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# When Should Microwaves Be Used To Process Technical Ceramics?

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## Abstract

This paper attempts to shed light on why the stand alone microwave processing of technical ceramics, despite being one of the most popular field with respect to volume of research performed, is still struggling to achieve priority status with respect to commercialisation. To obtain some answers to this enigma and determine when microwaves should be used to process technical ceramics, three case studies are explored. The conclusion is that microwaves should be used to process technical ceramics when specific advantage can be taken of the intrinsic nature of microwave energy and not simply as an alternative energy source. In addition, it is concluded that from a commercialisation view point hybrid processing is often a better approach than the use of pure microwaves.

## Introduction

The use of microwave frequency radiation as an alternative energy source for ceramic processing has been examined since the early 1950's. Initially the work focused on drying [1], however in the mid-1970's the first attempts were made to utilise microwaves in ceramic sintering [2]. Research over the next ten years showed that substantial heating effects could be generated and materials densified, however the work was too uncoordinated for substantial progress to be made. It wasn't until the late 1980's when a substantial, global effort was initiated [3,4], with interest in the use of microwaves being associated with the both the attainment of new or improved properties and in achieving economic benefits, the latter often via claims of faster processing rates and/or the ability to use lower temperatures. Since then, although there have been inevitable peaks and troughs in the number of papers published, interest in the use of microwaves for processing ceramics has remained remarkably high. Disproportionately high, in fact, given the small number of niche applications in which microwaves are being used commercially in ceramic processing some 30 years after the first serious laboratory experiments were performed. This begs the question, why? When *should* microwaves be used to process technical ceramics? The answers to these questions will be sought by studying three case studies.

## Case Study One: Microwave Sintering

Microwaves have been used to densify a very wide range of ceramic materials via sintering [5], however perhaps the ceramic that has seen the greatest amount of effort over the decades is alumina,  $\text{Al}_2\text{O}_3$ . It is the most common engineering ceramic used by industry as a result of exhibiting excellent hardness and strength, a very low electrical conductivity and its low cost compared to many of its potential competitor ceramics. Despite its highly refractory nature, it is relatively straight forward to sinter to full densification via the use of well established sintering aids. However, for the microwave sintering enthusiast it is a low loss material that is very difficult to heat from cold using a standard, multimode microwave cavity. To overcome this intrinsic processing difficulty, a number of 'solutions' have been investigated, such as:

1. **Mixing in high loss additives:** Examples range from sodium nitrate and glycerol [6] to silicon carbide whiskers [7] amongst many others. Whilst they work in terms of being more lossy than the alumina and so, when added in sufficient quantities, improve the ability to heat the ceramic from cold and hence be heated and densified, in terms of the final properties achieved, they range from potentially property-enhancing, e.g. SiC whiskers, to rather questionable, e.g. NaNO<sub>3</sub>. Sodium-based compounds, for example, have been well known for very many years to yield glassy grain boundaries that can significantly impair both the mechanical strength and the electrical resistivity of the alumina to the extent that the ceramic can no longer be used in any practical application. However, whilst composites based on Al<sub>2</sub>O<sub>3</sub> with SiC are known to offer potentially superior mechanical properties, unfortunately they are also significantly more expensive than the monolithic version of alumina, restricting the uses for the end product to high value applications.
2. **Use of high E-field applicators and/or high microwave frequencies:** Whilst applicators such as single mode cavities achieve a much higher electric field in the sample, and often one that can be calculated quite precisely, it is at the cost of a very much smaller spatial size for the microwave heating zone. This means that the approach, which often works very well in terms of being able to heat even very low loss materials, e.g. extremely high purity alumina, to sintering temperatures [8], the ability to scale up such equipment to handle actual engineering components, rather than very small laboratory samples, at commercial production levels (e.g. thousands of components per week for an engineering ceramic such as alumina) is not even remotely feasible. Similarly, research has been undertaken at much higher microwave frequencies than the 2.45 GHz or 915 MHz traditionally used [9]. Once again, this is an approach that works extremely well in the laboratory, but the economics of the process are more questionable for industrial scale processing [10].
3. **Use of caskets:** An idea originally developed at Oak Ridge National Laboratories in the USA, these are ceramic insulation boxes that contain high loss ceramics, for example, SiC rods, that act as susceptors [11]. These heat up first in the microwave field, in turn heating the lower loss alumina or other ceramic samples. In some cases, at elevated temperatures the changes in the dielectric characteristics of the samples and the susceptors can mean that the former actually start to absorb more than the latter, improving the energy efficiency of the process. Once again, there is little doubt that the principle works – until it is desired to scale the process up. When a very valiant effort was made to construct a prototype industrial kiln based on the susceptors approach [12], it was demonstrated that not only was the design of the casket system extremely critical, but it was slow to build and strip down and hence required considerable labour time. In addition, the dielectric properties of the casket materials, including the susceptors rods, were found to change with repeated use, preventing long-term consistency being achieved and meaning that almost every sintering run required a different power-time profile.

So, given how easy it is to sinter even very high purity (i.e. very low dielectric loss) alumina by conventional means – use appropriate additives and hold it in a furnace at 1500-1600°C for a few hours – have microwaves any role to play at all? The answer is yes and the first conclusion can be drawn.

Microwaves heat volumetrically, that is, throughout the volume of the material. However, the air surrounding the materials remains unheated by the microwaves and hence cooler. The surface of the material thus loses heat and an inverse temperature profile is developed, figure 1, that is, the centre of the body becomes hotter over time (typically seconds) than the surface. Combine this with conventional heating in the correct proportion (typically only a fraction of the total power required is needed from the microwave source, which is helpful since microwaves are generally not a cheap

source of energy) and a uniform temperature profile can be achieved, figure 2. This allows heating and cooling rates to be significantly faster than conventional processing since the thermal stresses developed are very much reduced since the need to rely on thermal conduction to avoid sharp temperature gradients is very significantly reduced [13].

This approach, known as hybrid heating or, in the USA, microwave assist technology (MAT), was developed by EA Technology Ltd (now C-Tech Innovations Ltd) in the UK during the 1990s. Products investigated ranged from advanced ceramics to bricks, sanitary ware to tableware, and included abrasives, pigments and refractories. Almost all products could be produced at twice the speed with equivalent or better quality and the results of cost benefit analyses showed that the payback period was typically less than 3 years [14]. A more recent analysis performed for a brick company in 2006 showed a payback of only 13 months, partly because of an increase in gas prices. The design of hybrid, or MAT, kilns also has advanced, leading to decreased kiln costs and encouraging more companies to investigate the potential for their products. One recent example, the firing of SiC sleeves for Blasch Precision Ceramics by Ceralink, the exclusive agents for MAT technology in the USA, has revealed that the temperature uniformity achievable in the part permitted five time faster heating rates to be utilised, resulting in 500% savings in time and an estimated 41% saving in energy costs over the existing process [14].

However, this is not the only benefit that can be observed from the use of hybrid sintering approaches. For example, research on the firing of zinc oxide varistors yielded results that showed that hybrid sintered devices exhibited more homogeneous and finer microstructures that exhibited superior electrical properties [15]. In addition, the combination of hybrid heating with a new firing strategy known as two stage sintering [16] has yielded the ability to achieve nanostructured zirconia with densities >99.5% of theoretical whilst retaining final average grain sizes as fine as just 65 nm using precursor nanopowders with an average grain size of ~16 nm [17], figure 3. In other words, keeping grain growth during densification to just approximately a factor of 4, a remarkable achievement using a pressureless sintering approach, especially for components up to 50 mm in diameter. It is believed that one of the primary advantages offered by the hybrid heating approach was the ability to use a much faster initial heating rate, 20 versus just 7°C min<sup>-1</sup>, since the bulk of the grain growth observed using two stage sintering occurs during heating to the first sintering temperature, known as T<sub>1</sub>. These nanostructured ceramics have since been observed to display very significantly enhanced properties, results that are currently the basis for a patent application [18].

*The conclusion that can be drawn is that hybrid heating, which takes advantage of the volumetric nature of microwave heating, can allow faster, and consequently, lower energy and hence cheaper firing of ceramic components as well as yielding superior properties.*

### **Case Study Two: Microwave Enhanced Chemical Vapour Infiltration**

Chemical vapour infiltration (CVI) is a process route that can be used to produce ceramic matrix composites (CMCs), though the process is very slow and hence expensive. The technique relies on the infiltration of a gas throughout a ceramic fibre preform. On heating, the gas decomposes to yield a ceramic, e.g. methyltrichlorosilane (CH<sub>3</sub>Cl<sub>3</sub>Si) yields SiC, which forms a matrix around the fibres.

With conventional heating the outer surface of the preform heats preferentially, figure 4a, causing deposition of the matrix material to occur preferentially at or near the outer surface. This eventually leads to the blockage of the surface channels which, in turn, prevents the gaseous reagents from further penetrating the preform [19]. This necessitates the stopping of the process, removal of the piece and the machining of its surface to reopen the channels. As a result, it can take up to 2 months (1500 hours) and several, expensive machining operations to produce a component. This leads to the

whole process being slow and very expensive. Techniques designed to alleviate these problems require the use of temperature and pressure gradients. However, when a thermal gradient is combined with a forced-gas flow, non-uniformly densified composites can also result, even though overall higher densities have been achieved.

The search for more efficient methods that yield rapid and complete densification continues and the use of microwave heating in the processing of ceramic materials has been recognised as a promising alternative [20] since they can be used to generate an inverse temperature profile, figure 4b that allows much faster processing [21]. Preferential densification of the composite from the inside out was clearly observed. Whilst an average relative density of only 55% was achieved in 24 h, representative of a ~26% increase over the initial fibre vol.%, the centre of the preform densified to 73% of theoretical in this period. Further densification was inhibited as much by the size of the macroporosity within the samples, which would have necessitated relatively long infiltration times to fill, even with the enhancement arising from the use of microwaves. One solution to this approach is to impregnate the fibre preform with SiC powder first, effectively yielding denser preforms that can be subsequently densified efficiently by MECVI [22].

As has already been seen, figure 2, microwaves can be combined with conventional heating to generate a controlled temperature profile. If, however, instead of focusing on uniform temperature profile across the body, microwaves were used preferentially at the start of the infiltration process then an inverse temperature profile, or a hotter centre, can be generated. This can be maintained until the centre of the component is suitably densified when the fraction of microwave and conventional energy can be changed to promote densification towards the surface of the component. This allows the chemical vapour infiltration of the fibre preforms to be performed from the inside out, resulting in a more uniform infiltration of the matrix. Microwave enhanced CVI (MECVI) also avoids surface pore closure and reduces deposition times to an order of magnitude less than can be achieved using conventional CVI with the production of uniformly and highly densified fibre-reinforced ceramic matrix composites.

Although this variable temperature profile approach has yet to be confirmed experimentally, the results achieved to date with the use of microwaves [21,22] are sufficiently promising to indicate that the 'inside out' heating available from using microwave heating can be exploited to significant advantage.

A different, but related, application arises during the synthesis of ceramic powders via, for example, the direct reaction of metal powders with an appropriate gas, e.g. nitrogen. Taking aluminium nitride, AlN, a ceramic that has many attractive properties for electronics and refractory applications [23], as an example, it is synthesised using two main industrial processes. These are the carbothermal reduction of aluminium oxide and the direct nitridation of aluminium [24]. The former consists of heating a mix of alumina and carbon powders to above 1100°C in nitrogen. Unreacted carbon is removed by controlled oxidation at ~650°C in dry air whilst a second heat treatment at ≥1400°C in vacuum reduces oxygen pickup and stabilises the powder. Although this method has the advantages of readily available raw materials and the production of powders that are homogeneously sized and suffer low levels of agglomeration, avoiding carbon and oxygen impurities is difficult [23]. The nitridation process also allows large quantities of powders to be produced with relatively low energy and raw materials' costs. Being highly exothermic, once the reaction starts it is able to proceed without any additional supply of external heat. However, it is difficult to produce fine, fully nitrided powders because during the reaction the Al powder can form large aggregates due to its melting point (660°C) being lower than the nitridation temperature (≥800°C) [25]. In addition, AlN formation occurs first on the surface of the Al particles inhibiting the diffusion of the nitrogen to the unreacted metal. As for the chemical vapour infiltration process, extended reaction times are therefore required

to allow adequate diffusion whilst intermittent grinding steps are generally necessary to break the agglomerates and expose fresh surfaces of unreacted Al [26]. However, when microwaves are used to ignite the combustion synthesis process, ignition is initiated in the centre of the body and the combustion wavefront propagates radially outward [27] – towards the source of fresh nitrogen gas. As a result, notionally complete conversion to AlN could be observed after just 15 minutes at temperatures in the range  $1220\pm 60^\circ\text{C}$ . This compared very favourably with results from more conventional processing in which complete conversion to AlN could not be achieved even after three passes through a transport flow reactor at up to  $1650^\circ\text{C}$  and several hours processing [26].

*The conclusion that can be drawn is that the inverse temperature profile can be exploited successfully to allow much faster processing, particularly where reactions between gases and solid phases is required.*

### **Case Study Three: Ceramic Joining**

The exploitation of ceramics in an expanding field of engineering applications has resulted in the need for changes in both component design and fabrication. However, the high hardness and lack of ductility in ceramics limits the complexity of shapes that can be formed without extensive, and hence expensive, machining. One alternative is the fabrication of smaller, simpler shapes that can be formed with better quality and then joined together to form the final component. This approach places the emphasis on the need to establish bonding techniques that are simple, fast and inexpensive and yet yield bonds that will deliver the performance required of the ceramic component. To achieve this requires techniques that will:

- Only heat the ceramic locally in the join region; this avoids risking damage to the microstructure or deformation of the component other than in the immediate vicinity of the join where such changes are probably unavoidable.
- Be fast and efficient, thus keeping the time required to produce the component as short as possible.
- Result in high quality bonds, thus ensuring that the join has the maximum possible strength and so the component has maximum integrity.

The ability to form rapid, high quality bonds between a range of ceramic materials using microwave energy has been demonstrated by a number of researchers using two main approaches, viz. direct and indirect joining [28]. In the latter case, use is made of some form of interfacial layer to assist in achieving bonding. Both multimode [29] and single mode [30] approaches have been used; the former suffer from the problem that the whole ceramic part heats up so potentially affecting the microstructure and/or component deformation. The latter approach, of using single mode applicators, such as a  $\text{TE}_{10n}$ , have the advantage that they can be used to heat only the parts of the ceramic at the immediate location of the join, figure 5.

As already discussed under microwave sintering above, a further advantage of single mode applicators is that they have much stronger electric fields than multimode devices. This can ensure that components heat rapidly, even when their dielectric losses are relatively low, such as with alumina. Finally, research has shown that bonding times can be as short as 10 minutes, with total processing times of only 30 – 45 minutes. This is much faster than can be satisfactorily achieved using diffusion bonding and results in significantly less deformation of the samples. The operational mechanisms however, appear to be almost identical between the two techniques and are based on viscous flow of a grain boundary phase, for example, glass in the case of oxides such as low purity aluminas or silicon in case of reaction bonded silicon carbide [28,31]. Provided sufficient migration

across the bond line of both glassy phase and grains occurs, then a fully homogeneous microstructure can be obtained. In such cases, the mechanical strength of the bond can be at least as high, often higher, than that of the parent material with the joined samples never breaking at the bond line during 4-point bend tests [28].

Scaling up of this process could be envisaged by using the cavities in much the same way as glass bottle forming machines work. Known as IS (independent section) machines, they produce only one bottle at a time but are arranged in banks such that a large number (e.g. 20-50) bottles can be produced at the same instant. One could thus envisage a whole bank of simple, inexpensive cavities, all powered off the same generator, each producing only one join at a time but collectively producing a large number of finished components.

*The conclusion from this example is that microwaves offer the ability to design applicators to put energy where it is most needed.*

## **Summary**

The three case studies examined have each highlighted a different advantage of microwave heating for ceramic processing, viz.:

- Volumetric heating
- 'Inside out' heating
- Ability to design an applicator to put energy where it is most needed.

There are other advantages not represented here, for example, the ability to selectively heat high loss phases in a matrix of a low loss phase (provided non-equilibrium conditions are maintained) and the ability to take advantage of the so-called 'microwave effect', which has now been clearly demonstrated for ceramics [32,33]. Also excluded from the discussion are the areas of microwave assisted synthesis/processing of electrical/magnetic ceramics, powder metals, organic materials, microwave drilling etc and the advantages offered. However the purpose of this paper is not to simply list the advantages of using microwaves, but to highlight a more fundamental consideration. That is, to answer the question 'When should microwaves be used to process technical ceramics?'. The answer is believed to be:

*Microwaves should be used to process technical ceramics when specific advantage can be taken of the intrinsic nature of microwave energy. They should not be used simply as an alternative to conventional heating approaches.*

This implies that careful thought and consideration needs to be exercised to ensure that there will be an advantage and that the research is not merely leading to an alternative approach. Thorough and rigorous analysis of costs versus benefits, including ecological issues, offered by the microwave assisted approach would also help to lead the way for early commercialisation.

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