A NOVEL APPROACH TO UNDERSTANDING MICROWAVE HEATING OF ZIRCONIA

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ABSTRACT

Savings in processing time (up to 90%) and energy (20-80%) are expected in microwave sintering of ceramics, as this technology breaks through into industrial firing processes. Linn High Therm had developed a high temperature hybrid microwave system in anticipation of industries needs. Typically, silicon carbide susceptors are used to initiate heating from room temperature, where many ceramics have low dielectric losses. The loss increases with temperature, and at some "kick in" transition temperature, the ceramic load heats preferentially over the susceptors. In this work the effect of dopant type and crystal structure of zirconia on the "kick in" temperature was observed using silicon carbide susceptors.

INTRODUCTION

Researchers have demonstrated that direct microwave coupling is a feasible processing method that significantly reduces the firing time in many ceramic materials[1-11]. Benefits in microstructural control have been indicated including the potential to densify nanoceramics. The scale-up of this technology to commercial processes is underway.

One bottleneck in the scale-up, is the need for affordable microwave furnaces that are designed specifically for the ceramics industry. Linn High Therm has 15 years of experience with modular microwave drying equipment and has recently undertaken the development of a hybrid microwave-resistance furnace for sintering. A laboratory scale high temperature microwave furnace is also available for the first time with a combination of 2.45 and 5.8 GHz frequency magnetrons. Linn High Therm developed the 5.8 GHz magnetron to improve uniformity in the microwave field. In some cases the need for susceptors will be eliminated with the higher frequency of 5.8 GHz.

The ability of a dipole in a given material to reorient in a field (to cause heating), depends on the temperature and frequency. Experimentally, it appears that the frequency range from 2.45 to 30 GHz is appropriate for heating semiconducting and electrically insulating (dielectric) materials. The millimeter wave frequencies can produce extremely uniform fields, however millimeter waves are produced via gyrotrons or klystrons, which are expensive technologies compared to magnetrons. The advantages of higher frequency at the low cost of a magnetron greatly enhances the capabilities for research and product development of ceramics and related materials.

The new 5.8 GHz magnetrons were designed to have the same dimensions and similar electrical characteristics as the common 800W 2,45 GHz magnetrons. The 5.8 GHz magnetrons have a microwave power of 500W at the moment and will be available with 600W in the next few months and are expected to reach 800W in the near future. These magnetrons can be used to easily change the frequency of either new or existing microwave systems that are based on 800W 2,45 GHz magnetrons to 5.8 GHz.

This frequency is expected to improve the heating of especially thin materials as the energy transfer at this frequency is higher than at lower frequencies. Also some materials that do not readily couple at 915 MHz or 2,45 GHz are expected to be more easily heated by 5.8 GHz microwaves.

frequency	**e“ of water at 20°C**	**e“ of water at 40°C**	**e“ of water at 80°C**	**theoretical energy transfer in comparison to 2.45 GHz**	**penetration depth in water at 80°C**
915 MHz	4.3	2.4	0.9	0.15	16.9 cm
2.45 GHz	10.9	6.3	2.3	1	6.6 cm
5.8 GHz	22.9	14.0	5.3	5	2.9 cm

Table 1. Comparison of microwave frequencies 915 MHz, 2.45 GHz and 5.8 GHz

In this work, the new Linn High Therm dual frequency microwave was tested using the 2.45 GHz magnetron with zirconia samples of different dopant types and amounts. The results will be compared to future work using 5.8 GHz. The heating behavior of the porous zirconia compacts in a microwave field was observed.

Typically, it is assumed that the starting stabilizer doped zirconia powders, already have the crystal structure of the sintered material. This is rarely the case. For a given composition, the microwave heating of a zirconia powder compact can differ from the heating of a sintered piece, due to the different 1) dielectric properties of the phases, 2) phase changes, 3) density, 4) volume, 5) emissivity, and 6) thermal conductivity.[6,9,11] In addition, different impurity levels from the powder source and different dopant types and amounts can affect the microwave heating of zirconia compacts. Direct comparisons of the heating behavior of various zirconia types gives greater insight into the real problem of microwave heating, rather than focusing on the dielectric characteristics.

Zirconia was chosen due to the wide range of phases and because it is a ceramic material with widespread uses. In the partially stabilized tetragonal phase, zironia is used in structural and wear parts and it is bio-compatible. The cubic phase of zirconia is used in oxygen sensors and is also important in the emerging technology of solid oxide fuel cells. Previous work[5] indicates that zirconia is an excellent candidate for commercial microwave sintering.

PROCEDURES

Samples were prepared by dry pressing and cold isostatic pressing to a green density of approximately 50 %theoretical. X-ray data were collected with a Siemens diffractometer and a Phillips goniometer using copper K_α radiation. Phase analysis was accomplished using MDI Jade 6.0.

A fiber-insulation housing was placed inside the microwave chamber as shown in Figure 1. The inside dimensions of the housing were 100 x 100 x 60 mm. Four SiC susceptors were placed in the edges of the fiber housing. The susceptors were tubes with a height of 50 mm and a diameter of 35 mm, cut in half. In the middle of the housing, the sample was placed on a fiber-insulation block, so that it was approximately in the center of the susceptors.

The temperature of the sample was measured by an infrared pyrometer, type Keller Optix with a measuring range of 250°C to 2000°C, as shown in Figure 2. The pyrometer is connected to a computer that stores one measurement per second. The measuring spot had a diameter of approximately 2 mm at a distance of approximately 50 cm. The sample was viewed through a tube on top of the chamber (for microwave protection) and a hole in the roof of the housing. The microwave system was equipped with one 800W 2.45 GHz magnetron and one 500W 5.8 GHz magnetron.

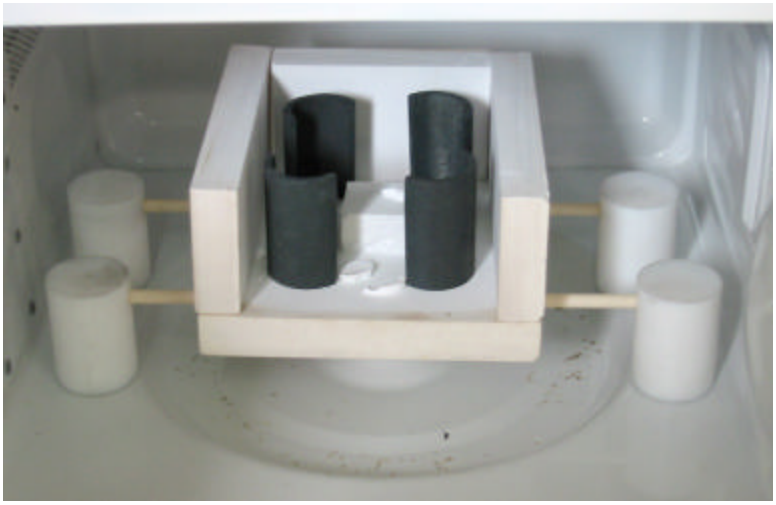


Figure 1. Experimental set-up, including refractory housing and four susceptors.

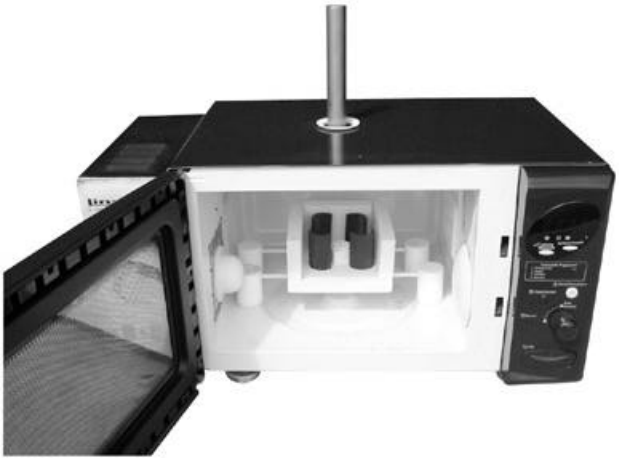


Figure 2. Linn High Therm Dual-Frequency 2.45 GHz/5.8 GHz Test Microwave Sintering Furnace.

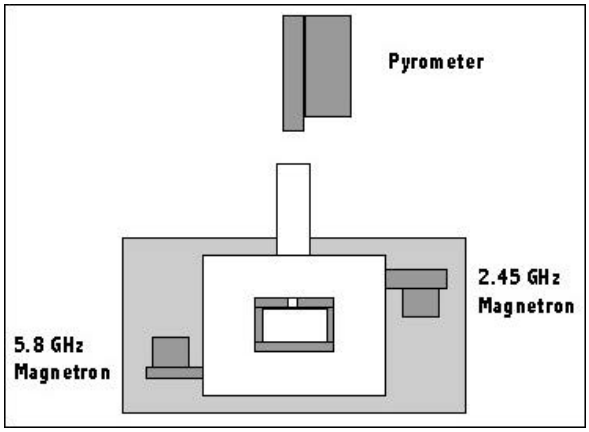


Figure 3. Experimental Setup

RESULTS AND DISCUSSION

In the absence of stabilizers, monoclinic zirconia (Baddelyte) converts to tetragonal at ~1200 °C and to cubic at ~2300 °C. Stabilizers, such as yttria and ceria, form solid solutions with zirconia, such that the cations substitute for the Zr and form oxygen vacancies. This promotes stabilization of the higher temperature phases at much lower temperatures.

Table 2 gives a summary of the phases in the starting powders as detected by x-ray diffraction. It can be noted that the phases of the starting powders differ from the target phase. Phase changes can be expected at some temperature during sintering for each of these compositions. It can also be noted that the starting phases from each composition have different levels of substitution. They represent four different “types” of zirconia for comparisons.

Zirconia Source	Stabilizer Type	Stabilizer Amount	Detected Phases Before Sintering	Expected Sintered Phase
Tosoh	Y2O3	3 m%	Monoclinic (Baddeleyite) Tetragonal ($Zr_{0.92}Y_{0.08}O_{1.96}$)	Tetragonal
Tosoh	Y2O3	8 m%	Tetragonal ($Zr_{0.84}Y_{0.16}O_{1.92}$)	Cubic
Z-Tech	Y2O3	5 m%	Monoclinic (Baddeleyite) Tetragonal,Cubic	Cubic/ tetragonal
Zircoa	CeO2	10 m%	Monoclinic (PDF file 83-0940) Tetragonal [$(Zr_{0.188}Ce_{0.12})O_2$]	Tetragonal

Table 2. Summary of X-Ray Diffraction Analysis of Starting Zirconia Phases.

The zirconia compacts were heated in the insulation housing in the microwave chamber. Figure 3 shows a comparison of the temperature (at the sample surface) for the four different zirconia types. All types had distinctly different behaviors. All were heated at full microwave power and showed identical ramp rates until ~900 °C, where Tosoh 3Y showed a sharp increase and then a peak in temperature. Tosoh 8Y showed a similar peak at a slightly higher temperature, but shorter time. The delay in heating for Tosoh 3Y was reproduced. The behavior appears to be characteristic of the materials. It can also be noted from Figure 3 that the Z-Tech 5Y displayed a similar peak at a higher temperature (~1100 °C) and much longer time, while the Zircoa 10Ce did not show a peak at all for these measurement conditions.

It is proposed that the peaks correspond to the transition from the zirconia heating predominantly by radiation, to preferential coupling of the zirconia over the silicon carbide susceptors. This is supported by modeling work by Lazri, et al.[11] which predicts that blackbody radiation plays a major role in heating zirconia until a critical temperature (Tc) occurs at a characteristic time. The transition temperature occured at approximately 1050 °C as illustrated in Figure 4, for the given conditions[11].

A decrease in temperature after a sharp jump (Figure 3) would not be expected, however, the low thermal conductivity of zirconia (~2 W/mK) may have

created the condition where the surface was originally hotter than the bulk (by radiation). The optical pyrometer, reading from the surface, would record this temperature. After the small volume from the skin began to couple, the bulk would quickly catch up as the surface cools by radiation, i.e. create an inverse temperature profile, with insufficient applied power (high enough ramp rate) to prevent cooling. The cooling effect after the transition was more pronounced for the Tosoh 8Y than the 3Y or Z-Tech 5Y. This behavior requires further investigation.

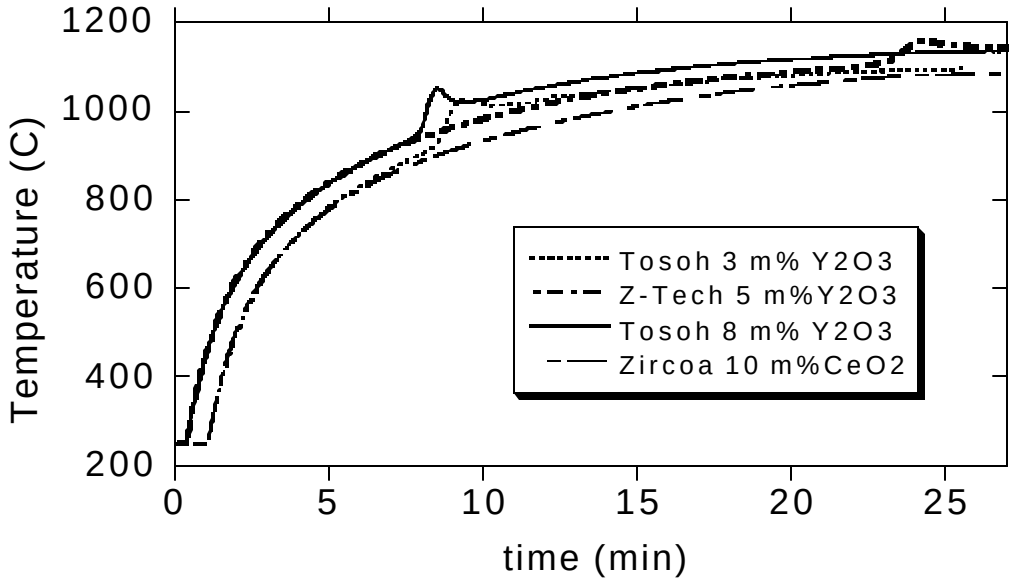


Figure 3. Relative Temperature Time Behavior for Microwave Heating of Zirconia using SiC Susceptors Showing the Critical Temperature (T_c or "Kick-in Temperature").

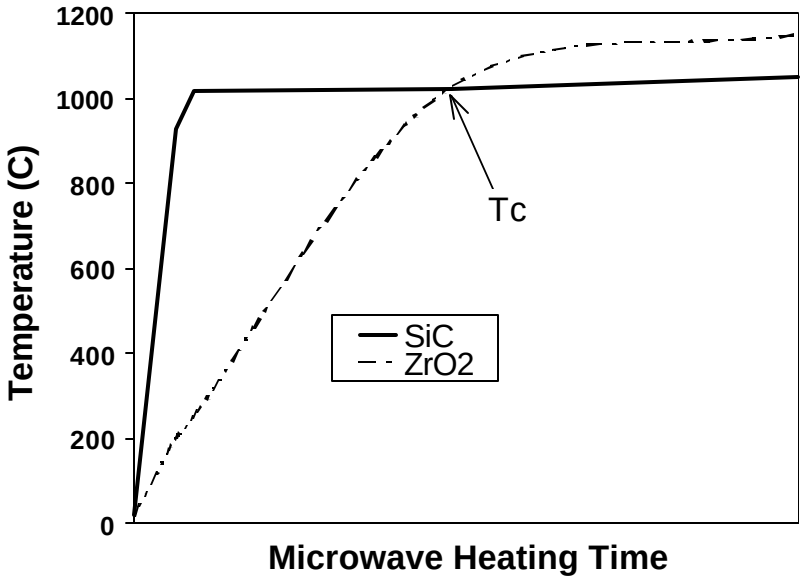


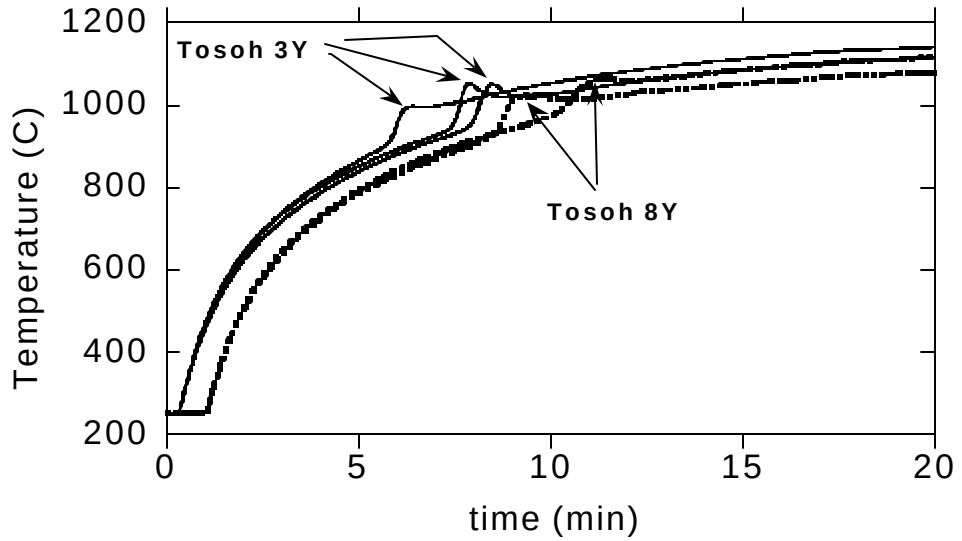
Figure 4. Illustration of the Critical Temperature (Tc) for transition between radiative heating and coupling in the zirconia (after Lazri, et al.[11] Note: The temperature time dependence was predicted for a model that contained silicon carbide, zirconia, and alumina.)

It was important to determine the reproducibility of the transition temperature, to see if this was a clear fingerprint of the material, for the given conditions. Figure 5 shows repeat runs for Tosoh 3Y and 8Y. It can be seen that there was enough variability to prevent a clear conclusion, as to which of these two materials "kick in" at the lower temperature. There does seem to be a different characteristic shape between the curves for the different materials, however, further experiments are required to understand this phenomena. It is interesting to note that the heating delay was reproducible for Tosoh 8Y, as mentioned previously.

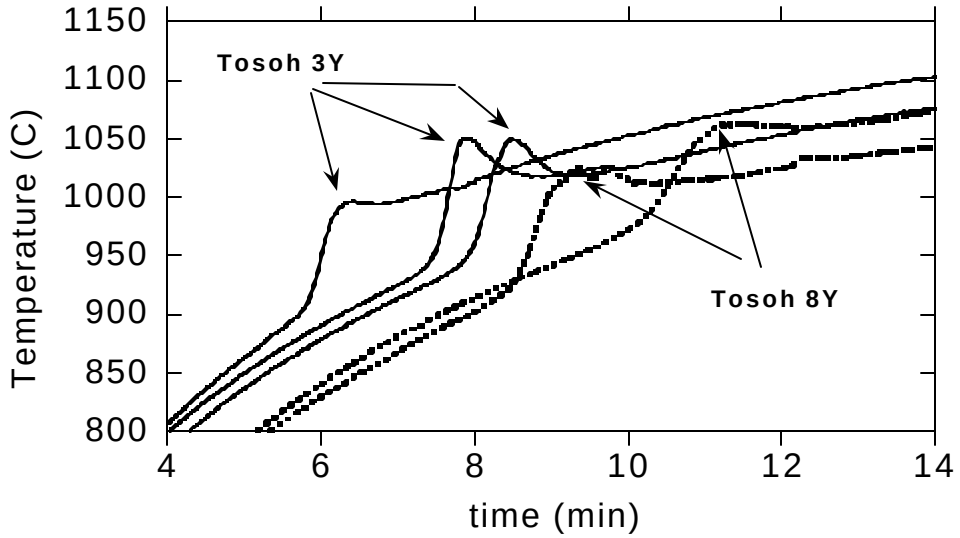
It is clear from Figures 4 and 5 that the different zirconia starting phases heated differently from one another in a microwave field. It is understood that dielectric relaxation mechanisms result in heat. At room temperature, the dielectric loss, ε'', of tetragonal zirconia (PSZ) is ~0.04. At ~1000 °C the loss increases to $\varepsilon'' \sim 100$, similar to SiC. This is consistent with the observed range of "kick in" temperatures.

It can be expected that loss at room temperature is predominantly due to ionic polarization. The ionic jump relaxation mechanism may become more active as the material heats. In the substituted phases, one might expect greater heating with a greater contribution of oxygen vacancies (e.g. $2Y'_{Zr} - V_o^{\bullet\bullet}$). At temperatures greater than 500 °C, there is a significant contribution to the loss

through O2- ionic conductivity. From this reasoning, one would expect the Tosoh 8Y to show the lowest temperature "kick in" at the shortest time, however, the differences observed cannot be predicted or easily explained from the dielectric properties. Further work is underway to derive a better understanding of this behavior.



a) Temperature by microwave heating using an optical pyrometer as a function of time.



a) close up of a)

Figure 5. A Study of the Reproducibility of the Critical Temperature at which Zirconia Heats Preferentially over the SiC Susceptors ("Kick–in Temperature").

CONCLUSIONS

It is useful to know how the microwave heating of zirconia is effected by different additives. In this work, the microwave heating behavior of zirconia doped with 3, 5, and 8 mole% yttria and 10 mole% ceria was compared. It was found that the general temperature/time profiles were similar for all the materials studied, however distinct differences were also observed in the heating behavior of the four types of zirconia doped compacts. The observed anomalies in the temperature/time profiles may be related to the critical temperature or "kick in" of zirconia absorbing energy by coupling preferentially over the silicon carbide susceptors. Further work is required for a better understanding of the mechanisms behind these behaviors.

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