Effect of electric field (2.45 GHz) on sintering behavior of fully stabilized zirconia

Raghunath R. Thridandapani¹, Diane C. Folz, David E. Clark

Department of Materials Science and Engineering
213 Holden Hall, Virginia Tech, Blacksburg, VA 24060, USA

Abstract

Numerous reports presented in the literature have shown that microwave sintering results in reduction of processing temperature/time required for densification in some materials when compared to conventional sintering. While faster sintering regimes may look promising, it is important to understand why microwaves appear to enhance the sintering phenomena. It is speculated that the electric field associated with microwave energy is enhancing flux, leading to accelerated densification. Enhancement in flux is a result of an increase in driving force, in the transport coefficient, or both. This study examines the sintering behavior of 8 mol % yttria-zirconia at various values of electric field intensity (frequency being constant, 2.45 GHz) to understand whether the driving force or transport coefficient terms in the flux equation lead to enhanced densification. The transport coefficient term shows an increasing trend with an increase in electrical field intensity. These results indicate that the underlying reason for the increase in the transport coefficient term is due to a shift in diffusion path, from volume to grain boundary diffusion.

Keywords: Electric field, Microwave sintering, Activation energy, 8 mol % Yttria-stabilized zirconia

1 Introduction

Numerous reports (as well as the work presented here) have shown an acceleration in densification and grain growth during microwave sintering [1, 2]. Microwave heating is a conversion of electromagnetic energy to heat, mainly due to the formation and displacement of dipoles [3, 4].

¹r4thrida@gmail.com

Presently there is not a clear understanding as to why microwave processing enhances the rate of sintering.

Typically, densification (during sintering) is quantified using Eqn. (1), derived from a two-sphere sintering model [5, 6].

$$\frac{\Delta\rho}{\rho} \approx \left(\frac{\Delta L}{L_o}\right)^3 = - \underbrace{\left(\overbrace{D_o \exp\left(-\frac{Q}{RT}\right)}^{\text{Transport Coefficient}} \underbrace{\frac{\gamma_{sv}}{n} \frac{dA}{dx}}^{\text{Driving Force}} \frac{c}{RT} \right)}_{\text{Flux}} \underbrace{\left(\frac{2\pi V_m x^2}{a^3} \right)}^{\text{Material Constants}} t^{\frac{3}{2}} \quad (1)$$

where, $\frac{\Delta\rho}{\rho}$ and $\frac{\Delta L}{L_o}$ represent the relative change in density and linear shrinkage, respectively. The D_o term represents the coefficient of diffusion, Q is the activation energy, R is the universal gas constant, T is the temperature, $\frac{\gamma_{sv}}{n}$ is the surface free energy per mole, a is the radius of the particle, c represents the concentration of the diffusion species, V_m is the molar volume, dA is the change in the surface area, and dx is the change in radius of the neck region.

As seen in Eqn. (1), the rate of sintering is dictated by flux, which is defined as a product of the *transport coefficient* and the *driving force* [8]. The negative sign indicates a spontaneous flux of material in the direction of decreasing driving force. Enhanced flux could result from an increase in the transport coefficient, the driving force, or both. Several studies investigated enhanced flux by focusing on one of these terms, assuming that the other term was unaffected by the microwave field [1, 7, 9, 10].

Freeman et al [10] observed enhanced ionic currents in single-crystal sodium chloride with an increase in the intensity of the applied microwave field. These ionic currents were attributed to the presence of an additional driving force induced by ponderomotive electric field forces along structural non-uniformities. A basis for understanding ponderomotive phenomena was established by Rybakov and Semenov [11, 12], and Booske et al [13]. Based on a series of sintering studies in a hybrid furnace (that include microwave heating and conventional heating sources), Wroe and Rowley [9] attributed enhanced microwave sintering to an additional driving force induced by the electric field component of the microwaves. Many reports have found that microwave sintering has resulted in a reduction of the measured activation energies that led to an increase in the transport coefficient [1, 7], thereby enhancing flux. Presently, it remains unclear whether an alteration of the transport coefficient, the presence of an additional driving force, or some other reason is responsible

for the observed enhancement in sintering.

The main goals of this work were two-fold. First, to examine the sintering behavior of 8 mol % yttria-zirconia (8YZ) with respect to the electric field to which the sample is exposed during microwave processing. Second, to attempt to understand which of the terms, if any, in the flux equation (transport coefficient or the driving force) lead to enhanced densification during microwave sintering.

2 Experimental Procedure

Commercially available spray dried granules of 8YZ (Tosoh Corporation, Grove city, OH, USA) produced through a hydrolysis process, with specific surface area of $16 \pm 3 \frac{m^2}{g}$, were used for this study. Approximately 3.5g of the as-received powder was poured into a cylindrical rubber mold (2.5mm x 40mm) that was subjected to a maximum isostatic pressure of 200 MPa. The green pellets selected for this study were 46 ± 5 % of the Theoretical Density (TD). The powder characterization, compaction, and sintering behavior (both conventional and microwave-assisted heating) of these powders have been reported previously [2, 14].

The magnitude of the sintering driving force (change in surface area) and the electric field driving force were estimated theoretically (numerical calculations). The driving force for sintering a mole of 8YZ particles is estimated via $\frac{\gamma_{sv}}{n} \frac{dA}{dx}$. The electric field driving force is equivalent to the product of charge (of the diffusing ion), the Faraday constant, and the root mean square of the applied electric field [8].

The transport coefficient term consists of a pre-exponential term, D_o , and an exponential term, $\exp(-\frac{Q}{RT})$. The pre-exponential term is a product of materials constants, such as attempt frequency, ν_o , inter-atomic distance, λ , and correlation factor, g [17], none of which should be influenced by the microwave field. Thus it is assumed that the term, D_o , is unaffected by the microwave field. Therefore, activation energy measurements at various values of electric field intensities should represent the changes in transport coefficient term. The activation energy required for sintering 8YZ powders was estimated using the Master Sintering Curve (MSC) approach [18].

Su and Johnson [18] developed a MSC model for predicting the sintering behavior of ceramics for a given processing method and particle size. Since its inception, the MSC model has been used widely for studying the sintering behavior of several ceramic materials, including ThO_2 [19], $BaTiO_3$ [20], ZnO [21], and Al_2O_3 [22]. The MSC method was developed from a combined stage

sintering model that relates the instantaneous linear shrinkage to its process variables, *time* and *temperature* [18]. The rate of change in linear shrinkage is given in Eqn. (2) and is dictated by the dominant diffusion mechanism (either volume or grain boundary diffusion) [18].

$$-\frac{1}{L_o} \frac{dL}{dt} = \frac{\gamma\Omega}{kT} \left(\frac{\Gamma_v D_v}{G^3} + \frac{\Gamma_b \delta D_b}{G^4} \right) \quad (2)$$

where, L_o is the initial length of the sample, $\frac{dL}{dt}$ is the rate of change in linear dimension during sintering, γ is the surface energy of the material, Γ is the scaling factor, k is the Boltzmann constant, Ω is the atomic volume, G is the grain size, D_v and D_b are coefficients of volume and grain boundary diffusion, R is universal gas constant, T is temperature, t is time, and δ is the width of the grain boundary. Assuming either volume or grain boundary diffusion is dominant and re-arranging Eqn. (2) results in the separation of variables that affect the microstructural properties and process variables. This relationship is shown in Eqn. (3).

$$\underbrace{-\frac{1}{L_o} dL \left(\frac{\gamma\Omega}{k} \frac{\Gamma(\Delta L)}{G(\Delta L)^n} D_o \right)^{-1}}_{\text{Microstructural variables}} = \underbrace{\frac{1}{T} \exp \left(-\frac{Q}{RT} \right) dt}_{\text{Process variables}} \quad (3)$$

The value of n , in the above equation, approximately is three for volume diffusion and four for grain boundary diffusion. The scaling factor $\Gamma(\Delta L)$ and the grain size $G(\Delta L)$ are a function of linear shrinkage ΔL , while D_o is equivalent to D_v when volume diffusion is dominant and D_b when grain boundary diffusion is dominant. The equality between shrinkage (microstructural variables) and process variables is defined as a *Master Sintering Curve* [18]. A series of sintering experiments at different heating rates is required for determining a single-valued function between density and heating rate. This single-valued function is a representation of Q for the diffusion process that is dominant during sintering [18].

2.1 Microwave Hybrid Dilatometry

Generating MSC requires a dilatometer for estimating the activation energy during sintering. As microwave dilatometers are not commercially available, sintering experiments were conducted in a microwave hybrid dilatometer built in-house. Patents on microwave dilatometry date back to 1994 and were developed by Kimrey et al [23]; these instruments used a contact method for measuring

thermal dilation. Most recent work by Marinell et al [24] and Barber et al [25] used non-contact methods. The dilatometer set-up developed for this study used a push-rod assembly (see Figure 1) due to ease of availability and to avoid issues with emissivity, which is a function of temperature. The applicator used for this study was a tunable TE₁₀₃ cavity. The flexibility with tuning allowed us to compensate for any electric field perturbations caused by the insertion of the thermocouple and the push rod.

The material system used for this study was polycrystalline fully stabilized cubic-zirconia. The deviation from isotropic shrinkage is due to non-homogenous microstructure of the green body caused by asymmetric-particles. The anisotropic coefficient after sintering was observed (ratio of percent change in radial to linear shrinkage) to be 1.11 ± 0.5 on all fully sintered samples irrespective of the heating method. As the anisotropic coefficient is close to a value of one it was assumed that the linear shrinkage was a representative of isometric volume shrinkage. The relevant hardware, software, and the calibration procedure developed for this instrument were documented previously [26].

The absorption of microwave energy and conversion to heat is due to polarization and conduction would result in a rise in temperature, $\frac{\Delta T}{\Delta t}$, and this is given by the following equation:

$$\frac{\Delta T}{\Delta t} = \frac{2\pi f \varepsilon_o \varepsilon_{eff}'' E_{rms}^2}{\rho C_p} \left(\frac{^\circ C}{s} \right) \quad (4)$$

where, ε_o is the permittivity of free space ($8.85 \times 10^{-12} \frac{V}{m^3}$), ε_{eff}'' is the relative effective dielectric loss due to ionic conduction and dipolar reorientation, f is the frequency ($\frac{1}{s}$), E_{rms} is the root mean square of the electric field within the material ($\frac{V}{m}$), ρ is the bulk density of dielectric material ($\frac{kg}{m^3}$) and C_p is the heat capacity of the material at constant pressure ($\frac{J}{kg \cdot ^\circ C}$) [3]. For a given microwave frequency it can be observed from Equation 4 that microwave absorption depends on the effective dielectric constant, ε_{eff}'' , and the magnitude of the internal electric field, E_{rms} . The higher these values are the more energy (microwave) is absorbed. A power meter (435B, Hewlett-Packard) consisting of a sensing unit (8418, Hewlett-Packard) and an attenuator (20 dB), was used for measuring the microwave electric field in the vicinity of the sample, based on a method developed by Folgar [28].

Microwave-assisted sintering experiments were performed by placing susceptors (20 wt% SiC and 80 wt% Al₂O₃ cement) directly into the microwave cavity. With the aid of susceptors (20, 10, and 5

wt% of SiC in Alumina) different heating rates (20, 10, and $5 \frac{^{\circ}\text{C}}{\text{min}}$) were achieved while maintaining the desired electric field along the sample. A schematic of this design is shown in Figure 1. A detailed description of fabricating silicon carbide-alumina cement susceptors and their behavior under a microwave field is described by Leiser [27]. The direct microwave sintering experiments (no susceptors) were performed in the same applicator by varying the input power to attain the desired heating rate.

2.2 Temperature Measurements during Microwave Heating

Thermocouples are widely used for measurement and control of the sintering process inside a furnace. The electromagnetic fields associated with microwaves will interact with metallic elements of thermocouples resulting in erroneous readings. Lack of proper shielding to the thermocouple leads has resulted in simultaneous arching and melting of leads in short periods of time inside microwave furnaces [1]. The necessity of using thermocouples as a primary means of measuring temperature led researchers [29] to investigate different ways of positioning the thermocouples inside microwave cavities with minimum interaction. It was observed that placing thermocouples (in well-grounded metallic sheaths) perpendicular to the electric field resulted in reliable and accurate measurements [28, 29].

For this study, a platinum-rhodium thermocouple with a platinum sheath was used (XPA-P30R-U-062-30-M-SX-6, Omega Engineering) for measuring temperature. Figure 2 shows the $\frac{1}{16}$ inch stainless steel compression fitting used to provide grounding to the cavity wall. All of the conventional sintering experiments were performed using a single-end push rod dilatometer (P 367, Theta Industries, Inc.). For both conventional and microwave sintering experiments, the thermocouple was placed in close ($\sim 5 \text{ mm}$) proximity to the surface of the sample to ensure that the sintering regime was controlled by the sample temperature.

Figure 3 shows the microstructures along the cross section of a direct microwave sintered sample (99% TD) with a heating rate of $10 \frac{^{\circ}\text{C}}{\text{min}}$. The grain sizes measured (using stereological point count method) along these locations were equivalent to $6 \pm 1 \mu\text{m}$. The variation in grain size measurement between the surface and the interior was negligible, suggesting no difference in thermal treatment along the cross-section.

3 Results and Discussion

3.1 Microwave sintering at various electric field intensities

The microwave hybrid dilatometer developed for this study was used to monitor the densification behavior as a function of applied electric field (associated with microwave energy at 2.45 GHz). Figure 4 shows the densification behavior (of 8YZ) as a function of temperature for conventional sintering at three different heating rates (10, 15, and 20 $\frac{^{\circ}C}{min}$). Similar densification curves were generated as a function of electric field intensity, and these results are presented in Figure 5. The densification curves reported at 104 $\frac{V}{cm}$ (see Figure 5(d)) represents direct microwave sintering; all other electric fields intensities were achieved using microwave-assisted heating. It can be observed that for a given heating rate (i.e., 20 $\frac{^{\circ}C}{min}$) the temperature required to attain 90 % density was decreased with an increase in the electric field intensity (see Figure 5). These results indicate that the increase in the magnitude of the applied electric field was accelerating densification. This result is in agreement with Wroe and Rowley's [9] observation; they observed a shift in linear-shrinkage curves to lower temperatures with the increase in applied microwave power (i.e., increase in the applied electric field).

A similar observation was made by Cologna et al [30] during sintering of 3 mol % yttria at various intensities of D.C. electric fields. The field intensities used in Cologna's [30] work were similar to the ones used in this study (0 to 120 $\frac{V}{cm}$). The linear shrinkage graphs presented by Cologna et al [30] as a function of D.C. electric field show that full densification is observed at 100 $\frac{V}{cm}$ at 900°C. The present study showed full densification at 1300°C. The differences in densification between the present study and Cologna's work are due to the differences in the material systems (3 mol % vs. 8 mol % yttria-zirconia) and the nature of the electric field. Cologna et al's work and the present study indicate that the presence of electric fields (be they static or oscillating) enhances densification during sintering.

3.2 Role of electric field (2.45 GHz) on driving force

The change in density, as quantified by Eqn. (1), is controlled by three independent terms: the transport coefficient, the driving force, and the concentration of diffusing species. For a given diffusing species, the concentration, c , typically is considered to be a constant. Thus only the presence of the electric field (during microwave sintering) will need to be accounted for, in addition

to the surface area (sintering) driving force. This relationship is shown in Eqn. (5).

$$\frac{\Delta\rho}{\rho} \approx - \underbrace{\left(\overbrace{D_o \exp\left(-\frac{Q}{RT}\right)}^{\text{Transport Coefficient}} \underbrace{\left(\overbrace{\frac{\gamma_{sv}}{n} \frac{dA}{dx}}^{\text{Surface Area}} + \overbrace{z_i F \vec{E}_{rms}}^{\text{Electric Field}} \right)}^{\text{Driving Force}} \right)}_{\text{Flux}} \underbrace{\left(\frac{c}{RT} \frac{2\pi V_m x^2}{a^3} \right)}^{\text{Material Constants}} t^{\frac{3}{2}} \quad (5)$$

The electric driving force consists of the following terms: z_i is the charge on the ion, F is the Faraday constant, and $\vec{E}_{rms}$ is the root mean square of the electric field.

In 8YZ, the diffusion of anions (O^{-2}) is much faster than the diffusion of cations (Zr^{+4} or Y^{+3}); due to the presence of a large number of oxygen vacancies [6]. Between the two cations, Zr^{+4} and Y^{+3} , Swaroop et al [31] showed that the Zr^{+4} is the slowest diffusing species. As sintering is rate limited by the slowest diffusing species, Zr^{+4} would control the overall rate of sintering. Therefore, the electrical driving force and the transport coefficient measurements performed on 8YZ most likely represent either the volume or the grain boundary diffusion of Zr^{+4} ions.

The driving force, $\frac{d\mu}{dx}|_{\gamma}$, required for sintering 8YZ compacts used for this study is described below. The initial diameter of the particles was $0.1 \mu m$ (these particles were spray dried with an agglomerate size of approximately $10 \mu m$); detailed analysis of these powders has been reported previously [14]. A total of $5.96 g$ of 8YZ powder was used for making the powdered compact. The change in neck region (dx) before and after sintering was approximated to the final grain size i.e., $0.12 \mu m$ [14]. The change in surface area before and after sintering (dA per mole of particles) was $\sim 1.9 \times 10^6 cm^2$. Substituting the values of $\gamma_{sv} = 10^{-7} \frac{kJ}{cm^2}$ [6], dA and dx resulted in a driving force value of $1.5 \times 10^4 \frac{kJ}{mol \cdot cm}$.

Table 1 compares the magnitude of the driving force due to the surface area energy, and that of the electric field intensity. It can be observed from Table 1 that the driving force on Zr^{+4} due to the electric fields is comparable to that of the surface area.

During microwave sintering the direction of the electrical field within the sample would change for every half cycle. As a result, net movement of the Zr^{+4} ion from oscillating electrical fields should be close to zero, suggesting that the driving force alone is not a major contributor to enhanced sintering. The electric field force term (in Eqn. (5)) assumes that electric force fields are in-phase and that they nullify over time. However, a time averaged out-of-phase electric force fields may result in net movement of ions. Numerous reports [11, 12, 13] have shown that inhomogenous

electric fields result in non-linear ponderomotive forces. Bykov et al [15] and Rybakov et al [16] work have shown that electric fields intensify along surfaces and grain boundaries. This component provides additional flux within near surface layer of each grain providing additional driving force that would enhance mass transport as compared to conventional sintering.

3.3 Role of electric field (2.45 GHz) on transport coefficient

The transport coefficient term is exponentially dependent on the activation energy [8]. The change in activation energy with electric field intensity must represent the transport coefficient changes. The activation energies for sintering (using microwave-assisted heating) 8YZ were generated using the MSC method as a function of various electric field intensities: 25, 50, and 83 $\frac{V}{cm}$. Sintering curves presented in Figure 5 were used for estimating the activation energy. Furthermore, the value of Q was estimated by use of the best convergence of these sintering curves for each electric field condition (for details, see Eqn. (3)).

Figure 6 shows the MSC. A Q value of $\sim 500 \frac{kJ}{mol}$ was recorded for conventional sintering, while the MSC method for direct microwave sintering yielded an activation energy value of $\sim 200 \frac{kJ}{mol}$. The shift in the direct microwave sintering MSC is due to the increase in slope of the densification curves (see Figure 5), suggesting enhanced sintering under the influence of a direct microwave field. The activation energy values presented in Figure 6 have been plotted with respect to the applied electric field in Figure 7. As a baseline comparison, the volume ($515 \frac{kJ}{mol}$) and grain boundary diffusion ($200 \frac{kJ}{mol}$) of Zr^{+4} ions (in zirconia lattice) have also been added to Figure 7 [31, 32, 33].

It can be observed from Figure 7 that the activation energy value for sintering 8YZ decreased with an increase in the applied electric field. These results imply that the magnitude of the transport coefficient term increases with the increase in applied electric field.

Activation energy, by definition is the potential energy barrier that a diffusing species must overcome for flux to occur [8]. These activation energy values are constant for a given diffusion path (volume diffusion or grain boundary diffusion). The presence of a driving force will create chemical potential gradients leading to diffusion along the direction of decreasing chemical potential gradients. The data shows that conventional sintering was dominated by volume diffusion of Zr^{+4} ions, while direct microwave sintering was dominated by grain boundary diffusion. It is evident that at intermediate values of electric field intensity, the activation energy represented a combination of both volume and grain boundary diffusion. The results presented in this study show that enhanced

sintering was a result of active grain boundary diffusion during microwave sintering and that it was not due to a physical change in the activation energy barrier by the microwave field.

Cologna et al's [30] work on D.C. field sintering attributes the activation of grain boundary diffusion to preferential heating of the grain boundaries by electric fields. A model developed by Meek [34] for sintering a system of alumina particles under a microwave field showed that the heating rate of grain boundaries was approximately two times that of the grains. This difference in temperature is attributed to the relative variation in dielectric property between a grain and the grain boundary region [34].

Grain size measurements were performed for direct microwave and conventionally sintered samples to observe the grain size variation with temperature. These results are presented in Figure 8. The grain size values recorded for direct microwave sintering were between $0.64 \mu m$ (at $1100^{\circ} C$) and $8.86 \mu m$ (at $1500^{\circ} C$). For conventional sintering, an appreciable grain structure could only be seen at temperatures greater than $1300^{\circ} C$. The structural integrity of the conventionally sintered samples below $1300^{\circ} C$ was poor, as they did not survive the sectioning and grinding stage.

Figure 9 shows the SEM images of the grain structure for 97 % dense samples processed using direct microwave and conventional heating. The direct microwave sintered sample (see Figure 9b) shows that grain size is about five times higher than that of the conventionally sintered sample. The large grain size observed in Figure 9b imply that the densification (powder compaction) stage was completed at lower temperatures (between 1100 and $1200^{\circ} C$) during direct microwave sintering, as compared to conventional sintering (see Figure 4 and 5).

It may be possible that the electric field is coupling with the grain boundary regions and preferentially heating them through ionic conductivity and space charge polarization losses (in the case of the A.C. field). The low thermal conductivity ($2 \frac{W}{m.K}$) of this material limits the heat transfer from grain boundaries to lattice regions. This phenomena results in large temperature gradients between the grain and the grain boundaries that are "averaged out" by the thermocouple. The preferential rise in temperature along the grain boundary within a short time scale is acting as a "short-circuit" to the transport of ions. It should be noted that all researchers would not agree with this argument. For example, Johnson's [35] theoretical calculations (for sapphire) showed that the temperature differences between the grain and grain boundaries could be sustained only if the heating rate were greater than $100 \frac{^{\circ}C}{min}$. It could be argued that, even though the temperature of the grain boundaries might be higher than that of the grains, the volume of the grain boundary

through which transport occurs is small and enhanced densification might not be expected. However, the volume occupied by a 10 nm grain boundary, as approximated to the final grain size of the material system under investigation (i.e., 0.5 μm Figure 8), is about 50 % that of the bulk. As a consequence half of the material is preferentially heated, enhancing diffusion along these regions. This phenomena allows for substantial matter transport along the grain boundary region.

4 Summary

In summary, the magnitude of the electric field influenced the rate of densification. As the electric field intensity (at 2.45 GHz) increased, so did the rate of densification. The magnitude of the driving force for the electric field was comparable to that of the surface free energy. The non-linear pondermotive forces acting along the surfaces and the grain boundaries may result in additional driving force during microwave sintering. A value of $500 \pm 25 \frac{\text{kJ}}{\text{mol}}$ was observed for non-isothermal sintering of 8YZ with conventional heating. This value was close to the volume diffusion of Zr^{+4} ion ($500 \frac{\text{kJ}}{\text{mol}}$). The direct microwave sintering resulted in activation energies values of $200 \pm 27 \frac{\text{kJ}}{\text{mol}}$. This value was close to the grain boundary diffusion of Zr^{+4} ions, while microwave-assisted sintering at lower values of electric field intensities showed activation energy values between volume and grain boundary diffusion. It is believed that the electric field preferentially raised the temperature of grain boundaries resulting in the enhanced diffusion along these regions. Based on the results of this study, the activation energy measurements show that microwave sintering caused a shift in the primary diffusion mechanism (volume to grain boundary). The enhancement in diffusion is not due to a physical change in the activation energy barrier. Variation in the measured activation energy with the electric field intensity was due to the relative magnitude of the contribution from each mechanism of diffusion.

5 Acknowledgments

The authors wish to acknowledge Department of Energy for supporting this work under project no. DE-FC07-06-ID14731.

References

- [1] K. H. Brosnan, G. L. Messing, D. K. Agrawal, "Microwave Sintering of Alumina at 2.45 GHz," J. Am. Ceram. Soc., [86] 1307-1312 (2003).
- [2] R. R. Thridandapani, C. E. Folgar, A. Kulp, D. C. Folz, D. E. Clark, "Effect of Direct Microwave Sintering on Structure and Properties of 8 Mol % $Y_2O_3ZrO_2$," Inter. J. App. Ceram. Technol., 8 (2011) 1229-1236.
- [3] R. C. Metaxas, R. J. Meredith, Industrial Microwave Heating, Peter Peregrinus Ltd., London, 1983.
- [4] National Research Council, Microwave Processing of Materials, Technical Report, 1994.
- [5] R. R. Thridandapani, The Effect of Microwave Energy on Sintering, Ph.D. Dissertation, Virginia Polytechnic Institute and State University, 2011.
- [6] M. N. Rahaman, Ceramic Processing and Sintering, Marcel Dekker, New York, 2003.
- [7] M. A. Janney, C. L. Calhoun, and H. D. Kimrey, "Microwave Sintering of Solid Oxide Fuel Cell Materials: I, Zirconia-8 mol % Yttria," J. Am. Ceram. Soc., [75] 341 (1992).
- [8] W. D. Kingery, H. K. Bowen, and D. R. Uhlmann, Introduction to Ceramics, John Wiley (1976).
- [9] R. Wroe and A. T. Rowley, "Evidence for a Non-thermal Microwave Effect in the Sintering of Partially Stabilized Zirconia," J. Mater. Sci., [31] 2019-2026 (1996).
- [10] S. A. Freeman, J. H. Booske, R. F. Cooper, "Microwave Field Enhancement of Charge Transport in Sodium Chloride," Phy. Rev. Lett., [74] 2042 (1995).
- [11] K. I. Rybakov and V. E. Semenov, "Possibility of Plastic Deformation of an Ionic Crystal due to the Nonthermal Influence of a High Frequency Electric Field," Phys. Rev. B., [49] 64-68.
- [12] K. I. Rybakov and V. E. Semenov, "Mass Transport in Ionic Crystals Induced by the Ponderomotive action of High-frequency electric field," Phys. Rev. B., [52] 3030-3033.
- [13] K. I. Rybakov, V. E. Semenov, J. Freeman, H. Booske, and R. F. Cooper, "Dynamics of Microwave-induced Currents in Ionic Crystals," Phys. Rev. B., [55] 3559-3567.

- 1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
- [14] R. R. Thridandapani, C. E. Folgar, D. C. Folz, D. E. Clark, K. Wheeler, P. Peralta, "Microwave sintering of 8 mol% Yttria-Zirconia (8YZ): An Inert Matrix Material for Nuclear Fuel Applications," J. Nucl. Mater., [384] 153 (2009).
 - [15] Y.V. Bykov, K.I. Rybakov and V.E. Semenov, "High-temperature microwave processing of materials," J. Phys. D: Appl. Phys. [34] R55-R75 (2001).
 - [16] K. I. Rybakov, E. A. Olevsky, and E. V. Krikun, "Microwave Sintering: Fundamentals and Modeling," J. Am. Ceram. Soc., [96] 1003-2010 (2013).
 - [17] H. Meher, Diffusion in Solids: Fundamentals, Methods, Materials, Diffusion-controlled Processes, Springer (2007).
 - [18] H. Su and D. L. Johnson, "Master Sintering Curve: A Practical Approach to Sintering," J. Am. Ceram. Soc., [79] 3211 (1996).
 - [19] T. R. G. Kutty, K.B. Khan, P.V. Hegde, J. Banerjee, A.K. Sengupta, S. Majumdar, H.S. Kamath, "Development of a Master Sintering Curve for ThO₂," J. Nucl. Mater., [327] 211-219 (2004).
 - [20] M. V. Nikolic, V. P. Pavlovic, V. B. Pavlovic, N. Labus, B.D. Stojanovic, "Application of the Master Sintering Curve Theory to Non-Isothermal Sintering of BaTiO₃ Ceramics," Mater. Sci. Forum., [494] 417 (2005).
 - [21] K. G. Ewsuk, D.T. Ellerby, B. DiAntonio, "Analysis of Nanocrystalline and Microcrystalline ZnO Sintering using Master Sintering Curves," J. Am. Ceram. Soc., [89] 2003 (2006).
 - [22] O. Guillon, J. Langer, "Master Sintering Curve Applied to the Field-Assisted Sintering Technique," J. Mater. Sci., [45] 5191 (2010).
 - [23] H. D. Kimrey, M. A. Janney, and M. K. Ferber, "Microwave furnace having microwave compatible dilatometer," US patent 5,099,096
 - [24] S. Marinel, E. Savary, "In situ measurement of the shrinkage during microwave sintering," J. Mater. Proc. Tech., [209] 4784-4788 (2009).

- [25] J. Barber, A. Klimera, F. Raether, "In situ measurement of dimensional changes and temperature fields during sintering with a novel theroptical measuring device," J. Euro. Ceram. Tech., [27] 701-705 (2007).
- [26] R. R. Thridandapani, D. C. Folz, D. E. Clark, Development of a Microwave Dilatometer for Generating Master Sintering Curves, J. of Meas. Sci. and Techn. [22] 105706 (2011).
- [27] K. S. Leiser, Microwave Behavior of Silicon Carbide/High Alumina Cement Composites, Ph.D. Dissertation, University of Florida, 2001.
- [28] E. F. Carlos, Structure Evolution of Silica Aerogel under a Microwave Field, Ph.D. Dissertation, Virginia Polytechnic Institute and State University, 2010.
- [29] G. Roussy, J. Pearce, Foundations and Industrial Applications of Microwave and Radio Frequency Fields: Physical and Chemical Processes, Wiley (1995).
- [30] M. Cologna, B. Rashkova, R. Raj, "Flash Sintering of Nanograin Zirconia in 5S at 850 ° C," J. Am. Ceram. Soc., [93] 3556-3559 (2010).
- [31] S. Swaroop, M. Kilo, C. Argirusis, G. Borchardt, A. H. Chokshi, "Lattice and Grain Boundary Diffusion of Cations in 3YTZ Analyzed using SIMS," Acta Mater., [53] 4975 (2005).
- [32] D. Yang and H. Conrad, "Enhanced sintering Rate and Finer Grain Size in Yttria-Stablized Zirconia (3Y-TZP) with Combined DC Electric Field and Increased Heating Rate," Mater. Sci. and Eng. A, [528] 1221-1225 (2011).
- [33] K. Maca, M. Trunec and P. Dobsak, "Bulk Zirconia Nanoceramics Prepared by Cold Isostatic Pressing and Pressureless Sintering," Rev. Adv. Mater. Sci., [10] 84-88 (2005).
- [34] T. T. Meek, "Proposed Model for the Sintering of a Dielectric in a Microwave Field," J. of Mater. Sci. Letters [6] 638-640 (1987).
- [35] D. L. Johnson, "Microwave Heating of Grain Boundaries in Ceramics," J. Am. Ceram. Soc., [74] 849-850 (1991).

List of Tables

Table 1: Magnitude of the driving force for surface free energy and several electric fields used in this study.

Driving force, $\times 10^4 \frac{kJ}{mol.cm}$			Total driving force, $\times 10^4 \frac{kJ}{mol.cm}$
Surface energy	$\frac{\gamma_{sv}}{n} \frac{dA}{dx}$	1.5	1.5
Electric Field	$\vec{E}_{rms} = 25 \frac{V}{cm}$	0.9	2.4
	$\vec{E}_{rms} = 50 \frac{V}{cm}$	1.9	3.4
	$\vec{E}_{rms} = 83 \frac{V}{cm}$	3.2	4.7
	$\vec{E}_{rms} = 104 \frac{V}{cm}$	4.0	5.5

Figure1

Figure2

Figure 3

Figure4

Figure 5

Figure 6

Figure7

Figure8

Figure 9

List of Figures

Figure 1: Schematic of the microwave hybrid dilatometer specifically designed for this study.

Figure 2: Stainless steel compression fitting ($\frac{1}{16}^{th}$ inch) set-up used for grounding the thermocouple to the microwave cavity.

Figure 3: (a) Optical image of 8YZ processed at $10 \frac{^{\circ}C}{min}$ using microwave dilatometer, (b) Scanning electron image of grain structure at edge location 1, (c) at center location 2, and (d) at edge location 3.

Figure 4: Densification versus temperature for 8 mol % yttria-zirconia as a function of heating rate for conventional sintering.

Figure 5: Densification versus temperature for 8 mol % yttria-zirconia as a function of heating rate for microwave sintering at electric field values of (a) $25 \frac{V}{cm}$, (b) $50 \frac{V}{cm}$, (c) $83 \frac{V}{cm}$ and (d) $104 \frac{V}{cm}$.

Figure 6: Master Sintering Curve approach for measuring the activation energy for sintering (with microwave-assisted heating) 8YZ at various values of electric field intensity.

Figure 7: Plot of measured activation energy, Q_{Zr} , (diffusion of Zr^{+4} ion) as a function of applied electric field (oscillating at $2.45 GHz$). Bars on each data point represent standard deviation surrounding the mean value for four samples.

Figure 8: Change in grain size with temperature during direct microwave sintering and conventional sintering. The lines on each bar represent a 95 % confidence interval surrounding the mean value.

Figure 9: Scanning electron microscopy images of 8YZ processed at $1400^{\circ}C$: (a) conventionally sintered, and (b) direct microwave sintered samples.