

SINTERING UNIFORMITY AND REPRODUCIBILITY WITH 2.45 GHZ MICROWAVES IN AN INDUSTRIAL SIZED CHAMBER

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ABSTRACT

The scale-up of microwave processes for production requires the systematic study of 1) the uniformity of microwave sintered materials and 2) the reproducibility of material properties for given processing parameters. In this study, a microwave power versus time recipe for sintering zirconia ceramics to full density was successfully transferred from a 1.0 kW modified kitchen microwave to a large 3 kW chamber (1.7 cubic ft or 0.045 m³). The effects of increasing the load and refractory box volume were investigated. The uniformity and reproducibility of the density, hardness, and microstructure were explored.

INTRODUCTION

It has been demonstrated by research laboratories around the globe that microwave heating is a viable method for sintering many types of advanced ceramics¹⁻¹⁷. For example, an excellent study by Katz and Blake¹² addresses some of the issues in the production scale-up using microwaves. They showed that large quantities of high quality alumina ceramics could be microwave sintered with a very low reject rate, at a significant savings in energy. The commercial application of microwaves in high temperature sintering and melting processes has been slow, considering the tremendous opportunities, such as saving in time and energy, improved properties, and densification of nanoceramics.

In the past, the barriers to commercialization have included 1) a lack of microwave furnace suppliers, 2) the need for quick, convincing proof of concept studies prior to investment in equipment, and 3) a need for inexpensive process development. Recently, these barriers have been greatly reduced. There are increasing numbers of well designed microwave systems available with adequate power for small production runs. There are personnel at several universities and national laboratories with considerable experience in high temperature microwaving of materials. Projects can be established to perform feasibility studies and process development with universities, national laboratories, or private testing centers, such as Ceralink Inc.

Ceralink's focus is to provide a practical, methodical approach to microwave firing with the goal of solving problems of scale-up relevant in ceramics and glass. The breakthrough of microwave technology into the ceramics industry will generate new profit, through process cost reduction and new products. Collaboration as well as competition is useful to stimulate the uptake of this technology.

There are many excellent texts on microwave interactions with materials.^{1,2} Microwave heating is predominantly caused by material coupling in the field, e.g. reorientation of dipoles in the material. The complex permittivity, ($\epsilon^* = \epsilon' - i\epsilon''$), is a measure of the time dependent polarizability, or behavior of the dipoles. The dielectric loss or loss tangent, ($\tan\delta = \epsilon''/\epsilon'$) indicates the tendency of the material to convert absorbed energy into heat. In general, the more covalent the bonding, the less polarizable, and the more difficult to couple to microwaves, unless the material is a semiconductor. Microwave heating is volumetric through the material, avoiding the problem of thermal gradients inherent in conventional firing. This allows the application of high heating rates (>100 °C/min) and drastically reduced firing time.

The purpose of this study was to explore the transfer and scaling up of a microwave sintering process from a modified kitchen microwave to a larger more powerful microwave furnace. Process reproducibility, material uniformity, and

product quality were critically evaluated in this study, as they are necessary requirements for the advanced ceramic industry.

EXPERIMENTAL PROCEDURES

Microwave Test Set-up

Microwave Equipment: Preliminary work was performed on a modified kitchen microwave^{*}, (MRS ThermWAVE) with nominal power of 1.0 kW, 2.45 GHz frequency and chamber size of 12" X 13" X 14" (30 x 20 x 10 mm). The working volume was approximately half of the internal space. The unit was water cooled and equipped with a controller and thermocouple. A stepped or full power schedule was applied and temperature was recorded as a function of time. The glass plate and turning mechanism were left intact from the original product.

Scale-up studies were performed in a CPI Autowave system^{**} with 3 kW nominal power at 2.45 GHz frequency. The external dimensions of the cylindrical applicator chamber was 35" x 35" x 54" (89 cm x 89 cm x 138 cm) with a designated working volume of 12" x 12" x 20" (30 cm x 30 cm x 50 cm). The microwaves were applied from the back face of the cylindrical chamber. The front face pulls out from the chamber with a large plate to place refractory containers. Power and time were recorded in the Autowave. A temperature measurement system was not used for these experiments. A detailed description of the Autowave equipment can be obtained from CPI.

Refractory containers: Two types of high temperature (1700 °C) fibrous alumina refractory materials from Zircar^{***} were used in this study, 1) Al-1700 and 2) ECO-25B, (now discontinued). Several box sizes were fabricated from the 1.5" thick boards, using dovetail joints. Boxes were held together with either alumina cement or fiberglass ribbon.

Susceptors: Silicon carbide susceptors⁺ in the shape of discs were fabricated using a proprietary process. Susceptors were mounted on alumina refractory holders. The mass of each susceptor was approximately 45 g. At least two susceptors were placed in the refractory boxes with samples spaced evenly in between them.

Zirconia samples: Zirconia discs (5 and 25 g) were prepared from Tosoh 3Y powder⁺⁺ (without binder) by uniaxially pressing in a 1" diameter steel die to approximately 10,000 psi (70 MPa). Discs were then cold isostatically pressed to 20,000 psi (138 MPa).

^{*}The next generation of this machine, the ThermWAVE (1.3 kW) is now being marketed by Materials Research Systems, Alfred, NY.

^{**} Communications and Power Industries, Beverly, MA. (<http://www.Autowave.tv>)

^{***} Zircar Ceramics, Inc. Florida, NY

⁺ Microwave Research Systems, Alfred, NY.

⁺⁺ Tosoh, Bound Brook, NJ.

Materials Analyses

The green and sintered weight and dimensions were recorded for the zirconia discs. Shrinkage was calculated from the dimensions. Density was measured 1) using the Archimedes method and 2) from the weight and dimensions. Select samples were polished in cross section and thermally etched for microstructural analysis by scanning electron microscopy. Vickers hardness was measured on polished surfaces using a 20 kg load. Five indents were used for each sample measurement.

RESULTS AND DISCUSSION

Microwave Furnaces

The actual maximum power (100%) in the ThermWave (ModII) was approximately 0.65 kW. The percentage power was converted to kWatt assuming a linear relationship. A power/time profile of 5 minutes at 0.52 kW, 5 minutes at 0.59 kW and 35 min at 0.65 kW power was sufficient to produce fully dense (>99.5% of theoretical) zirconia for the 10 gram load in a refractory box volume of 680 cc with 2 SiC susceptors (described in more detail elsewhere).

The same power/time profile (5 minutes at 0.52 kW, 5 minutes at 0.59 kW and 35 min at 0.65 kW) was applied in the CPI Autowave and repeated for four runs. The average density (8 samples) was 99.8 +/- 1.1% of theoretical density (6.08 g/cc). Considering the approximations involved, this was an encouraging result, indicating that the power/time requirements can be used as a guide to transfer processes between microwave furnaces.

Refractory Container Type

Commercial fibrous refractory material used to insulate conventional furnaces will have a range of densities and compositions. It is usually assumed that high alumina refractories are microwave transparent, however, there will be some degree of absorption of microwaves, especially at elevated temperatures as the dielectric loss of the refractory increases. It is important to determine the effects of the refractory material type on the power/time profile for sintering ceramics. A thorough investigation comparing refractories from many commercial sources is underway. Preliminary results are reported here.

Zircar ECO25B refractory was used for the transfer from the ThermWave (ModII) to the Autowave. This material is no longer available and has been replaced by a slightly denser more rigid grade, A125/1700. A box with the same dimensions was fabricated with Zircar A125/1700 and the same power/time profile was applied in the Autowave using the same sample and susceptors set-up. The resulting zirconia samples were 96.8 +/- 0.1% dense (average of 6 runs, 12

samples). A slight increase in the maximum power (~ 4%) was applied in the Autowave to produce fully dense (>99.5%) zirconia.

Refractor Container Volume

An important aspect to consider is the effect of refractory box volume on heating using microwaves. If the box volume is significantly larger than the sample, an inverse temperature profile can develop, where the inside of the sample is hotter than the surface. The sample radiates and cools from the surface, behaving like a heating element. This condition can lead to thermal shock and non-uniform densification.

Figure 1 shows the effect of increasing the box volume by ~3 times on the density of zirconia samples. It can be seen that with the increased box volume, more microwave power would be required to densify the same load. It is more energy efficient to develop a “good fit” between the desired load and the refractory container.

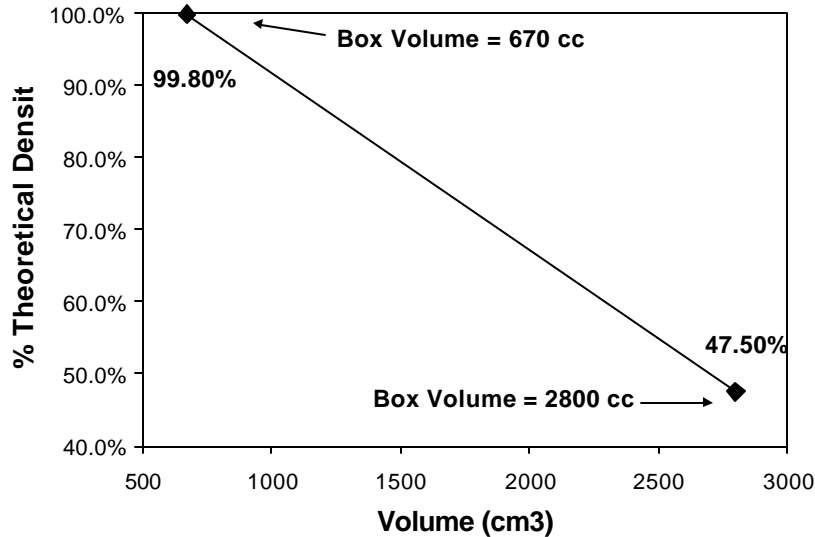


Figure 1. Effect of increasing the refractory container volume on density of zirconia samples.

Load Size Scale-up

Increasing the load size must require an increase in energy and microwave power to achieve densification. This relationship is one of the subjects of an ongoing study. Preliminary results are shown in Figure 2. It can be noted that density decreased slightly with increase in the mass of the load, and then dropped

sharply for further increase. This behavior may be related to the experimental set-up. Initially, the susceptor mass (90 g) was higher than the load. Microwave energy must be absorbed by the susceptors as well as the sample load. As the mass of the load increased, the energy absorbed by the susceptors would account for a smaller percentage of the total energy absorbed.

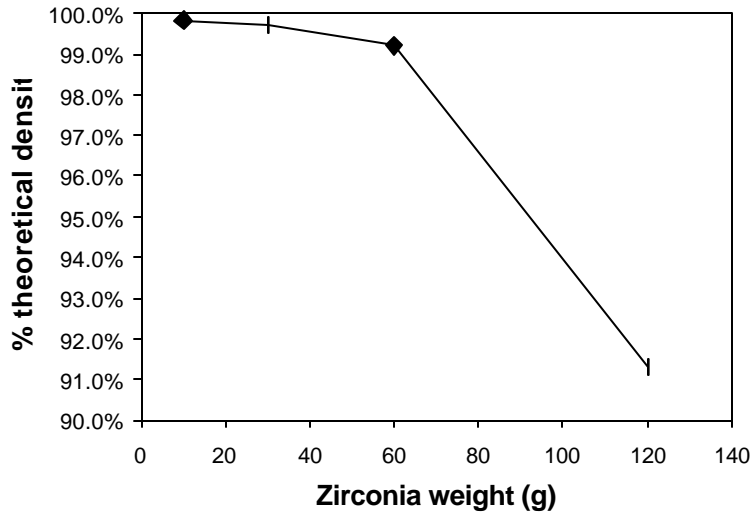


Figure 2. Graph showing density as a function of zirconia load (mass) for given microwave power/time profile, box volume and susceptor set-up.

Uniformity and Reproducibility

One of the important questions about firing with microwaves, concerns the uniformity and reproducibility of the density and microstructure. The microstructure has a drastic effect on the properties of ceramics. It is not obvious from the scientific literature that microstructures can be readily reproduced and controlled, however, this is a key issue for scale-up and production.

A series of experiment were performed to observe the resulting densities and microstructures from a given power/time profile. A set of experiments using the Zircar A125/1700 refractory box and 2 susceptors, was repeated five times with two samples in each run. The resultant density from the 10 samples was 96.3 +/- 0.6%. Table I contains data for these runs, showing the density, shrinkage, grain size, and hardness. The grain sizes were approximated from the scanning electron micrographs. No attempt at quantitative grain size analysis was made at this stage, however, several of the corresponding micrographs can be found in Figures 3-5.

Table I also gives the position of the samples as top or bottom, so that a comparison can be made between these different positions. The samples were stacked, such that the top position was exposed to the atmosphere and the bottom sample was insulated (or heated) by the sample on the top and by the refractory on the bottom.

Table I. Data from five identical microwave runs containing two samples in each run.

RUN-Sample	Position	Grain Size (um)	%Shrink (dia)	%Shrink (thick)	%Shrink (vol)	% Green Dens	% Fired Density	Hardness (GPa)
A-200	Bottom	0.15-0.35	21.3%	23.7%	52.7%	48.1%	96.7%	12.2 (0.1)
A-201	Top	0.35-0.55	21.2%	22.9%	52.1%	48.2%	97.1%	12.3 (0.0)
B-202	Bottom	0.20-0.40	21.1%	22.2%	51.6%	46.9%	95.2%	
B-203	Top	0.55-0.90	21.4%	24.2%	53.2%	45.3%	95.8%	11.9 (0.2)
C-204	Bottom	0.25-0.45	21.1%	20.3%	50.4%	48.5%	96.1%	
C-205	Top	0.30-0.45	21.6%	20.0%	50.8%	48.2%	96.5%	
D-206	Bottom	0.35-0.65	21.0%	21.7%	51.1%	46.8%	96.1%	12.3 (0.1)
D-207	Top	0.45-0.90	21.5%	21.4%	51.6%	47.3%	96.1%	12.1 (0.1)
E-208	Bottom	0.30-0.75	21.2%	20.6%	50.7%	47.4%	96.7%	
E-209	Top	0.30-0.70	21.2%	21.5%	51.3%	47.1%	96.9%	

From Table I, it can be seen that the shrinkage in the thickness and diameter was fairly uniform and reproducible between runs and between the samples in one run. The density was reproducible with some variation apparently caused by variation in green density (e.g. B-203). The hardness of one sample (B-203) was slightly lower (11.9 GPa) than the rest (~12.2 GPa), which may also be related to the slightly lower green and sintered density. The small differences in grain size observed by SEM did not effect the hardness as detected by the Vickers hardness measurement. The low standard deviation from the Vickers indents suggests a high degree of uniformity.

A sample with a typical microstructure from the series described in Table I (A-201) is shown in Figure 3. The disc was cut in half, and the cross section polished and thermally etched to reveal the microstructure. The sample was on the top of the stack, therefore, there was a question whether an inverse temperature profile would affect the microstructure, (i.e. the sample would have been cooling preferentially from the top surface). It can be seen that in fact, the microstructure was extremely uniform throughout the sample. Excellent uniformity was observed for all samples studied, regardless of position in the stack or density. This is consistent with observations from other researchers¹².

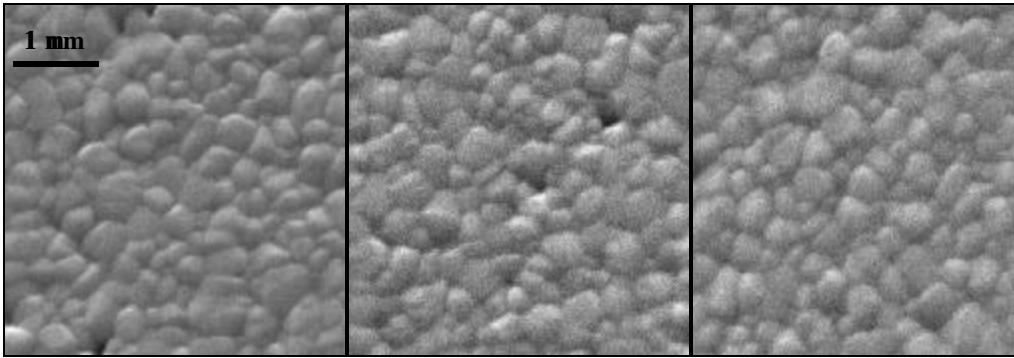
Figure 4 shows the most frequently observed microstructure for this test series. It can be seen that there is excellent uniformity between the top and bottom samples in this run. Figures 5 and 6 show another set of samples from one run. Each samples showed uniform microstructure throughout, however there

was a difference between the top and the bottom microstructures. The bottom sample in the run (Figure 5) showed a finer microstructure than the top sample (Figure 6) in the same run. It is interesting that one of these microstructures was slightly finer than the typical microstructure, while the other was slightly coarser. This may indicate a difference in the absorption of microwave energy between these two positions, with the total absorption remaining constant.

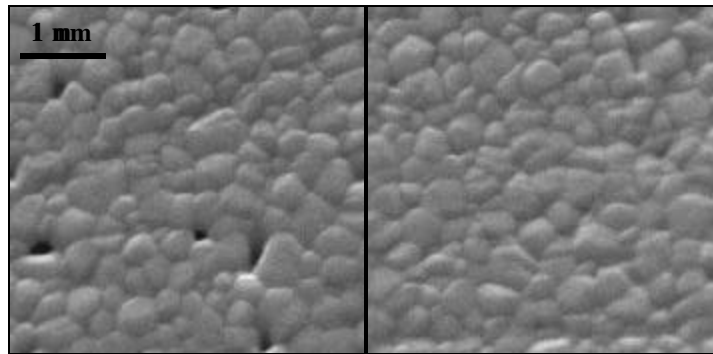
It will be important to understand how the power/time profile affects the uniformity between sample positions. Figure 7 shows samples of similar density microwave sintered with more power for shorter time. It can be seen that the microstructures were extremely reproducible both from top to bottom positions and between two different runs.

In Figure 8, the density variation between positions in a stack of six samples was explored for two power/time profiles. There is a slight indication that the top samples may have a higher density, especially at the higher power setting, indicating slightly higher temperature. Apart from this possible slight variation, the density was fairly reproducible and did not seem dependent on position in the run or between runs. The higher apparent variability in the set of runs at 0.70 kW is probably due to the measurement method, since the density of these samples was measured by the weight and dimensions while the other set (0.65 kW) was done by Archimedes method.

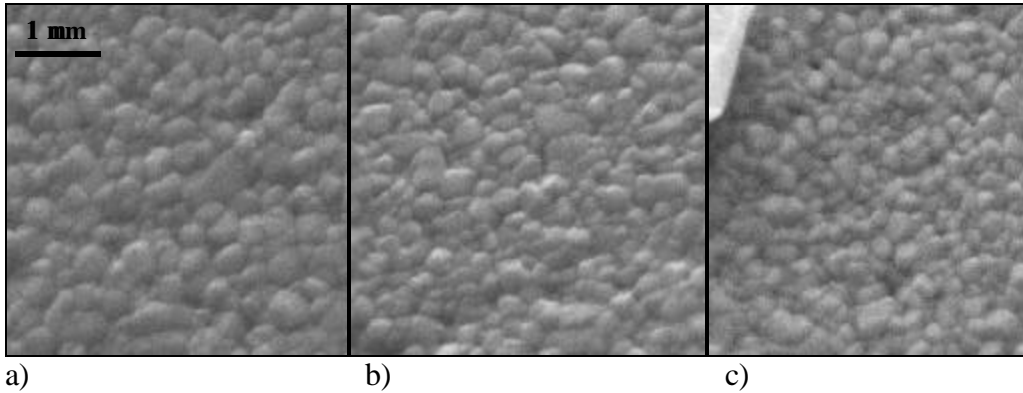
From the summary of microstructure data in Table I (comparing top and bottom), including the microstructures in Figures 5 and 6, and the density data in Figure 8, there is a possible indication that samples sintered on the top of a stack achieve a slightly higher temperature. Further study will be required to confirm this, however, if it is real, it is a very minor problem and easily remedied by using setting powder or setters on top of the load as well as beneath.



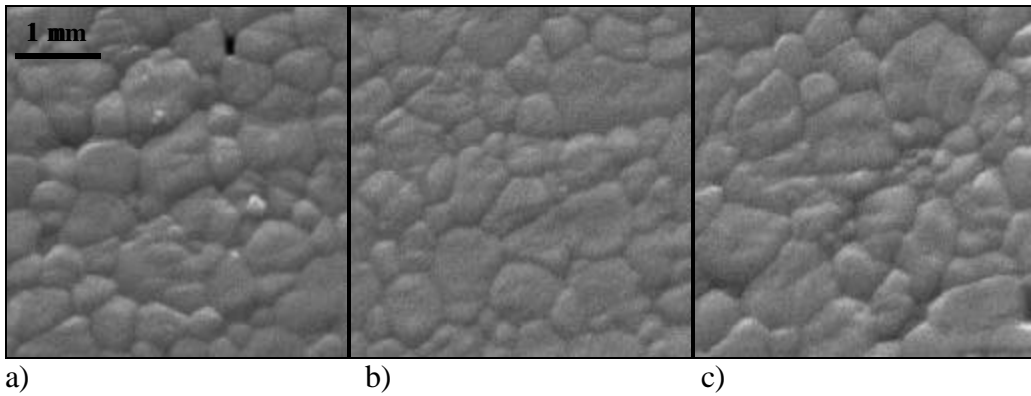
a) b) c)
Figure 3. Typical microwave sintered Tosoh-3Y Zirconia microstructure (by SEM 20,000x) taken from the cross section of a 5 gram disc a) near one face, b) center, c) near opposite face, showing extremely uniform grain size. (sample 201).



a) top position (sample 204) b) bottom position (sample 205)
Figure 4. Comparison of microstructure (by SEM) for Tosoh-3Y Zirconia from a) top and b) bottom position for 5 gram discs, microwave sintered together in one run, showing uniformity between positions.



a) b) c)
 Figure 5. Microstructure of a sample microwave sintered on the *bottom* of a two sample run, showing *finer* than the typical grain size, with high degree of uniformity in the cross section a) near one face, b) center, and c) near opposite face. (sample 202)



a) b) c)
 Figure 6. Microstructure of the sample microwave sintered on the *top* of the sample shown in Figure 3, showing *coarser* than the typical grain size. Note the uniformity in the cross section a) near one face, b) center, and c) near opposite face. (Sample 203)

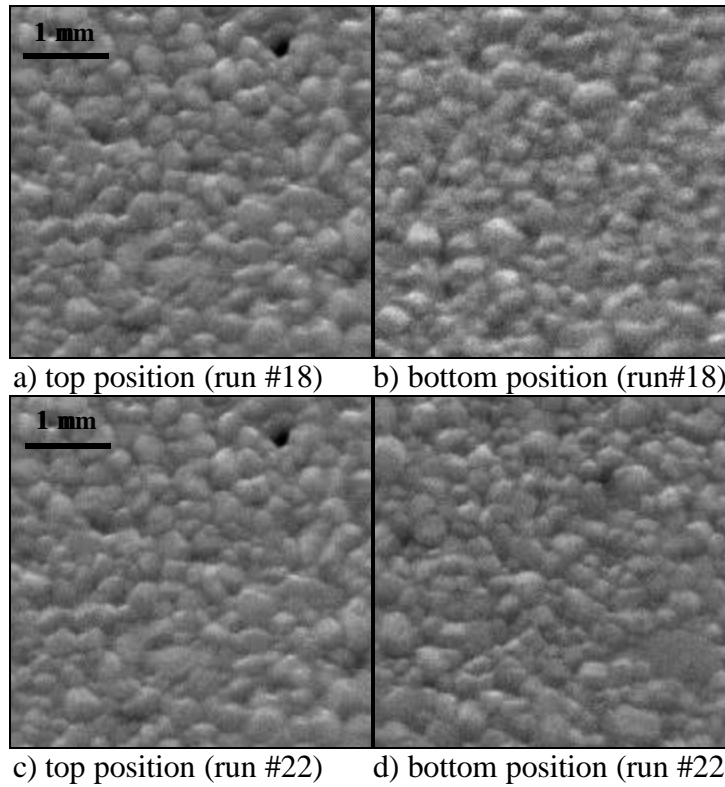


Figure 7. Four samples sintered in two runs with *shorter time at higher power* than samples shown in Figure 3-6, showing fine, uniform grains and no variation in microstructure with position or between runs.

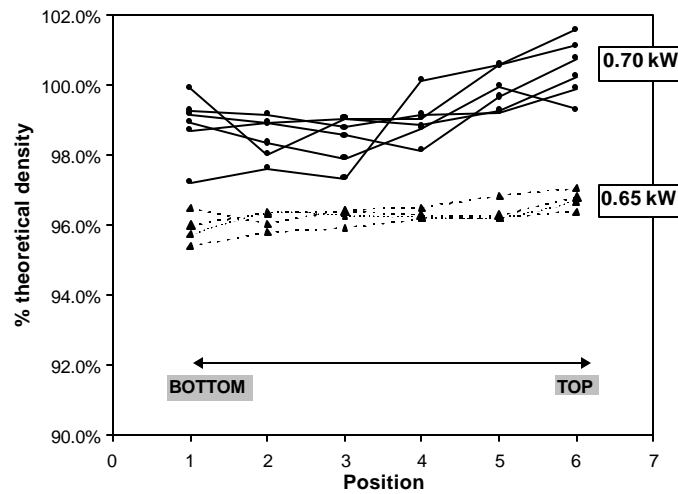


Figure 8. Graph of theoretical density as a function of position in a 6 sample stack in for two different power settings.

CONCLUSIONS

It was demonstrated that a given refractory container, susceptors, and sample set-up can readily be transferred between different microwave furnaces to give predictable densification behavior.

In this study no special care was taken to produce “good” samples. Instead, the focus was to apply a simple, easily scalable procedure and 1) study the reproducibility and uniformity and 2) observe the effects of different variables, including container volume, sample position, and load size.

It was found that extremely uniform microstructures were obtained by microwave sintering. A high degree of reproducibility in density, microstructure and hardness was observed. There was a slight indication that samples exposed at the top of a stack may have been at a higher temperature. This would not represent a strategic problem for scale-up, and can likely be remedied by using setting power or setting plates.

Increasing the refractory container volume or the mass of the load, requires an increase in the microwave power. The relationship between microwave power/time for densification, refractory volume, load size and material type requires further exploration to develop a predictive model. This understanding will assist scale-up efforts.

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