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Microwave Fast Sintering of Ceramic Materials

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1. Introduction

Microwaves are electromagnetic waves with wavelengths ranging from 1m to 1 mm, which correspond to frequencies between 0.3 and 300 GHz. This frequency range lies just above radio waves and just below visible light on the electromagnetic spectrum (Katz, 1992). The possibility of processing ceramics by microwave heating was discussed over 50 years ago by Von Hippel (1954a), and experimental studies on microwave processing of ceramics were started in the mid 1960s by Tinga and Voss (Tinga & Voss, 1968). Since then, the results of many investigations into microwave sintering and joining of ceramics have been reported (Bykov et al., 2001). Activity in this field began to accelerate in the mid-1970s because of a shortage of natural gas, prompting the investigation of microwave heating and sintering of several ceramic materials in the late 1970s and 1980s.

While most of today's industrial microwave applications involve the relatively low-temperature processing of food, wood, rubber, polymers, etc., interest in high-temperature microwave processing of materials has been growing. In recent years, microwave heating has been widely employed in the sintering and joining of ceramics (Bykov et al., 2001; Huang et al., 2009).

Most of the reposts published in the literature assert that microwave-driven processes are faster than conventional heating processes. This faster speed is manifested as a reduction in the densification time of ceramic powder compacts, often allied to lower sintering temperatures (Bykov et al., 2001). In general, the kinetics of synthesis and sintering reactions are reportedly augmented by two or three orders of magnitude or even more when conventional heating is substituted for microwave radiation (Oghbaei & Mirzaee, 2010).

Microwave heating is a process whereby microwaves couple to materials, which absorb the electromagnetic energy volumetrically and transform it into heat. This differs from conventional methods in which heat is transferred between objects through the mechanisms of conduction, radiation and convection. Because the material itself generates the heat, heating is more volumetric and can be very rapid and selective (Sutton, 1989). Thus, microwave sintering techniques allows for the application of high heating rates, markedly shortening the processing time.

Microwave processing eliminates the need for spending energy to heat the walls of furnace or reactors, their massive components and heat carriers. Hence, the use of microwave processing methods significantly reduces energy consumption, particularly in high-temperature processes, since heat losses escalate considerably as processing temperatures increase. However, the advantages of using microwave energy in high-temperature processes are by no means limited to energy savings. In many cases, microwave processing can improve the product quality (Bykov et al., 2001).

High heating rates not only shorten processing time and reduce energy consumption. Many high-temperature processes involve a sequence of steps that follow each other as the temperature rises. These sequences occur in multistage thermally activated processes, in which separate stages are characterized by different values of activation energy. Some of these stages may have a negative effect on the properties of the final product. In such cases, rapid heating may be vital in reducing the effects of undesired intermediate stages of the process. An example of such a multistage process is the sintering of ceramics. Various diffusion processes, such as surface, grain boundary and bulk diffusion, determine mass transport in different sintering stages.

Harmer and Brook (1981) postulated that rapid sintering produces a finer grained microstructure. This theory applies to all rapid sintering techniques, including microwave sintering. The theory of rapid sintering is based on the assumption that densification and grain growth are thermally activated processes and that the activation energy for grain growth is lower than for densification.

In fast firing, the objective is to enhance the densification rate in detriment to the coarsening rate by a rapidly approaching to the sintering temperature. Because coarsening mechanisms (e.g., surface diffusion and vapor transport) usually prevail over densification mechanisms (e.g., lattice and grain-boundary diffusion) at lower temperatures, it has been suggested that rapid heating to higher temperatures can be beneficial to achieve high density allied to fine grain size. In this case, the shorter time spent at lower temperatures serves to reduce the extent of coarsening, while the driving force for densification is not decreased significantly (Menezes & Kiminami, 2010), resulting in high densification and fine microstructures, which is a factor of paramount importance in the sintering of nanostructured ceramic and composite materials.

However, various fundamental problems are usually encountered when sintering materials by direct microwave heating. Most of the research on material processing by microwaves is based on conventional low-frequency (2.45 GHz) microwave applicators. However, such applicators do not couple microwave power efficiently to many ceramics at room temperature, and poor microwave absorption characteristics make initial heating difficult. Thermal instabilities may occur, which can lead to the phenomenon of thermal runaway; i.e., the specimen overheats catastrophically. The temperature gradients inherent in volumetric heating can lead to severe temperature non-uniformities, which, at high heating rates, may cause non-uniform properties and cracking.

These problems have led researchers to develop hybrid heating techniques that combine direct microwave heating with infrared heat sources. Increasing the temperature (with radiant heat) is a common method used by many researchers to couple microwaves with poorly absorbing (low-loss) materials. Once a material is heated to its critical temperature,

microwave absorption becomes sufficient to cause self-heating. This hybrid method can result in more uniform temperature gradients because the microwaves heat volumetrically, and the external heat source minimizes surface heat losses. Hybrid heating can be achieved by using either an independent heat source such, as a gas or electric furnace in combination with microwaves, or an external susceptor that couples with the microwaves. In the latter, the material is exposed simultaneously to radiant heat produced by the susceptor and to microwaves (Clark & Sutton, 1996).

There is growing evidence to support the use of microwave hybrid heating in ceramic sintering and to justify continued research and development for its use in many ceramics manufacturing processes. In this context, this chapter discusses microwave interactions with ceramic materials, dielectric properties of ceramics, and theoretical aspects of microwave sintering, as well as results that highlight the successful application of microwaves to the rapid sintering of ceramic materials.

2. Fundamentals of microwave heating

Microwaves are electromagnetic waves in the frequency band of 300 MHz (3×10^8 cycles/second) to 300 GHz (3×10^{11} cycles/second), which correspond to a wavelength range of 1 m to 1 mm. Within this portion of the electromagnetic spectrum there are frequencies that are used for cellular phones, radar, and television satellite communications (Thostenson & Chou, 1999). Typical frequencies for materials processing are 915 MHz, 2.45 GHz, 5.8 GHz, 22.00 GHz, 24.12 GHz, 28GHz and 60GHz, but only 915 MHz and 2.45 GHz are widely applied ((Katz, 1992; Committee on Microwave Processing of Materials: An Emerging Industrial Technology et al., 1994). The advantages of higher frequencies are more uniform electric field distribution in the cavity and higher power dissipated in dielectric materials. However, microwave apparatus is available on a very limited basis and at extremely high cost.

The interaction of an electric field with a material may elicit several responses, and microwaves can be reflected, absorbed and/or transmitted by the material. In a conductor, electrons move freely in the material in response to the electric field, resulting in electric current. Unless the material is a superconductor, the flow of electrons will heat the material through resistive heating. However, microwaves will be largely reflected from metallic conductors, and therefore such conductors are not effectively heated by microwaves. In insulators, electrons do not flow freely, but electronic reorientation or distortions of induced or permanent dipoles can give rise to heating (Committee on Microwave Processing of Materials: An Emerging Industrial Technology et al., 1994).

Because microwaves generate rapidly changing electric fields, these dipoles change their orientations rapidly in response to the changing fields. If the electric field change takes place close to the natural frequency at which reorientation can occur, the maximum amount of energy is consumed, resulting in optimum heating. In microwave processing terminology, this event is described by the term "well-coupled" material.

It is known that in dielectric materials the external electric field causes a redistribution of internal bound charges, which results in the polarization of the material. A measure of the response of a material to an external electric field is its dielectric permittivity, ε. If the

external electric field is alternating (ac), the dielectric response of the material follows it, generally with some lag behind the field changes. To describe this phenomenon quantitatively, a complex dielectric permittivity that depends on the field frequency, ω (ω is equal to $2\pi f$, where f is the frequency in cycles per second), is formally introduced:

$$\varepsilon(\omega)^* = \varepsilon(\omega)' - i\varepsilon(\omega)'' = \varepsilon_o\,(\varepsilon_r(\omega)' - i\varepsilon_r(\omega)'') \tag{1}$$

where $i = (-1)^{1/2}$, ε′ is the permittivity (or dielectric constant), ε′′ is the dielectric loss factor, ε_o is the permittivity of a vacuum, and ε_r is the relative permittivity (or relative dielectric constant) (ε_r' equals $\varepsilon'/\varepsilon_o$ and ε_r'' equals $\varepsilon''/\varepsilon_o$).

The real component of complex permittivity, ε′, is commonly referred to as the dielectric constant. However, because ε′ is not constant but may vary significantly with frequency and temperature, it is generally referred to simply as permittivity.

However, microwave propagation in air or in materials depends on the dielectric and magnetic properties of the medium. Thus, the electromagnetic properties of a medium are characterized by complex permittivity and also complex permeability, μ* (Equation 2). In magnetic materials, the dipoles may be able to couple with the magnetic component of the electromagnetic field and provide an additional heating mechanism. Similarly to the dielectric properties of materials, their magnetic permeability, μ′, and magnetic loss, μ″, must be considered in microwave processing,

$$\mu(\omega)^* = \mu\,(\omega)' - i\,\mu\,(\omega)'' \tag{2}$$

where μ' and μ'' are the permeability and magnetic loss factor, respectively.

In an ideal dielectric, the electric charge adjusts instantaneously to any change in voltage or field. In practice, however, there is an inertia-to-charge movement that shows up as a relaxation time for charge transport. Relaxation time, τ, can be defined as the time interval in which a disturbed system is restored to its equilibrium configuration after the application of a microwave field. The behavior of τ determines the frequency and temperature dependencies of ε′ and ε″ and varies widely in liquids and solids (Committee on Microwave Processing of Materials: An Emerging Industrial Technology et al., 1994). Thus, when an alternate electric field interacts with a dielectric, the time required for polarization appears as a phase retardation of the charging current. Instead of advancing by 90°, it advances by some angle, δ, other than 90°. This phase shift, which corresponds to a time lag between an applied voltage and induced current, causes loss of current and dissipation of energy in the material (Kingery et al, 1976). The imaginary term in equation (1), ε′′, which quantifies the power dissipated in the material, is known as the dielectric loss factor.

Another term sometimes used to quantify the "lossiness" of a material is the loss tangent (Equation 3). The inverse of the loss tangent is the quality factor, Q, which is widely used in waveguide technology (Von Hippel, 1954a).

$$\tan\delta = \frac{\varepsilon''\mu' - \varepsilon'\mu''}{\varepsilon'\mu' + \varepsilon''\mu''} \tag{3}$$

For negligible magnetic loss (μ'' = 0) the loss tangent is expressed as:

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} = \frac{\varepsilon_r''}{\varepsilon_r'} \tag{4}$$

The charging current for a simple dielectric plate with a sinusoidal applied voltage is given by $I_c = i\omega\varepsilon' E$ and the loss current by $I_l = \omega\varepsilon'' E = I_l = \sigma E$, where σ is the dielectric conductivity. Engineers concerned with dielectric heating will generally use the dielectric constant, ε', and the dielectric conductivity, σ, to characterize the processed material and express its response at a given frequency.

The power absorbed per unit volume, considering that the electric field is uniform throughout the volume, can be expressed by:

$$P = \frac{1}{2}\left(\omega\varepsilon''\mathrm{E}^2 + \omega\mu''\mathrm{H}^2\right) = \omega\left(\varepsilon''\mathrm{E}^2_{rms} + \mu''\mathrm{H}^2_{rms}\right) \tag{5}$$

where E_{rms} and H_{rms} are the root mean squares of the internal electric and magnetic fields.

Equation (5) shows that the power dissipated in a ceramic body during microwave processing is directly related to the applied frequency (ω = 2πf) and the material's conductivity, σ (σ = ωε"). For instance, 25 times more power can be dissipated in alumina at 28 GHz, than at 2.45 GHz.

Depending on their electrical and magnetic properties, materials can be divided into three categories according to their microwave absorption properties. Materials with a very low dielectric loss factor (or conductivity) allow microwaves to pass through with very little absorption and are said to be transparent to microwaves. Materials with an extremely high dielectric loss factor, i.e. metals, reflect microwaves and are said to be opaque. Materials with intermediate loss tangents will absorb microwaves (Katz, 1992).

Ceramics with loss factors between the limits of $10^{-2} < \varepsilon'' < 5$ are good candidates for microwave heating. Ceramics with $\varepsilon'' < 10^{-2}$ would be difficult to heat, while those with $\varepsilon'' > 5$ would absorb most of the heating on the surface and not in the bulk.

Absorption energy is quantified by the absorbed power per unit volume and by the attenuation distance, D (or depth of penetration), which expresses the magnitude of the energy attenuation inside the material.

A plane wave varying periodically in time with the frequency f = ω/2π and advancing in the + x direction through space presents a complex propagation factor, γ (Metaxas & Binner, 1990):

$$\gamma = j\omega\sqrt{\varepsilon^*\mu^*} = \alpha + j\beta \tag{6}$$

where α is the attenuation factor and β is the phase factor of the wave.

Equating the real and imaginary parts of Equation (6), the attenuation and phase factors can be expressed in terms of permittivity and permeability (Von Hippel, 1954a):

$$\alpha = \frac{\lambda\omega^2}{4\pi}(\varepsilon'\mu'' + \varepsilon''\mu') \tag{7}$$

$$\beta = \omega \sqrt{\frac{\varepsilon'\mu' - \varepsilon''\mu''}{2} \left(1 + \sqrt{1 + \left(\frac{(\varepsilon'\mu'' + \varepsilon''\mu')}{(\varepsilon'\mu' + \varepsilon''\mu'')} \right)^2} \right)} \tag{8}$$

where λ is the wavelength of the plane wave inside the material.

The attenuation produced by a dielectric is frequently expressed as the attenuation distance (or penetration depth or skin depth), D, defined as $1/\alpha$, through which the field strength decays to 1/e (0.368) of its original value. For materials with negligible magnetic loss ($\mu'' = 0$), and considering the permeability of the vacuum ($\mu' = \mu_o$):

$$D = \frac{1}{\alpha} = \frac{c}{\omega} \sqrt{\frac{2}{\varepsilon_r' \left(\sqrt{1 + \tan^2 \delta} - 1 \right)}} \tag{9}$$

where c is the speed of light.

Another parameter that can be defined is power penetration depth, D_P, which is the distance at which the power drops to 1/e (0.368) from its value at the surface (Metaxas & Binner, 1990):

$$D_P = \frac{1}{2\alpha} = \frac{D}{2} \tag{10}$$

It is important to differentiate between power penetration depth and electric field attenuation distance or skin depth (D), because at frequencies allocated for industrial use in the microwave regime, the power penetration depths could be very small indeed and the size of the ceramic to be treated, particularly when it is fairly lossy, could be many times larger than Dp, resulting in unacceptable temperature non-uniformities (Metaxas & Binner, 1990).

The index of absorption, k, can be expressed in terms of the attenuation, α, and the phase factor β, according to Equation (11). The reflection coefficient, R (the fraction of reflected power), for a normal incidence of the electromagnetic wave on a plane boundary between material and vacuum can also be expressed in terms of loss tangent (Equation 12) (Von Hippel, 1954b; Bykov et al., 2001):

$$k = \frac{\alpha}{\beta} = \sqrt{\frac{\sqrt{1 + \tan 2\delta} - 1}{\sqrt{1 + \tan 2\delta} + 1}} \tag{11}$$

$$R = \frac{1 - \sqrt{2\varepsilon_r' [1 + \sqrt{1 + tg^2\delta}]} + \varepsilon_r' \sqrt{1 + tg^2\delta}}{1 + \sqrt{2\varepsilon_r' [1 + \sqrt{1 + tg^2\delta}]} + \varepsilon_r' \sqrt{1 + tg^2\delta}} \tag{12}$$

The absorption properties of non-metallic materials vary greatly in the microwave frequency range. The loss tangent, tan δ, varies at room temperature from 10^{-4}–10^{-3} (for example in pure alumina and silicon nitride) up to 1 and higher (in carbides, borides, some oxides, and intermetallic compounds). Correspondingly, the penetration depth varies from

tens of meters to fractions of a millimeter. For example, at 2.45 GHz and room temperature, graphite and alumina have skin depths of 38 μm and 25 m (according to data in Von Hippel, 1954b; Metaxas & Binner, 1990), respectively.

In general, at room temperature, many ceramics do not absorb microwaves appreciably at 2.45 GHz, and thus present high attenuation distances. However, their absorption can be increased by raising the temperature, adding absorbents (e.g., SiC, carbon, binders), altering their microstructure and defect structure (Agrawal, 1998) by changing their form (e.g., bulk vs. powder), or by changing the frequency of incident radiation (Clark & Sutton, 1996).

The dielectric properties of ceramic materials are highly dependent on temperature, and their loss factor generally increases with temperature, improving the ability of "transparent" materials to couple with microwaves. The rate of temperature increase depends upon the type of ceramic and the operating frequency, but a sharp increase in microwave losses begins at temperatures of about 0.4–0.5 T_m (where T_m is the melting temperature of the material). In this temperature range, the bonds between ions in ionic crystals begin to break, and the electrons in covalent materials begin to populate the conduction bands. Due to this sharp increase in dielectric losses, "transparent" materials couple efficiently with microwaves. This is characteristic of solids with both ionic (Al_2O_3, ZrO_2) and covalent (Si_3N_4, AlN) bonds. For instance, the attenuation distances of alumina and zirconia (Y-stabilized) change from meters at 20°C to 23 and 1 cm at 1200°C, respectively.

When the skin depth is greater than the dimension of the sample, this effect may be neglected. Conversely, when dimensions of samples are greater than its penetration depth penetration of microwave energy will be limited, making uniform heating impossible

Historically, there is a paucity of data on the dielectric properties of most materials as a function of temperature in the microwave range. The data reported in the literature indicate that there is a complex interdependence of dielectric properties on temperature and frequency (Clark & Sutton, 1996). Figures 1 and 2 illustrate the behavior of loss tangent, attenuation distance and reflection coefficient according to complex permittivity data published in the literature (Andrade et al., 1992; Arai et al., 1993; Batt et al., 1995).

Von Hippel (1954b) compiled the first tabulation of measurements for numerous materials over a wide range of frequencies (10 Hz - 10 GHz). The materials he characterized were both organic and inorganic in nature and both liquid and solid. Subsequently, dielectric data on high temperature solid materials, including oxides, nitrides, silicates, rocks and minerals were obtained by Inglesias and Westphal (Inglesias & Westphal, 1967, as cited in Metaxas & Binner, 1990). Since then, four reports have been produced at the same MIT Laboratory for Insulation Research where Von Hippel obtained his results as described by Metaxas & Binner (Metaxas & Binner, 1990). These reports contain much valuable information on the frequency and temperature dependence of the dielectric properties of a large number of ceramic materials (both oxide and some non-oxide), as well as various minerals, many organic compounds and some foodstuffs. The frequency and temperature varied up to 25 GHz and 1000°C, respectively (Metaxas & Binner, 1990).

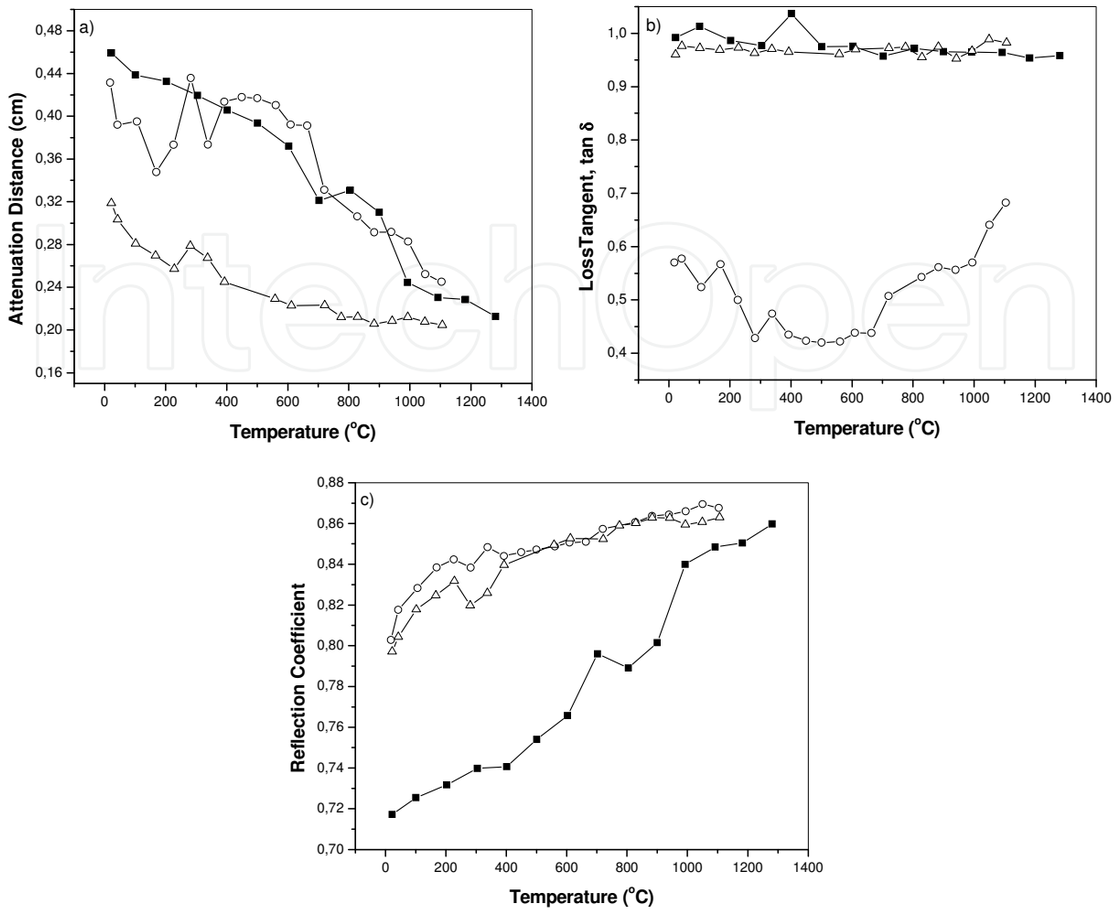


Fig. 1. a) Attenuation distance b), loss tangent, and c) reflection coefficient of SiC.

Studies (Sutton, 1989; Meredith, 1998) showed that when low-loss dielectric materials exhibit an abrupt increase in ε" with increasing temperature, the potential exists for very rapid changes in temperature. The temperature at which this abrupt change in ε" occurs is known as critical temperature, *Tc*. Above this temperature, the dielectric loss factor begins to increase, and the material begins to couple with microwaves. Figure 2 illustrates this behavior is when the loss tangent of zirconia increases significantly increases after 600°C.

However, many researchers have shown that thermal runaway in microwave-heated materials often occurs when critical temperature is reached. The sharp increase in microwave absorption with temperature may cause thermal instability, which is commonly known as temperature runaway.

The rapid rise in the dielectric loss factor with temperature is the main issue in thermal runaway (unstable accelerated heating). An increase in local temperature is accompanied by an enhanced microwave energy absorption, which results in local acceleration of heating, a further rise in temperature and the development of thermal runaway. This instability develops when microwave power exceeds some threshold value, which corresponds to an S-type dynamic curve of temperature versus power (Bikov et al., 2001). Below a "critical power level", the material will heat in a stable manner to a steady state value on the lower

branch of the response curve. If the power is increased to exceed the upper critical power, the temperature will jump to the upper branch of the temperature-power curve, giving rise to thermal runaway.

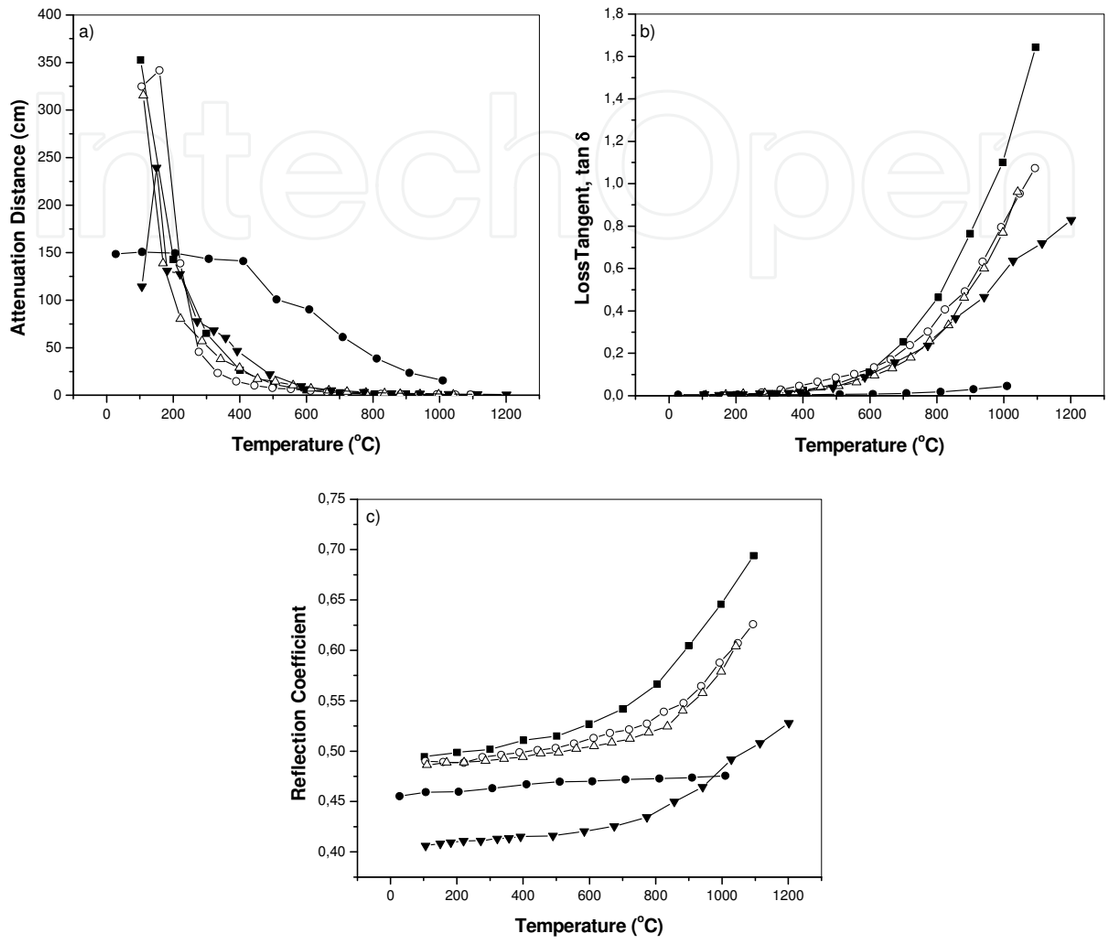


Fig. 2. a) Attenuation distance b), loss tangent, and c) reflection coefficient of ZrO_2.

Another important characteristic of the interaction of microwaves with ceramic materials is the non-thermal influence of microwave fields on mass transport. Many investigators have reported unexpected effects resulting from the use of microwave radiation as an alternative energy source during the processing of materials. This has included apparent evidence for accelerated kinetics for a range of processes in ceramic, polymeric, and organic systems, including the microwave sintering of ceramic materials. This unexpected effect was named "microwave effect". As a general rule, the kinetics of synthesis and sintering reactions of ceramic materials is reportedly augmented by two or three orders of magnitude or even more when conventional heating is substituted for microwave radiation.

In principle, the term "microwave effect", or, more strictly, "microwave field non-thermal effect", should be reserved for the deviations of microwave processes from conventional processes that occur given the identical temperature dynamics of these processes. Over the last decade, considerable effort has been focused on the development of theoretical models

for microwave non-thermal enhancement of transport phenomena in solids and experimental justification of these models (Bikov et al., 2001). Studies (Rybakov & Semenov, 1994a, 1994b; Freeman et al., 1994; Booske et al., 1997) observed that, through an amplification and rectification process, the electric fields inside a microwave oven are sufficient to significantly affect the sintering behavior of ceramics, inducing an additional driving force for diffusion in solid materials (Clark & Sutton, 1996). They demonstrated that, under certain conditions, microwave-induced oscillating vacancy fluxes are rectified, leading to directional macroscopic mass transport; and that when the electromagnetic field interacts with the free surfaces of interfaces, an additional driving force for diffusion is created. This driving force has been named "ponderomotive" driving force. This force can compete with different thermochemical driving forces and significantly affect mass transport in solids during sintering.

3. Microwave fast sintering of ceramics

The initial surge in the development of microwave technology was driven by the military needs of World War II. The tremendous effort that went into the development of radar during World War II generated am enormous body of knowledge on the properties of microwaves and related technologies (Committee on Microwave Processing of Materials: An Emerging Industrial Technology et al., 1994). In the post-war years, further development resulted in microwaves used for heating, especially for domestic purposes (Meredith, 1998). The first commercial microwave oven was a large floor-standing model was developed by the Raytheon Company of North America in 1951. Microwave ovens for domestic use were launched on the market in the early 1960s, initiating the mass market for this product. Soon thereafter, industrial microwave applications began to emerge, beginning with rubber extrusion, plastic manufacturing, and the treatment of foundry core ceramics.

Microwave processing of materials is a technology that has proven useful in a number of applications, presenting some important advantages over conventional heating methods. The main benefits of exploiting microwave energy in thermally activated processes stem from the specificity of microwave energy absorption. In contrast to all the other methods commonly used, microwaves allow for volumetric heating of materials. Microwave energy transforms into heat inside the material, which generally result in significant energy savings and shorter processing times. This factor plays a decisive role in most applications that have gained industrial acceptance to date.

Studies on microwave processing of ceramics started in the mid 1960s by Tinga (Tinga & Voss, 1968; Tinga & Edwards, 1968) and, since then, interest in the use of microwaves for heating and sintering ceramics has grown steadily. However, the particular requirements for ceramic powder sintering make this process one of the most challenging applications for microwave processing. These requirements often include high temperatures, high heating rates, uniform temperature distribution, etc. (Menezes et al., 2007). Moreover, during microwave heating, the absorption of electromagnetic energy raises the temperature of the entire sample, but heat loss from the surface causes the near-surface temperatures to become lower than the internal temperatures. Thus, in ceramics with poor thermal conductivity, large temperature gradients can develop in the body. The shape of the ceramic body and the microwave frequency strongly influence the temperature gradients, and achieving

sufficiently uniform heating of the body can be difficult. High heating rates can lead to localized heating, which can cause non-uniform properties and even cracking of the sample; as well thermal runaway when the temperature of the sample increases rapidly (Rahaman, 1995).

In microwave sintering, heat is generated internally through the interaction of the microwaves with the atoms, ions, and molecules of the material, which produces an inverse heating profile. Figure 3 presents a schematic diagram of heating by conventional and microwave processes. The microwave heating process is more volumetric, thus allowing higher heating rates. However, most research to date is based on conventional low-frequency (2.45 GHz) microwave applicators, and at this frequency, many ceramics present poor microwave absorption characteristics. Thus, materials, that are transparent to microwaves, such as SiO_2 and Al_2O_3 (ceramics with low-loss, as pure oxides and nitrides), are difficult to heat at room temperature.

Many ceramic materials that are difficult to heat at room temperature possess electrical conductivity or dielectric loss factors that rapidly increase in magnitude as the temperature rises. Thus, these materials will absorb microwave energy if they can be preheated to a suitable temperature using another heat source. This has led to the development of hybrid heating methods (Krage, 1981; Kimrey et al., 1991). Hybrid heating can be achieved by using either an independent heat source, such as a gas or electric furnace in combination with microwaves, or an external susceptor material (high-loss material) that couples with the microwaves. In the latter case, the material is exposed simultaneously to radiant heat produced by the susceptor material and to microwaves (usually, the susceptor material is simply named as "susceptor").

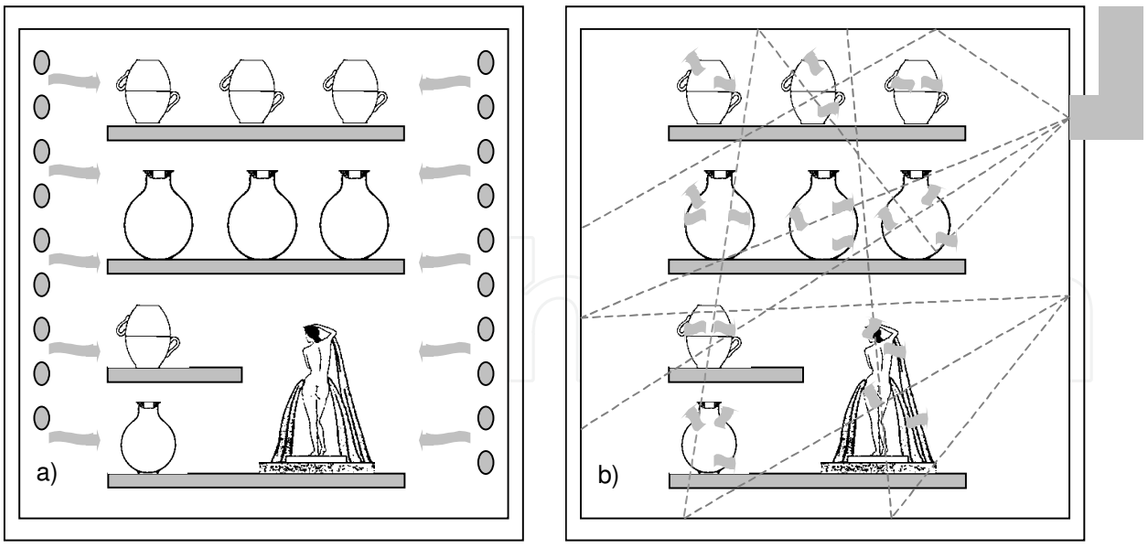


Fig. 3. Heating patterns in: a) conventional, and b) microwave furnaces.

Increasing the temperature (with radiant heat) is a common method many researchers employ to couple microwaves with poorly absorbing (low-loss) materials. Once a material is heated to its critical temperature, *Tc*, microwave absorption becomes sufficient to cause self-heating. This hybrid method can result in more uniform temperature gradients because the

microwaves heat volumetrically and the external heat source minimizes surface heat losses. Therefore, one of the most important characteristics associated with the use of microwave hybrid heating (MHH) is the potential to achieve uniform heating throughout the cross-section of a material, as illustrated in Figure 4. In the early 1990s, Dé (Dé et al., 1991a, 1991b) showed that microwave hybrid heating (MHH) could result in samples with no significant density gradient throughout the cross-section and that this phenomenon was enhanced with increased sample size. The consequences of more uniform temperature gradients are homogenous microstructures and improved properties of the final body.

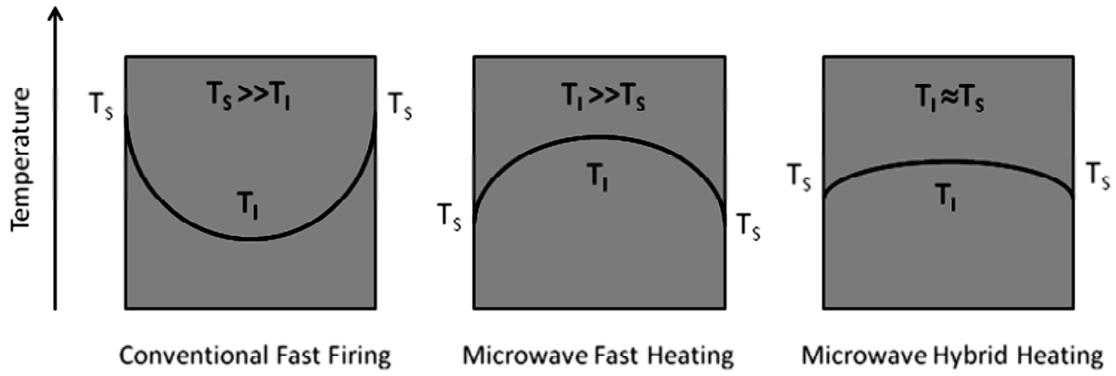


Fig. 4. Temperature distribution in ceramic material heated by conventional fast firing, microwave fast firing and microwave hybrid heating (T_S – Surface temperature, T_I – Internal temperature).

Figure 5 displays homogeneous microstructures of microwave hybrid fast sintered (MHFS) alumina samples (low-loss material). The samples sintered for 20min reached 97% densification and presented internal and surface microstructures with a similar grain size distribution, which reinforces the efficiency of hybrid fast firing in the densification and uniform heating of low-loss ceramic materials. Using hybrid heating, our research group has also microwave fast sintered other ceramic materials, such as mullite, zirconia, ZnO, porcelains, ferrites, and zirconia (Menezes et al., 2005, 2007, 2008, 2010; Souto et al., 2007; 2011), which has yielded similar homogenous microstructures in fast sintering cycles.

On the other hand, our researchers have also observed that, in two conditions, microwave hybrid fast heating can produce non-uniform microstructures. This was verified when susceptor material responded very rapidly to microwaves and the sample presented a very low loss, leading to a heating behavior similar to that of the conventional fast firing. The other condition was detected when processing high-loss materials. These materials coupled very efficiently with microwaves and their temperature rose very rapidly without similar heating of the susceptor. However, both conditions can be controlled by using different susceptors or by optimizing the sintering cycle. Figure 6 depicts the homogeneous microstructure of microwave hybrid fast sintered Ni-Zn ferrite (high-loss material). Using heating rates of up to 100oC/min up to 1000oC allied with lower heating rates at higher temperatures it was possible to reach high densification, 99% and uniform microstructures. Grain size distribution in the region near the surface and in the core of the samples was practically equal, highlighting the uniform temperature distribution inside the material, notwithstanding their high loss and rapid sintering.

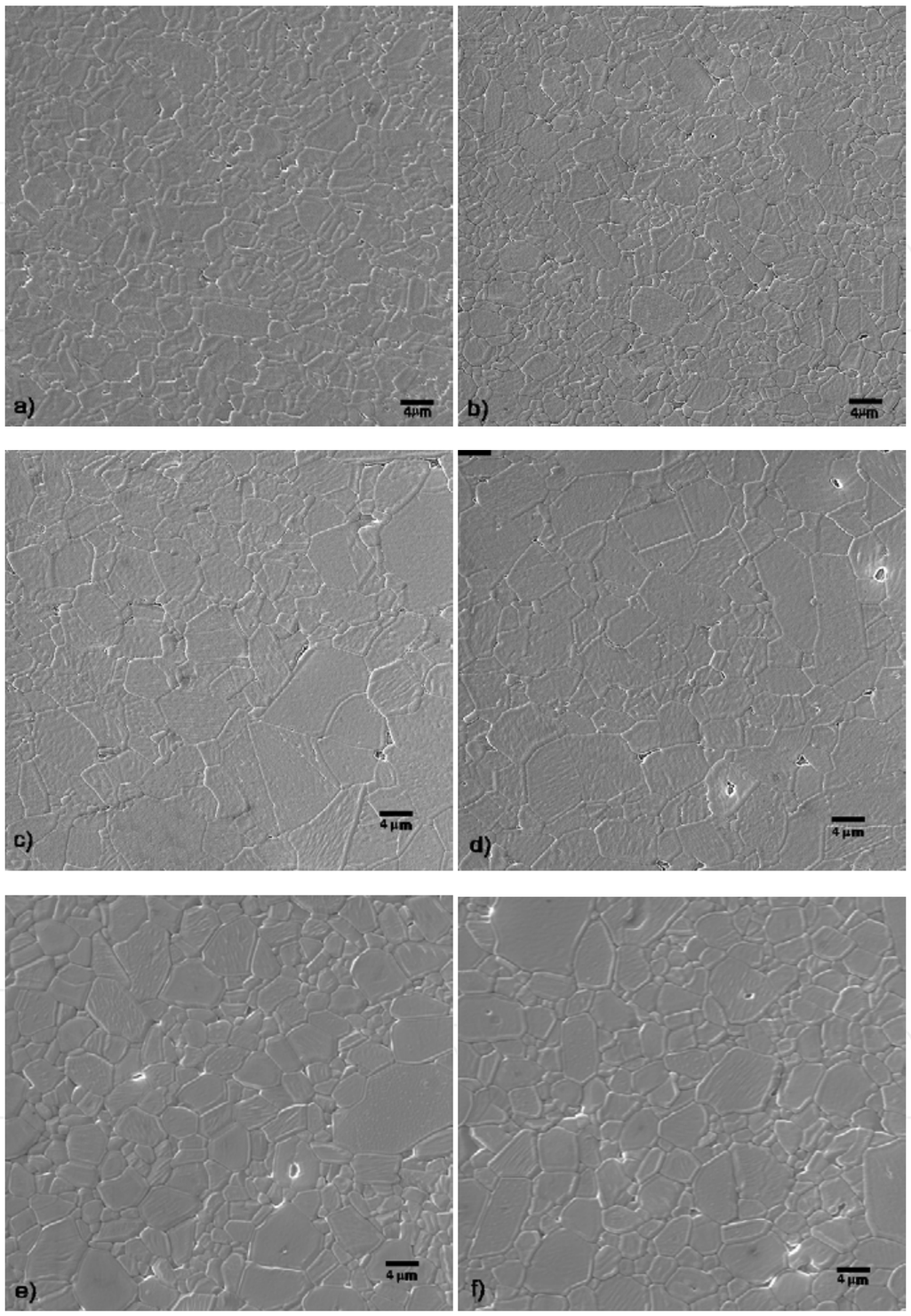


Fig. 5. SEM micrographs of MHFS alumina (Alcoa - A1000SG): at 1550°C (100°C/min up to 1100°C and 50°C/min up to 1550°C, soak time of 30 min – density of 95.3%) a) interior, b) surface; using 1.5kW for 25min (density of 96.6%), c) interior, d) surface; using 1.8kW for 20 min (density of 97.1%), e) interior, and f) surface.

An outstanding example of the use of microwave hybrid heating was the sintering of, ZrO_2/8% Y_2O_3 and zirconia/12% CeO_2 at 2.45 GHz by Janney (Janney et al., 1992). Although these materials could be sintered readily at 28 GHz, attempts to use 2.45 GHz, which involves lower equipment costs, were unsuccessful until SiC rods were inserted into the insulation surrounding the specimens, in what is referred to as the "picket fence" arrangement (Figure 7). The microwave energy initially heated the SiC rods, which resulted in uniform heating of the zirconia, and hence, in a homogenous coupling with microwaves after the critical temperature was reached.

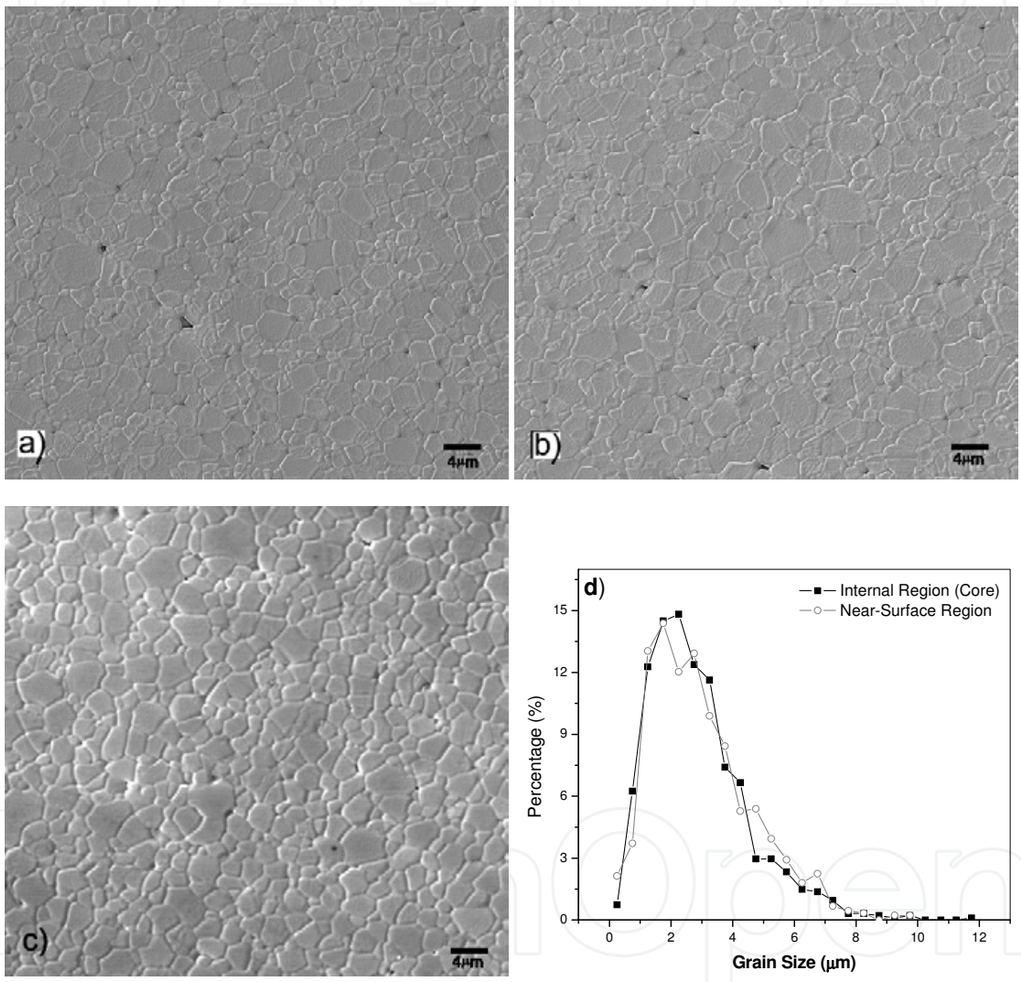


Fig. 6. SEM micrographs of homogeneous microstructures of Ni-Zn ferrite ($Ni_{0,5}Zn_{0,5}Fe_2O_4$): microwave hybrid fast sintered at 1220°C (100°C/min up to 1000°C and 50°C/min up to 1200°C, soak time of 20 min – density of 99%): a) sample interior (core), b) sample surface, c) sintered conventionally at 1200°C (5°C/min, soak time of 120min – density of 95.4%), and d) internal and near-surface grain size distribution of microwave-sintered sample.

Inside the insulation system, the thermal uniformity provided by susceptors plays an important role in reducing thermal runaways during fast sintering. Catastrophic overheating (thermal runaway) of processed material was observed in a large variety of

ceramics (such as Al_2O_3, SiO_2, Fe_2O_3, ZrO_2, etc.), and was a serious problem in the processing of materials whose dielectric properties are abruptly altered with rising temperature. Studies (Spotz et al., 1995) demonstrated that the insulation normally used to contain heat inside the cavity can exacerbate the problem of thermal runaway. However, the data also suggested that thermal runaway may be minimized or controlled by hybrid heating, thus allowing low-loss ceramic materials to be processed using rapid firing.

However, care must be taken in designing the shape and size of the susceptor arrangement, because some susceptor materials, e.g., SiC, have high loss factors and therefore low penetration depths. Raising temperature leads to higher dielectric losses and significantly decreased penetration depths (see Figure 1). In this condition, it may not be possible to determine what the fraction of the sintering resulted from the interaction with microwaves and what fraction was sintered conventionally (by radiation of the susceptor material), as illustrated in Figure 8.

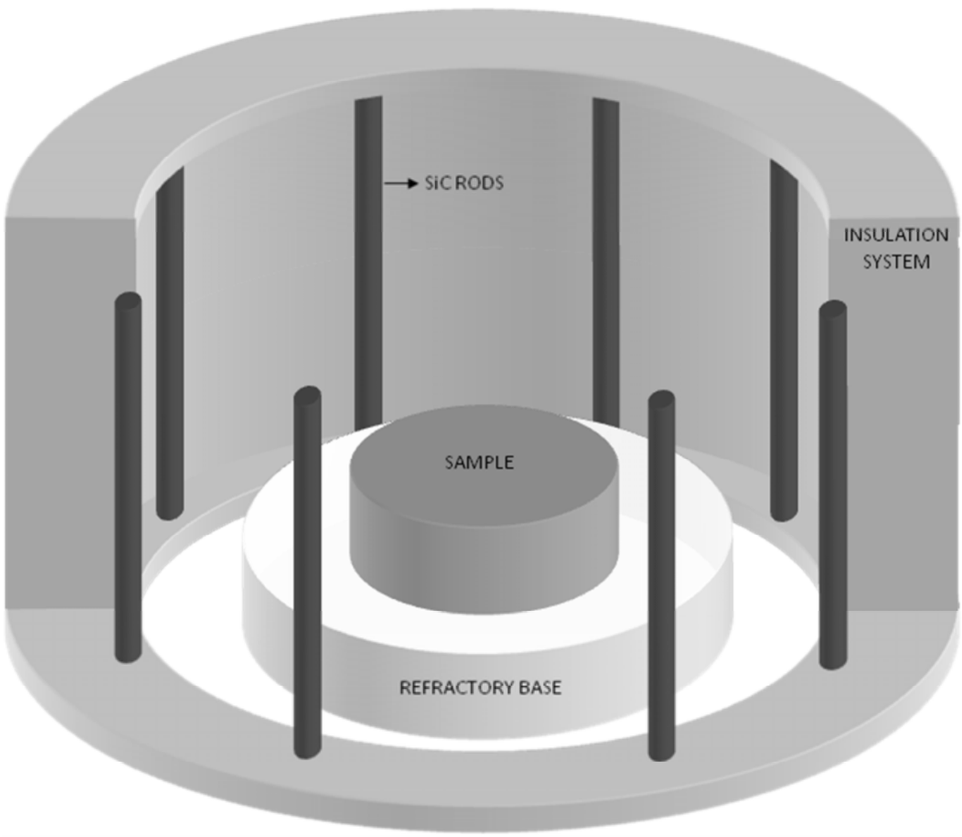


Fig. 7. Illustration of the "picket fence" arrangement.

Nanostructured materials have received much attention in recent years, due to their potential unusual physical and mechanical properties, such as superplasticity in ceramics at elevated temperatures, high hardness and mechanical strength, transparency for usually opaque materials, etc. However, one of the most challenging goals of modern ceramic technologies is still the manufacture of dense ceramic parts with submicrometric or nanostructured grains. Thus, controlled grain growth during the final steps of densification

is an extremely important processing concern that requires the development of processing routes to effectively suppress grain growth during densification.

When ceramic materials are processed by traditional sintering techniques, the high temperatures required to fully densify ceramic powders result in large grain sizes due to Ostwald ripening. This makes it extremely difficult to obtain dense materials with nanometric and submicrometric grain sizes. Thus, although suitably uniform nanophase powder materials are becoming increasingly available, the fabrication of fully dense nanostructured products still offers challenges. In this context, the microwave fast sintering appears as an alternative for the sintering and densification of ceramics with suppressed grain growth.

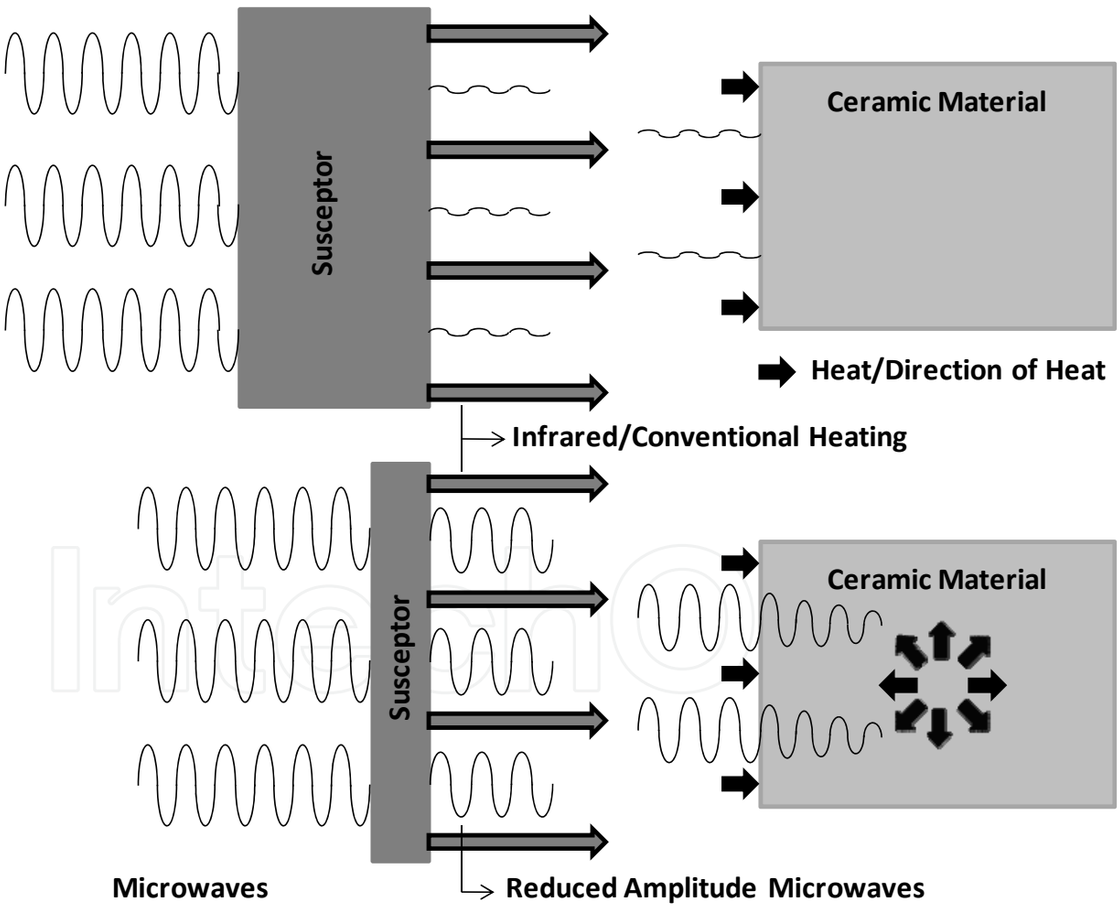


Fig. 8. Microwave hybrid heating arrangement/effect of susceptor material volume on the final heating pattern.

As mentioned early, the objective of fast firing is to enhance the densification rate in detriment to the coarsening rate by a rapidly approaching to the sintering temperature. Because coarsening mechanisms (e.g., surface diffusion and vapor transport) commonly prevail over densification mechanisms (e.g., lattice and grain-boundary diffusion) at lower temperatures, it has been suggested that rapid heating to higher temperatures can be beneficial to achieve high density allied to fine grain size. In this case, the shorter time spent at lower temperatures serves to reduce the extent of coarsening while the driving force for densification is not decreased significantly.

The authors' research group employed microwave hybrid fast heating to sinter submicrometric alumina (Sumitomo, AKP 53 – average particle size of 0.2 μm and surface area of 10.4m²/g). Rapid densification, 98.9%, suppression of grain growth, and submicrometric grain size microstructures were achieved (SEM micrographs in Figure 9)

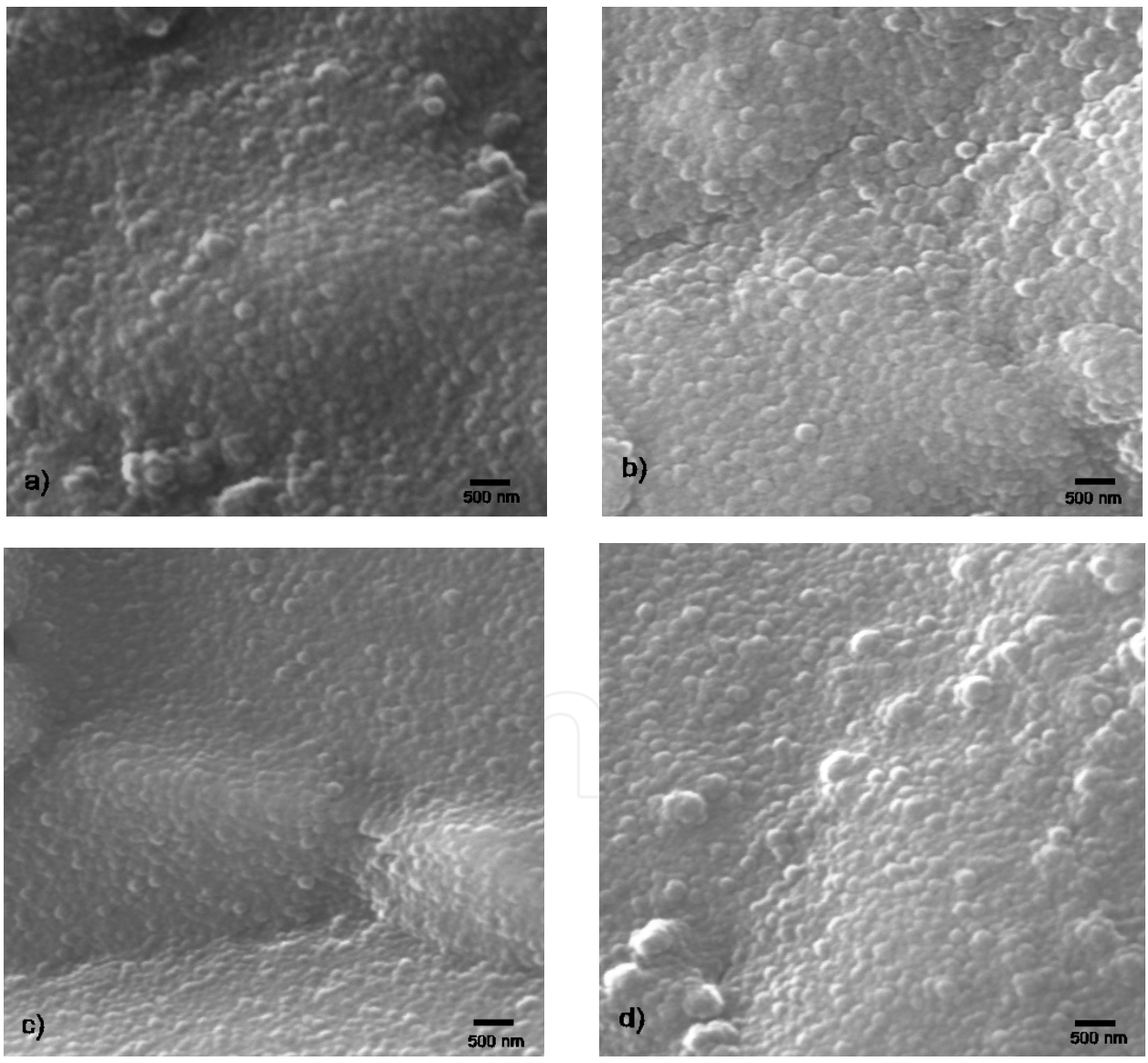


Fig. 9. SEM micrographs of the fracture surface of MHFS alumina (Sumitomo AKP - 53) processed at 2.45GHz with power level of 1.8kW for 26min (98.9% density): a) and c) grains in a internal region, b) and d) grains in a near-surface region.

Figure 10 shows samples of these alumina bodies sintered in a multimode furnace operating at 2.45 GHz. Microwave fast sintered alumina bodies were devoid of cracks, which is a reliable indicator of homogeneous temperature distribution in the bodies. In contrast, conventionally fast fired samples (50°C/min) presented cracks and non-uniform microstructures.

A alumina-zirconia nanocomposites were also rapid-sintered using the heating system developed for fast heating of alumina samples. Alumina (Sumitomo AKP 53)/ zirconia (yttria-stabilized zirconia powder, 3YSZ, Nanostructured & Amorphous Materials Inc., 58–76nm particle size) nanocomposites containing up to 5 vol.% zirconia, reached densities of approximately 99% in 35 min. Uniform microstructures and suppression of grain growth were obtained using rapid hybrid sintering. Figure 11 presents SEM micrographs of sintered nanocomposite containing 5%vol.% zirconia.



Fig. 10. Alumina samples processed by microwave hybrid fast sintering.

Grain growth suppression was also achieved in the processing of submicrometric zirconia (Zirconia Tosoh TZ-3Y, Tosoh Corporation, $D_{50} \approx 0{,}4\mu m$), which yielded a high densification of 99% a fine-grained microstructure with an average grain size of 0.6μm. The micrographs (Figure 12) of the internal and near-surface regions are practically identical, showing intergranular fracture, uniform grain size distribution, and no visible cracks, pores or abnormal grain growth.

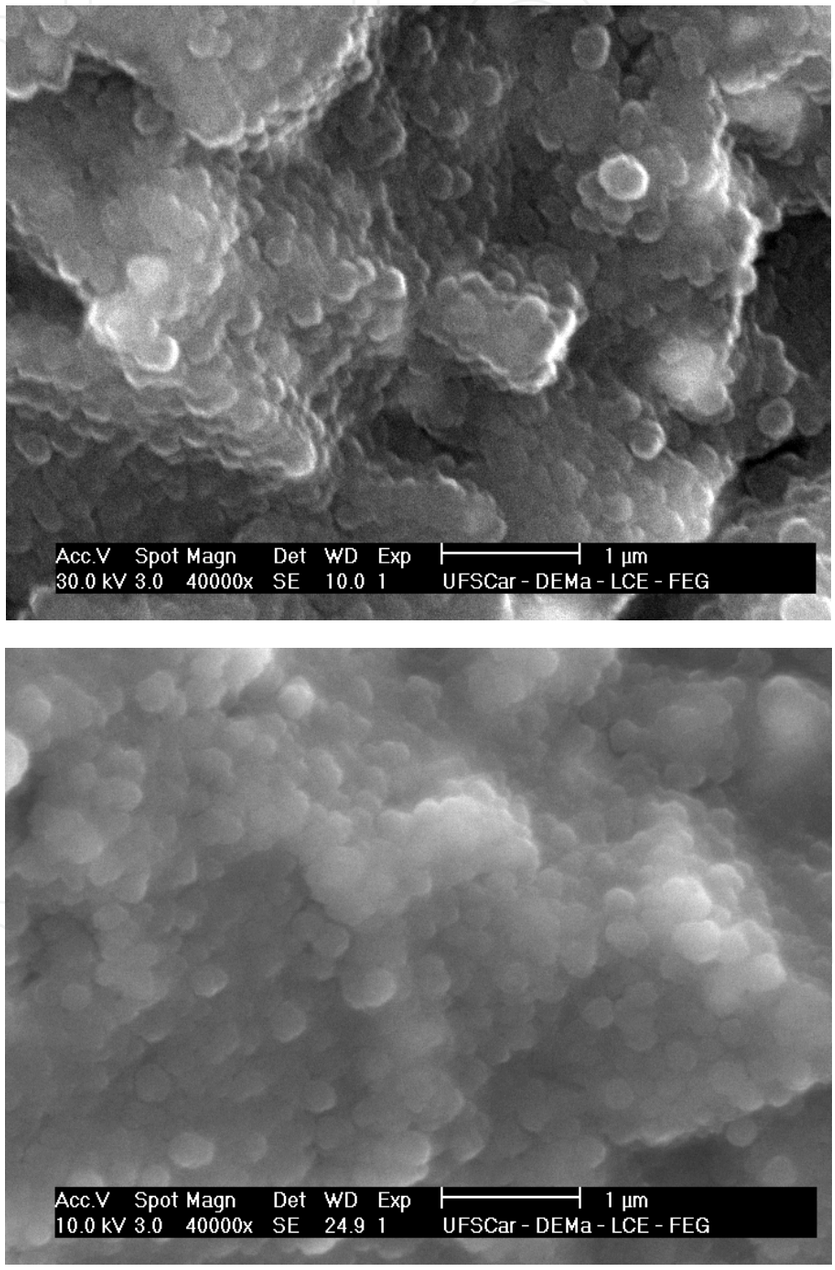


Fig. 11. SEM micrographs of the fracture surface of MHFS nanocomposite alumina (Sumitomo AKP - 53)/zirconia (Nanostructured & Amorphous Materials, 3YSZ) (3 vol.% zirconia) processed at 2.45GHz with power level of 1.8kW for 35min (99% density).

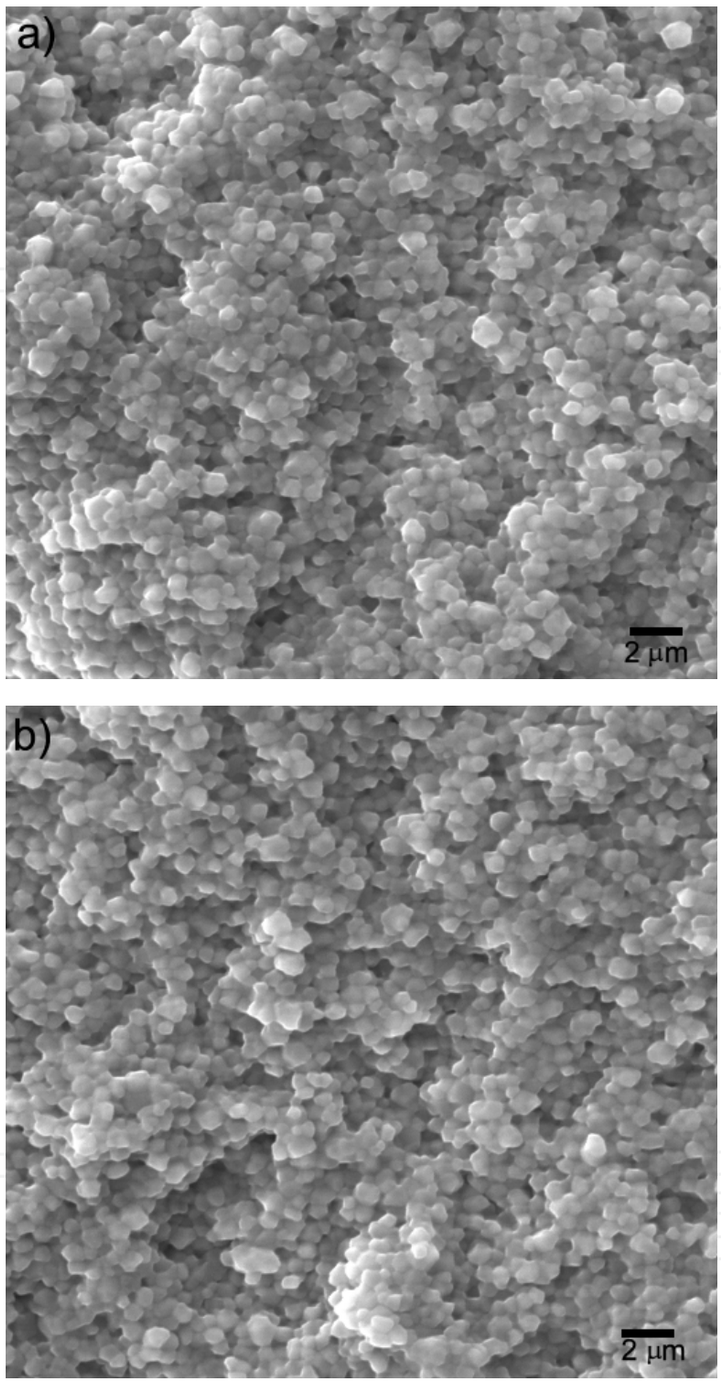


Fig. 12. SEM micrographs of the fracture surface of MHFS zirconia (Tosoh TZ-3Y) processed at 2.45GHz with power level of 1.8kW for 20min (99% density), a) internal region, b) near-surface region.

It is difficult to process zirconia in a 2.45GHz microwave furnace because the dielectric properties of this material change rapidly with temperature (see Figure 2) and its thermal conductivity is very low. Therefore, the use of hybrid heating is very important to produce

uniform heating, thus avoiding thermal runaway and cracks. The rapid sintering of zirconia specimens without cracked, allied to the high densities achieved (> 97%), indicate a highly uniform distribution of temperature in the processed bodies. The non-uniform distribution of temperature in zirconia hinders its densification and may lead to thermal runaway may.

The results obtained by our research group indicate the successful use of microwave hybrid fast sintering in the densification of ceramic bodies and its effectiveness in suppressing grain growth in the final stages of sintering. The rapid densification achieved, accompanied by only minor grain growth, seems to be an indication of the microwave effect. However, regardless of the presence or absence of the microwave effect, the results of our research group indicate that microwave hybrid heating is a great potential method for rapid sintering of low and high-loss ceramic materials, yielding uniform microstructures and allowing for suppressed grain growth (when necessary).

4. Conclusions

Studies by our research group confirm that microwave hybrid fast sintering can be employed successfully to sinter low and high dielectric loss ceramics, producing highly dense ceramics and suppressing grain growth in the final stages of sintering. Controlled heating schedules and the use of suitably designed susceptor materials yield uniform microstructures without stress-related cracking or the development of incipient fusion, hot spots or thermal runaway. Thus, successful microwave fast sintering depends on the strict control of sintering conditions, striking an adequate balance between power and time or temperature and time to obtain highly dense and homogeneous microstructures.

5. Acknowledgements

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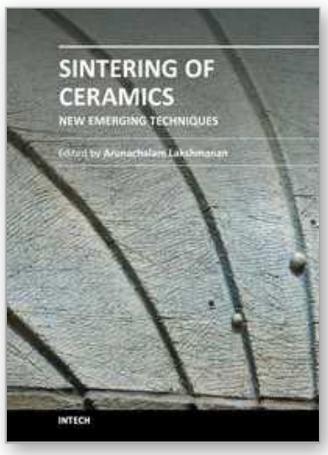
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The chapters covered in this book include emerging new techniques on sintering. Major experts in this field contributed to this book and presented their research. Topics covered in this publication include Spark plasma sintering, Magnetic Pulsed compaction, Low Temperature Co-fired Ceramic technology for the preparation of 3-dimesinal circuits, Microwave sintering of thermistor ceramics, Synthesis of Bio-compatible ceramics, Sintering of Rare Earth Doped Bismuth Titanate Ceramics prepared by Soft Combustion, nanostructured ceramics, alternative solid-state reaction routes yielding densified bulk ceramics and nanopowders, Sintering of intermetallic superconductors such as MgB2, impurity doping in luminescence phosphors synthesized using soft techniques, etc. Other advanced sintering techniques such as radiation thermal sintering for the manufacture of thin film solid oxide fuel cells are also described.

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