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Evidence for a non-thermal microwave effect in the sintering of partially stabilized zirconia

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A hybrid furnace, which allows the simultaneous application of microwave and radiant energy, has been used to investigate the sintering of partially stabilized zirconia (doped with 3 mol % yttria). Microwave-enhanced sintering is clearly demonstrated with densification occurring at a lower temperature when a high-frequency electric field is applied. By considering the variation of electric field strength with furnace temperature, this enhancement is shown to be non-thermal in nature, being dependent on the electric field strength and not the power density (heating) of the microwaves. This dependence on electric field is consistent with an additional driving force term in the equation which describes the diffusion of vacancies through the material during sintering.

1. Background

1.1. Microwave enhanced sintering of ceramics

The thermal sintering of a ceramic is a complex process, with a number of diffusion mechanisms taking place which together produce the required increase in density, and changes in mechanical (and other) properties of the material. Through this diffusion, ions move into vacancies within the crystal lattice, resulting in a net transport of empty space from the bulk of the sample to the surface, causing an eventual reduction in volume. Although it is the ions which move within the material, it is convenient to regard the process as a diffusion of vacancies out of the sample. These vacancies can diffuse through the bulk of the crystal grains, along grain boundaries, and over particle surfaces within the material (volume diffusion, grain-boundary diffusion and surface diffusion, respectively). In conventional sintering, the dominant force driving the diffusion is due to the capillary stresses which exist within the material associated with the reduction of surface energy. The diffusion of ions or vacancies along a gradient in species concentration is described by Fick's law [1]

$$J = -D\mathrm{grad}(n) \qquad (1)$$

where J is the particle flux, n is the species concentration and D is the diffusion coefficient, given by

$$D = \nu_0 a^2 e^{-\frac{\Delta g_m}{kT}} \qquad (2)$$

here, ν_0 is the characteristic lattice vibration frequency, a is the lattice constant, k is Boltzmann's constant, T is the absolute temperature, and Δg_m is the Gibbs free energy for motion through the lattice (the activation energy). In a given material, the activation energy, and hence the diffusion coefficient, will be different for each diffusion mechanism – surface and grain-boundary diffusion normally have significantly lower activation energies than volume diffusion. The vacancy flux, represented by Fick's law, can be thought to be the product of a mobility term, D, and a driving force term, $-\mathrm{grad}(n)$. If either term is increased, then the diffusion will be enhanced. Other force terms are possible, such as that due to an electric or an electrochemical potential gradient.

There is now a growing amount of experimental evidence to support the fact that microwave heating of ionic crystalline solids leads to an enhancement of the sintering processes taking place in these materials (see [2] for a review of microwave processing). Samples processed within a microwave furnace are observed to sinter at a faster rate or a lower temperature than those processed in a conventional system. Wilson and Kunz [3] demonstrated that partially stabilized zirconia (with 3 mol % yttria) could be rapidly sintered using 2.45 GHz microwaves with no significant difference in the final grain size. The sintering time was reduced from 7200 s to about 600 s – shorter times resulted in cracking of the samples. Kim and Kim [4] successfully sintered yttria-doped zirconia samples (3, 6.6 and 8 mol %) in a microwave furnace at very high heating rates (up to 5000 °C min^{-1}) with near maximum theoretical final densities (> 99%). (These high densities were only achieved if care was taken to remove any residual chlorine before sintering.) Many authors have incorporated this enhancement into the conventional theories of sintering through the introduction of an effective activation energy for the diffusion processes taking place during sintering (increasing the vacancy mobility through the lattice). Most notably, Janney and Kimrey [5, 6] have shown that, at 28 GHz, the microwave-enhanced densification of high-purity alumina proceeds as if the activation energy reduced from 575 kJ mol^{-1} to 160 kJ mol^{-1}. Similarly, the same authors [6] have shown that when

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stabilized zirconia (with 8 mol % yttria) is processed in a 2.45 GHz microwave furnace, the sintering curve is shifted by ~ 150 °C with respect to the conventional sintering curve – equivalent to an apparent reduction in the activation energy for this sintering process. Furthermore, the grain size of the final dense zirconia was finer in the microwave-fired sample. Despite the potential implication for the ceramics industry, there has been little work published which discusses the possible physical mechanisms for such a large reduction in activation energy.

The most obvious explanation for this enhancement would be simply the inaccurate measurement of temperature [7] in the microwave sintering experiment (T would need to be underestimated by about 100–200 °C to account for observed results). In conventional sintering, heat is applied through the surface of the sample and thermal conduction is relied on to transport this energy throughout the bulk of the sample. In microwave sintering, heat is generated volumetrically throughout the sample and heat losses at the surface could result in the bulk temperature being substantially higher than that measured at the surface. In this case, using the lower surface temperature in the analysis would lead to an apparent reduction in the activation energy. However, careful analysis of microwave sintered samples shows a fairly uniform grain size throughout the sample, indicating uniform processing temperature [8]. The microwave enhancement of sintering seems to be a genuine non-thermal effect, i.e. even if conventional heat could be applied in the same volumetric way as microwave heating, the same enhancement of the sintering process would not be observed.

Increasing the temperature of the grain boundaries relative to the grains would increase the diffusion coefficient in the boundary regions and, consequently, lead to an apparent reduction in the overall activation energy for the sintering process. However, Johnson [9] demonstrated that, although the microwave energy might be initially absorbed in these areas, the material dimensions involved are too small to sustain a significant temperature gradient unless the rate of heating is extremely rapid ($> 6000\,^{\circ}\mathrm{C\,min^{-1}}$) – much faster than that used in sintering.

Given that the sintering temperature is measured accurately, the microwaves must interact with the ceramic so as to reduce the actual activation energy or to increase the effective driving force experienced by the diffusing species. Bookse *et al.* [10] suggested that the microwaves interact with the crystal lattice in such a way as to render the Boltzmann approximation used in the derivation of the diffusion coefficient (2) invalid. However, in later calculations by the same group, Freeman *et al.* [11] indicated that extremely high microwave electric field strengths would be required for this to occur ($\sim 10^7\,\mathrm{V\,m^{-1}}$) – much higher than typical field strengths in a microwave applicator ($\sim 10^3$–$10^4\,\mathrm{V\,m^{-1}}$). In the same paper, Freeman *et al.* published results of conductivity measurements made on a single crystal of NaCl which indicated that the vacancy mobility is not enhanced by the application of microwaves, but that the diffusion driving force is enhanced. This result is consistent with the calculations of Rybakov and Semenov [12] who show that the driving forces for vacancy motion can be enhanced near a surface or boundary.

When an electric driving force, due to a gradient in the electric potential, is present in addition to those due to capillary stresses, the total particle flux becomes

$$J = -D\,\mathbf{grad}(n) - D\frac{nq}{kT}\,\mathbf{grad}(V) \qquad (3)$$

where q is the electronic charge on the ion or vacancy and V is the local electric potential. The particle flux is enhanced by the presence of an electric field, $E = -\mathbf{grad}(V)$. Because the applied field is oscillatory, in the first approximation the particle flux in the electric field will cancel out. However, if the diffusion coefficients for positive and negative diffusing species are different, a non-zero field can result from space charge formation near to crystal surfaces and grain boundaries. The magnitude of this space charge field will depend on the applied electric field strength.

1.2. Microwave heating of ceramics

When a dielectric material with complex relative permittivity ε_r'–$\varepsilon_r''j$ is placed in a high-frequency electric field, the power per unit volume, P_v, dissipated within it is given by (e.g. [13])

$$P_v = \omega\varepsilon_0\varepsilon_r''E^2 \qquad (4)$$

where ω is the angular frequency of the applied field, ε_0 is the permittivity of free space ($8.854\times10^{-12}\,\mathrm{F\,m^{-1}}$), and E is the local electric field strength. The electric field within the material depends on both the applied electric field (due to the microwave applicator) and the real part of the permittivity, ε_r', also known as the dielectric constant. The imaginary part of the permittivity, ε_r'', is often referred to as the dielectric loss factor of the material.

There are a number of mechanisms which can lead to a dielectric material absorbing energy from a microwave field, and the value of ε_r'' used in Equation 4 actually represents the sum of the losses due to all loss mechanisms, i.e.

$$\varepsilon_r'' = \sum_i \varepsilon_r''(i) \qquad (5)$$

Dielectric loss mechanisms which contribute to the total value of ε_r'' (and to ε_r') can be characterized by a dipole moment (or bulk polarization) and a relaxation time. These are resonant loss mechanisms and will only be significant if the natural relaxation times are of the same order of magnitude as the reversal time of the applied electric field. Katz *et al.* [14] gives a review of the dielectric loss mechanisms in crystalline insulators.

At microwave processing frequencies, ionic conductivity is an important loss mechanism in ceramic materials, and can be incorporated into the analysis through the introduction of an equivalent loss factor, $\varepsilon_r''(\mathrm{cond}) = \sigma'/\omega\varepsilon_0$ (σ' is the real part of the complex

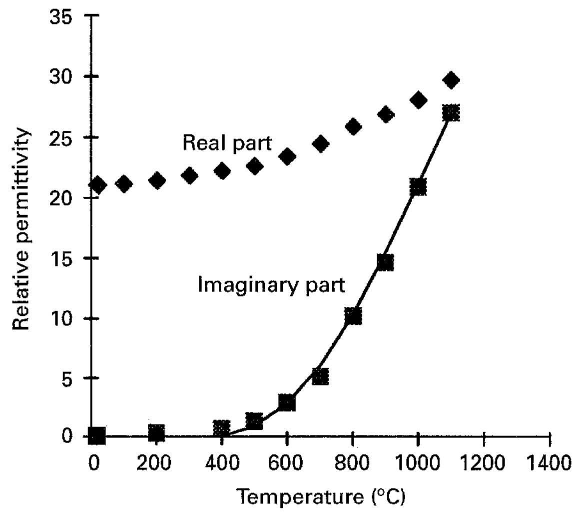

Figure 1 Temperature variation of real and imaginary parts of complex relative permittivity for partially stabilized zirconia sample (3 mol% yttria). Measurements made at 2.45 GHz.

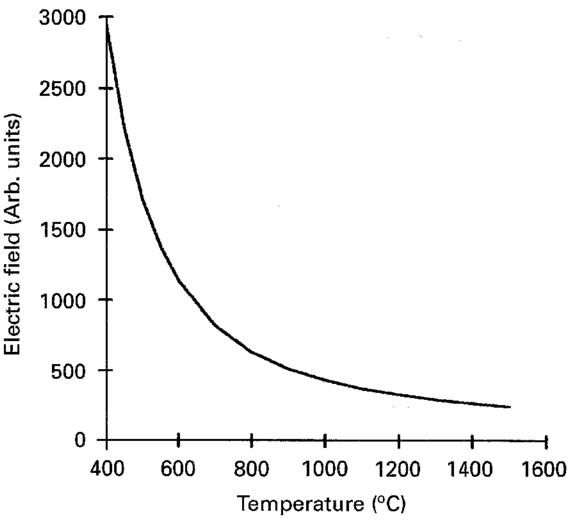

Figure 2 Temperature variation of electric field strength in partially stabilized zirconia sample (3 mol% yttria) during microwave-assisted sintering processes. $E \propto Te^{1/2(\Delta g_m/2kT)}$.

a.c. conductivity). When ions diffuse through a ceramic, they will carry electrical charge and, consequently, electric current will flow. The material will thus possess a non-zero electrical conductivity which will depend on the diffusion coefficient for the ion motion through the material. The Einstein relation ($\mu = qD/kT$) defines the mobility, μ, of a charge carrying species in terms of the diffusion coefficient, D. Using this relation, and substituting for the diffusion coefficient, allows the electrical conductivity, σ, to be written as

$$\sigma = nq\mu = \frac{nq^2 \nu_0 a^2}{kT} e^{\frac{-\Delta g_m}{kT}} \tag{6}$$

and hence

$$\varepsilon_r''(\text{cond}) = \frac{\sigma}{\omega\varepsilon_0} = \frac{nq^2 \nu_0 a^2}{\omega\varepsilon_0 kT} e^{\frac{-\Delta g_m}{kT}} \tag{7}$$

Fig. 1 shows the temperature dependence of the real and the imaginary parts of permittivity of zirconia measured at 2.45 GHz. If resonant absorption mechanisms were making a significant contribution to the total loss factor, the dielectric constant, ε_r', at 2.45 GHz would be significantly less than its value at zero frequency. However, the measured values of ε_r' at 2.45 GHz are approximately the same as the accepted zero frequency value (~ 22.00 [15]), indicating that the microwave frequency is not high enough for resonant absorption mechanisms to become significant. Consequently, ionic conductivity is the dominant loss mechanism in this material, and Equation 6 can be used for $\varepsilon_r''(T)$. The solid line through the imaginary part of the permittivity data corresponds to the best fit of a function of the form $\varepsilon_r''(T) = (A/T)\, e^{-\Delta g_m/kT}$ For these data, $A = 3.87 \times 10^6$ K and the activation energy, $\Delta g_m = 8.8 \times 10^{-20}$ J (0.55 eV).

If the microwave power density is assumed to be constant throughout the sintering process, then, from Equation 4, the electric field will be varying approximately as $[\varepsilon_r''(T)]^{-0.5}$. Consequently, the temperature variation of the electric field will be $E \propto T^{1/2} e^{\Delta g_m/2kT}$, shown in Fig. 2.

1.3. Microwave-assisted sintering

In previous measurements of microwave-enhanced sintering, two different furnaces have had to be used, one for the conventional radiant heating experiments and the other for the microwave experiments. The operation of the microwave furnaces has been further complicated by the need for a microwave susceptor (usually zirconia) to provide the initial heating of the sample. The development of a combination (hybrid) furnace removes the need for such a susceptor, and allows the relative amounts of microwave and conventional heating to be varied during processing. Consequently, for the first time, non-thermal effects can be separated from thermal effects by varying the electric field while keeping the heating rate constant during sintering.

The variations of power density and electric field with temperature will be very different (due to the strong dependence of ε_r'' on temperature), and the electric field will be falling away rapidly towards the end of the sintering process (Fig. 2) whereas the power density will remain approximately constant (or even may be increasing). Consequently, if there is a non-thermal effect present (dependent on E), any enhancement of the sintering would be expected to be reduced towards higher temperatures. In contrast, an enhancement resulting from a thermal effect should be approximately constant throughout the whole process.

The mechanisms occurring in the initial (pre-densification) stage of sintering are different from those occurring during the densification stage, with surface diffusion thought to be dominating at the lower temperatures. During densification, volume and grain-boundary diffusion are the preferred mechanisms. The ability to switch the microwaves on and off during the sintering process should provide information on which stage of sintering is most affected by the microwaves. Furthermore, pulsing the microwave power during sintering should allow thermal, P_v, and non-thermal, E, effects to be separated, since $P_v \propto E^2$. For

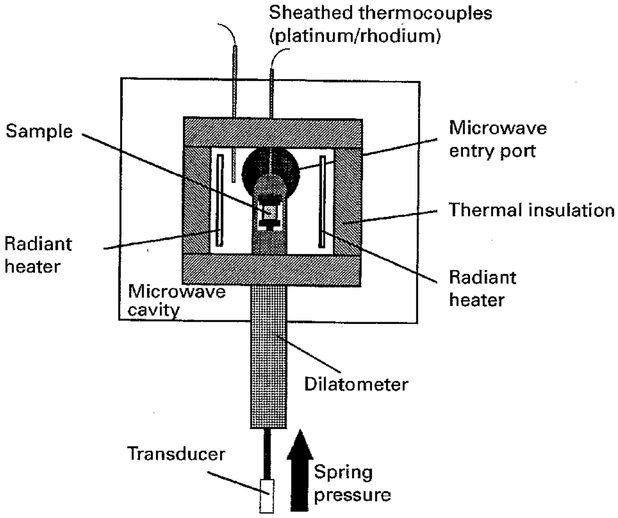

Figure 3 The microwave-assisted furnace used in sintering experiments.

example, pulsing the microwave power with a 50% duty cycle halves the average microwave power, but reduces the average electric field by $1/\sqrt{2}$ i.e. to ~ 70% of its original value. Consequently, if the microwave-effect was proportional to the electric field strength, pulsing with a 50% duty cycle should be equivalent to constant processing at 70% of maximum microwave power.

2. Experimental procedure

2.1. Furnace design

The furnace used for these sintering experiments was specially designed to allow microwave and conventional heating sources to operate simultaneously [16]. The system, shown schematically in Fig. 3, is essentially a conventional furnace built within a multi-mode 2.45 GHz microwave cavity powered by a 1.2 kW industrial standard magnetron. Care must be taken in the design and construction of the radiant heating elements to avoid any undesirable interaction between the two heating sources. For example, the radiant heating elements can severely affect the distribution of the high-frequency fields within the cavity. Similarly, the dilatometer used to measure sample shrinkage has been modified to avoid its operation being affected by the application of microwaves, and to minimize its effect on the microwave field distribution within the sample space.

The thermocouples used in the furnace are encased in metal sheaths, and are positioned to minimize their effect on the microwave field distribution. Two thermocouples are used: one to measure the ambient furnace temperature and one to measure the actual sample temperature. Either thermocouple can be used to control one or both heating sources (microwave and radiant).

During furnace operation, sample and ambient furnace temperatures, dilatometer output, microwave power (forward and reflected) and radiant power are continuously recorded.

2.2. Sample preparation

All samples used in this work were prepared from Tosoh TZ3Y partially yttria stabilized zirconia (YSZ) powder supplied by Tosoh Corporation. This powder has a very fine crystallite size of 0.02–0.03 μm. The samples were prepared by wet-milling the powders with 1% polyethylene binder. The powder was then dried, crushed and sieved, prior to uniaxial pressing using a 12 mm tool-steel die at a pressure of 96 MPa. The binder was then burnt out of the compacts in a muffle furnace using a slow heating cycle. The resulting compacts had a green density of approximately 50%–55% of the optimal final sintered density.

Approximately 2.5 g of powder were used producing a sample with a length of about 6 mm.

2.3. Sintering experiments

For each sintering experiment, whether conventional or microwave-assisted, two runs are required. The first run is the actual sintering experiment, and the second run is a calibration experiment (with a fully sintered sample in place) to allow compensation for the effects of thermal expansion on the readings from the dilatometer. In the microwave-assisted trials, the microwave power was also applied during the calibration run. During each experiment, the sample temperature, ambient furnace temperature, dilatometer reading, microwave power and radiant power are all continuously recorded. The sample temperature was controlled by the radiant heating elements, and the microwave power (if used) was kept approximately constant throughout the sintering process. For most experiments, the sample was heated at $10\,^\circ\mathrm{C\,min^{-1}}$ to 1500 °C, held there for 1 h and then ramped down at $20\,^\circ\mathrm{C\,min^{-1}}$ to room temperature.

Relatively small samples of partially stabilized zirconia were used (~ 700 $\mathrm{mm^3}$) to ensure that any temperature variation throughout the sample was small (< 20 °C at these heating rates). However, this means that the samples under test only make up a relatively small part of the total microwave absorption load of the whole furnace, and it is therefore difficult to measure the exact amount of microwave energy dissipated in the sample. Consequently, when the microwave power is specified in the results, it is only given as a percentage of the maximum power available, and not as an absolute power in watts.

The difference in the sample and ambient furnace temperatures during equivalent conventional and microwave-assisted experiments can be used as an indication of the actual proportion of power absorbed by the sample. In fact, the microwave power dissipated in the sample is reasonably constant over the temperature range of interest (~ 800–1400 °C).

3. Results and discussion

3.1. Microwave-assisted sintering of partially stabilized zirconia

Fig. 4 shows the normalized linear shrinkage, $\Delta l/l_0$, plotted as a function of temperature (l_0 is the original

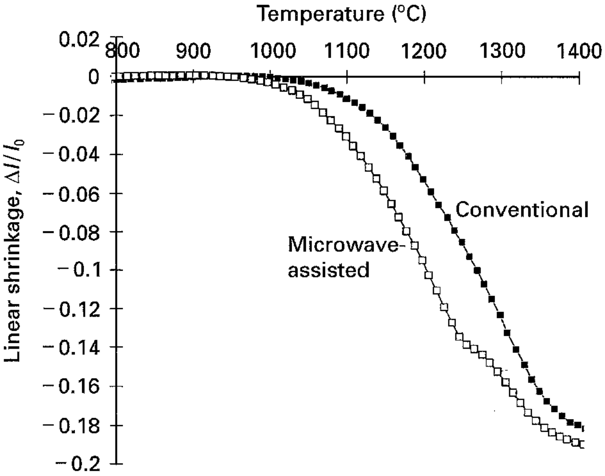

Figure 4 Normalized linear shrinkage of zirconia (3 mol % yttria) plotted as a function of temperature for conventional (radiant heat only) and microwave-assisted sintering.

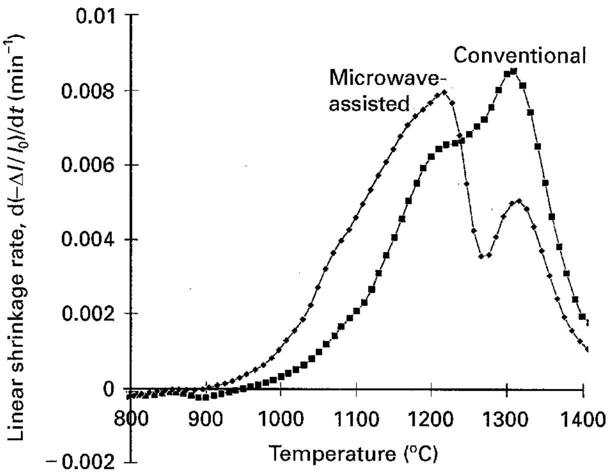

Figure 5 Normalized linear shrinkage rate of zirconia plotted as a function of temperature for conventional (radiant heat only) and microwave-assisted sintering.

sample length) for conventional and microwave-assisted sintering of partially stabilized zirconia (3 mol % yttria). The enhancement of the sintering is clearly demonstrated, the microwave-assisted curve is displaced by ~ 80 °C from the conventional shrinkage curve. Furthermore, the total shrinkage is greater in the microwave-assisted cases, leading to an increase in the final sample density. At about 1250 °C, there is a significant change in gradient in the microwave-assisted curve. Towards the end of the microwave-assisted sintering, although the applied microwave power is still approximately constant, the electric field will be falling due to the increase in the dielectric factor, ε_r''. Consequently, the additional microwave-induced electric field driving the diffusion process will be falling rapidly (see Fig. 2), and the sintering will proceed, dominated by the conventional, capillary driving force. (Although the microwave power density increases as the sample shrinks, this effect on the electric field is much smaller than that due to exponential increases in ε_r''.)

The enhancement is more clearly demonstrated in Fig. 5, which plots the rate of shrinkage $d(\Delta l/l_0)/dt$ as a function of sintering temperature for the two processing routes. In the conventional case, the peak in the sintering rate occurs at about 1300 °C, with a minor peak around 1200 °C. When microwaves are applied the peak sintering rate is shifted down in temperature to 1200 °C. However, the second peak in the sintering rate at 1300 °C is still evident (although it is much smaller) when the microwave enhancement is reduced, and the densification is mainly driven by the conventional capillary forces.

Xing-Xiang *et al.* [17] attributed the presence of two peaks in the conventional sintering of yttria-doped zirconia to a two-stage densification process. In the first stage, the shrinkage is mainly dominated by inner-sintering with agglomerates, and in the second stage, shrinkage is mainly due to sintering between the already densified agglomerates. Because the microwave electric field will be much higher at lower temperatures, most enhancement should be observed in the first stage of densification (the first peak).

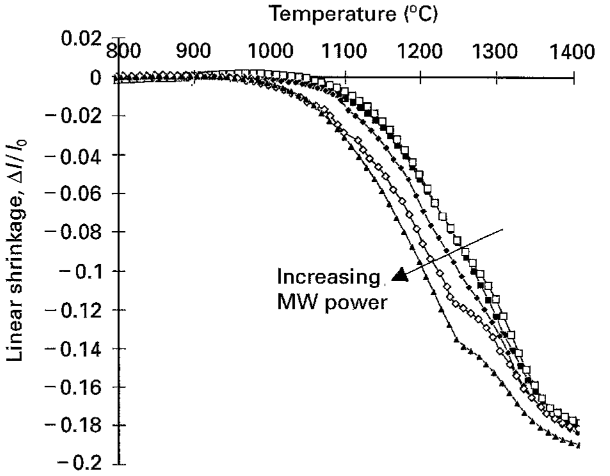

Figure 6 Normalized linear shrinkage of zirconia plotted as a function of sintering temperature for a number of microwave powers. The sintering enhancement increases with increasing microwave power.

The effect of microwaves at different power levels (and hence different electric field strengths) is shown in Figs. 6 and 7. As the proportion of microwave power is increased, the enhancement to the sintering is increased. The shrinkage rate curves (Fig. 7) indicate a gradual enhancement of the peak at 1200 °C, and the reduction of the dominant conventional peak at 1300 °C.

It is interesting to compare the effect of microwave power on the sintering process with the effect of conventional sintering at a slower heating rate. In both cases, the shrinkage occurs at lower temperatures, and there is an increase in the final sample density. It seems as though the microwave-assisted sintering is effectively proceeding in a similar way to conventional sintering, but at a much faster heating rate. This conclusion is emphasized in Fig. 8, where the shrinkage rate for microwave-assisted sintering at 10 °C min^{-1} is compared with conventional sintering at 1 °C min^{-1} (conventional sintering at 10 °C min^{-1} is also shown for reference). In the initial stages of sintering the microwave-assisted process almost exactly follows the 1 °C min^{-1} conventional curve. The shrinkage rates

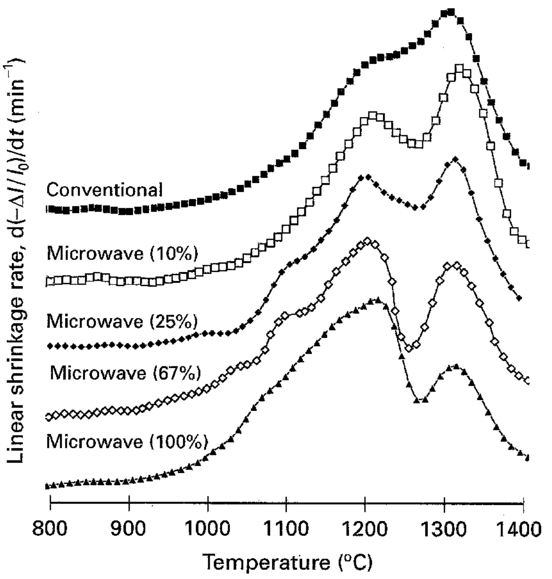

Figure 7 Normalized linear shrinkage rate of zirconia plotted as a function of sintering temperature for a number of microwave powers. (The curves are displaced along the *y*-axis.)

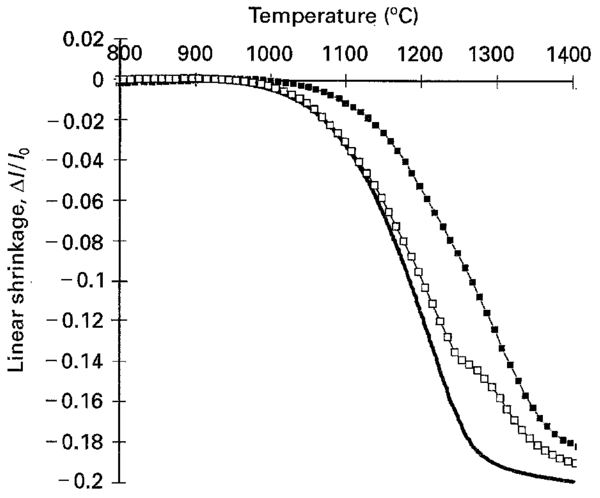

Figure 8 Normalized linear shrinkage of zirconia plotted as a function of sintering temperature for (■) 10 and (——) 1 °C min^{-1} heating rates. (□) Microwave-assisted sintering at 10 °C min^{-1} displays similar characteristics to the much slower (1 °C min^{-1}) radiant only heating.

corresponding to these curves are shown in Fig. 9. In the initial stages of densification, the microwave-assisted 10 °C min^{-1} curve fits remarkably well to the 1 °C min^{-1} conventional sintering curve. These curves imply that if the electric field could be maintained throughout the whole of the sintering process, then the microwave-assisted sintering would almost exactly follow the conventional sintering curve, but at about ten times the speed. The possibility of faster (and therefore more efficient) processing is very attractive to the ceramics industry and, in many cases, should lead to microwave-assisted sintering becoming the accepted processing route. This the main reason for the interest being shown in the technology by the ceramics industry world-wide.

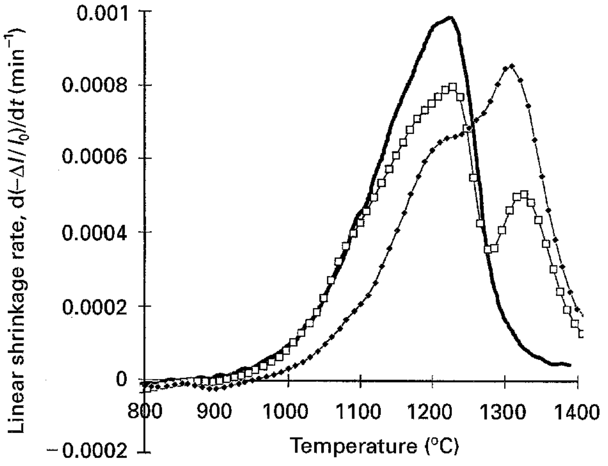

Figure 9 Normalized linear shrinkage rate (scaled with temperature) of zirconia plotted as a function of sintering temperature for (◆) 10 and (——) 1 °C min^{-1} heating rates. (□) Microwave-assisted sintering at 10 °C min^{-1} displays similar characteristics to the much slower (1 °C min^{-1}) radiant only heating.

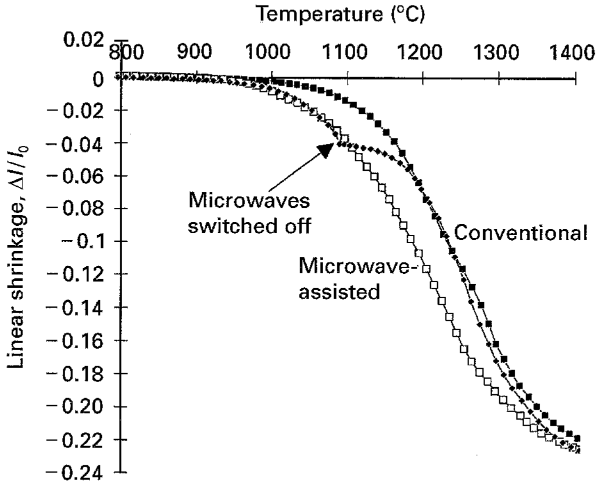

Figure 10 Normalized linear shrinkage of zirconia plotted as a function of sintering temperature for conventional and microwave-assisted sintering showing the effect of switching off the microwaves during the process (~ 1080 °C).

3.2. Effect of switching microwaves on or off during sintering

Fig. 10 shows the effect of switching the microwaves off at 1080 °C, when the microwave enhancement of densification is already established. Quite clearly, the densification slows down substantially until the sintering temperature is high enough for conventional densification to take over. However, the final sample density is still higher than the purely conventionally sintered sample. This effect is also apparent in Fig. 11, where the shrinkage rate almost falls to zero when the microwaves are turned off. A similar experiment in which the microwaves were switched off at 975 °C, approximately at the end of the initial stage of sintering, demonstrated that microwaves did not enhance this stage significantly – although the final sample density was slightly higher.

Fig. 12 shows the results of the complimentary experiment, with the microwaves switched on at about 1080 °C. At this point, densification proceeds extremely rapidly and eventually "catches up" with the

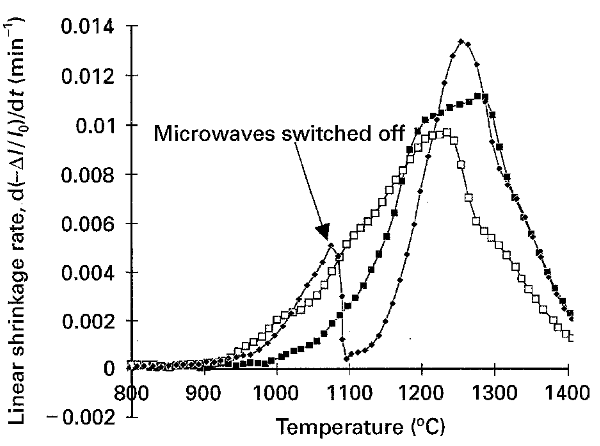

Figure 11 Normalized linear shrinkage rate of zirconia plotted as a function of sintering temperature for conventional and microwave-assisted sintering, showing the effect of switching off the microwaves during the process (~ 1080 °C).

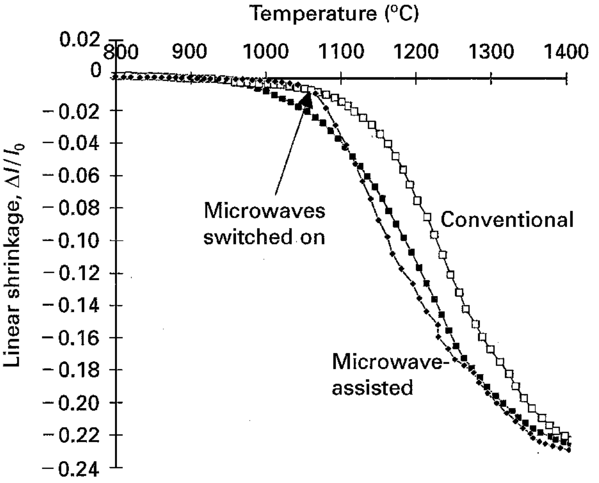

Figure 12 Normalized linear shrinkage of zirconia plotted as a function of sintering temperature for conventional and microwave-assisted sintering, showing the effect of switching on the microwaves during the process (~ 1080 °C).

continuous microwave-assisted sample. The final sample density was slightly higher in the sample in which the initial stage of sintering proceeded conventionally.

3.3. Pulsed microwave power

In the experiment described by Fig. 13, the microwaves were pulsed at maximum power with a duty cycle of 50%, and the results were compared with those for continuous microwave power at 67% of the maximum. As predicted in Section 1.3, the two shrinkage curves are similar indicating that the enhancement depends on electric field and not the microwave power density. The shrinkage rate curves shown in Fig. 14 further emphasize the similarity between the two microwave-assisted processes.

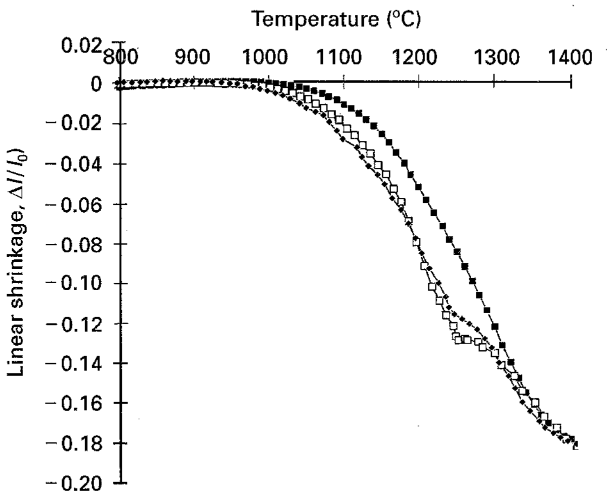

Figure 13 Normalized linear shrinkage of zirconia plotted as a function of sintering temperature for (□) pulsed microwave (50% duty cycle, maximum power), (◆) continuous microwave (67% of maximum power), and (■) for radiant heating only. Pulsed microwave produces approximately the same enhancement as continuous 67% microwave power.

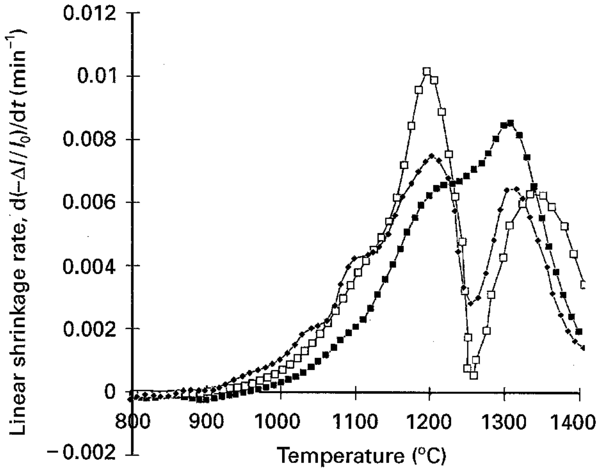

Figure 14 Normalized linear shrinkage rate (min^{-1}) of zirconia plotted as a function of sintering temperature for (□) pulsed microwave (50% duty cycle, maximum power), (◆) continuous microwave (67% of maximum power), and (■) for radiant heating only.

4. Conclusion

In all cases, the microwave-assisted sintering of partially stabilized zirconia demonstrates an enhancement relative to conventional sintering in the same furnace. Typically, the microwave-assisted processing leads to a reduction of ~ 80–100 °C in the sintering temperature for a given value of linear shrinkage. Moreover, the final density of the samples sintered in a microwave field is slightly higher.

This enhancement is non-thermal in nature; even when the microwave power is held constant throughout the whole process, there is clear evidence that the enhancement falls away towards higher temperatures. This is consistent with the enhancement being dependent on E (non-thermal) rather than P_v (thermal). More dramatically, when the electric field is switched off in the initial stages of densification, the shrinkage almost halts before resuming along the conventional curve. This supports the theory of an additional driving force induced by the microwave field. If this force is removed, the vacancy flux again is given by Fick's law, and becomes that corresponding to the conventional sintering temperature.

There is some evidence to suggest that the majority of the enhancement occurs during the densification stage of sintering, rather than the initial stage. This implies that the microwave field enhances either the volume or grain-boundary diffusion mechanisms more than the surface-diffusion process which dominates at lower temperatures. Because the induced driving field is likely to be due to the accumulation of space charge at boundaries, the microwaves will preferentially increase the flux of vacancies within grain boundaries in the sample. In most cases, the mobility of species in grain-boundary diffusion is higher than that for volume diffusion due to the lower activation energy for vacancy motion in the boundary regions. The increased driving force, coupled with the preferential enhancement of a mechanism with a lower activation energy, could account for the large reductions in effective activation energy measured previously. However, the actual activation energies for any given diffusion process are not affected by the microwave field.

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