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MODELING OF POROUS CERAMICS DURING MICROWAVE SINTERING

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8.1 Introduction

Ever since Tinga and Voss [1968] showed the feasibility of sintering of ceramics in the mid-sixties, a significant amount of research has been focused on identifying and understanding the problems associated with the sintering of various types of ceramics [Bertaud and Badot, 1976; Meek, 1984; Borom and Lee, 1986; Brodwin et al., 1987; Sutton et al., 1988]. It is not very well understood how the parameters, such as the shape, and the size, etc., of ceramic particles in green samples, affect sintering. Experimental verification is very time consuming since various types of samples have to be made and sintered. This suggests theoretical research involving computer simulation using various approximations.

Ceramics can be modeled as multi-phase random media [Varadan et al., 1988]. A green sample of porous ceramic material may be modeled as particles or fibers (discrete inclusion phase) of one or various kinds randomly dispersed in a host medium (connected matrix phase). Or, it can be considered in terms of randomly distributed pores in a matrix material. Although the modeling can involve a number of details of both phases, for clarity, we try to avoid these complexities and

present a simple model for microwave sintering.

The average dielectric constant of porous ceramics to be sintered, which are complex in the microwave frequency band, usually plays a key role in the whole sintering process. The imaginary part of the dielectric constant is an indicator of the energy absorbing capability through the heat diffusion equation while its real counterpart may represent the level of energy distribution inside the material. Although the mechanisms coupling thermodynamics and the concentrations and sizes of pores or particles are, unfortunately, not very clear to the materials research community, the change of dielectric constants due to the change of concentrations and sizes of pores may be predicted by the proposed model and, as a result, our understanding of the microwave sintering process may be improved.

In this paper we begin addressing the problems associated with mixture theories and use rigorous multiple scattering theory to compute the average dielectric constants of porous ceramics. A power law is introduced in the scattering formalism in order to count the concentration (volume fraction of either pores or ceramic particles) dependent particle and pore sizes. Values of computed complex dielectric constant of sintered alumina with different densities compare quite well with those measured at the room temperature. In addition, thermal runaway conditions may be studied using the heat-diffusion equation with appropriate initial and boundary conditions.

8.2 Multiple Scattering and Dispersion Equation

In most applications involving multiple scattering, the discrete and continuous phases are well defined. The physical sizes of the discrete phase remain unchanged no matter how the concentration is varied. Due to the selection of models, results by switching the phases will be different. Nevertheless, in a previous study [Varadan et al., 1988], it was shown that, without lossy mechanism in both phases, the choice of discrete phase may not be critical beyond the concentration threshold if a concentration dependent size variation is incorporated into the theory. However, when associated with any lossy mechanism, the selection of inclusion phase does affect multiple scattering results which will be presented in this paper.

The complex dielectric constant can be, in general, obtained for any microwave composite through the effective wavenumber which is

derived using multiple scattering theory [Ma et al., 1988]. The role of the imaginary part of the dielectric constant is generally neglected in mixture theories but plays an important role in the sintering process.

In multiple scattering formalism, by assuming that the exciting microwave to be a plane wave with an effective wavenumber K (the average dielectric constant ε is directly proportional to K^2), we can obtain the following dispersion equation

$$|I - \sum \int \sigma(\bar{r}_i - \bar{r}_j) T^j p(\bar{r}_j | \bar{r}_i) e^{i\bar{K} \cdot (\bar{r}_i - \bar{r}_j)} d\bar{r}_j| = 0 \quad (1)$$

Equation (1) is a determinantal equation and I is an identity matrix. The roots of (1) can be solved numerically to yield the values of the effective wave number $K = K_1 + iK_2$ as a function of microwave frequency ω , the shape, size and orientation of the scatterer via the T -matrix T^j , and the statistics of the distribution via the joint probability distribution function $p(\bar{r}_j | \bar{r}_i)$.

In microwave sintering of ceramics, we are interested in the imaginary part of the dielectric constant ($\varepsilon = \varepsilon' + j\varepsilon''$) of ceramics which appears in the source function of the heat diffusion equation. For a nonmagnetic material, the relation between K and ε is

$$\varepsilon/\varepsilon_o = K^2/k_o^2 \quad (2)$$

in which ε_o and k_o are the dielectric constant and wavenumber of free space, respectively.

8.3 Approximation of Grain and Pore Sizes

During microwave sintering, the sizes of both grains and pores vary with the concentrations of grains and pores. Here, we review and modify a previously proposed concentration dependent power law for grain or pore size [Varadan et al., 1988]. Although the present power law of grain size is preliminary and empirical, it turns out to be a fairly good approximation. Based on this, the dielectric constants of porous ceramics calculated using multiple scattering formalism agree quite well with those measured. With the increasing temperature, the concentration of the pores (grains) decreases (increases) and a direct but an implicit relationship between the sizes of particles and the sintering temperature may be visualized but remains to be explored and is beyond the scope of this study.

Before sintering, the porous ceramic samples have definite grain as well as pore sizes which remain constant (or the change of size can be neglected) even after the start of sintering as long as the temperature runaway has not been triggered. A critical concentration c_{cr} which depends on the runaway temperature and the material properties determines the start of the growth of grain and pore sizes [for experimental observations, see Figs. 8 and 9 of Varadan et al., 1988]. By microwave sintering, beyond the critical concentration, the green samples begin to densify much more effectively than by mechanical compaction or by conventional oven heating.

The size of grain particles, after the critical concentration, can be assumed to be a function of concentration and has the following form

$$a = \begin{cases} a_i (\varepsilon_r)^{(c-c_r)\alpha/(c_f-c_{cr})} & ; \text{ if } c > c_{cr} \\ a_i & ; \text{ if } c < c_{cr} \end{cases} \quad (3)$$

where $\alpha = \ln(\varepsilon_r)/(\ln a_f - \ln a_i)$, ε_r is the relative dielectric constant (real part) between the grain and the pore. The parameters a_f and a_i are the sizes of particles after and before sintering, respectively. The final sintering concentration c_f is, in general, in the range of 0.95 to 0.98 or even higher which means the total volume fraction occupied by the pores in the sintered ceramics has been reduced to about 2 to 5 percent of the total volume, or less.

Although the purpose of sintering is to reduce the concentration of pores in ceramics, the pore sizes, according to SEM obtained from sintered samples, increase with the decreasing concentration of pores. Therefore, we assume the pore size during sintering process is also a function of concentration and can be written as

$$b = \begin{cases} b_i (\varepsilon_r)^{(c-c_{cr})\beta/(c_f-c_{cr})} & ; \text{ if } c > c_{cr} \\ b_i & ; \text{ if } c < c_{cr} \end{cases} \quad (4)$$

where $\beta = \ln(\varepsilon_r)/(\ln b_f - \ln b_i)$, and b_f and b_i are the sizes of pores after and before sintering, respectively. In order to avoid confusion, c again is the concentration of grains as in (3) and the corresponding concentration of pores is simply $1 - c$. During the sintering of the alumina, the average grain grows from about one micron to about fifty microns. Meanwhile, the average pore size is increased from about 0.05 micron to about one micron.

One notices that a priori information, in the form of the critical concentration c_{cr} , is required in order to use (3) and (4). The critical

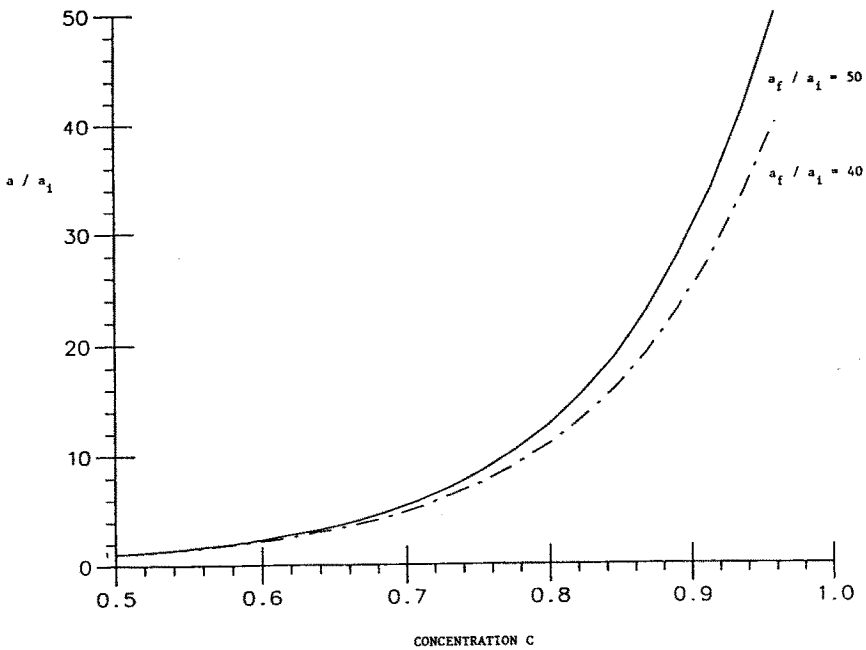


Figure 8.1 Normalized size vs. concentration based on the power law (2).

concentration can be predicted by finding the maximum attenuation due to pure scattering, i.e., both discrete and continuous phases are lossless, through solving the dispersion equation (1) using the following linear relationship between the grain size and the concentration

$$a = a_i + (c - c_i)\gamma \quad (5)$$

where $\gamma = (a_f - a_i)/(c_f - c_i)$.

Unless an absolute magnitude is required in the final results, the ratios of a_f/a_i and b_f/b_i are sufficient because all the values can be normalized with respect to those in the initial state of sintering. The size ratio a/a_i vs. concentration c for two different ratios of a_f/a_i are depicted in Fig. 8.1.

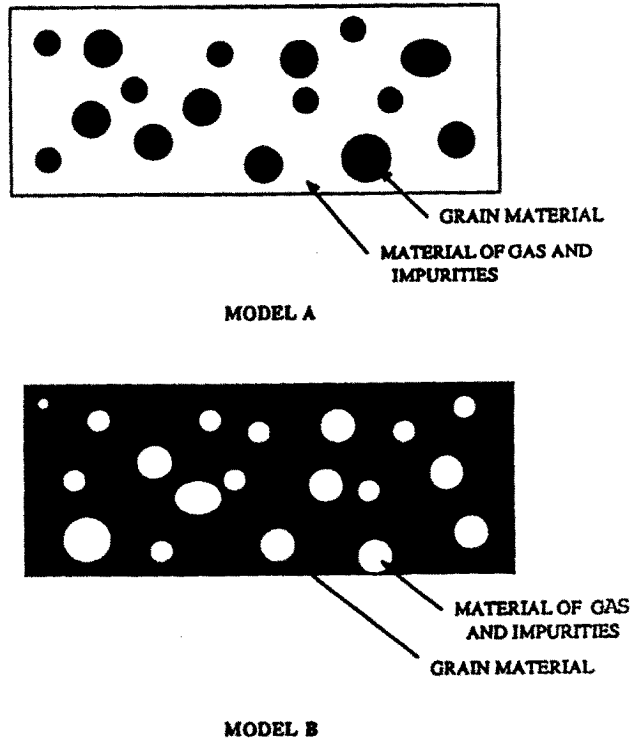


Figure 8.2 Schematic of two models considered in microwave sintering.

8.4 Modeling-Dependent Effective Dielectric Constants

Two models can be used for sintering ceramics and the choice of the continuous and discrete phases. Figure 8.2 depicts the models considered in the calculations. Model A uses air as the matrix material and the grains are dispersed in it while model B takes the matrix having the properties of grains and the discrete phases are the randomly distributed pores.

In the calculations, the microwave frequency is taken to be 3 GHz. At low gigahertz frequencies, both sizes of grains and pores are very small compared with the microwave wavelength. Therefore, the details of the grain and pore geometry are not very sensitive at these fre-

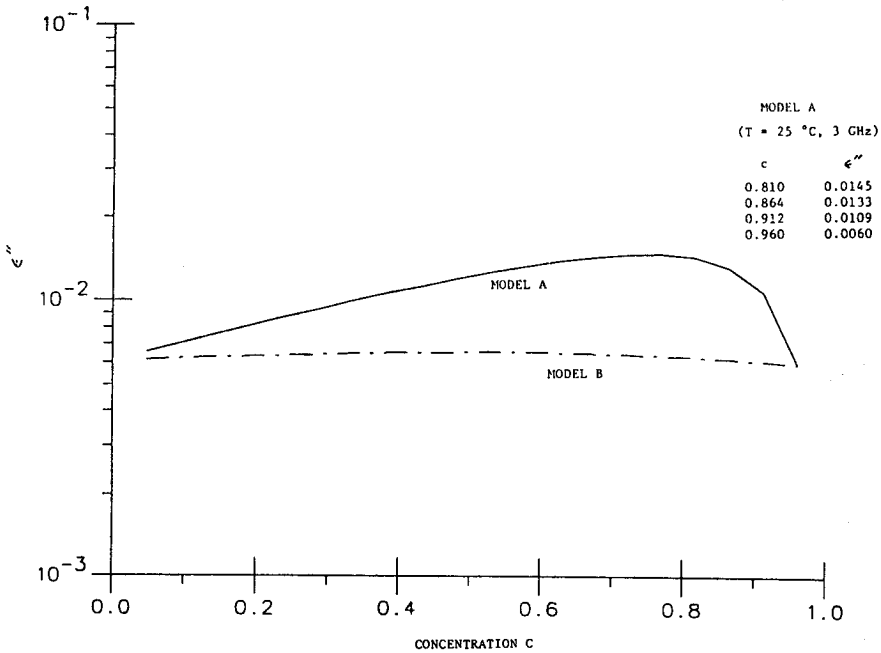


Figure 8.3 Computed ϵ'' vs. concentration for porous alumina.

quencies; hence we assumed them to be spherical in shape. The porous ceramic material considered here is alumina whose dielectric properties have been well documented.

Based on the reported dielectric constants of alumina, we know that a lower purity alumina has a higher dielectric loss factor [Westphal and Sils, 1972]. In order to predict this phenomenon, we consider both phases in the modeling have intrinsic loss mechanism. To do this, we assume the grains have the relative dielectric constant $\epsilon = 9.5 + 0.006i$ (an average value of sintered alumina having 95-96% of theoretical mass density at the room temperature) and the pores which may consist of lossy gas and impurities have $\epsilon = 1.0 + 0.006i$. The critical concentration c_{cr} is taken as 0.5 from a previous study [Varadan et al., 1988].

Computed values of ϵ'' vs. concentration c , which is defined as the volume fraction of grains, are presented in Fig. 8.3. As can be seen from

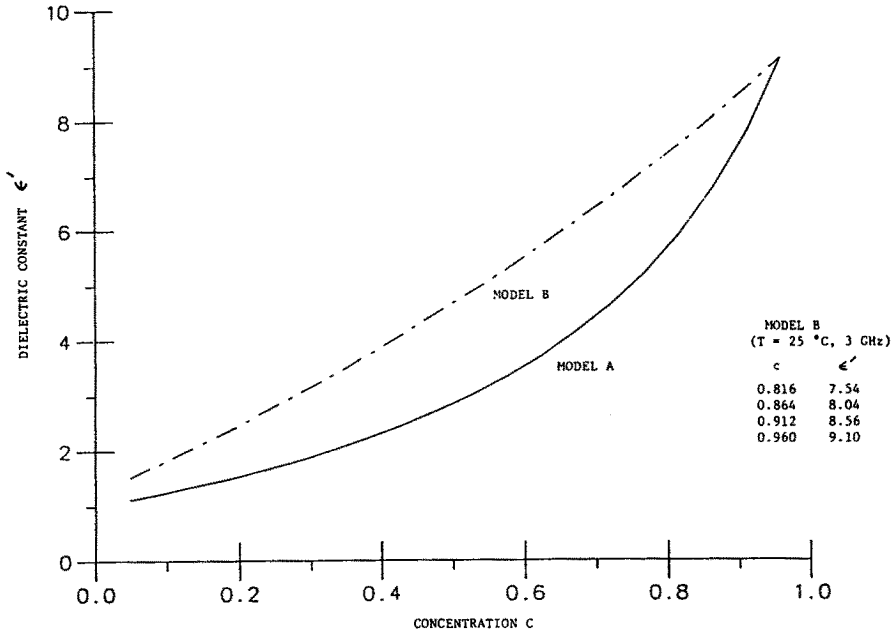


Figure 8.4 Computed ϵ' vs. concentration for porous alumina.

the figure, model A predicts the loss factor quite well if compared with those reported while model B is inferior in this case. However, when one looks at Fig. 8.4 in which the computed dielectric constants ϵ' are plotted against the concentration, the dielectric constant obtained using model B are, instead, in much better agreement with those measured [Westphal and Sils, 1972]. As apart from previous discussion on different scattering models [Varadan et al., 1988], depending on the real or the imaginary part of the dielectric constant to be predicted, different models should serve for different purposes and different scattering models give different results if the intrinsic loss mechanism is introduced into the modeling.

The effectiveness of microwave sintering can be explained using Fig. 8.5. With the increasing temperature, the concentration of the grains is increasing and the concentration of the pores is decreasing. This results in an increasing ϵ'' as well as an increasing ϵ' . The in-

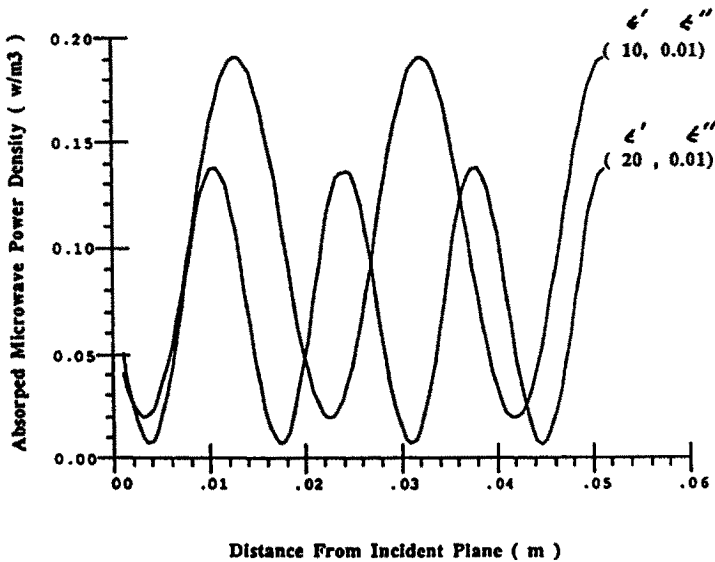
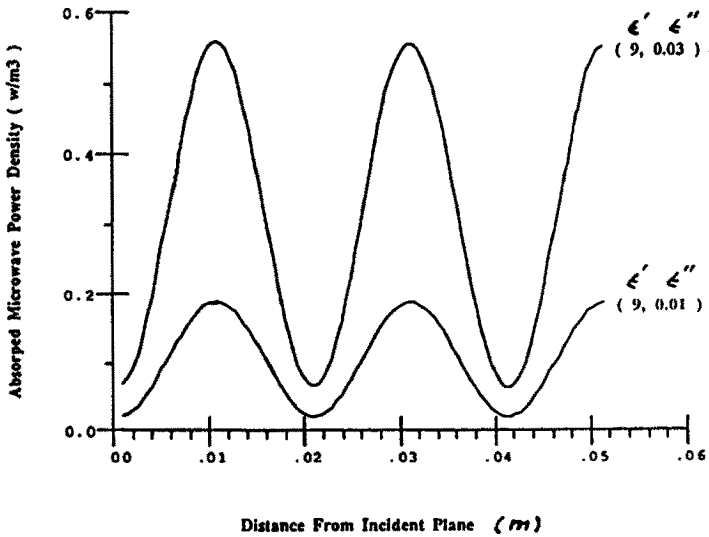


Figure 8.5 Power density vs. penetration distance for samples with different relative dielectric constants.

creasing loss factor ε'' gradually increases the sample absorbing capability while the increasing ε' makes the heat distribution inside the sample more even.

8.5 Chaos in the Heat-Diffusion Equation

Once the profile of ε'' as a function of temperature and other parameters has been obtained through multiple scattering studies, it may be possible to study the thermal runaway conditions through the source-incorporated heat-diffusion equation. The diffusion of thermal energy in a homogeneous bounded volume V , with constant thermal conductivity K_h , is determined by the partial differential equation

$$\rho C_p \partial T / \partial t - K_h \nabla^2 T = \varepsilon''(\omega, T) |E|^2 \quad (6)$$

in which ρ is the mass density, C_p is the specific heat capacity, $\varepsilon''(\omega, T)$ is the dielectric loss factor, E is the applied electric field, and $T(\bar{r}, t)$ is the temperature at a point \bar{r} at time t . On the boundary S of the volume V , the boundary condition

$$K_h \bar{e}_n \cdot \nabla T = H(T - T_o) \quad (7)$$

must hold, in which H is the convection heat coefficient, \bar{e}_n is the unit inward normal to S , and T_o is the ambient temperature. The initial condition is, obviously,

$$T(\bar{r}, 0) = T_o \quad (8)$$

it being assumed that the change in the temperature of the surroundings is negligibly small.

It can be seen that (6) is analogous to the forced Fisher equation

$$\dot{T}_t = T_{xx} + G(T) \quad (10)$$

which is known to exhibit chaotic behavior for specific initial and boundary conditions [Fisher, 1937; Rothe, 1981]. Additional work on the chaotic response of the two-dimensional form is available in the work of Bruch and his colleagues [Mitchell and Bruch, 1985; Waccholz and Bruch, 1987]. Although further work is necessary, knowing that $\varepsilon''(\omega, T)$ is an increasing function of T for sinterable ceramics, it is conjectured that the chaos inherent in (6) gives rise to the temperature runaway conditions observed by Roussy et al. [1985] during the microwave irradiation of EPDM rubber.

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