

Microwaves Enhanced Sintering Mechanisms in Alumina Ceramic Sintering Experiments

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Abstract

The results from the use of microwaves for ceramic synthesis have showed different results than that of conventionally synthesis method. One of the group results consists of indirect evidence of diffusion such as observations of enhanced sintering, grain growth, or reaction zones. The other group consists of direct measurements of diffusivities and activation energies for diffusion during microwave processing. Understanding the physical mechanisms of microwave effect is play an important role in the synthesis of materials technologies employing microwave energy. Many different physical phenomena including thermal and non-thermal are involved in the microwave processing of ceramics known as 'microwave effect'. This paper describes analysis of recent research on microwave sintering of an oxide ceramic, a high purity α -alumina. The experiment data used involved a wide range of microwave frequencies up to sub-

millimeter range which have been reported previously. Existing evidence as to that microwaves enhanced diffusions has been reviewed and will be discussed.

Keywords: Microwave effect, enhanced sintering, alumina, non-thermal effect

1 Introduction

Microwave sintering has emerged in recent years as a new method for sintering a variety of materials that has shown significant advantages over conventional sintering procedures. Since 1950s, microwaves have been used for food processing [1], mainly at a low microwave frequency, 2.45 GHz and 0.915 GHz. Recently, it has been developed gyrotrons as a high frequency and high power radiation source with more available frequencies [2]. In 1990s, the use of gyrotron with a power output of several kW and frequencies within a range of millimeter waves was reported by some researchers [3]. Moreover, a very high frequency microwave processing system within a range of sub-millimeter waves with a frequency of 300 GHz has been developed at FIR Center [4]. This device has been successfully used for sintering alumina, zirconia, and silica [5-8]. Researchers believe that the use of higher frequencies possesses greater microwave effects and the existing problems found in lower frequencies would be more easily solved.

The results from the use of microwaves for ceramic synthesis showed enhancement results. Those enhancements are grouped into two. The first enhancement consists of indirect evidence of diffusion such as observations of enhanced sintering, grain growth, or reaction zones [3, 5-10]. This type of observations does not provide clear evidence of enhanced diffusion due to its difficult in interpretation for complex processes such as sintering, grain growth, phase change, and chemical reaction. The second enhancement consists of much weaker evidence and comprises of direct measurements of diffusivities and activation energies for diffusion during microwave heating. An increase in width of the reaction zone for the ion exchange of potassium into a sodium-aluminum-silicate glass[11] and a significant decrease of activation energies for the sintering in alumina annealed using microwaves [3,12] have been reported. The obtained activation energies were 710 and 410 kJ/mol for the conventional and microwave samples, respectively, which is equivalent to an increase of approximately two orders of magnitude in the diffusivity for the temperatures studied. Recently, FIR Center of the University of Fukui calculated apparent activation energy of alumina for very high microwave frequency of 300 GHz [13].

Understanding the physical mechanisms of microwave effect is play an important role in the synthesis of materials technologies employing microwave energy. Many different physical phenomena including thermal and non-thermal are involved in the microwave processing of ceramics known as 'microwave effect'. Microwave effects have been used in order to explain unusual observations in microwave material processing. The effects are not to require the

transfer of microwave energy into thermal energy and the microwave energy itself directly couples to energy modes within the atom, ion, molecule or lattice known as non-thermal effect. To investigate microwave effects, experiments on the synthesis of oxide materials, alumina(Al_2O_3) and silica(SiO_2) as well as magnetic materials for ceramics, sensor, and microwave absorber via both conventional synthesis and microwave have been conducted by several groups of researchers as well as by authors [5-8, 14-17].

Non-thermal effects in solids are still part of an ongoing debate. Recently, several researchers have tried to develop theories to explain experiment results on microwave synthesis of materials, such as some group researchers supposed that electric fields focus at non-crystalline part area (interfaces) where microwaves cause plasma formation [18-19]. Booske, *et al.* believe that microwaves enhance diffusion in solids via second-order effects [20-21], and Rybakov, *et al.* explained that the effects are because of microwave ponderomotive force [22-23]. The non-thermal effect in relation to selective heating related to Debye relaxation theory of loss mechanism is recently discussed [24]. As a result, all possible effects may enhance solid-state sintering processes. The numeric and simulation of microwave-materials interaction have been also performed and published in this field [25-27]. This paper is to attempt to explain results of high frequency microwave alumina sintering from existing theories.

2 Microwave Sintering Results

A series of sintering experiments on alumina ceramics performed at a wide range of microwave frequencies have been reported by Sudiana *et al.* and Mitsudo *et al.* [5-6, 13, 28]. Alumina was chosen because sintering alumina mechanisms had been so widely studied earlier that comparative data were available [3,11-12]. Moreover, there are much information is available including diffusion data from several studies [29-30]. The alumina used in the work was Sumitomo AES-11C. The microwave annealing was performed under various frequencies of microwave sintering facilities consisting of a 2.45GHz, 28 GHz, and 300 GHz at kilowatts of microwave power. The detail experimental procedures and comparisons between results of microwave and conventional sintering have been analyzed and reported previously [5-6, 28]. The one of those results is presented in Fig. 1. The graph shows the relative density of the alumina samples with temperature variations for a sub-millimeter wave (300 GHz), a millimeter wave (28 GHz), and conventional processing. In comparison with the conventional case, samples sintered by microwave showed more rapid sintering. Effect of microwave frequency is also clearly shown in the densification graph. Effect of microwave on microstructures, grain growth, and others alumina properties have been published previously [6, 28].

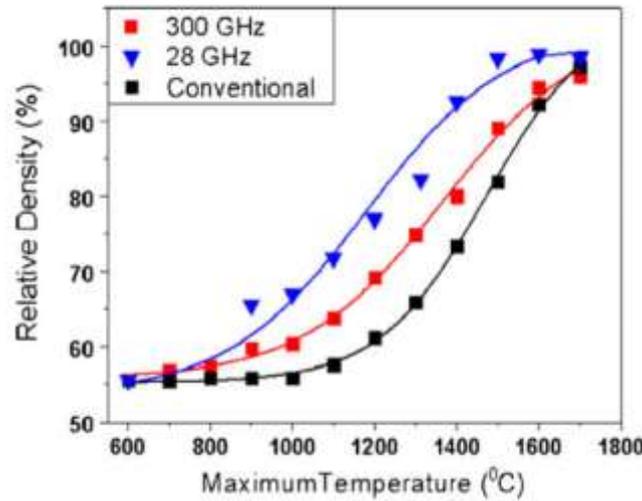


Fig. 1 Densifications of alumina sintered by various microwave frequencies [4]

3 Discussion

Properties of microwave sintered alumina showed different from conventional heating as reported by several scholars. The experiment results also exhibited effect of microwave frequency. To explain the results let us consider several possibilities. According to the microwave absorption theory, the power absorbed per unit volume $P(\text{W}/\text{m}^3)$ is,

$$P = \omega \varepsilon_0 \varepsilon_r' \tan \delta |E|^2 \quad (1)$$

which depends on the intensity of electric fields E , frequency f , dielectric constant $\varepsilon = K\varepsilon_0$ and loss factor $\tan \delta$ [31]. Because generally ceramic materials are structurally inhomogeneous, to keep the electric field flux on the interface between region 1 and 2 continuous ($\phi_{12} = \phi_{21}$), the field E must also be not homogeneous. Thus, it is clear that the electric field is higher in a region with a lower permittivity. Furthermore, to explain microwave enhanced sintering, it is required that microwave effects on atomic diffusion be analyzed. Moreover, to understand how a microwave field might influence atomic diffusion, it is helpful to look at the factors which control diffusion.

Generally, diffusion in solid state can be represented by the following atomistic equation:

$$D = f \lambda^2 N \Gamma \quad (2)$$

where D is the diffusivity, f is the correlation factor, λ is geometric constant (the distance between adjacent lattice planes), N is the concentration of vacancies (i.e., the probability that an ion has a vacant next to the nearest neighbor) and Γ is the jump frequency. Since λ and N are material and constant, microwaves might only

affect 2 components, i.e. the correlation factor f and the jump frequency, Γ are dependent on its previous jumps because all jumps are inter correlated and affect one another.

Electromagnetic energy can be dissipated in a crystalline dielectric through several loss mechanisms. These mechanisms can be associated with the microwave by the following processes: Polarization, short range formation and displacement of dipoles present in the material, quantified as (ϵ_d'') and Conduction, long-range displacement of charged particles, quantified as (ϵ_c''), electronic polarization (ϵ_e''), ionic polarization (ϵ_i''), and interfacial polarization (ϵ_s''). Because of the experimental limitation with differentiating each type of polarization, a term referred to as effective loss, (ϵ_{eff}''), has been introduced [1].

$$\epsilon_{eff}'' = \epsilon_d'' + \epsilon_c'' + \epsilon_e'' + \epsilon_i'' + \epsilon_s'' \tag{3}$$

Of all the possible loss mechanisms, for alumina and all most commonly ceramics used in microwave frequency applications, their predominant polarization are because of the dipole and ion polarization. These polarization types can be described by Debye's relaxation polarization model, as follows [32],

$$\epsilon^* = \epsilon' - i\epsilon'' = \epsilon_{optical} + \frac{\epsilon_s - \epsilon_{optical}}{1 + i\omega\tau} \tag{4}$$

where

τ = the relaxation time

ϵ_s = the static permittivity

$\epsilon_{optical}$ = the high frequency/optical permittivity

In alumina, the ion jump relaxation is a result of the formation of intrinsic Schottky or Frenkel pairs of aluminium ions and ion oxygen, for example, as follows,

$$V_{null} = V_{Al^{3-}} + 1.5V_{O^{2+}} \tag{5}$$

Each aluminium ion would associate with an average of 1.5 ion oxygen vacancies to form a dipole. Effect of this formation is shown in loss tangent properties of alumina [33, 36]. The loss tangent of alumina at microwave frequencies as is reported by Ho at frequency of 3.5 and at frequency of 35 GHz [34]. At room temperature the loss tangent of alumina is shown in Table 1. Unfortunately, data at high temperatures at this frequency have yet to be available.

Table 1 Loss tangents of alumina at different frequencies (T=25 °C)

f(GHz)	λ_0 (mm)	$\tan\delta$
2.45	122.4	1.7×10^{-4}
28	10.7	8.0×10^{-4}
35	8.57	3.0×10^{-4}
300	1.0	2.2×10^{-3}

Since both intrinsic vacancy formation and lattice jumps are thermally activated process, they then follow the Arrhenius type equations. From Eq. 2, the jump frequency Γ follows the equation [35],

$$\Gamma = v \exp\left(\frac{-\Delta G^\ddagger}{kT}\right) \quad (6)$$

Microwave frequencies are within a range of 3×10^8 to 3×10^{11} Hz and the ion jump frequency is of the order of the Debye frequency which is about 10^{13} Hz for the case of bulk crystal. Because Debye frequency is much higher despite the highest frequency from the microwaves used in sintering experiments (i.e. 300 GHz), it is not plausible if microwaves affect the jump frequency in the case of ceramics. However, in grain boundaries or on across surfaces where frequency factors are less well defined, the effects of microwaves on atom jump frequency will be more reasonable.

Other possibility by which microwave affects the diffusion is atomic vibration loss. Starting from the general equation of the resonance theory 1-D [36],

$$m \frac{d^2x}{dt^2} + c \frac{dx}{dt} + kx = F(t) \cos(\omega t) \quad (7)$$

where m is mass, c is friction/damped coefficient, k is the material constant, and $F(t)$ is an external force acting on the mass. If the equation is applied to the interactions between microwaves that have electric field E and materials, it is given:

$$\frac{d^2x}{dt^2} + \gamma \frac{dx}{dt} + \omega_0^2 x = \left(\frac{q}{m}\right) E \cos(\omega t) \quad (8)$$

Absorption occurs when the oscillation characteristic frequency of the molecules within the materials (ω_0) is approximately the same as the frequency of the microwave radiation. For bulk crystals ω_0 is about three to four orders of magnitude than different microwave frequencies ω within a range of GHz, therefore, it is also not reasonable for the ionic vibration loss mechanism to occur. However, since during the sintering alumina experiments, very high microwave frequency (i.e. 300 GHz) were used, this factor could not be ignored. The microwave absorption dependence on frequencies is shown in Fig. 2 which indicates the effects of electromagnetic frequencies on polarization mechanism.

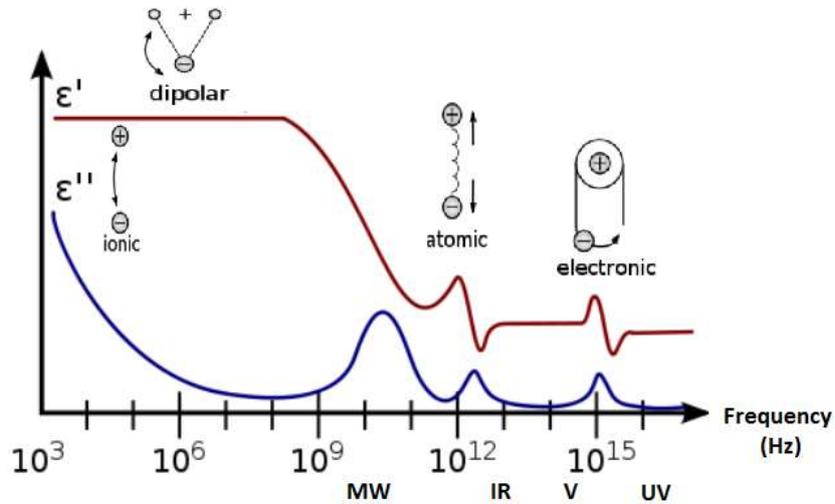


Fig. 2 Frequency dependence of the polarization mechanism in dielectric [33]

Since the electronic polarization occurs at even higher frequencies than the ionic vibration, thus be concluded that electronic polarization and ionic vibration are not important loss mechanisms for microwave heating. Other more plausible way is ion jump relaxation. An aliovalent ion-vacancy pair has a dipole moment associated with it which responds to the applied electric field. The vacancy is thought to jump around the aliovalent ion to align its dipole moment with the electric field. Interfacial polarization occurs at a structural inhomogeneity such as a grain boundary, dislocation, or vacancy cluster. In an ionic lattice there will be a localized disruption in electric neutrality at such a structural inhomogeneity with a net dipole moment which will align itself with the applied field. This is in agreement with the proposed model suggested by Meek [19] where in the grain boundary, coupling microwave and material are stronger than that in the grain itself.

4. Conclusion

The results of sintering alumina using various microwave frequencies up to 300 GHz showed microwave enhanced sintering of alumina. Moreover, there was dependence on microwave frequencies. It is thought that microwave enhanced diffusion during synthesis. The theoretical analyses indicate that several probable interactions between microwaves and ceramic materials. Some loss mechanisms are thought to be operable during microwave heating of crystalline ceramics. These loss mechanisms will influence the correlation factor for diffusion. In order for resonance type loss mechanisms to occur, unrealistically high damping forces would have to be present because of the large difference between the natural lattice vibration frequency and the microwave heating frequencies. For this reason, resonance type loss mechanisms are not thought to occur

during microwave heating. However, when sintering alumina at very high microwave frequencies (i.e. 300 GHz), the factor needs to be considered. The second way by which the diffusivity might be altered is by changing the correlation factor. Any alteration to the correlation factor would show up as a change in the pre-exponential factor of the diffusivity. The observed enhancement was minimal and may have been caused by an increase in the correlation factor as a result of a relaxation type loss mechanism. Of all theory suggested that microwaves effect is stronger in structural inhomogeneity area such as in the grain boundary.

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