TOPICAL REVIEW

High-temperature microwave processing of materials

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Abstract

This article reviews the physical aspects of a cross-disciplinary science and
technology field: the microwave processing of materials. High-temperature
microwave processing has a clear industrial perspective in such areas as the
production of advanced ceramics, the deposition of thermal barrier coatings,
the remediation of hazardous wastes etc. This review starts with the relevant
fundamental notions regarding the absorption of electromagnetic waves,
heat transfer and the electrodynamics of single- and multimode microwave
cavities. Useful formulae, estimates, and interrelations between process
variables are presented. This is followed by a review of process examples
illustrating the specific features of microwave processing: reduction in
energy consumption and process duration, rapid and controllable heating,
peculiar temperature distribution, and selectivity of energy deposition.
Much attention is given to the advantages of higher-frequency
millimetre-wave processing, which include the enhanced absorption in many
materials of industrial interest, improved uniformity of electromagnetic
energy and temperature, and the possibility of surface treatment. The
phenomenon of microwave process rate enhancement is addressed in
connection with the problem of the non-thermal microwave effect on mass
transport in solids. Both experimental and theoretical approaches to the
identification of the mechanism responsible for this effect are illustrated.
Finally, the physical and technical factors influencing microwave technology
scaleup and transfer to industry are discussed.

1. Introduction

Processes based on microwave heating find many industrial
applications. The main benefits of exploiting microwave en-
ergy in thermally activated processes stem from the specificity
of microwave energy absorption. In contrast to all other com-
monly used methods, microwaves allow *volumetric* heating of
materials. Microwave energy transforms into heat inside the
material, which results, as a rule, in significant energy savings
and reduction in process time. This factor plays a decisive role
in most applications that have gained industrial acceptance to
date. The wide availability of microwave power sources of fre-
quencies $\leqslant 2.45$ GHz and good microwave absorption proper-
ties of many materials have led to the emergence of industrial
facilities for various applications with hundreds of megawatts
in total of installed microwave power [1].

While most of today's industrial applications of mi-
crowaves are centred around the relatively low-temperature
processing of food, wood, rubber, polymers etc, there is grow-
ing interest in the high-temperature microwave processing
of materials. The term 'high-temperature processing' has a
rather general meaning and can hardly be defined by some
characteristic temperature. It refers primarily to the process-
ing of solid, inorganic materials by activating mass trans-
port phenomena based on diffusion. These processes are
of significant general interest due to the clear physical na-
ture of their driving forces and the relatively simple struc-
ture of the materials, as compared to the aforementioned
low-temperature processing of organic substances. Yet, the
general physical issues pertinent to microwave heating are
equally relevant for all processes, independent of their tem-
perature.

This article is a review of the physical aspects of microwave processing of materials. It has the following structure. Section 2 contains a general consideration of the basic physical notions underlying microwave processing. Subsection 2.1 introduces the microwave absorption properties of materials, which govern energy deposition during microwave processing. Particular features of microwave absorption in low-loss, high-loss, and composite materials are described briefly in this subsection. The issues of heat transfer and temperature distribution during microwave heating are addressed in subsection 2.2. The dependence of temperature uniformity on the heating schedule and the thermal properties of material is discussed. The thermal instability peculiar to microwave heating and ways to prevent it are analysed. Subsection 2.3 contains a brief account of the types of applicators used for microwave processing, including a single-mode resonator and a multimode untuned cavity.

Efficient diffusion in inorganic solids starts at temperatures above 0.5–0.6 of the melting temperature, T_m. In most materials of practical importance, which are not single crystals, the transport of mass can occur by various mechanisms, including surface, grain boundary or bulk diffusion, evaporation–condensation etc. These mechanisms constitute the basis for the high-temperature macro-processes, such as sintering of ceramics, joining of ceramics and metals, synthesis of new materials, deposition of coatings etc. Subsection 2.4 briefly recalls some basic concepts from solid-state physics that are relevant to high-temperature processes in materials. These concepts are further used throughout the article.

Section 3 deals with high-temperature microwave processing itself. It describes how the specific features of microwave heating can be exploited in particular processes. The review of microwave applications is deliberately restricted to high-temperature processing of inorganic solid materials. This field has received the greatest attention of researchers to date. Even within this limited area we do not try to give an all-embracing review but select only those processes which instructively illustrate the peculiar features of the microwave treatment of materials.

Among the microwave applications considered, an important place is occupied by ceramics processing. This is explained by both the authors' primary interests lying in this field and the prevailing activity of the high-temperature microwave processing community. The possibility of ceramics processing by microwave heating was discussed over 40 years ago by Von Hippel [2], and experimental studies started in the middle of the 1960s by Tinga and co-authors [3, 4]. Since then the results of many investigations in microwave ceramics sintering and joining have been reported. In the majority of the papers the authors claim acceleration of microwave-driven processes as compared with processes performed using conventional heating. The acceleration commonly manifests itself as a reduction in the densification time of ceramic powder compacts, which is often accompanied by a decrease in the temperature of sintering. References to the published works on microwave sintering and joining of various ceramics and specific procedures and techniques can be found in the reviews by Sutton [5], Katz [6], and Clark [7]. Section 3 of this article surveys how high-temperature processing can benefit from such peculiar features of microwaves as reduced

energy consumption and process time (subsection 3.1), rapid and controllable heating (subsection 3.2), inverse temperature distribution (subsection 3.3), and selective heating (subsection 3.4). Specifically, high rates of volumetric heating, not limited by thermal diffusion, prevent recrystallization grain growth and result in a finer and more uniform microstructure of ceramic materials. It is well known that a fine, homogeneous, and fault-free microstructure is a necessary prerequisite for enhanced material performance. Similarly, a decrease in the duration of the high-temperature stage of the ceramics joining process leads to reduced grain growth in the joint zone and, as a result, to the higher mechanical strength of the joint. The inverse temperature profile with a maximum in the core of the body results from the combination of volumetric heating and surface heat loss. It is especially advantageous in processes that involve the reaction of a porous solid matrix with a gas or liquid phase, such as the synthesis of reaction-bonded ceramics or infiltration. Selective absorption of microwave energy and inertialess heating make up an added bonus of microwave processing. Selective microwave absorption can be purposely used for the synthesis of composite materials with desired functional properties. The inertialess nature of microwave volumetric heating offers the opportunity of the *in situ* control over the microstructure of the material undergoing processing.

Section 3 ends with a discussion of the surface processing of materials (subsection 3.5). This type of processing becomes possible when higher-frequency millimetre waves are used. Surface treatment has great potential in such processes as joining and coating. However, this promising area remains largely unexplored, probably due to the lack of millimetre-wave sources in materials research laboratories.

Even relatively simple microwave processes, for example solid phase sintering of single-component powder compacts, encounter fundamental problems that are widely discussed in the microwave processing community. As mentioned above, numerous experimental results suggest that microwave heating causes acceleration of processes as compared to conventional heating. In the search for a physical explanation of this phenomenon, two essential factors which distinguish microwave-driven processes can be considered as starting points. One of them is the abovementioned inverse temperature profile. Another fundamental difference is the presence of alternating electromagnetic fields in the volume of materials undergoing microwave heating. The problem of direct electromagnetic influence on mass transport, the so-called microwave non-thermal effect, is discussed in section 4. Subsection 4.1 outlines the problem of the experimental identification of non-thermal effects and describes selected experimental findings. Subsection 4.2 discusses the fundamental approaches to the mechanisms of non-thermal microwave action. It introduces the concept of non-equilibrium excitations and gives an estimate of their significance. It is shown that nonlinear effects in the microwave-driven motion of charged vacancies can affect mass transport under the microwave processing conditions. Although theoretical models have been suggested that attempt to explain the enhanced mass transport under microwave heating, further research is still needed to clarify the mechanism of microwave–materials interaction.

Section 5 briefly discusses the physical and technical factors influencing the transfer of laboratory results to industry.

Finally, it should be noted again that this article is not intended as a detailed survey of the numerous results that have been achieved in the field of high-temperature microwave processing of materials. The interested reader will find a much more complete list of references in the above cited reviews. On the other hand, this article contains a number of original estimates and illustrations. A primary focus of this article is those physical aspects and experimental results that can play a decisive role in further developments in this area.

2. Basic physical concepts of microwave high-temperature processing

2.1. Microwave absorption

Microwave heating is based upon the capacity of a material to absorb the electromagnetic energy. 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 such a response of a material to an external electric field is the dielectric permittivity, ε[1]. 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, is formally introduced: $\varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega)$. The imaginary part of the dielectric permittivity is greater the larger the lag. The change of polarization, i.e. the redistribution of internal charges, is accompanied by the motion of electric charge, i.e by the electric ac current, which generates heat inside the material. The effective high-frequency conductivity, σ, can be introduced in order to characterize the power of heating, similar to the case of a dc current. The power of heating per unit volume, which equals the absorbed microwave power, is

$$w = \sigma E^2 \qquad (2.1)$$

where E is electric field strength inside the material. The effective high-frequency conductivity is unambiguously linked to the imaginary part of the dielectric permittivity, $\sigma = \omega\varepsilon_0\varepsilon''$, where ε_0 is a constant called the permittivity of free space.

Because of absorption, the electromagnetic fields decrease as the wave passes through the material. The dissipation of electromagnetic energy is commonly characterized by the so-called loss factor, $\tan\delta = \varepsilon''/\varepsilon'$. The attenuation of the electromagnetic wave can also be characterized by a penetration depth (or skin depth), on which the field strength is reduced by a factor of $e = 2.71\ldots$:

$$l = \frac{c}{\omega}\sqrt{\frac{2[1 + \sqrt{1 + (\tan\delta)^2}]}{\varepsilon'(\tan\delta)^2}}, \qquad (2.2)$$

where c is the velocity of light [8].

When the electromagnetic wave is incident (from air or vacuum) onto a plane surface of material, it is partly reflected from the surface and partly penetrates into the material.

For a normal incidence of the electromagnetic wave on a plane boundary between material and vacuum, the fraction of reflected power (reflection coefficient) is [8]

$$R = \frac{1 - \sqrt{2\varepsilon'[1 + \sqrt{1 + (\tan\delta)^2}] + \varepsilon'\sqrt{1 + (\tan\delta)^2}}}{1 + \sqrt{2\varepsilon'[1 + \sqrt{1 + (\tan\delta)^2}] + \varepsilon'\sqrt{1 + (\tan\delta)^2}}}. \qquad (2.3)$$

Any of the heating processes that use the electromagnetic energy can be characterized by the two parameters, l and R. The frequency dependence of the dielectric permittivity determines the peculiar features of heating by electromagnetic radiation of different frequency ranges. In conventional furnace heating, energy is transferred to the materials by thermal electromagnetic radiation, with its maximum intensity being in the infrared range. The penetration depth of infrared radiation ($\omega \geqslant 10^{13}$ s^{-1}) is very small ($l \ll 10^{-4}$ m) in a majority of solids. Therefore, energy deposition is localized within a thin layer near the surface of material. As a result, conventional heating essentially depends on heat transfer from the hotter near-surface region to the colder bulk of the material.

In the microwave frequency range the absorption properties of non-metallic materials vary greatly. The loss factor, $\tan\delta$, 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 metres to fractions of a millimetre. Thus, knowledge of the dielectric properties of materials, as well as their dependence on frequency, temperature, chemical composition, and microstructure is of paramount importance for the intelligent use of microwave energy for high-temperature processing.

The physical mechanisms of microwave absorption have long been studied, and an exhaustive account of them can be found in practically any monograph on electromagnetic waves in dielectrics (see, for example, [2]). However, the theory of interaction between microwave electromagnetic fields and materials is capable of giving only qualitative information on the dielectric properties of materials and their frequency dependence. The reason is that the mechanisms of interaction and their effectiveness are strongly dependent on the structure of materials, type and strength of chemical bonds between atoms. At most, the theoretical considerations are able to predict the character of the dependence $\varepsilon(\omega)$ but fail to calculate the magnitude of the dielectric permittivity at a given frequency. Therefore, the direct measurement of the dielectric properties appears the only method to obtain quantitative information on them. Various experimental techniques exist for measuring dielectric properties in a wide frequency range up to several hundred gigahertz. With increase in frequency, the experimental methods vary from the coaxial line and waveguide techniques commonly used for decimetre wavelengths to open quasioptical resonators and interferometers exploited in the millimetre-wave range [9].

The materials commonly subjected to microwave processing can be categorized according to their microwave absorption properties (expressed by either the imaginary part of dielectric permittivity, ε'', loss tangent, $\tan\delta$, or effective conductivity, σ). The problems encountered in the microwave

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[1] In most dielectric materials the magnetic component of the electromagnetic field does not contribute to microwave absorption, and will not be considered here. However, magnetic effects are important in the interaction of microwaves with metals and can be determining in the microwave absorption of metal–dielectric composites.
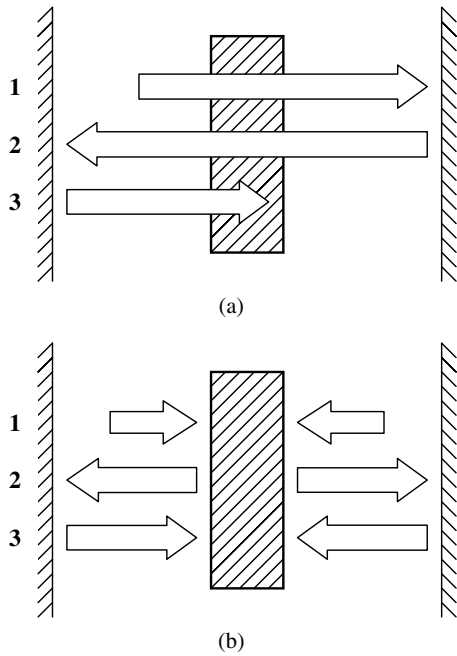
Figure 1. Illustration of resonant cavity operation. (a) Case of a low-loss sample: 1, incident radiation; 2 and 3, radiation returned to the sample after reflection from resonator walls. (b) Case of a high-loss sample: 1, incident radiation; 2, radiation reflected from the sample; 3, radiation returned to the sample after reflection from resonator walls.

heating of materials exhibiting low ($\tan\delta \leqslant 10^{-3}$) and high ($\tan\delta \geqslant 10^{-1}$) absorption are quite different, as are the methods for their solution. It is therefore instructive to consider the cases of low-loss and high-loss materials separately[2].

At room temperature, dielectric losses of low-absorption materials are caused by the displacement of bound charge carriers in such processes as atomic lattice vibrations and dipole reorientation. Among these materials are pure oxides (Al_2O_3, BeO, SiO_2) and nitrides (BN, Si_3N_4, AlN). Low microwave absorption makes it generally inefficient to heat these materials by the radiation of the decimetre-wave range ($\leqslant 2.45$ GHz), traditionally used for microwave applications. However, even at these low frequencies the heating of these materials is possible if the sample undergoing processing is placed into a resonant cavity which concentrates the electromagnetic field within the sample (figure 1(a); see subsection 2.4). In this case heating is achieved owing to multiple passes of the electromagnetic wave through a sample, even if its size is much less than the penetration depth of radiation, l. Another approach employs the so-called hybrid heating schemes. In essence, they involve introduction of additional heat sources into the system. In particular, the role of these sources can be played by microwave-absorbing objects (susceptors), from which the microwave-generated heat is transferred to the low-loss material undergoing processing [5].

[2] It is worth noting that no significant resonant effects can occur in the microwave heating of solid and liquid materials. Even though microwave radiation might be in resonance with some energetic state of the material undergoing processing, the relaxation time (i.e. the time of energy exchange between various energetic states) in solids and liquids is so small that all excited states are in thermal equilibrium. The relaxation becomes even faster with an increase in the temperature of the materials.

At elevated temperatures, microwave absorption in most materials grows sharply, primarily due to an onset of another absorption mechanism. This is characteristic for both solids with ionic (Al_2O_3, ZrO_2) and covalent (Si_3N_4, AlN) bonding. A sharp increase in the microwave loss starts 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 start to break, and the electrons in covalent materials begin to populate the conduction bands. Due to the sharp increase in the losses, there is no need for hybrid heating at elevated temperatures. A correctly designed susceptor system would provide heating at the initial stage, and reflect most of the power at high temperatures when microwaves are absorbed directly by the material undergoing processing.

The sharp increase in microwave absorption with temperature can cause a thermal instability, which is commonly known as a temperature runaway. The problem of a temperature runaway is widely discussed in the literature on the microwave processing of materials (see, for example, [10]). It is pertinent not only to high-temperature processes. The nature of this instability is easy to understand. An increase in the local temperature is accompanied by an enhancement of microwave energy absorption, which results in the local acceleration of heating and further growth of temperature. The instability develops provided that the microwave power exceeds some threshold value, which corresponds to an S-type dynamic curve of the temperature versus power [11]. An illustration to this phenomenon is shown in figure 2. Further discussion of thermal instabilities is given in subsection 2.3.

Heating of low-loss materials becomes much easier at higher frequencies of microwave radiation, i.e. in the millimetre-wave range. This is due to the fact that the dielectric losses of these materials increase with frequency. For example, the sintering of high-purity Al_2O_3 ceramics, one of the least-absorbing materials, at a frequency of 30 GHz has demonstrated that the heating rates of about several tens of degrees centigrade per minute can be easily achieved by direct absorption of the microwave energy by the material [12–14]. There is also evidence [15, 16] that in many materials the temperature dependence of dielectric losses in the millimetre-wave range is not so sharp. Therefore, the problem of a temperature runaway becomes less severe with an increase in the frequency of the radiation used for heating. If this phenomenon is of a general nature, it can be a major argument in favour of using millimetre-wave power for the high-temperature processing of materials.

In principle, the dependence of the microwave absorption of materials on frequency opens a way to controllably shape the temperature distribution by simultaneously using radiation of two different frequencies. The simultaneous application of microwaves of frequencies 2.45 GHz and 30 GHz was discussed in [17]; however, no experimental results of an attempt to accomplish double-frequency heating have been reported to date.

In the case of highly absorptive materials (with $\tan\delta \geqslant 10^{-1}$) the effective conductivity is typically so large that a strong reflection of radiation from the surface inhibits microwave heating (figure 1(b)). The absorbed fraction of the incident microwave power can be estimated approximately as

$$1 - R \approx 2\sqrt{\frac{2}{\varepsilon' \tan\delta}}. \tag{2.4}$$
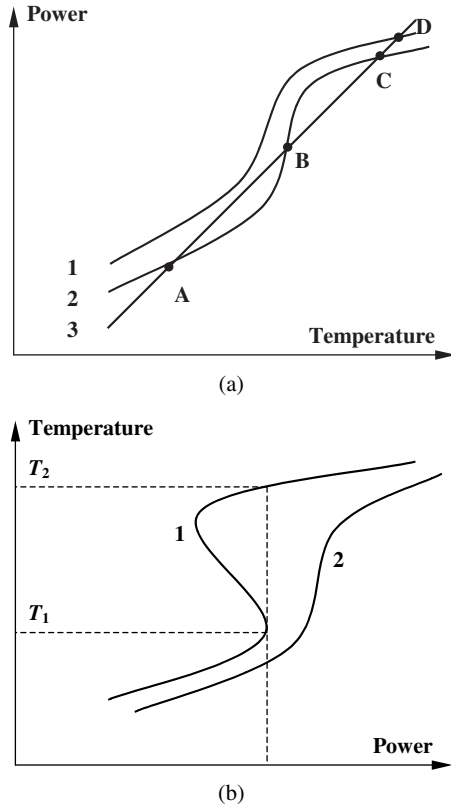
(a)

(b)

Figure 2. (a) Power balance under microwave heating as a function of temperature. 1 and 2, absorbed microwave power at two different levels of power from microwave source; 3, power removed via heat losses. A, C, and D, stable points; B, unstable point. Controlled heating possible at microwave power level 2 (point A) but impossible at level 1. (b) The resulting temperature versus power curves for two levels of power from microwave source. Note that temperatures between T_1 and T_2 are not accessible at power level 1, which means that controllable heating is impossible.

Usually the absorbed power does not exceed several per cent at a frequency of about 1 GHz and increases in direct proportionality to the square root of frequency. Efficient microwave heating becomes possible only when the sample is covered with an absorbing layer that facilitates coupling with the incident electromagnetic waves and/or is placed inside a high-quality cavity providing multiple passes of radiation. For optimum performance the absorbing layer must have high values of the imaginary part of the dielectric permittivity, $\varepsilon'' \gg 1$, and an even higher real part,

$$\varepsilon' \sim \left(\frac{\pi}{4}\varepsilon''\right)^2. \qquad (2.5)$$

The optimum thickness of the absorbing layer is

$$d \sim \frac{2c}{\omega\varepsilon''}. \qquad (2.6)$$

In microwave processing practice most of the materials are heterogeneous. For example, ceramic materials at all stages of densification remain a two-component mixture of solid material in the grains and voids between the grains. The heterogeneous composition of many other materials is dictated by their applications. For example, metal–ceramic composites are commonly used for producing hardmetal machine tools

[18]. Composites formed as a dielectric matrix with metal particle inclusions are known as good absorbers of microwave and infrared radiation [19]. Functionally graded materials with specially tailored composition are promising for the development of high-temperature thermal barrier coatings [20]. In fact, applications of heterogeneous materials are much more diverse compared to materials of homogeneous composition.

If the scale of microstructure non-uniformity is much less than the electromagnetic wavelength in the material, one can use the averaged description of the electromagnetic field interaction with the material. Within this description the material is treated as homogeneous and characterized by effective dielectric and magnetic permittivities, ε_{eff} and μ_{eff}, which play the same role as the ordinary permittivities in homogeneous material. The effective properties of a heterogeneous material depend upon the properties of the constituent materials, the ratios of the constituent parts, size and shape of particles composing a mixture, etc. A detailed review of the methods developed for simulating the dielectric and magnetic properties of heterogeneous materials by introducing effective parameters can be found, for example, in [21]. The most popular among these methods are the Maxwell–Garnet theory (MGT) and the effective medium approximation (EMA). The MGT describes a heterogeneous material as some host (matrix) material containing spherical inclusions of other material(s). In this case the value of ε_{eff} is determined as a root of the equation

$$\rho_h(\varepsilon_h - \varepsilon_{eff}) + \sum_k \rho_k(\varepsilon_k - \varepsilon_{eff})\frac{3\varepsilon_h}{2\varepsilon_h + \varepsilon_k} = 0 \qquad (2.7)$$

where ε_h and ε_k are the complex dielectric permittivities of the host material and the inclusion of sort k, respectively; ρ_h and ρ_k are the volumetric fractions of these materials; and summation is taken over all sorts of inclusions. This approximation gives results that agree well with the experimental data when the concentration of inclusions is rather small so that separate particles of inclusions do not contact each other. If the content of inclusions is high enough and contacts between particles are likely to occur, the selection of one of the materials as a host becomes unjustified. In this case, the EMA methodology can be used. Within this approximation, each material is considered as spherical inclusions in the host material whose properties are the effective properties that are sought. The effective dielectric permittivity, ε_{eff}, is then obtained as a root of the equation

$$\sum_k \rho_k(\varepsilon_k - \varepsilon_{eff})\frac{3\varepsilon_{eff}}{2\varepsilon_{eff} + \varepsilon_k} = 0 \qquad (2.8)$$

where the summation is taken over all constituents. A comparison between the dielectric permittivity, ε_{eff}, calculated within these approximations and the data of measurements for particular ceramic and composite materials can be found, for example, in [22]. This comparison demonstrates the feasibility of methods of average description for predicting the properties of heterogeneous materials. A more refined approach to simulating the effective properties of ceramics based on the concept of fractal boundaries between the grains can also be found in [22].

When a composite material contains conductive (metal) particles embedded in a low-loss host material, it may absorb microwaves due to the magnetic polarization of particles [23]. The oscillating magnetic component of the microwave electromagnetic field induces electric currents within the particles. Depending on the particle size, these currents may be much stronger than those driven directly by the electric component of the field. The process of heating by the current induced by an oscillating magnetic field is usually termed induction heating.

One of the promising applications of microwave processing is the development of functionally gradient materials in which composition changes continuously from pure ceramic to pure metal [24]. Along with the composition, the microwave absorption properties of such materials change from low loss at the ceramic end to full reflection on the metallic end. It can be shown (e.g., by the EMA) that the dielectric loss of a gradient ceramic–metal material exhibits a sharp increase at the percolation threshold value of the metal concentration (corresponding to the onset of connectivity between individual metal particles). In gradient materials most of the microwave power is absorbed within a narrow spatial region where concentration is about this threshold value. If an initially porous gradient material undergoes microwave sintering, the region of high absorption moves with densification towards the ceramic end [25].

2.2. Thermophysical properties and heating

The main properties of any heating process are its characteristic time τ_T, determined by the heating rate ($\tau_T \sim T/(\partial T/\partial t)$), and the uniformity of temperature within the body undergoing heating. These properties depend significantly on the heating mode. For conventional heating, heat enters the sample through its surface and propagates inside due to heat transfer processes—mainly thermal conduction. The temperature inside the sample is therefore always lower than on the surface, with an exception of the case when a constant temperature is maintained ($\tau_T \rightarrow \infty$). The heat transfer process takes a certain time (longer the larger the sample), which limits from above the heating rate.

A distinguishing feature of microwave heating is its volumetric nature. The heat is deposited directly inside the sample, and the heating rate is limited only by the power of the microwave source. On the other hand, the heat is dissipated to the environment through the surface. Therefore, the temperature inside the sample is always higher than on the surface (including the case when a constant temperature is maintained). This microwave-specific temperature distribution is known as an inverse temperature profile.

The differences between conventional and microwave heating can be described mathematically within a simple model based on the thermal conduction equation with a volumetrically distributed heat source:

$$c_p \rho \frac{\partial T}{\partial t} = \nabla (\kappa \nabla T) + w \qquad (2.9)$$

where c_p is specific heat capacity, ρ is density, κ is thermal conductivity of the material, and w is local density of heat

sources. For conventional heating w is localized within a thin near-surface layer of the sample, whereas for microwave processing w, determined by equation (2.1), is distributed in the sample more or less uniformly (if the sample size does not exceed the characteristic penetration depth, equation (2.2)).

Equation (2.9) can be used as a basis for estimates of temperature uniformity for various processes. A main parameter of the conventional heating process is the characteristic time of temperature equalization on a scale length Λ due to thermal conduction:

$$\tau_\Lambda \sim \Lambda^2/\chi \qquad (2.10)$$

where $\chi = \kappa/c_p\rho$ is the thermal diffusivity of the material. If Λ_s is the dimension of the sample and χ_s its thermal diffusivity, then $\tau_s \sim \Lambda_s^2/\chi_s$ is the minimum possible characteristic time of conventional heating for this sample (typical values of χ_s in dielectric materials are on the order of 10^{-2} cm^2 s^{-1}, therefore for 1 cm samples $\tau_s \sim 10^2$ s). In order to reduce temperature differences in the sample, the characteristic heating time, τ_T, should be chosen much larger than τ_s. In this case the temperature difference, ΔT, can be estimated as

$$\Delta T \sim T \frac{\tau_s}{\tau_T}. \qquad (2.11)$$

When constant temperature is maintained, $\tau_T \rightarrow \infty$ and hence $\Delta T \rightarrow 0$.

Under microwave heating, as mentioned above, the temperature difference in the sample is non-zero even in the steady state. In order to reduce this temperature difference the sample is usually surrounded by a layer of a thermally insulating material which reduces heat losses from the surface of the sample. In thermal insulation arrangements various porous materials are used, their thermal conductivity, κ_{ins}, being much lower than the thermal conductivity of the material of the sample, κ_s. Introducing the characteristic thermal conduction time for the thermal insulation arrangement, $\tau_{ins} \sim \Lambda_{ins}^2/\chi_{ins}$ (where Λ_{ins} is the characteristic thickness of the insulating layer and χ_{ins} is its thermal diffusivity), we find that for slow heating ($\tau_T > \tau_{ins} > \tau_s$) the temperature difference in the sample, ΔT, can be estimated as

$$\Delta T \sim T \frac{\kappa_{ins}}{\kappa_s} \qquad (2.12)$$

provided that microwave absorption in the thermally insulating material is negligible.

The temperature difference in the sample grows with the heating rate, but not as rapidly as under conventional heating. In the case $\tau_{ins} > \tau_T > \tau_s$ the temperature difference grows with the heating rate in inverse proportion to $\sqrt{\tau_T}$:

$$\Delta T \sim T \sqrt{\frac{\tau_{ins}}{\tau_T}} \frac{\kappa_{ins}}{\kappa_s}. \qquad (2.13)$$

If the heating is so rapid that $\tau_T < \tau_s$, the growth of ΔT saturates at

$$\Delta T \sim T \sqrt{\frac{\chi_s}{\chi_{ins}}} \frac{\kappa_{ins}}{\kappa_s}. \qquad (2.14)$$

This entire temperature difference is localized in the latter case within a near-surface layer of thickness $\sqrt{\chi_s \tau_T} < \Lambda_s$.
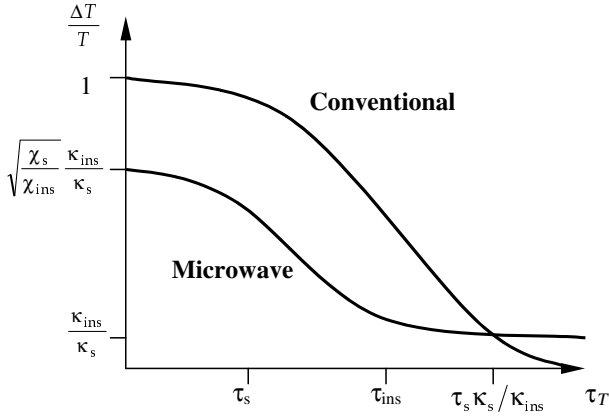
Figure 3. Temperature difference (normalized) versus characteristic heating time for microwave and conventional heating.

Thus, microwave processing is, in principle, capable of heating the sample in times shorter than τ_s, and improving the temperature uniformity provided that the heating is not too slow, $\tau_T < \tau_s \kappa_s / \kappa_{ins}$. On the other hand, slow microwave heating results in temperature differences larger than conventional heating. Figure 3 shows schematic dependences of temperature differences on the characteristic heating time for conventional and microwave processing.

Another source of temperature gradients under microwave heating is the inhomogeneous distribution of the microwave power dissipated in the sample. This can originate from both the inhomogeneous absorptivity of the material and the inhomogeneous electric field strength. Using the thermal conduction equation, equation (2.9), it is possible to estimate the temperature differences arising due to these factors. Let a be the scale length and Δw_a be the amplitude of the dissipated power non-uniformities. If the heating is very rapid, so that $\tau_T < \tau_a = a^2 / \chi_s$, the temperature non-uniformities follow those of the dissipated power,

$$\Delta T \sim T \frac{\Delta w_a}{w}. \qquad (2.15)$$

If the heating is not so rapid, $\tau_a < \tau_T < \tau_s \kappa_s / \kappa_{ins}$, thermal conduction reduces the fluctuations of temperature:

$$\Delta T \sim T \frac{\Delta w_a}{w} \frac{\tau_a}{\tau_T}. \qquad (2.16)$$

If, finally, the heating is slow, $\tau_T > \tau_s \kappa_s / \kappa_{ins}$, the fluctuations of temperature stabilize at a low level,

$$\Delta T \sim T \frac{\Delta w_a}{w} \frac{\tau_a}{\tau_s} \frac{\kappa_{ins}}{\kappa_s}. \qquad (2.17)$$

Based on the above estimates it can be argued that the small-scale non-uniformity of the dissipated power due to the granular structure of a material never results in any observable temperature differences (with the grain size $a \leqslant 10 \ \mu$m the corresponding ΔT is $\ll 1$ K) [26]. The influence of the electric field non-uniformity with the scale length on the order of the wavelength, λ, decreases rapidly with increasing frequency, $\Delta T \propto \lambda^2 \propto 1/\omega^2$. For example, at a frequency of 2.45 GHz and $\tau_T \sim 10^3$ s ($|\partial T/\partial t| \sim 100$ K min^{-1}, $T \sim 10^3$ K) the

expected relative temperature difference in the sample, $\Delta T / T$, is on the order of 10^{-1}, whereas at a frequency of 24 GHz under same heating conditions $\Delta T / T \leqslant 10^{-3}$.

The increase of microwave absorptivity of materials with temperature can lead to a significant deterioration of the uniformity of microwave heating. In particular, if the parameter $\beta = (T/w)(\partial w / \partial T)$ exceeds some critical value, β_c, the development of a specific thermal instability is likely. This leads to the formation of so-called 'hot spots' [27], i.e. overheated areas of small size. The critical value, β_c, depends significantly on the properties of the thermal insulation arrangement and the heating rate. A very rough estimate is

$$\beta_c \approx \left(\frac{\tau_s}{\tau_T} + \frac{\kappa_{ins}}{\kappa_s} \right)^{-1}. \qquad (2.18)$$

It should be noted that the models of 'thermal runaway' discussed in the literature [11] do not provide an adequate description of the process of 'hot spot' formation since they do not account for the spatial structure of the temperature field. In other words, these models describe the *global* overheating of the sample that occurs in the absence of control over the input microwave power. This kind of overheating can be eliminated by introducing temperature sensors and automatic power control systems [28]. *Local* overheating leading to hot spot formation is much more difficult to control since surface temperature sensing is insufficient for this purpose. The use of the higher-frequency (millimetre-wave) radiation is therefore preferred when heating materials that have a sharp temperature dependence of the absorptivity, since the values of β for most dielectric materials are generally smaller in this range than at frequencies $\leqslant$2.45 GHz.

2.3. Applicators

Microwave processing of a sample(s) enclosed in a thermal insulation arrangement is usually performed in a closed chamber with metal walls, which is called an applicator. The electrodynamic term for such a chamber is a cavity resonator for electromagnetic oscillations. The metal walls of the applicator return the radiation reflected from the sample or transmitted through it back to the sample (see figure 1). This improves the efficiency of microwave heating for both low- and high-loss materials. In fact, the resonator increases the microwave field strength in its volume due to multiple passes of the electromagnetic waves through each point. However, such constructive interference of the electromagnetic waves leading to an increase in the field strength is only possible when the field frequency is close to one of the resonant frequencies of the resonator, which depend on its dimensions and shape.

Each resonator possesses a series of discrete eigenmodes that differ in the structure of the electromagnetic field. Each eigenmode has its resonant frequency, ω_n, and quality factor, Q_n, which characterizes its excitation efficiency. The density of the eigenmode frequency spectrum depends on the resonator volume and frequency. An estimate of the frequency difference between two adjacent eigenmodes, $\Delta \omega$, is

$$\Delta \omega = \frac{\pi^2 c^3}{V \omega^2} \qquad (2.19)$$

where V is resonator volume. The quality factor of an eigenmode depends on the reflectivity of resonator walls, resonator volume, and the absorptivity of the material inside the resonator. A rough estimate of the quality factor is

$$Q_n \approx \frac{\omega_n}{(1 - R)(cS)/V + \omega \varepsilon_s''(V_s/V)} \qquad (2.20)$$

where R is the reflection coefficient of the resonator wall for microwaves, S is the surface area of the wall, V is the resonator volume, ε_s'' is the imaginary part of the dielectric permittivity of the sample, and V_s is the volume of the sample. The energy of the electromagnetic field in the resonator, W_n, given a constant absorbed power, P, is higher the larger the quality factor of the excited eigenmode:

$$W_n = \int \frac{E^2}{4\pi} \, dV = \frac{P Q_n}{\omega_n}. \qquad (2.21)$$

In order to excite an eigenmode efficiently, the frequency of the microwave source, ω, should be within the band $|\omega - \omega_n| < \omega_n/Q_n$. At low frequencies the eigenmode resonance bandwidth is less than the frequency difference between adjacent eigenmodes, $\omega_n/Q_n < \Delta\omega$ (figure 4(a)), which means that only a single resonator eigenmode is excited. In this case, in order to obtain efficient coupling it is necessary to finely tune the resonator so that one of its resonant frequencies coincides with the operating frequency. It should be remembered that the resonant frequencies generally depend on the dimensions, shape, and dielectric properties of the sample introduced into the resonator. Therefore coupling depends on temperature, and repeated tuning is necessary for each new sample. Another problem with single-mode microwave processing is a pronounced non-uniformity of the microwave field in the resonator volume, exhibiting maxima and minima with a distance between them of about one-quarter of the wavelength. This non-uniformity makes it difficult to process large samples and batches of samples.

In the millimetre-wave range the eigenmode resonance bandwidth, ω_n/Q_n, is usually larger than the frequency difference between adjacent eigenmodes, $\Delta\omega$ (figure 4(b)). This is the case of multimode operation, when a number of eigenmodes are excited simultaneously. The advantages of this regime are the absence of strict tuning requirements and the possibility to achieve a significantly more uniform distribution of microwave power in the resonator volume. The latter feature is due to the fact that the positions of the maxima and minima do not coincide for different eigenmodes. The multimode regime allows further improvement of the microwave power uniformity by introducing mobile metal objects (mode stirrers) into the resonator. A change in the mode stirrer position changes the eigenmode structure, including the locations of the maxima and minima. However, the excitation efficiency is not affected, due to the large eigenmode resonance bandwidth. Thus, the rotation or vibration of mode stirrers, with typical frequencies on the order of 1 Hz, results in the efficient compensation of the small-scale interference-related non-uniformity of the millimetre-wave heating.

The optimization of microwave systems involves extensive numerical modelling. If the ratio of the resonator
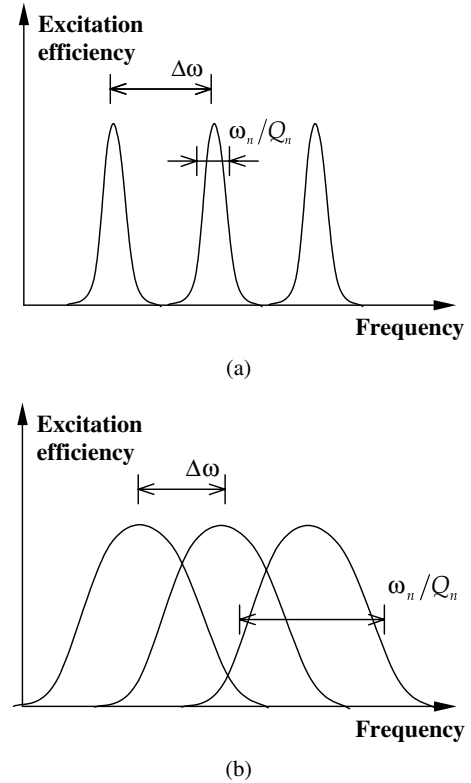

Figure 4. Illustration of the cavity excitation regimes: (a) single-mode operation and (b) multi-mode operation.

volume to the cube of the wavelength, V/λ^3, is under approximately 10^3 (which typically holds for the 2.45 GHz microwave systems), the electromagnetic field distribution in the resonator, including the case of a load inside it, can be computed via finite difference methods [29, 30]. However, for the millimetre-wave systems ($V/\lambda^3 > 10^5$) finite difference methods require prohibitively large computer resources and computation time. For this case approximate methods of numerical modelling based on the ray tracing approach have been under development in recent years [31, 32]. The results obtained within this approach have been tested by comparison with both experimental data and exact solutions for simple resonator configurations [32]. The comparison, illustrated by figure 5(a)–(c), has proved the usefulness of the geometric optic approach in solving practical tasks of millimetre-wave system optimization. In particular, the suggested modifications to the resonator design have resulted in significant improvements of the electromagnetic field distribution (figure 5(d)). Currently numerical modelling is increasingly used to simulate the entire microwave process, including the calculation of the temperature distribution inside the sample and its densification during sintering [25].

2.4. High-temperature processes in solids

This short subsection briefly reviews some fundamental concepts that are necessary to obtain an understanding of basic high-temperature processes in solids. In general, the idea of the high-temperature treatment of solid materials is to activate mass transport phenomena and use them for the
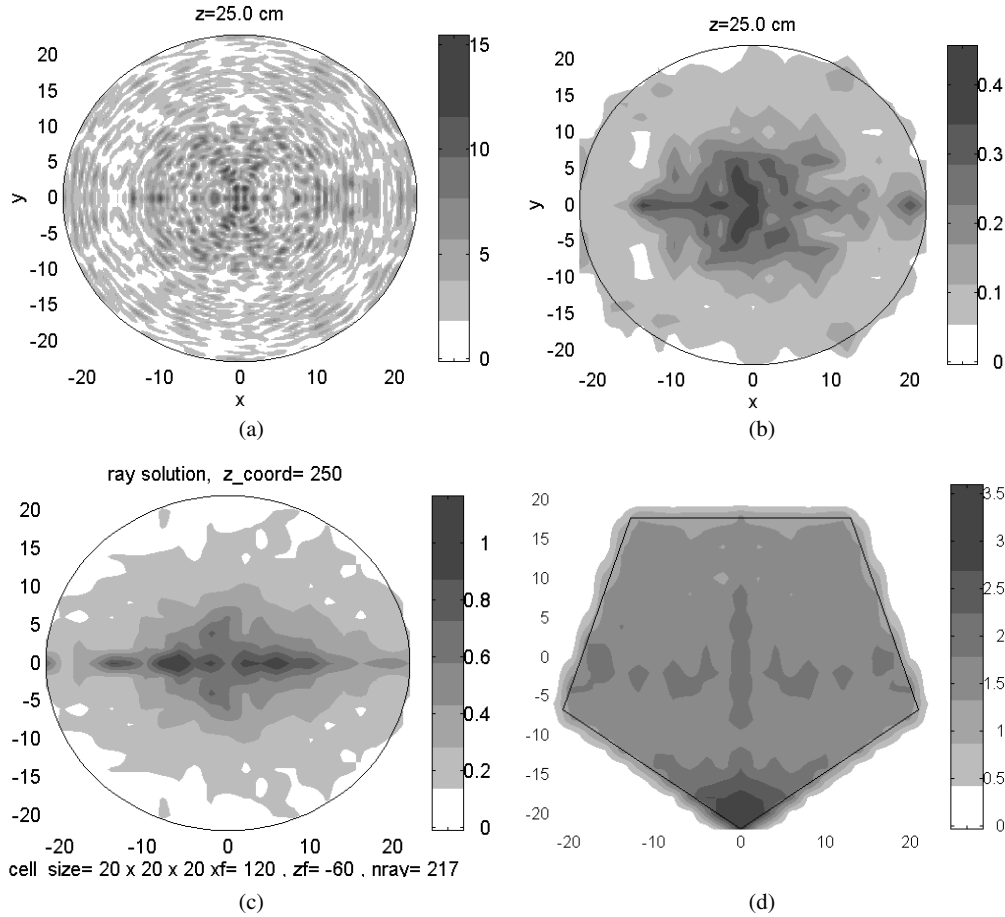
Figure 5. Simulated spatial distribution of millimetre-wave power in the central cross section of the cylindrical cavity (46 cm in diameter and 50 cm in height) of a 30 GHz gyrotron system: (a) exact solution and (b) exact solution averaged over $2 \times 2 \times 2$ cm^3 cells (averaging eliminates small-scale inhomogeneities of power. In practice the same is achieved using mode stirrers): (c) solution by the method of averaged geometric optics; (d) solution by the method of averaged geometric optics with a pentagonal insert in the cavity. Improved uniformity of the power distribution can be seen.

modification of the material properties. Mass transport in the solid phase is mostly accomplished by means of diffusion. One of the most important yet simple mass transport mechanisms in crystalline solids is vacancy diffusion. The formation of the vacancies requires some amount of energy, U, to deform the lattice; yet it increases the entropy, S, of the system. Therefore, at equilibrium, unless the temperature, T, is zero, there exists some equilibrium concentration of vacancies that is determined by the minimum in the free energy, $F = U - TS$. This concentration depends upon the temperature and stresses acting on the crystalline body (since the latter influence the energy of vacancy formation).

Vacancies in the crystalline lattice provide a path for diffusion motion of atoms[3]. Since the concentration of vacancies in the lattice is usually small, any interaction between vacancies can be neglected, making the ideal gas approach applicable. It is generally more convenient to describe the process in terms of vacancy diffusion as opposed to the diffusion of atoms. The vacancy diffusion coefficient is proportional to the probability of atom transfer into a

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[3] Other defects, such as interstitial atoms, can also participate in diffusion. However, in most solids the vacancy mechanism of diffusion requires the lowest energy and therefore usually prevails.

neighbouring vacant lattice site:

$$D \sim a^2 \nu_0 \exp\left(-\frac{\Delta F}{kT}\right) \qquad (2.22)$$

where a is the lattice parameter, ν_0 is the vibration frequency of the atom, ΔF is the potential barrier between the equilibrium positions of the atom in the lattice, and k is Boltzmann's constant. It can be seen from equation (2.22) that diffusion is a thermally activated, or Arrhenius-type, process, i.e. it becomes significant only when the temperature exceeds some critical value determined by the activation energy.

The transport of vacancies (or atoms) in a solid mostly leads to the transport of mass. For example, mass transport occurs in crystalline solids when they are inelastically deformed under the action of mechanical stresses. The stresses change the local concentration of vacancies (e.g., compressive stresses decrease it). This causes diffusion flows of vacancies that are directed against the concentration gradients. The corresponding transport of atoms leads to the inelastic deformation of the solid (which is termed high-temperature creep). A measure of the 'deformability' of the solid is the diffusion coefficient. Therefore, most high-temperature processes of structural modification in solids have an Arrhenius-type dependence upon the temperature.

An important high-temperature process based on thermally activated mass transport is sintering [33, 34]. Sintering is the process of densification of compacted powder bodies that occurs below the melting temperatures via shape accommodation of powder particles. The main driving force for sintering is capillary stress, which acts to minimize the free energy associated with the surface area. The materials obtained by sintering (e.g., ceramics) have a density almost equal to the density of corresponding single-crystalline material, and usually possess high hardness and mechanical strength, which are the greater the smaller the grain size. The latter is not necessarily equal to the particle size in the starting powder, since the diffusion phenomena during sintering cause recrystallization grain growth. It should be noted that the sintering and grain growth processes, being of diffusion nature, have an Arrhenius-type dependence upon the temperature and are often characterized by the corresponding activation energies.

3. Advantages of microwave high-temperature processing

3.1. Reduced energy consumption and process time

The main advantages of microwave heating stem from direct energy deposition in the volume of a material. This eliminates the need for spending energy on heating the walls of the furnace or reactor, its massive components, and heat carriers. As a result, the use of microwave methods significantly reduces *energy consumption*, especially in high-temperature processes, since heat losses grow dramatically with an increase in the process temperature. The volumetric nature of energy deposition accelerates heating, which reduces the *time* needed to complete a process. An idea of the energy saving potential of microwave processing can be inferred from the results of a number of comparative studies in sintering. According to one of them [35], the specific energy consumption in the process of sintering alumina-based ceramics at a temperature of 1600 °C is about 4 kWh kg^{-1} for microwave heating versus 59 kWh kg^{-1} for fast conventional heating in a resistive oven. For the sintering of silicon nitride-based ceramics, the specific energy consumption is 3 kWh kg^{-1} over a 2 h process of microwave sintering versus 20 kWh kg^{-1} over a 12 h conventional process [36].

The reduction in process time under microwave heating is especially significant when the process involves *endothermic chemical reactions* and/or phase transformations and the temperature is limited from above (either by the capabilities of the system or by product quality). In this case a sufficient energy supply is a prerequisite for a high process rate, which is determined at each point by the local temperature. Conventionally, the energy supply rate is always limited by slow heat transfer processes. Due to volumetric energy deposition, microwave heating is, in principle, capable of providing any desired rate of an endothermic process, limited only by the power of the microwave source.

However, it should be emphasized that the advantages of using microwave energy in high-temperature processes are by no means reduced only to energy saving. In many cases microwave processing is capable of improving the product quality or leads to results that cannot be achieved conventionally. The following sections discuss other specific features peculiar to microwave processing and give examples of processes to which microwave heating can be applied most advantageously.

3.2. Rapid and controllable heating

High rates of heating lead not only to reductions in process time and energy consumption. Many high-temperature processes include a sequence of various steps which replace each other with the rise of temperature. Such sequences occur in multistage thermally activated processes, in which separate stages are characterized by different values of the activation energy. Some of these stages may have a negative influence on the properties of the final product. In such cases rapid heating may be vital for reducing the role of undesired intermediate stages of the process.

An example of such a multistage process is the *sintering of ceramics*. At different steps of sintering the diffusion processes of various natures, viz surface, grain boundary, and bulk diffusion, determine the mass transport. It is well-known [33] that inhibition of surface diffusion at the initial stage of densification is favourable for sintering. An increase in the rate of heating at the onset of densification can reduce the formation of a rigid neck structure between grains, which occurs primarily by surface diffusion, and retain high enough Laplace driving forces for densification.

An advantageous method for ceramics sintering based on the idea of inhibiting surface diffusion is *rate-controlled processing* [37]. In this approach the heating rate is varied during the process to keep the prescribed densification rate. The implementation of rate-controlled sintering by conventional methods is often complicated by thermal inertia. The direct deposition of microwave energy is highly relevant to the task of inertialess control over heating. The temperature of the sample undergoing sintering is controlled, in this case, by means of a feedback loop that uses data from *in situ* density and temperature measurements and that varies the microwave power according to the prescribed schedule of densification versus temperature. In fact, many experiments on the microwave sintering of ceramics, although not pursuing rate-controlled processing, use variable heating rates to decrease the detrimental effect of surface diffusion during the initial phase of densification [38].

At the intermediate and final stages of sintering high rates of microwave heating help overcome grain growth, resulting in ceramic materials with fine microstructure, which in turn enhances their mechanical properties. For example, figure 6 compares the microstructures of alumina ceramics sintered with millimetre waves at different heating rates [39].

It appears that the capability of accomplishing fast microwave heating is a factor of paramount importance in the sintering of *nanostructured ceramic* and *composite materials*. The growing interest in the nanostructured materials is associated with the recognition of their great potential for various applications, such as near net shape forming, diffusion bonding, and layered composite structures. All these applications are based on the enhanced plasticity of nanostructured materials. The theory of plasticity predicts a
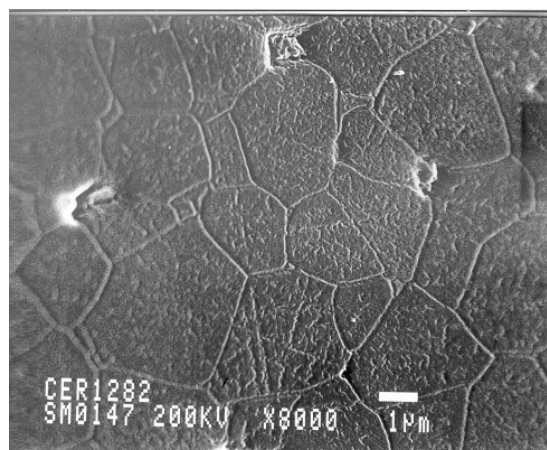
(a)
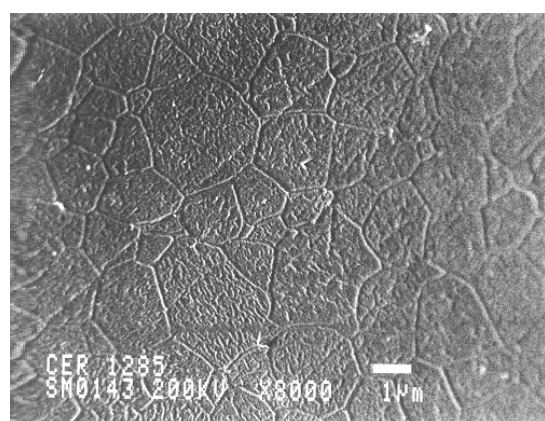
(b)
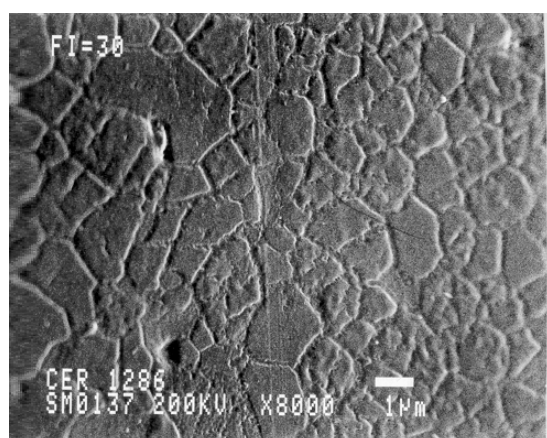
(c)

Figure 6. Microstructure of alumina ceramic samples (99.5% $Al_2O_3 + 0.5\%$ MgO) sintered with millimetre waves at the heating rate of (a) $50\,^\circ$C min^{-1}, (b) $100\,^\circ$C min^{-1}, and (c) $300\,^\circ$C min^{-1}.

sharp increase of the strain rate in polycrystalline solids with a decrease in the crystallite size. A decrease in the grain size from 1 μm, which is characteristic of the up-to-date fine ceramics, to 10 nm is expected to increase the strain rate by several orders of magnitude [40]. The enhanced plasticity can overcome, to a certain extent, the brittleness of ceramic and composite materials, the most serious drawback that limits their application in technology. The capability of specimens
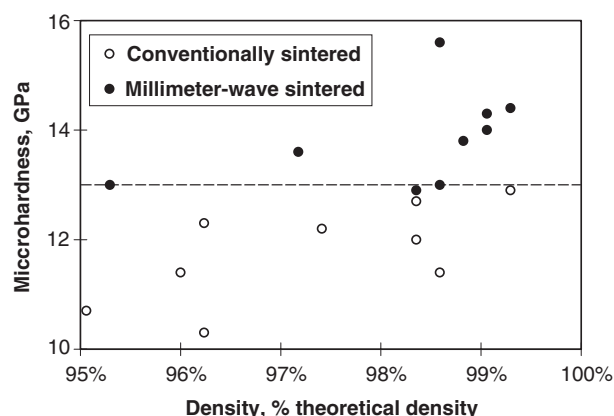

Figure 7. Microhardness of millimetre-wave and conventionally sintered titania samples versus their final density after sintering. The broken horizontal line shows the microhardness of single-crystalline titania (rutile).

to deform at moderate temperature can solve the problem of the fabrication of the net shape ceramic components. Today the cost of component machining to the final size is usually more than 50% of the total product cost. Therefore net shape processing can result in substantial savings, as well as reduced environmental impact associated with the final machining processes.

The main obstacle for the fabrication of nanostructured ceramic materials via high-temperature sintering is the problem of grain growth by recrystallization. Since the first attempt to use fast microwave heating for the sintering of nanostructured materials, when 90% dense TiO_2 ceramics with average grain size of less than 20 nm were obtained [15], substantial research in this field has been accomplished [14, 41, 42]. Shown in figure 7 are the data on the microhardness of titania ceramic samples sintered in identical regimes under millimetre-wave and resistive heating [42]. The microhardness of samples sintered with millimetre waves was systematically higher than that of the conventionally sintered samples. In samples of high density the microhardness of sintered sample exceeded the microhardness of single-crystalline titania (rutile) by about 10%. Such enhancement of the microhardness in the millimetre-wave sintered samples can be explained by the presence of a significant portion of material in the form of nanosized grains. The deformation of material under indentation mostly occurs via generation of dislocations in grains, and it is accepted that dislocations can be generated only in the crystals whose size exceeds a certain value (on the order of tens of nanometres) [43]. In a recent compressive deformation study [44] an appreciable strain rate was observed in the samples of millimetre-wave sintered TiO_2 at a temperature of $850\,^\circ$C, whereas no strain was detected in the samples sintered conventionally. This is evidence for the enhanced plasticity of the millimetre-wave sintered nanostructured ceramic samples.

The absence of inertia and the controllability of heating are of great importance in the processes that exhibit a strong dependence on temperature, for example exothermic chemical reactions. Among such reactions are the carbonization of tungsten, W + C $\rightarrow$ WC which is part of the process of sintering WC–Co hardmetals [45], and the nitridation of silicon

$Si + N_2 \rightarrow Si_3N_4$ [46]. In the latter case, the reaction rate can be controlled by a feedback loop that uses data on the weight gain of the sample during nitridation and varies the microwave power input to the reactor.

3.3. Inverse temperature profile

As was mentioned above (see subsection 2.2), microwave heating results in a specific temperature distribution with a maximum within the body. For many processes this temperature non-uniformity is an unambiguous disadvantage since it may result in the non-uniformity of product properties. In particular, in ceramics sintering, which has probably attracted the greatest amount of interest in microwave processing research, temperature non-uniformity is especially undesirable since the internal stresses caused by non-uniform densification [47] may lead to destruction of the product. Therefore various measures are taken in order to overcome temperature non-uniformities, including thermal insulation and the use of additional heat sources. There is no universal solution to this problem; it should be sought specifically for any particular application. A straightforward approach is to surround the body with additional electric heaters, the power in which is controlled to make up for the surface heat losses [48]. However, this approach encounters great difficulties in implementation. A number of issues such as microwave and environmental compatibility, temperature control, product shape etc make this method feasible only at the expense of loss of universality. Another approach, most commonly used in the high-temperature microwave processing, is based on thermally insulating the material undergoing processing. In some cases the material is surrounded by microwave susceptors, i.e. by objects possessing strong microwave absorption which provide additional heat flow to the surface of the sample. Since these techniques use only one source of energy, viz microwaves, it is difficult to adjust the properties of the thermal insulation arrangement or microwave susceptors so that they would compensate accurately enough the heat losses in the entire temperature range of the process.

Experimentation on microwave ceramics sintering and joining consists largely of a search for the optimal process conditions, which include the temperature–time schedule of microwave heating, the frequency of microwave radiation, thermal insulation properties, possible use of susceptors or additional heat sources, etc. One example of a study where this problem was successfully solved is in the millimetre-wave sintering of alumina and silicon nitride ceramic buckets 200 mm in diameter and 200 mm in height [49].

One should not assume that the microwave-specific temperature distribution has only a detrimental effect on the process of ceramics sintering. In fact, due to the outward temperature decrease from the core of a ceramic body its porous structure remains open to a higher average value of density [12]. This effect contributes both to the acceleration of densification under microwave heating and achieving a higher final density (which is in fact often observed in comparative studies of microwave and conventional sintering). Unfortunately, no attempt has been made to find a quantitative correlation between the major parameters that characterize the evolution of the porous structure in a inhomogeneous

temperature field and the effect of sintering enhancement under microwave heating.

There are many other processes in which a microwave-specific distribution of temperature plays a positive role. As a rule, they involve the reaction of a porous solid matrix with the gas phase. One of these processes is the synthesis of reaction-bonded silicon nitride (RBSN). The RBSN ceramic is an attractive candidate for high-temperature applications. Since RBSN is made without the addition of oxide sintering aids which form a glassy grain boundary phase, it retains mechanical strength to a higher temperature as compared to other types of silicon nitride ceramics. RBSN is produced via the nitridation of pressed silicon powder compacts, which proceeds during their heating to the reaction temperature (1150–1450 °C) in an atmosphere of nitrogen. Under microwave heating the silicon powder tends to react faster in the interior, where the temperature is higher, than near the surface of the compact. As a result, nitrogen diffuses into interior more easily compared to the isothermal heating because the nitridation reaction propagates from the interior outward and the porosity at the surface remains open for longer. This means that the processing of compacts having a higher initial density can be accomplished, which increases the strength and toughness of the final product. This fact, in combination with the ability to control the exothermic nitridation reaction by changing the input microwave power, allows a significant reduction in the time needed to obtain RBSN [50]. The specific temperature distribution plays a similar role in the microwave sintering of YBCO high-temperature superconductors, where the presence of oxygen in initially porous mixed oxide compacts is required to prevent oxygen loss during processing [51].

Another type of process benefiting from microwave-specific temperature distributions is the *infiltration of porous matrices* with products of solid–liquid or solid–gas chemical reactions. For example, a promising method for the synthesis of ceramic–ceramic fibre composites is the chemical vapour infiltration of matrix preforms. In the fabrication of SiC composites the vapour-phase precursor, such as trichlormethylsilane, infiltrates the fibre preform and reacts at a high temperature (1100–1200 °C) on the fibre surface. Gaseous reaction products diffuse out of the pores:

$$CH_3SiCl_3(g) \rightleftharpoons SiC(s) + 3HCl(g) \qquad (in\ H_2).$$
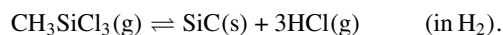
The solid product of reaction (SiC) is deposited on the fibre preform. Isothermal infiltration inevitably leads to the preferential deposition of SiC at the pore mouths and premature sealing of pores. The advantages of utilizing a temperature profile inherent in volumetric microwave heating for microwave-assisted chemical vapour infiltration of ceramic matrix composites are demonstrated in [52]. Other applications involving the gas phase which beneficially exploit the microwave-specific temperature profile are chemical decompositions in fluidized bed reactors [53] and waste remediation processes [54].

3.4. Selectivity

The dependence of the deposited microwave power upon the absorption properties of materials opens the way to

the implementation of selective heating, i.e. the formation of desired inhomogeneous temperature distributions in inhomogeneous materials. Sometimes inhomogeneous temperature distributions can also be formed during conventional heating, for example in layered structures. However, only the differences in the thermophysical properties of the components constituting a composite material can be used to control this process under conventional heating. The potential for selective heating is much higher with the use of the microwave energy, since in this case it becomes possible to form a desirable spatial distribution of heat sources and to control their power.

When a composite material is heated with microwave radiation, the temperature distribution forms in accordance with the absorption properties of the composite's components and the spatial distribution of components within the body. The utilization of the compositional selectivity of microwave heating in the processes of the fabrication of ceramic and composite materials has been extensively studied. The processing of composite materials consisting of a ceramic matrix impregnated with a metal–organic precursor is one of the promising applications in this field [55, 56]. Selective heating of a precursor and its subsequent pyrolysis makes it possible to obtain composite materials with microstructures quite different from those of conventionally produced materials. What is more, the selectivity of microwave heating allows efficient control over the microstructure and properties of the synthesized materials by choosing proper microwave absorption coefficients of the matrix material and precursor.

The high-temperature synthesis of metal–dielectric composites is another application based on the microwave selective heating [57]. Individual metal particles strongly absorb microwave radiation provided their size is comparable with the skin depth of radiation. Local overheating of metal particles greatly intensifies their bonding with the surrounding ceramic matrix. As a result, the synthesized materials have a peculiar microstructure and improved mechanical properties as compared with the materials produced conventionally [18].

Another trend in the development of methods utilizing the compositional selectivity of microwave heating is the synthesis of materials via high-temperature self-propagating chemical reactions. Microwave-assisted *self-propagating synthesis* is similar, to a certain extent, to conventional self-propagating high-temperature synthesis (SHS) while exhibiting a number of important distinctions. The microwave-specific temperature distribution with a maximum in the core allows ignition of the chemical reaction that propagates outward to the surface. Furthermore, the selectivity of microwave absorption makes it possible to maintain the propagation of a chemical reaction due to the selective heating of either an initial component or a product of reaction that has a strong microwave absorption. When the product of reaction has a low microwave absorption, self-controlled heating is observed. For example, silicon nitride which is formed in the reaction of synthesis at a temperature of about $1600\,^{\circ}C$,

$$SiC + O_2 + N_2 \rightarrow Si_3N_4 + CO_x \uparrow,$$
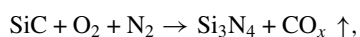
has a low microwave absorption. Therefore silicon nitride does not heat and is not oxidized in the course of the reaction,

in contrast to the SHS reaction conducted under conventional heating [58].

The synthesis of functionally graded materials (FGMs) is a promising new application area for the microwave processing. These materials which have spatially inhomogeneous microstructures and gradient functional properties are expected to exhibit improved performance in such fields as energy production, ceramic engines, gas turbines, nuclear fusion, etc [59]. These advanced technologies often demand properties that cannot be achieved by any single material. The principal idea of FGMs is to combine dissimilar materials in a way that takes advantage of each. The metal–ceramic FGMs are especially useful in high-temperature applications. One of the approaches for FGM fabrication is based upon the sintering of metal–dielectric powder mixtures with a gradually varying metal-to-dielectric concentration ratio. This approach is aimed at reducing the residual thermal stresses that do not allow direct deposition of a ceramic coating on metal. Currently, the research into the use of microwave heating for the synthesis of FGMs is at an early stage. Microwaves have already been successfully applied to the sintering of many metal–ceramic compositions of practical importance, such as Al_2O_3–steel, Al_2O_3–Mo, ZrO_2–$Ni_{80}Cr_{20}$ [24]. Still unexplored remains the possibility of the use of selective microwave absorption in the compositionally graded materials, resulting in graded deposition of the microwave energy. The compositional selectivity of microwave energy absorption makes it possible, in principle, to purposely create such profiles of the microwave energy deposition and, as a result, such temperature distributions that reduce thermal stresses in the FGMs.

The selective absorption of microwave radiation is utilized for the *joining of ceramic materials*. In the first experiment in this area, [60] two alumina plates were successfully joined using a glass interlayer. Today most researchers use a thin layer of material of relatively strong microwave absorption in order to obtain a joint between parts of a low-loss material. For example, for the joining of ceramic parts of pure alumina (99.5% purity) under 2.45 GHz microwave heating, a thin interlayer of technical grade (92–96% pure) alumina [61, 62] or nickel oxide [62] is used. Similarly, the microwave joining of silicon nitride ceramics at this frequency requires an interlayer of a high-loss grade of silicon nitride [61]. The use of such an interlayer facilitates the heating and joining but limits the performance of the product because at elevated temperature the glassy phase softens the joint. An alternative approach is to design applicators that concentrate the microwave field at the joint zone [63]. However, the attempts to directly join high-purity alumina parts using 2.45–6 GHz microwaves have been unsuccessful due to inability to reach the necessary temperature [64–66]. Yet it has been shown [66] that the presence of a glassy phase at the interface does not constitute a necessary prerequisite of joining, and high-quality joints can be obtained via solid-phase diffusion. Therefore, it appears attractive to use the millimetre-wave power for heating, which eliminates the need for a high-loss interlayer and allows the fabrication of products for high-temperature application via joining.

3.5. Possibility of surface processing

If, for a given material and frequency, the microwave penetration depth is small enough, then the deposition of the microwave energy takes place only in the near-surface layer of the material. This regime of microwave heating can be viewed as one more method for the surface treatment of materials by intense energy flows, which can be an alternative or additional to those widely used in practice, such as electron and ion beams, plasma processing, and laser irradiation. Here we will restrict our consideration to the surface processing solely with microwaves, as opposed to microwave-assisted plasma processing of materials [67] and other combinatory techniques. As a rule, a relatively high intensity of radiation is required to make high-temperature surface processing possible. As intensity is determined by the power of the radiation source divided by the area on which this radiation falls, in order to maximize the intensity one should increase the power and focus the radiation onto a spot of minimum possible size. Due to diffraction, the latter cannot be less than the wavelength of radiation. Therefore, microwave surface processing is most feasible in the millimetre-wave range, where gyrotron sources of power on the order of 10–30 kW cw are available for the frequency range 24–83 GHz [68]. Sharply focused wave beams can be formed using quasi-optical methods for transforming the structure of the electromagnetic field of the gyrotron operational mode into simpler configurations. Therefore, an intensity as high as 2×10^5 W cm^{-2} is achievable when the gyrotron output power is focused into a spot of size on the order of the wavelength.

It appears that the millimetre-wave beam processing has much in common with the methods of infrared laser treatment. At the same time, many features inherent in gyrotron wavebeam systems provide advantageous differences compared to laser-based systems:

- higher output power per device (>100 kW cw when necessary);
- higher efficiency of the radiation source (about 0.4 for regular gyrotrons and above 0.6 for the gyrotrons with a depressed collector);
- a much more robust system for the transport of radiation;
- very low heat load on mirrors and focusing components;
- possibility to form any desired pattern of intensity distribution in the wave beam cross section.

The most serious limitation of microwave surface processing is electric discharge on the surface. The threshold electric field strength for breakdown in air is much lower in this frequency range than in the infrared and visible parts of the spectrum. The presence of vapours of various substances at the hot surface of material makes the occurence of a discharge even more likely.

It should be noted that the term 'surface treatment' bears a rather conditional sense when applied to millimetre-wave processing of materials. In most dielectric materials that can be efficiently heated with millimetre waves the heat is generally deposited in a somewhat extended region beneath the surface. In fact, the characteristic microwave absorption length, equation (2.2), for $\omega \sim 2 \times 10^{11}$ s^{-1}, $\varepsilon \sim 10$ and tan ~ 0.1–1 is $l \sim 0.05$–0.5 cm. This situation is not typical for the surface treatment of materials by the other methods listed above, in which the incident energy is dissipated either on the surface itself or in a very thin (~ 1 μm) near-surface layer. Therefore, millimetre-wave beam heating can be of great importance in the processes of surface treatment when there is a restriction on the maximal temperature of the material.

In general, the problem of the efficiency of surface heating is solved in another manner than when the material is heated volumetrically in a microwave furnace. During surface processing it is necessary to provide the absorption of radiation in one pass of the incident wavebeam through the body undergoing processing. For this purpose the surface can be coated with a purposely designed absorbing layer, in largely the same manner as for infrared laser processing. Strong microwave absorption can be obtained in composite materials constituting a dielectric matrix impregnated with fine metal particles. The matching of the absorbing layer with the incident wave beam is achieved by optimizing the effective dielectric properties of the composite material, as described in subsection 2.2. It is often important not only to match the absorbing layer with the wave beam, but also to provide efficient heat transfer from the layer to the substrate. For example, fast heat transfer is a necessary condition in the transient high-temperature treatment of materials, where the deposited energy must be rapidly removed to prevent undesirable overheating of the processing zone. Concurrent fulfilment of both matching and fast cooling conditions imposes a limitation on the microwave frequency. Consider a layer of thickness d, which is optimized with respect to microwave absorption,

$$d \sim \frac{\pi c}{2\omega \sqrt{\varepsilon'}} \tag{3.1}$$

(cf equations (2.5) and (2.6)). The heat flow through the layer can be estimated as $q \sim \kappa \Delta T / d$, where ΔT is the characteristic temperature difference between the layer and substrate. The rate of temperature relaxation by thermal conduction is

$$\frac{\partial T}{\partial t} \sim \frac{4}{\pi^2} \frac{\varepsilon' \omega^2}{c^2} \chi \Delta T. \tag{3.2}$$

Taking typical values for transient thermal heating, $\partial T / \partial t \geqslant 10^3$ K s^{-1}, $\Delta T \sim 10^3$ K, and for a metal–dielectric layer $\varepsilon' \sim 10$ and $\chi \sim 10^{-2}$ cm^2 s^{-1}, we find $\omega \geqslant 1.5 \times 10^{11}$ s^{-1}, which corresponds to frequencies of 24 GHz and above. Thus, we again come to the conclusion that the high-temperature surface treatment of materials is most feasible with the millimetre-wave radiation.

The experiments on surface treatment were among the first processes in which the millimetre-wave radiation was used for materials processing [58, 69]. However, the research in this field has not yet received due attention. In all probability this fact is explained by relatively limited experience with gyrotron millimetre-wave sources in materials processing. However, the list of the processes that have successfully been tested with the use of the millimetre-wave radiation looks impressive [69, 70]: surface transient heating of metal alloys, joining of high-temperature superconductor ceramic coatings to metal substrates, coating of metal tubes with polymer films, joining of dielectric materials, etc.

4. Non-thermal microwave effects

4.1. Experimental identification of non-thermal effects

As long as microwave processes of high-temperature treatment differ from the processes that do not use microwaves, one of the questions arising is: is the difference due only to a different heat deposition pattern, or do microwave *electromagnetic fields* play a role in it? The problem of the so-called 'microwave effects' has become one of the most controversial issues in the recent literature on the microwave processing of materials. While some of the researchers tend to use the term 'microwave effect' to denote any and all distinctions of the microwave-assisted processes from those not using microwaves, others propose to limit its meaning to only those observations which cannot be explained in full on the basis of current knowledge in the field [71]. This section reviews the physical aspects of the effect of microwave electromagnetic fields on mass transport in solids.

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 identical temperature dynamics, $T(r, t)$, of these processes. In practice, at least two general problems challenge the identification of non-thermal effects. One of them is inaccurate or incomplete temperature measurements [72]. Thermocouple sensors generally measure the temperature of the thermocouple head, which may be close to the temperature of the material at the point which the head touches, but it can still differ substantially from the temperature in most other points of the material. The reasons are heat losses via the thermocouple, microwave absorption in the thermocouple, etc. Pyrometers measure temperatures on the surface of the material but these are different from those in the bulk. Millimetre-wave tomography methods [73] that can provide information on the temperature inside the material are hardly applicable to high-temperature processing conditions. In general, it is not feasible to obtain accurate data on the dynamics of temperature at all points.

The second problem is that it is impossible to devise a pair of a microwave and conventional processes that would have identical temperature fields. In particular, as discussed above, it is not possible to implement a microwave heating process with a uniform temperature distribution in the material undergoing processing. Temperature gradients are a fundamental attribute of microwave volumetric heating, and the effects caused by them indeed contribute to differences in the process flow. Possible mechanisms of the influence of temperature gradients are, for example, thermoelastic stresses [74], and thermal diffusion [75]. However, both experimental [76] and theoretical [77] studies suggest that temperature gradients are generally not the main reason for enhanced mass transport rates.

There are many experimental observations that suggest non-thermal influence of microwave fields on mass transport. One of the phenomena first observed and still not yet explained in full was the enhancement of oxygen diffusion in sapphire crystals heated in a 28 GHz millimetre-wave furnace [12, 78]. A 40% decrease in the apparent activation energy for bulk diffusion was observed under millimetre-wave heating as compared to conventional heating.

Many workers have observed an enhancement of the densification during microwave solid-phase sintering of ceramics. A systematic study of microwave sintering of zirconia [79] revealed a non-thermal nature of this enhancement. The authors used combined radiant and microwave heating, and varied the proportion of power between the two sources. The densification rate at each temperature was demonstrated to be sensitive to the proportion of microwave power. With full microwave power, the densification curve was shifted towards lower temperatures by approximately 100 °C, as compared to conventional heating.

The shifts of densification curves towards lower temperatures often observed in microwave sintering experiments may incur criticism from the standpoint of temperature measurement methodology and accuracy [72]. Therefore, of special importance are experiments that use natural reference points for the temperature, rather than rely on temperature data from instrumental measurements. A study of microwave-assisted oxygenation of melt-processed bulk YBCO ceramics [80] revealed significant enhancement of diffusion-controlled absorption of oxygen. The (highly temperature-dependent) equilibrium values of oxygen deficiency were found to be equal for the corresponding microwave and conventional processes, which proved that the observed diffusion enhancement was not due to erroneous temperature measurements.

Another diffusion-controlled process that has been tested for microwave effects is the spinodal decomposition of ionic solid solutions. Noticeable differences in the evolution of titanium oxide–tin oxide solid solution samples were observed under microwave and conventional heating [81]. This effect supposedly originated from the interaction of the microwave electric field with the space charge structure of compositional fluctuations.

An interesting observation of non-thermal effect of a microwave field on mass transport has recently been reported [82]. In this study, nanostructured porous alumina membranes were heated by millimetre waves in a gyrotron system and, for comparison, in a conventional furnace. The 25 μm thick amorphous alumina membranes were penetrated by a honeycomb-like structure of tubular pores with an average diameter of 60 nm. It was found that the porosity, observed by scanning electron microscopy, decreased consistently with increasing time of microwave exposure. By contrast, conventional heating caused no changes in the surface porosity of the membranes in the same process temperature and time ranges. The results of this comparative study suggest that microwave field enhances the rates of mass transport along the membrane surface by about two orders of magnitude.

This example illustrates the principles of devising a purposeful experiment to study the non-thermal effect of a microwave field on mass transport. The problem of inhomogeneous heating was avoided here by the choice of the material. Due to the small thickness of the membranes, temperature gradients across it were effectively eliminated, making microwave heating uniform in this particular case. The process under investigation involved only one mass transport path, surface diffusion. The nanoscale pore size reduced the time requirements for mass transport and allowed statistical processing of the data on hundreds of pores in each electron microscopy image. As a result, identification of the non-thermal nature of the observed enhancement of the mass

transport has become possible. Still, the specific mechanism of this effect needs further theoretical and experimental investigation.

4.2. Non-equilibrium excitations and ponderomotive effects

As follows from the above, experimental identification of the non-thermal effects of a microwave field poses a serious problem. This explains the limited number of direct experimental claims of having identified a non-thermal effect, as opposed to a large body of experimental work that demonstrates the difference itself between microwave and conventional processes. Even more difficult is the experimental identification of a particular mechanism of the non-thermal effect. Over the last decade, considerable effort has been spent on the development of theoretical models for microwave non-thermal enhancement of transport phenomena in solids and experimental justification of these models.

One of the hypotheses that seemed almost natural was based on the concept of non-equilibrium excitations [83]. To introduce this concept let us start from the observation that the primary difference between microwave and conventional processes is in the nature of their energy supply routes. In conventional processes, energy is mostly delivered to the material by means of equilibrium thermal electromagnetic radiation which has a continuous spectrum. Most of the energy of thermal radiation for temperatures on the order of 10^3 K is contained in the infrared region of the spectrum. The process of thermal radiation absorption by the material is usually viewed as the excitation of lattice oscillations which have an equilibrium spectrum. Changes in the temperature of the solid with heating mean the slow evolution of the spectrum which at all times remains in quasi-equilibrium.

In contrast to thermal radiation, the prevailing mechanism of microwave absorption in dielectric materials is the excitation of electron oscillation at the frequency of the microwave source. This means that all energy that is being absorbed is, for a certain time, contained in non-equilibrium excitations. The energy of electron oscillation is converted to the energy of lattice vibrations with an equilibrium spectrum via a number of steps. Electron oscillations induce periodic distortion of the lattice potential and thereby modify the spectrum of lattice vibrations—that is, drive it away from equilibrium. Due to the nonlinear interaction between lattice modes, the vibration spectrum then equilibrates. The fraction of energy stored in non-equilibrium excitations is determined by the time constant of the latter process.

It is easy to show that in a homogeneous and perfect crystalline solid the energy content of microwave-induced non-equilibrium excitations is negligible. Consider the vibration spectrum, $\omega(k)$, of a crystalline solid. It generally consists of several branches that belong to one of the two types: acoustic and optical (figure 8(a)). The maximum frequency of vibration, the so-called Debye frequency, is of the order of 10^{13} s^{-1}, which far exceeds the microwave frequencies. For the optical branches (which exist in crystals having more than one atom in the lattice cell) there is a minimum frequency of vibration, which is also of the order of the Debye frequency. The acoustic branches begin from zero frequency and in the long-wave ($k \rightarrow 0$) limit have the form $\omega = c_s k$, where c_s is sound velocity.
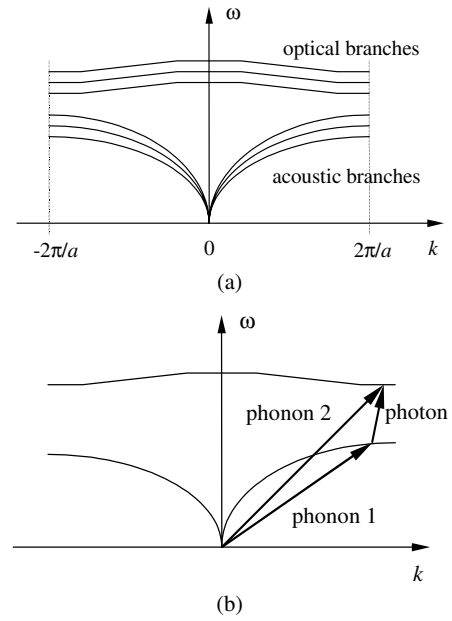

Figure 8. (a) Schematic view of a lattice vibration spectrum. (b) Schematic diagram of the photon–phonon three-wave mixing process leading to the excitation of a higher-energy phonon. The photon and phonons are shown as vectors with the components ω and k to illustrate the conservation laws. a is the lattice parameter.

The absorption of the energy of the microwave electromagnetic field can be viewed as the excitation of vibration modes due to the interaction of electromagnetic waves with the (induced) charge in the lattice. From the conservation of energy and momentum it follows that the sums of frequencies, ω, and wavevectors, k, of the interacting vibrations are conserved. This makes impossible the direct excitation of vibrations by microwaves both on the acoustic (since $c_s \ll c$) and optical (since microwave frequencies are much lower than the minimum vibration frequency) branches. At elevated temperatures at which mass transport processes are activated, a considerable contribution into microwave absorption is made by three-wave mixing interactions between electromagnetic waves and lattice vibrations. These processes are often termed three-quanta processes of electrophonon (or photon–phonon) interaction [84], with the corresponding conservation laws formulated as quantum selection rules.

The most likely to influence diffusion are the excess (above the equilibrium distribution) high-energy phonons that originate from the mixing between an electromagnetic wave and vibrational modes (in the short-wave region of acoustic branches and on the optical branches of the vibration spectrum, as shown in figure 8(b)). These phonons also participate in nonlinear relaxation processes (mostly of the three-wave type) which eventually equilibrate the vibration spectrum. An estimate of the microwave energy absorption rate, $\partial w/\partial t$, and relaxation time, τ, obtained within the Debye approximation for the vibration spectrum gives

$$\frac{\partial w}{\partial t} \sim |E|^2 \frac{kT}{\rho a^3 c_s^2} \frac{\omega^2}{\omega_D} \qquad \tau \sim \frac{\rho a^3 c_s^2}{kT} \frac{\omega_D}{\omega^2} \frac{1}{\ln(2\omega_D/\omega)}$$

$$(4.1)$$

where E is the microwave electric field strength, ρ is the density of the solid, and a is the lattice parameter. The product

of these two values gives an estimate of the energy contained in all excess high-energy lattice vibration modes:

$$w \sim |E|^2 \frac{1}{\ln(2\omega_D/\omega)}. \qquad (4.2)$$

The energy contained in non-equilibrium high-energy lattice vibrations is thus within the same order of magnitude as the energy of the electromagnetic field, $|E|^2/8\pi$. For the values of the field strength and temperature that are typical for microwave processing ($E \sim 10^3$ V cm^{-1}, $T \sim 10^3$ K) this energy is about 10^{-10} of the total thermal energy, NkT (where N is the number of atoms per unit volume), and about 10^{-6} of the total equilibrium energy of all atoms whose energies exceed the activation energy for diffusion. This estimate therefore suggests that the contribution of non-equilibrium lattice excitations into the enhancement of mass transport in microwave processing is absolutely insignificant.

No confirmation of microwave activation of ionic conductivity was found in the purposely designed experiments [85, 86]. Instead, it was discovered that microwaves induced a dc ionic current in a NaCl sample even with no dc bias voltage applied [85]. This suggested that the microwave field exerted a net driving force on the ions, rather than modified their mobility. At about the same time, a theoretical model predicting similar microwave net action on mass transport was proposed [87]. In terms of non-equilibrium excitations, its results can be understood if we note that the above estimates are valid for homogeneous, perfect crystalline solids. The presence of defects, however, can increase the lifetime of non-equilibrium excitations. The most obvious example is vacancy diffusion in ionic crystalline solids, which can convert a portion of the microwave field energy into the energy of the oscillatory migration of ions in the lattice. The authors of the theoretical model have demonstrated that under certain conditions the microwave-induced oscillatory vacancy fluxes are rectified, leading to directional, macroscopic mass transport. This so-called ponderomotive effect can be explained by the following considerations.

In the solids with an ionic crystalline structure, electrically charged vacancies can act as the recipients of the action of a microwave field. The vacancy flux, $\boldsymbol{J}$, contains, in addition to diffusion, a field-induced drift part:

$$\boldsymbol{J} = -D\nabla N + DNq\boldsymbol{E}/kT \qquad (4.3)$$

where D is the diffusion coefficient, N is the concentration, q is the effective electric charge of vacancies, and $\boldsymbol{E}$ is the vector of the electric field. Even in comparatively weak electric fields, the amplitude of the drift part of the vacancy flux exceeds the characteristic value of the diffusion part [87]. Macroscopic mass transport due to the vacancy drift has been observed in single-crystalline NaCl in a dc electric field as low as 70 V cm^{-1} [88]. However, since vacancy drift in microwave fields is oscillatory, a non-zero averaged effect can only exist due to the nonlinear rectification of currents. The nonlinearity in ionic crystals can originate from field-induced space charge perturbations. This effect can be described quantitatively within a model consisting of the continuity equations (for positively and negatively charged vacancies)

$$\partial N_{\pm}/\partial t + (\nabla \cdot \boldsymbol{J}_{\pm}) = 0 \qquad (4.4)$$

and the Maxwell equations

$$(\nabla \cdot \boldsymbol{E}) = 4\pi\rho_{sc}/\varepsilon \qquad (4.5)$$

$$(\nabla \times \boldsymbol{E}) = 0, \qquad (4.6)$$

where $\rho_{sc} = (|q_+|N_+ - |q_-|N_-)$ is the density of space charge and ε is the lattice dielectric constant of the material under consideration. The quasistatic approximation used in this model corresponds to an ionic crystalline body whose dimensions are small compared with the electromagnetic wavelength, for example, a particle of powder in ceramics.

In a homogeneous single crystal the electromagnetic field, varying sinusoidally in time, does not affect the concentration of vacancies and induces only oscillatory fluxes of vacancies. At the same time, in the vicinity of a grain boundary (or interface), oscillatory perturbations of the concentration of vacancies arise. These perturbations are in phase with the microwave electric field. As a result, the net (averaged over the field period) drift flux is non-zero. The direction of the net flux is the same for both positive and negative vacancies, which means that a transport of neutral mass occurs. Since the mobility of positive and negative vacancies is generally different there should also be charge transport, which has indeed been observed, as discussed above [85]. A subsequent detailed investigation of ionic current transient dynamics has demonstrated good agreement with this theory [89].

The final result for the net drift vacancy flux responsible for mass transport can be presented as a product of the effective mobility and the average volumetric force:

$$\langle \boldsymbol{J} \rangle = \frac{D_+ D_-}{D_+ + D_-} \langle \rho_{sc} \boldsymbol{E} \rangle. \qquad (4.7)$$

The force appearing in equation (4.7) is of the same physical nature as the ponderomotive force known in plasma physics [90, 91]. A general measure of the ponderomotive action is the magnitude of the pressure of the electromagnetic field, $\boldsymbol{E}^2/8\pi$. For the field strength on the order of 10^3 V cm^{-1} the radiation pressure is as low as 0.1 Pa. Usually much higher field strengths are needed to influence transport phenomena in condensed matter by electromagnetic field pressure [92]. However, there are factors that effectively result in the amplification of microwave action. The ponderomotive force in ionic crystalline solids is applied directly to mobile vacancies; it can be shown [87] that the equivalent stress that results from the ponderomotive effect is greater than the radiation pressure by a large factor, $N_0/N \geqslant 10^5$ (here N_0 is the concentration of atoms in the solid). An additional enhancement of the ponderomotive mass transport drive can occur at surfaces and grain boundaries due to the action of the tangential component of the microwave electric field [93]. This component induces net fluxes of vacancies only within the near-surface layer of each grain, where the space charge is localized and where the mobility of vacancies is much higher than in the bulk. This results in an additional mass transport enhancement factor, $(D_V/D_S + a/R)^{-1}$, which may reach several orders of magnitude (here D_S is the diffusion coefficient in the near-surface amorphized layer, D_V is the diffusion coefficient in the bulk crystal, a is the thickness of the amorphized layer, and R is a characteristic size of crystal). As a result, the ponderomotive action of an electric

field can compete with different thermochemical driving forces and significantly influence mass transport in ionic crystalline solids [94].

The efficiency of the ponderomotive effect on mass transport depends upon the correlation between the values of the frequency of radiation and the ionic conductivity of the solid. Estimates show that depending on the type of material and temperature, the optimum frequency range for the effect can vary from radio frequency to microwaves and millimetre waves.

Subsequent studies [91, 95] have revealed considerable intensification of the electric field in the neck regions between individual grains in ceramics undergoing microwave sintering. Depending upon the dielectric properties of the material and the relative neck size, the microwave energy density has been demonstrated to be one to three orders of magnitude higher in this region than the energy density averaged over the volume of the grain. Since the mass transport in the course of sintering occurs predominantly within the neck region, this result suggests that the role of ponderomotive forces in microwave sintering is even more significant than was anticipated.

In conclusion, the ponderomotive mechanism is, to date, the only model that has been confirmed quantitatively by experiments. However, not all experimentally observed non-thermal effects have been explained within this approach. Still more work is needed to explore the mechanisms responsible for non-thermal effects in microwave processing. This task is, however, rewarding, since its accomplishment will allow full utilization of the potential of microwave processing methods.

5. Conclusion and outlook to industry

Microwave high-temperature processing of materials is still at the laboratory stage of development. Commercialization of the microwave processing technology depends on many interrelated factors, consideration of which is largely beyond the scope of this review. We refer an interested reader to a number of publications discussing this problem [1, 96, 97]. Here we outline the physical and technical factors that are capable of affecting the transfer of laboratory results to industry.

The approaches proven to be efficient in the lower-temperature processes (in food, wood, pharmaceutical, polymer, and other industries) cannot be transferred directly to high-temperature processing. The implementation of high-temperature processing requires different and, as a rule, more sophisticated techniques regarding thermal insulation, temperature measurement and control, electromagnetic field and temperature uniformity etc. Although laboratory studies typically demonstrate significant reduction in process duration and energy consumption, to date only very few high-temperature microwave processes have found their way to industry. Apparently, this fact supports the observation made more than ten years ago at one of the first symposia on microwave processing of materials: 'Where microwave energy has been successfully adapted to materials processing, the capital cost of equipment has rarely, if ever, been justified on the basis of energy savings. More likely, microwave energy has been used because no other form of energy would

produce the same value added' [98]. Therefore, the research and development in this field concentrates largely on the fundamental physical specificity of the microwave processes and purposeful utilization of the microwave-specific effects.

It is difficult to make a prognosis concerning the most promising areas of high-temperature microwave applications, since too many factors other than physical can play the governing role in each particular case. It is more instructive to consider the industrial perspective of various microwave processing configurations from a technical viewpoint.

The methods based on the use of a single-mode applicator at a frequency of $\leqslant 2.45$ GHz, although wide spread at present, are in fact mostly restricted to laboratory research. Microwave heating of materials in a single-mode applicator has a number of fundamental limitations, probably the most serious of which is the strong non-uniformity of the electromagnetic field pattern. Uniform enough heating in such applicators can be provided only for specimens of a size much smaller than the wavelength. From the viewpoint of moderate-scale industrial production multimode applicators of a size much larger than the wavelength are more suitable. An example of an applicator with a volume of 4000 l ($L \sim 13\,\lambda$) fed with 48 kW power at a frequency of 2.45 GHz can be found in [99]. To make such systems acceptable for most applications of industrial interest, the factors that cause non-uniform heating, i.e. the volumetric heating and the non-uniform distribution of microwave energy in the applicator, should be accounted for. Thermal insulation arrangements reducing heat loss from the material are commonly used to address the first problem, as well as the hybrid heating, when microwaves are supplemented with conventional heat. The heat may come from separate heat sources (electric, gas etc.) [48] or from microwave absorption in high-loss elements of a hybrid heating system [38]. In both cases, the microwave power absorbed directly in the material undergoing processing is relatively small and the microwaves only modify the process to some extent. This method also works to increase microwave absorption in materials at the start of heating, and on the whole results in higher temperature uniformity, shorter production times and increased throughput [48]. However, hybrid heating, conceptually, is rather a modification of an established materials processing technology than a radically new approach to the fabrication of advanced materials, and it has many shortcomings pertaining to conventional heating. It is worth noting that any method pursuing complete elimination of temperature non-uniformity inevitably decreases the microwave power input to the material. Therefore, the development of each microwave-driven process can be viewed as a search for a trade-off between admissible non-uniformity and specific properties of materials obtained by microwave heating.

The problem of a uniform distribution of microwave energy in an applicator, as a prerequisite for homogeneous heating, seems to be less severe with applicator upscaling to industrial needs. When the applicator is a metal closed-wall cavity, the number of eigenmodes increases with its dimensions. The sweep of the mode interference pattern, which is commonly done using a mode stirrer, results in a rather uniform distribution of microwave energy if the number of modes is large enough. The movable interference pattern and highly uniform distribution of microwave energy can be
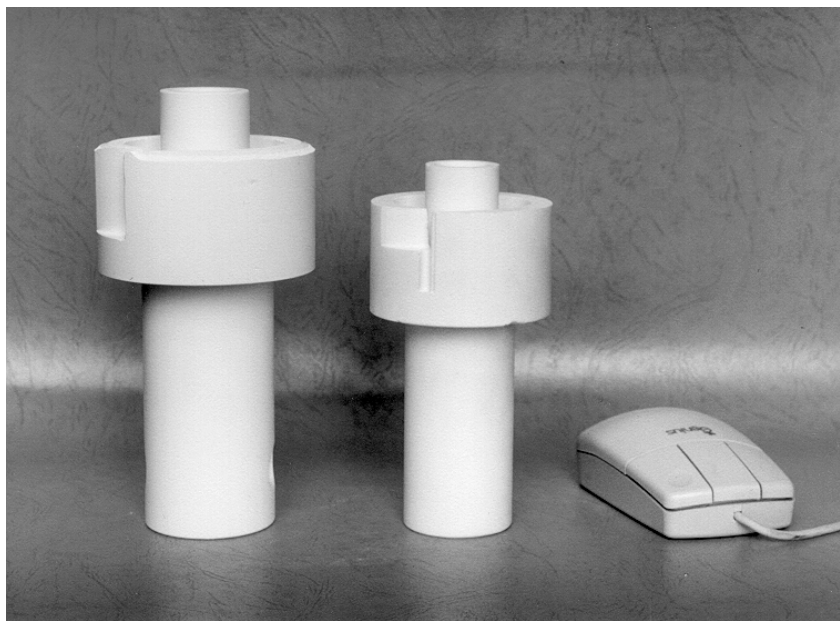
Figure 9. A 1 kg, 20 cm high pure alumina ceramic specimen sintered in a 30 GHz millimetre-wave gyrotron system. The sintering temperature was 1600 °C with a hold time at this temperature of 20 min; the maximum millimeter-wave power was 4 kW. For comparison, an unsintered specimen is also shown on the left.

obtained when an applicator is powered by variable frequency microwaves [100]. However, the output power of the variable frequency microwave sources is limited to 1–3 kW, and the processing systems exploiting several sources of this type can hardly be economically viable.

Many problems inherent in microwave heating can be more readily solved with the use of millimetre-wave power, for which the lowest standard ISM frequency is 24.125 GHz. The enhanced millimetre-wave energy absorption in most materials of practical interest, significantly higher uniformity of microwave energy distribution, even in moderate-size applicators, and better stability against the thermal runaway effect make millimetre-wave processing a unique technique. The purposeful utilization of all these factors is illustrated by figure 9, showing a pure alumina specimen of complex shape and large size sintered in a 30 GHz millimetre-wave system. The total process time was about 6 h (of which 3 h were taken by power-controlled cooling), in contrast to more than 30 h needed for a conventional sintering procedure. In addition to processes based on volumetric heating, many industrial expectations exist in connection with the use of focused millimetre-wave beams for surface processing of materials. In particular, this method has high application potential in the field of thermal barrier coatings.

An important issue for the development of microwave and/or millimetre-wave high-temperature processing technologies is broadening the range of materials and applications. While most of the research and development is currently within the area of dielectric ceramic and glass materials, there have been experimental studies on applying microwaves to the high-temperature processing of semiconductors [101] and powder metals [102]. Finding applications for the microwave processing methods in these well established and highly competitive industries is extremely difficult. In essence, only radically improved properties of the obtained products can lead to accep-

tance of the microwave technologies, which means that feasibility studies should be preceded by fundamental research efforts aimed at finding microwave-specific effects in the processing of these materials.

Both in the research and application development areas a crucial role is played by the modelling and simulation of microwave processes. While there exists plenty of commercially available software for simulating electromagnetic problems, not all of these codes can be combined with those for simulating heat transfer. In addition, although significant progress has been achieved in simulating 2.45 GHz microwave processing systems [30, 103], simulation of millimetre-wave processing in super-multimode cavities will for a long time remain a scientific problem, even if the power of computers continues to grow at the present rate. Even less investigated and understood is the effect of microwave heating on the evolution of materials (e.g., densification and grain growth in a microwave sintering process). All this suggests that application development must be accompanied by the development of appropriate models and simulation tools which will be indispensable for the actual implementation of microwave high-temperature processing technologies.

In conclusion, microwave methods of high-temperature processing of materials have substantial industrial application potential. The most promising applications are those which utilize the specificity of microwave processing and result in novel materials or radically improved material properties. Industrial mastering of microwave processing is therefore contingent upon high-level fundamental and applied research in the field of microwave–materials interaction.

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