THEORETICAL ANALYSIS OF MICROWAVE SINTERING OF CERAMICS

Muhammad Zamrun Firihi

Jurusan Fisika, Fakultas Matematika dan Ilmu Pengetahuan Alam, Universitas Halu Oleo, Kendari, Sulawesi Tenggara, 93231
email: muhammad.zamrun@uho.ac.id

ABSTRAK


Keywords: nonthermal effect, diffusi, microwave, polycristalline

I INTRODUCTION

Microwave processing of ceramics have been studied by some scholars in the last decade [1-7]. Some evidences indicated as ‘microwave effects’ were found.. The first remarkable results of microwave sintering ceramic have been reported by researchers Janney, et al., at Oak Ridge National Laboratory [2]. Indeed, their observations go beyond these bulk effects, suggesting that different microscopic mechanisms for the motion of ions are responsible for the differences between microwave and conventional sintering. For example, experiments with beta-alumina suggest an apparent reduction in activation energy of 70% during microwave sintering, when compared with conventional sintering. Specifically, the inferred activation energy for the conventional process was 575 kJ/mole, compared to an inferred activation energy of 170 kJ/mole for the microwave process. In FIR Center, University of Fukui, by using a very high frequency microwave sintering system of 300 GHz
calculated the activation energy of alumina of 196 kJ/mole. In both processes, equal bulk temperatures were maintained based on thermocouple measurements. In similar experiments with single crystal sapphire, microwave heating was observed to yield enhanced tracer diffusion kinetics for oxygen ions. Moreover, empirically inferred activation energies for ion diffusion based on a thermal process model were 20% lower for microwave versus conventional heating. No fundamental physical mechanisms have yet been established to explain these phenomena. For oxide ceramics, a physical explanation must concentrate on the effect of long wavelength (i.e., low-energy) radiation on the ionic diffusion that results in the densification of a powder compact. In sintering, the driving force for ionic motion is the decrease in surface energy that occurs as free surface area is replaced by solid-solid interfaces (i.e., grain boundaries) [8].

The diffusion fluxes involved can be analyzed from a Fick-Einstein perspective [9]

\[ j_i = - (C_i D_i / k_B T) \nabla \eta_i \quad (1) \]

Where \( j \) is flux, \( C \) is concentration, \( D \) is the chemical diffusion coefficient, \( \eta \) is electrochemical potential (all of the \( i \)-th species), \( k_B \) is Boltzmann's constant, and \( T \) is the temperature of the solid. As with all phenomenological descriptions of kinetic processes, Eq. (1) represents the product of a driving force and a species mobility: the driving force is the gradient in electrochemical potential; the mobility is contained in the chemical diffusion coefficient. Ionic mobility involves the motion of point defects, and the chemical diffusion coefficient can be described as a function of point defect concentration and point defect mobility. In a thermal process, the dependence is separable; that is, one can write:

\[ D \approx e^{-Q/k_B T} \approx [\text{defect concentration}] \cdot [\text{defect mobility}] \quad (2) \]

for diffusion driven by a Boltzmann distribution of ionic energies. A corollary to Eq. (2) is that, for thermal diffusion, the activation energy \( Q \) can be expressed as the sum of that for formation of point defects (\( Q_{PD} \)) and that for the mobility of defects (\( Q_M \)) [10-11]

\[ Q = Q_{PD} + Q_M \quad (3) \]

The plotting logarithms of microwave...
sintering rates against bulk inverse temperatures as measured by a thermocouple yields lower slopes than for conventional sintering has been interpreted as a decrease in activation energy. The microwave radiation generates a nonthermal phonon distribution in the (poly) crystalline lattice and thereby enhances the mobility of crystal lattice ions. This leads to enhanced diffusion and to enhanced sintering rates. It is also believed that similar nonthermal effects are responsible for unusual observations reported in other microwave heating processes. In this paper, we analyze theoretically the results of a series of microwave sintering experiments of ceramics.

II RESULTS AND DISCUSSION

In this part, we will discuss models of effect microwave on solid state oxide materials by using previous experimental data [3-4, 6-7,12]. Generally, we are looking for the most appropriate coupling formula between microwave and materials.

A. Linear coupling to elastic oscillations

The model uses a simplified kinetic model for oscillations in a perfect one-dimensional crystal lattice where be valid at temperature exceeds the Debye temperature for the solid compound. The Debye temperatures for most of the material compounds of interest will typically be less than or equal to 300 K.

In addition, each ion is coupled to a bound electron by an ideal spring. Each electron collectively represents an atomic electron cloud which can be displaced from the nucleus by an external electric field. To model the effect of the microwaves, we subject the charges (ion and electron masses) to a sinusoidal external electric field. The simplified model assumes that all of the ions in the lattice chain are identical. Allowing for the multiple ion species normally present in a compound will quantitatively refine, but not qualitatively alter, the essence of our arguments. Mathematically the system can be described as following equations [9-10],

\[ k_i = \frac{m_i}{2} \omega_i^2 \]  \hspace{1cm} (4)

\[ \kappa_e = \frac{m_em_i}{m_e+m_i} \omega_e^2 \approx m_e \omega_e^2 \]  \hspace{1cm} (5)

where \( k_i (\kappa_e) \) is the spring constant for one ion-ion (ion-electron) bond, and \( m_i \) (\( m_e \)) is the mass of a single ion (electron), \( \omega_i \) is the resonant oscillation frequency for the single spring connecting two ions, while \( \omega_e \) is
the resonant frequency for a single
ion-electron pair. Strictly speaking, the
linear force model is valid only for
small displacements $\delta_x$ of the ions (and
valence electron clouds) relative to their
equilibrium positions; i.e., $\delta_x/\rho_0 \ll 1$
where $\rho_0$ is the
equilibrium ion spacing. Accurately
modeling the phonon
distribution, including the irreversible
thermalization of microwave phonons,
would require the consideration of
nonlinear effects. In this model coupled
linear harmonic oscillators under the
influence of an external oscillatory
forcing function i.e. the microwave
electric field. Since damping effects are
neglected, the system dynamics may be
analyzed and understood in terms of the
two normal modes of oscillations of the
lattice driven by the microwave field as
follows [10,12]:

Small-resonant coupling. In this approach
the assumption is microwave radiation to
resonantly drive small-scale elastic
oscillations, involving only a few ions on
a localized scale (such sites could serve as
localized sources for excitation of
propagating phonons). this is unlikely to
occur within a perfect crystal lattice, as
ion-ion bonds are characterized by
resonant frequencies in the range of
infrared photons, while the electron-ion
bound are characterized by resonant
frequency approaching the optical regime.
for example, the resonant restrahl
frequency $\omega_l$ of a single spring and two
ion masses is typically of the order $\omega_l \sim 10^{12} - 10^{14} s^{-1}$ [11]. this is too
large for direct coupling from microwave
photos characterized by frequency $\omega_{em} \sim 10^{12} - 10^{14} s^{-1}$. thus, in perfect
single crystal compounds, should be only
slight coupling between microwave
energy and locally resonant perturbations
of the ions. In case of polycrystalline
compounds as have been used in our
experimental research materials [3,4,6,7],
however, the possibility for weaker
surface bond modes exists at the various
microscopic surface and grain boundary
interfaces. This is especially true for green
bodies prior to sintering. Hence we can
imagine the possibility of small scale or
localize microwave phonon excitation
through resonant coupling to weak surface
bounds. similarly, in both polycrystalline
and single-crystal compounds, the
presence of point defects (vacancies) can
lead to localized resonances at
frequency much lower than the typically
restrahl frequency $\omega_l$. So that microwave
effects can be observed.
Zero-frequency coupling. In this normal mode is a zero-frequency mode in which the center of mass of an aggregate of ions is displaced by the microwave field [15]. An individual ion’s displacement \( x_i \) is the sum of a center-of-mass displacement \( \mathfrak{R} \) plus a displacement \( r_i \) relative to the center of mass:

\[
x_i = \mathfrak{R} + r_i
\]

the center-of-mass motion for \( N_i \) ions and \( N_e \) electrons is determined by the equation

\[
(N_i m_i + N_e m_e) \ddot{\mathfrak{R}} = (N_i - N_e)Q \mathcal{E}
\]

where \( \mathcal{E} \) is the electric field strength and \( Q \) is the net charge on the ion (or electron cloud). Eq. (7) implies that there will be on coupling to this zero-frequency mode unless there exists some (local) charge imbalance in the chain of coupled atoms—i.e., \( N_e \neq N_i \). Associating an effective charge of \( (N_i - N_e)Q \approx N_{\text{eff}} |e| \) with a chain of identical (i.e., regular) atoms (where \( |e| = 1.6 \times 10^{-19} C \) ) leads to local displacement of every ion the chain according to:

\[
\mathfrak{R} \sim \frac{N_{\text{eff}} e \mathcal{E}}{N_i m_i a^2} = \frac{f e \mathcal{E}}{m_i a^2}
\]

where \( f \) represent the fractional charge imbalance, \( f = N_{\text{eff}} / N_i \)

Local charge will imbalance mostly in free surfaces, grain boundaries, and dislocations. It creates localized excess charges in the lattice; thus, in polycrystalline compounds, the possibility exists for stimulating microwave-frequency phonons near extended lattice defects. A relative small microwave deviations of ion kinetics from random thermal motions are sufficient to make substantial changes to ion jump probabilities and ion mobility [14]. A value of \( \mathfrak{R} / \rho \mathcal{E} \geq 0.001 - 0.01 \) should be considered a significant nonthermal effect, where \( \rho \mathcal{E} \) is the equilibrium lattice ion spacing, \( \rho \mathcal{E} \sim 1 \, \text{Å} \).

By using experimental data of sintering of oxide ceramics performed by Sudiana et al, Aripin, et al, Bykov, et al. and Janney, et al., [2-7], i.e. sintering temperatures: 1000 – 1700 °C, average grain size: 50-500 nm, the average ion’s thermal motion involves fluctuations \( \delta_x \) of order \( \delta_x \sim 0.1 \, \text{Å} \) [3]. For microwave-induced perturbations satisfying \( |\mathfrak{R}|/\delta_x \sim 1 - 10\% \), which is significant deviation from thermal equilibrium. To get order-of-magnitude estimates for the local charge imbalance concentrations needed to couple to a zero-frequency mode, we also consider the sintering parameter of the experiments [3,13-14]. For example,
based on a measured microwave cavity Q of \( \sim 300,000 \), input power of \( \sim 1.2 \) kW, volume of \( \sim 0.17 \) \( m^3 \), sample dielectric constant \( \varepsilon_r \sim 9.7 \) (alumina), and frequency of \( \sim 300 \) GHz, it can be estimated that the electric field strength was of the order of \( 10^6 - 10^{12} \) V/m during these sintering experiments. From (8) for a typical lattice ion spacing of \( \rho \sim 1 \) \( \AA \), significant nonthermal phonon effects from microwave heating requires local effective bound-charge concentrations of \( f \geq 0.001 \). This is consistent with the level of impurities expected in even the highest commercial grades of ceramic powders and compact (e.g., 99.8% for alumina and 97.5% for silica). Again, it is expected that this effect is more likely to exist locally near grain boundaries and microscopic surfaces (where impurities concentrate) within polycrystalline samples than within high purity single crystal samples.

Microwave frequencies one can find bulk phonon modes which satisfy frequency matching. However, the electromagnetic phase velocities greater several orders than elastic wave phase velocity. Thus direct linear coupling between microwave and elastic wave is unreasonable. Hence, nonlinear coupling should be considered. Nonlinear process such as microwave absorption through inverse Brillouin scattering may occurred [14-15].

Whether the three approximations discussed above is relevant to the our experimental parameters. First, it is expected that scattering within the overmoded cavity as well as within the ceramic sample will yield an electromagnetic k-spectrum that is essentially isotropic. Second, it has already been established that due to the large cavity Q with high microwave frequency of 300 GHz., the electric field strengths within the cavity are very high. Third, most high power microwave sources can be expected to produce a finite spectral bandwidth of order \( 10^{-6} \leq \Delta \omega/\omega \leq 10^{-2} \). Hence, it appears feasible that resonant (and thus nonthermal) transfer of microwave energy to crystal lattice phonons can occur between two high intensity electromagnetic waves to a low frequency elastic wave under the conditions present during the our experiments. Recent other theory of nonthermal effect of microwave radiation proposed by Rybakov and Semenov [15-16].
III CONCLUSION
The enhancements in material processing and reductions in apparent activation energy for microwave versus conventional sintering are due to nonthermal phonon distributions excited by the microwave field. These mechanisms favor polycrystalline over single crystal where consistent with reported experimental results. The higher temperature condition would enhance the probabilities these mechanisms. The experimental data were used to confirm the theory.

REFERENCES