10: infrared filter, 11: lens, and 12: infrared

camera. The proportions of the components' dimensions are not to scale. (B) Simplified flowchart of the gyrotron system for microwave processing of materials. (Reproduced with permission conveyed through Copyright Clearance Center, Inc.[15] 2022, Review of Scientific Instruments.)

4.4. Additive Manufacturing

Additive manufacturing is a fabrication process introduced in the 1980s wherein the part is made by depositing powder, liquid or solid sheets, typically in layers to achieve complex, near-net-shaped geometries.[72-74] For ceramic additive manufacturing, two approaches are generally used - direct and indirect.[16] Direct additive manufacturing is a one-step process wherein the ceramic parts are sintered during the printing process. Two commonly used direct additive manufacturing processes are selective laser sintering and selective laser melting.[75-76] However, the high temperature of sintering of ceramics limits the usage of direct additive manufacturing for ceramic samples. Indirect additive manufacturing of ceramics is a three step process where a ceramic green part is first printed with binder holding the ceramic particles together. Once the ceramic part is printed, the binder is removed in a debinding process and finally, the ceramic part is sintered (**Figure 6**A).[78] Indirect additive manufacturing is the most commonly used commercial process.[79] It is possible to print parts with multiple materials (**Figure 6**B) and complex geometries (**Figure 6**C) with and without support structures using indirect additive manufacturing. This makes creating complex prototypes economic as opposed to conventional manufacturing techniques which would need expensive dies or molds to shape the ceramic parts.[80-81] These additively manufactured green parts could be sintered using microwaves to produce complex, near-net-shaped ceramic parts (**Figure 6**D-F),[16] thereby transitioning the idea of microwave sintering of simple shapes to complex rapid prototyped parts.

5. Applications

The challenges associated with scaling up the microwave sintering of ceramics discussed in section 3 need to be addressed with the current advancements and state-of-the-art technologies discussed in section 4 due to the prevailing applications of ceramics in the diverse fields. Ceramics have applications in a multitude of areas due to their superior material properties.

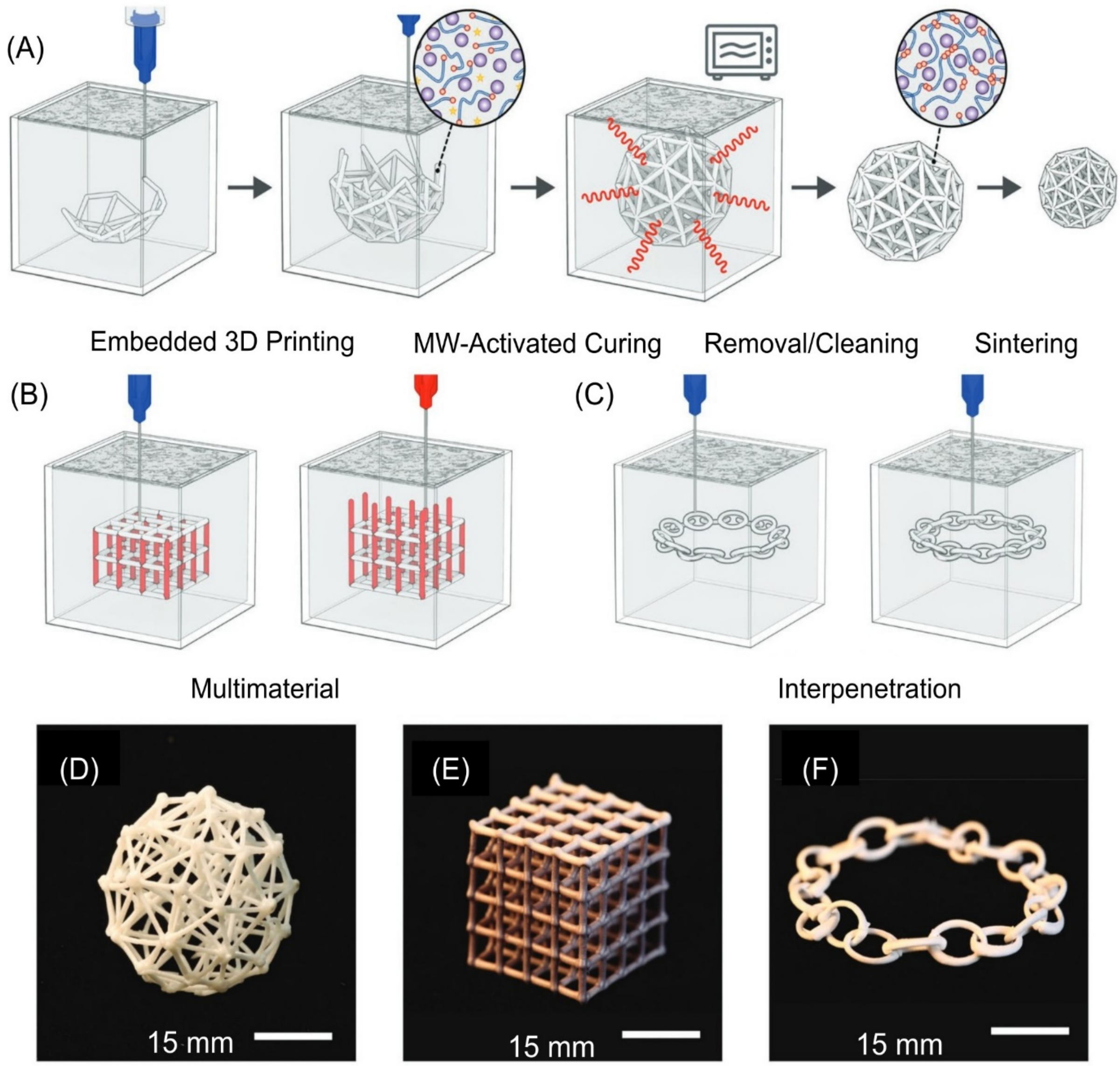

Figure 6. An example of the capabilities of additive manufacturing providing an extra dimension of geometric flexibility to microwave sintering. (A) Additive manufacturing and microwave sintering of architectured ceramic parts. (B) Schematic illustration of additive manufacturing of multimaterial ceramic lattices and (C) Interpenetrating (chainmail) architecture. (D-F) Optical images of additively manufactured and microwave sintered stochastic sphere, multimaterial lattice composed of pure (horizontal) and cobalt-doped (vertical) yittria stabilized zirconia (YSZ) struts and interpenetrating ceramic links patterned in the form of a closed chain respectively. (Reproduced with permission conveyed through Copyright Clearance Center, Inc.[71] 2023, Advanced Materials.)

Ceramics are materials that are known to be hard, resistant to wear and oxidation, thermally and chemically stable. Most of the ceramics are electrically insulating with some exceptions of semi-conducting ceramics.[82] They are used in domestic cookware, in automotive and aerospace industry for high temperature applications, in metallurgy industry as refractory materials due to the insulating properties of ceramics, and for mechanical applications such as cutting tools, turbine blades and bearings due to their mechanical hardness. Thermal effects observed in these high temperature applications, along with targeting the appropriate microstructure of the sintered ceramics are the most important challenges that need to be addressed with the advancements in simulation, automation and characterization specifically.

Ceramics have also applications in capacitors, piezoelectronics, batteries and telecommunication industry due to their electric and dielectric properties. Challenges associated with the heterogeneity in the ceramic material properties such as dielectric permittivity and residual stress in the ceramic sample when subjected to microwaves are of major concern in these applications which can be dealt with the advancements in simulation and additive manufacturing.

Furthermore, biomedical industry also depends on ceramics due to their biocompatibility and resistance to corrosion.[82-87] Microwave sintered ceramics have been explored extensively for applications in the biomedical field, especially as bone tissue scaffolds and as dental implants.[88-94] The complex near-net-shaped geometries are challenging to obtain for these applications which can be prototyped rapidly using additive manufacturing methods. By optimizing the microwave sintering process to address these challenges with the advancements categorized in **Figure 1**, we can truly make functional ceramic structures in a greener, more economic and more time and cost-efficient manner.

6. Future Outlook

This review work combines the current research breakthroughs in microwave sintering of ceramics that address the challenges prevailing since last 60 years in terms of scaling up this process. This review work thereby presents the scope of scaling up this efficient (~80-90% volumetric heat generation efficiency) technique at the industrial level.[35] Microwave sintering, being an energy and cost efficient ceramic part consolidation technique, can be exploited as an alternative to the current conventional sintering techniques. The ceramic part densification using microwaves provides a head start over other field-assisted sintering techniques in terms of geometric flexibility, processing time, associated cost and productivity, hence supporting the potential of scaling up this method.

Over the last two decades, the substantial progress reported in the simulation of microwave-ceramic interaction has opened new avenues that help us understand and address the issues, related to heterogeneous ceramic material properties and heating environment around the large ceramic parts, associated with this fast growing field-assisted sintering technique. With the recent improvements in the high power gyrotron based microwave reactors, researchers have also started automating the microwave sintering process.[20] Furthermore, most recent advancements in solid-state power generators have shown greater technical (in terms of uniform heating of larger samples with a higher quality assurance and better control of resonant conditions due to a narrow frequency range resulting in higher microwave power absorption inside the ceramic material) and economic (in terms of higher yield and increased lifetime with a lower replacement cost) benefits over the traditional magnetron-based microwave generators.[95] Moreover, the recent significant growth in the ceramic material characterization techniques confirms the durability of the microwave sintering process. Lastly, additive manufacturing of ceramics, especially indirect rapid prototyping methods, has provided microwave sintering of ceramics an extra dimension of geometric compliance for the near-net-shaped parts which is the need of the hour for the evolving mechanical, metallurgical, biomedical and telecommunication industry. Overall, this review paper presents the tremendous growth in the capabilities of ceramic additive manufacturing processes, simulation and automation of microwave sintering process, and characterization of the sintered ceramics which will provide the future enthusiasts an outlook of scaling up this field-assisted sintering technique.

Conflict of Interest Statement

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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