Project Title:	**MICROWAVE PROCESSING OF SIMULATED ADVANCED NUCLEAR FUEL PELLETS**
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Award Number:	**DE-FC07-06-ID14731**
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Project Team:	**Virginia Tech, Dept. of Materials Science & Engineering** **Univ. of Tennessee, Dept. of Materials Science & Engineering**
Project Objective:	**The objective of this work is to develop core principles and establish a quantitative basis for microwave sintering of simulate nuclear fuel pellets.**

BACKGROUND

In an effort to reduce current inventories of nuclear materials, the composition of an advanced nuclear reactor fuel has been designed to include these materials. It is expected that these materials will burn up during their use as reactor fuel. Various compositions have been developed and corresponding fabrication schemes developed to make sample fuel pellets.

While fuel pellets have been fabricated, there is a problem establishing a sintering profile that will result in pellets of the desired density without the loss of some of the volatile materials such as americium oxide or americium nitride. Using a conventional sintering approach requires the nuclear fuel material to be at a high temperature for many hours. Analysis of sintered material has revealed a loss of americium due to volatilization.

The conventional process by which green unsintered pellets are fabricated is described as follows. First, the mixed nitride, oxide feedstock powders (e.g. PuO_2, AmO_2 and ZrO_2) are blended and milled in the right ratios. Then the powder is pressed into briquettes and the briquettes are then thermally treated (e.g. 1700^0C in air) to form a solid solution oxide. The solutionized oxide will then be converted to nitide by the carbothermic reduction process. The nitride powder is then crushed, milled and formed into pellets and sintered at around 1600^0C in argon. At this temperature, Am boils off thus reducing the amount of Am in the pellets. In the conventional process no attempt to compensate for the lost Am is made and the range of compositions should be +/-5 wt% for the Zr, Np, Pu and U and +/-10% wt% for Am. Pellet density is to be 80% +/- 10% of theoretical and pellet geometry is that of a right cylinder with dimensions: 3.51-4.37 mm diameter, 4.32 mm in length and 1.09-7.64mm in height.

In order to reduce the loss of americium and shorten the overall sintering time, it is suggested that microwave sintering be used to process the fuel pellets.

Potential advantages of this thermal processing technique are: rapid sintering, less labor required to process the material, less energy required to process the material, different and in many cases superior microstructures, and more uniform material properties. This proposal addresses work of a fundamental

nature that needs to be performed in order to better understand how to achieve dense (>95% t_d) nuclear fuel pellets using 2.45 GHz and higher frequency electromagnetic radiation to sinter the material.

Sintered pellets will be characterized as to density and grain morphology. Sintered samples will be non-radioactive simulants that have properties similar to the materials of interest. Sintering parameters will be developed using these surrogate materials and these resulting parameters will be suggested as the starting parameters to sinter advanced nuclear fuel compositions.

PROJECT SUMMARY

Throughout the three-year project funded by the Department of Energy (DOE) and lead by Virginia Tech (VT), project tasks were modified by consensus to fit the changing needs of the DOE with respect to developing new inert matrix fuel processing techniques. The focus throughout the project was on the use of microwave energy to sinter fully stabilized zirconia pellets using microwave energy and to evaluate the effectiveness of techniques that were developed. Additionally, the research team was to propose fundamental concepts as to processing radioactive fuels based on the effectiveness of the microwave process in sintering the simulated matrix material.

In this final report, some of the highlights of the project are reported. Details of each aspect of the three-year project can be seen in the quarterly and annual project reports.

Task 1: Experimental Apparatus

Over the course of this three-year research project, several different microwave systems were used:

- two single mode systems
- one multimode cavity
- a cavity perturbation system for dielectric property measurements

One of the single mode systems and the multimode cavity were purchased during the project. Both single mode microwave ovens were fixed frequency (2.45Gz) and were equipped with peripheral equipment for controlling and monitoring temperature and applied power. Two single mode cavities were used: a TE103 rectangular cavity and a TM01x cylindrical cavity. Both systems were capable of employing grounded thermocouples and/or optical pyrometers for temperature monitoring and control. The rectangular TE system was equipped with a sliding short that allowed for precise location of the E-field maximum with respect to sample placement.

A cavity perturbation dielectric property measurement system was constructed with partial support from this project. This device could measure the dielectric properties of samples with moderate dielectric loss at 2.45 GHz, 4.0 GHz and 5.8 GHz and low power. The primary use of this system for the DOE project was in running cavity characterizations of the single mode cavities used for heat treatment experiments.

With the interest of our technical contact at Los Alamos National Laboratory, Dr. Ken McClellan, the past year and a half were spent in designing and developing a microwave dilatometer for performing Master Sintering Curve (MSC) experiments on the 8YZ pellets. The system (Figures 1 and 2) was used to generate initial data to compare with data generated from a conventional dilatometer on the same materials. (Though the project has concluded, work continues as the graduate research assistant on the project, R.R. Thridandapani finishes his doctoral work. The estimated date for completion of his degree is December 2010.)

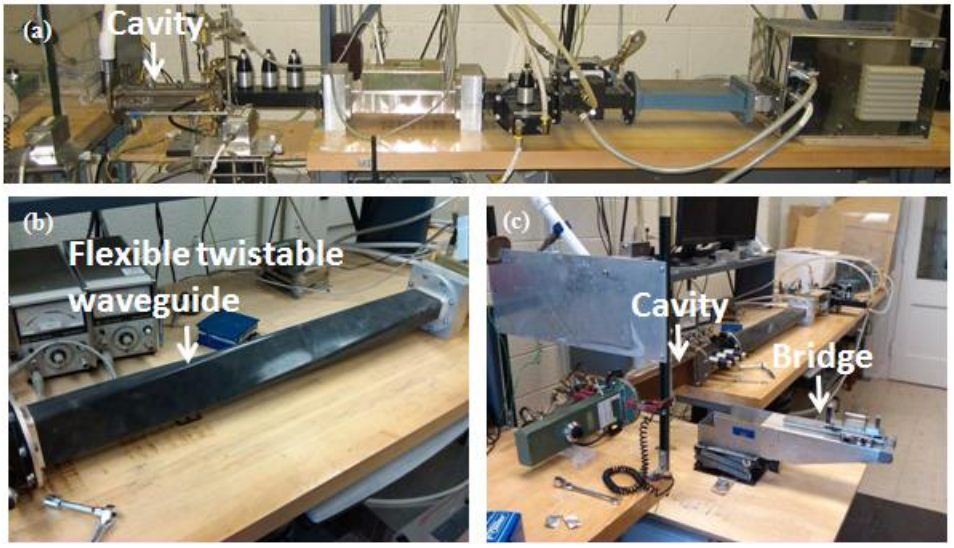

Figure 1: (a) A pictorial view of the standard TE_{103} single-mode microwave cavity, (b) flexible twistable waveguide, and (c) a modified version of TE_{103} with necessary changes for a dilatometer set-up.

In this design for the microwave dilatometer, the push rod (which senses the in situ shrinkage) was inserted into the cavity only along the vertical direction to minimize perturbation of microwave field in the cavity. For this design to work, the cavity had to be shifted by 90^{o}; accomplished by attaching a standard flexible twistable waveguide (Figure 1b), providing a 90^{o} rotation to the cavity. Figure 1c shows the modified design of the system with the cavity being in a vertical direction. A bridge for holding the push rod in place can also be seen in this picture. A close up view of the cavity is presented in Figure 2a.

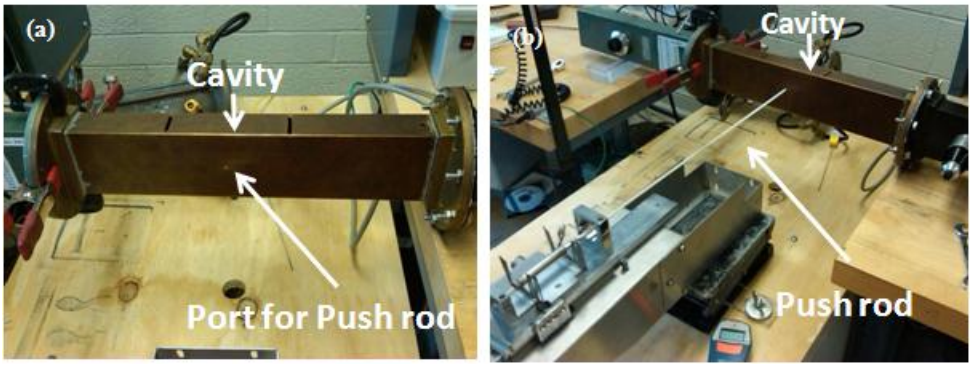

Figure 2: Close up view of (a) the machined TE_{103} cavity and (b) the push rod along with the bridge.

This cavity has been machined for incorporating the standard push rod. The arrows in Figure 2a show the port which is an entrance for the push rod. Figure 2b shows a complete view of the new set-up that has been designed for collecting in situ linear displacement of the sample during sintering. This new set-up will was termed as a single-mode microwave dilatometer.

A software package was designed for this new dilatometer. This software not only allows one to the control the microwave source, but also allows for continuous recording of the data from the temperature monitors and the digital read-outs. It could collect data at a precise interval of time that was necessary for constructing a Master Sintering Curve for 8YZ inside a single-mode microwave cavity.

The system was tested for measuring the in situ linear displacement of the 8YZ sample during sintering. The first experimental results lead to the next step; develop a standard calibration technique for this design. This was necessary for obtaining precise and accurate measurements.

Data was generated using the microwave system presented above. A MSC was constructed for 8YZ sintered in a conventional dilatometer. The activation energy reported was 1000 kJ/mol; this value was much higher than the values normally observed for sintering ceramics. It was observed that the dial gauge which was collecting the shrinkage data was out of calibration. A new set of linear shrinkage curves were generated after the installation of a new gauge. This data was used to generate a new set of MSC curves at different activation energy values and the results are presented in Figure 3.

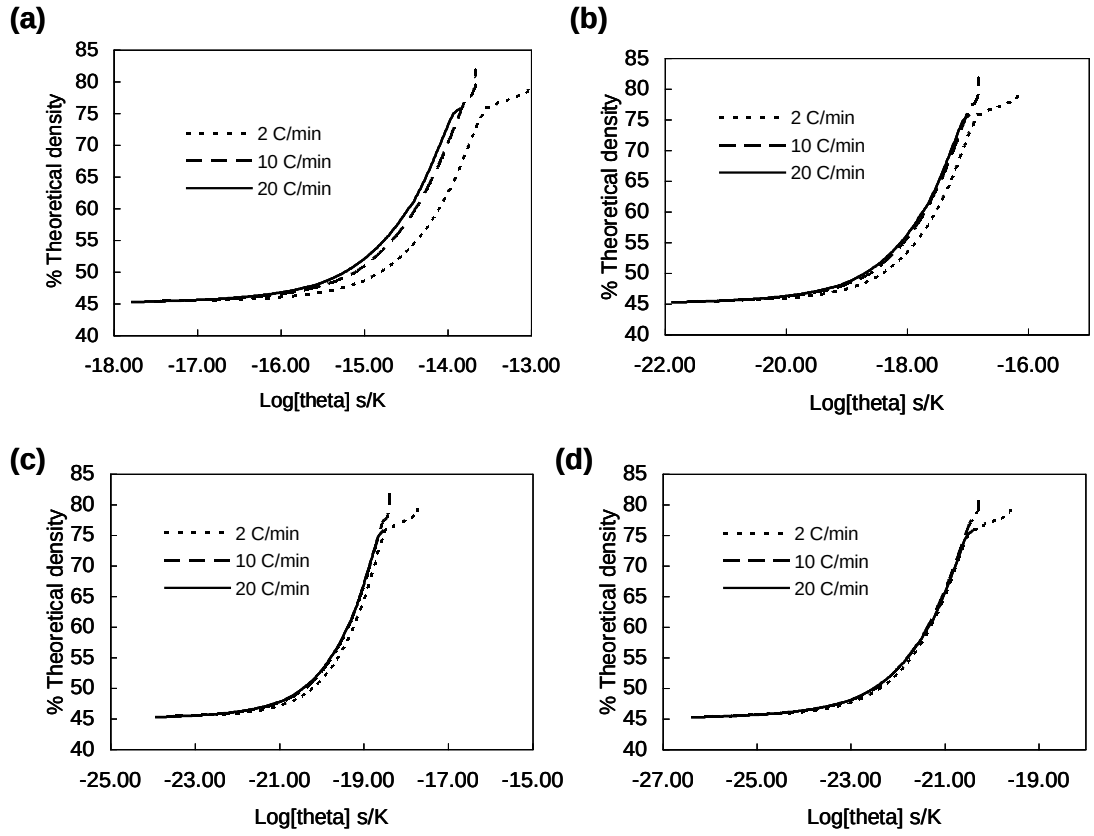

Figure 3: (a) % TD vs. temperature curve, Q = 300kJ/mol; (b) % TD vs. Log [Theta], Q = 400kJ/mol; (c) % TD vs. Log [Theta], Q = 500kJ/mol; (d) % TD vs. Log [Theta], Q = 600kJ/mol.

As can be seen from Figures 3(a) – (d), the best convergence of the density vs. theta curves occurs at an activation energy value of 600 kJ/mol. This value is the activation energy for sintering 8YZ inside a conventional furnace. This value (600 kJ/mol) is in close agreement to the activation energy value (~ 615 kJ/mol[4], calculated using constant rate heating experiments) reported in the literature for sintering of ZrO_2 - 2.8 % Y_2O_3.

Task 2: Fabrication of Green Pellets

Throughout the course of this project, researchers from the University of Tennessee (UT) and VT prepared cold isostatically pressed oxide pellets of ZrO_2 stabilized with 3 mol% Y_2O_3 (3YZ) and with 8 mol% Y_2O_3 (8YZ), pellets of the 8YZ containing Dy_2O_3 as a simulant for Am_2O_3, and a few pellets of ZrN. Based on meetings with Dr. Ken McClellan of Los Alamos National Laboratory (LANL), the 8YZ was selected as the focus composition for the bulk of the research at VT.

In addition to fabricating pellets for the microwave processing studies, Dr. Meek's team continued to study the characteristics of the various pellet compositions. The results of these studies are summarized in the 2009 annual report. The subcontract with the University of Tennessee ended in December 2009.

Tasks 3 and 4: Microwave Processing of Samples and Characterization of Samples

As this activity constituted the primary body of work for this project, some of the research highlights are described. For complete details, results are contained in annual and quarterly reports.

Methods for sintering included conventional resistance heating, single mode microwave heating, and multimode microwave heating. In single mode microwave heating, samples were placed in a cavity in such a way as to be exposed to microwave energy of a known field strength, while in multimode microwave heating, a wide distribution of energy is present in the cavity and the exact field strength at the sample position was not known. In both cases, the samples processed for this project were heated in a refractory housing (microwave hybrid heating, MHH).

Results of Density Measurements

As seen in Figure 4, samples of the 8YZ that were microwave-sintered reached higher density at lower temperature. Figure 5 illustrates the microstructures associated with these methods for the samples sintered at 1300°C. It can be observed from Figure 4 that, at 1300^{o}C, the microwave-processed samples showed a higher density; in particular, the single mode-sintered sample showed a 96% density. To obtain a similar density in the conventional furnace, we had to increase the temperature to 1400^{o}C. As confirmation of these higher densities at 1300^{o}C, we observed the fracture surface of these samples under SEM. The results can be seen in Figure 5.

As is evident in Figure 5, the conventionally processed sample is still in the green state, while the microwave-processed sample has shown a significant decrease in porosity. These results obtained for the 8YZ inert matrix material system indicate that higher densities (>95%) can be obtained using microwave energy than with radiant heating when then sample experiences the same soak temperatures for the same amount of time.

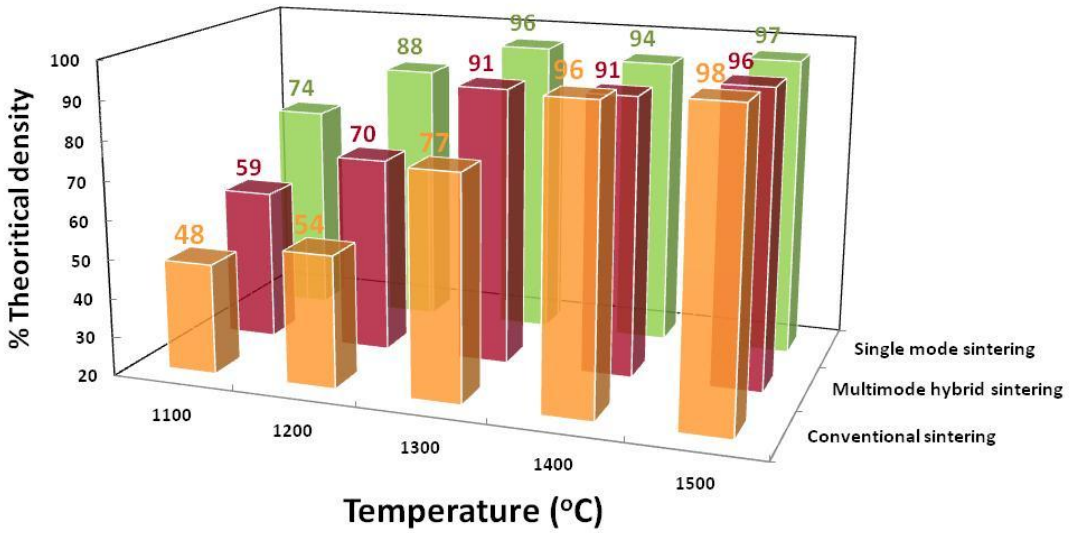

Figure 4: Effect of processing method and temperature on density of 8YZ.

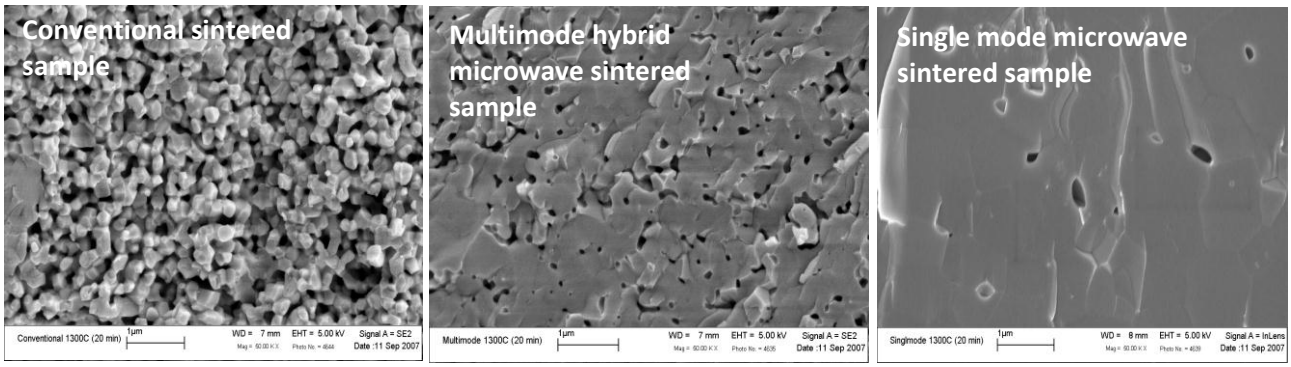

Figure 5: Fracture surface imaging of 8YZ sintered pellets at 1300°C for conventional, multimode hybrid and single mode samples.

Mechanical Testing

Hardness testing was performed at Virginia Tech and high temperature compression testing was performed at Arizona State University (ASU). These tests were done on the 8YZ samples sintered to 1300°C for 20 minutes.

Hardness testing

Vickers microhardness testing was used for testing the samples, as opposed to macrohardness which requires large sample sizes and a great deal of bulk material. Vickers microhardness testing uses a diamond indenter with the shape of a square based pyramid.

The sintering behavior of 8YZ in a microwave hybrid system and a conventional system was reported in previous quarterly reports. Attempts were made to predict the fatigue behavior of the 8YZ sintered pellets using micro-indentation techniques. These tests are inspired from the work done by Vaughan et al[1] and Govindan[2]. They predicted the mechanical cyclic fatigue behavior of alumina and uranium oxide fuel pellets using a micro-indentation technique. In this technique, a Vickers indentation is made on the

sample, as shown in Figure 6a. Indentations at the same spot are repeated until the corners of the indentation chips out (shown in Figure 6b).

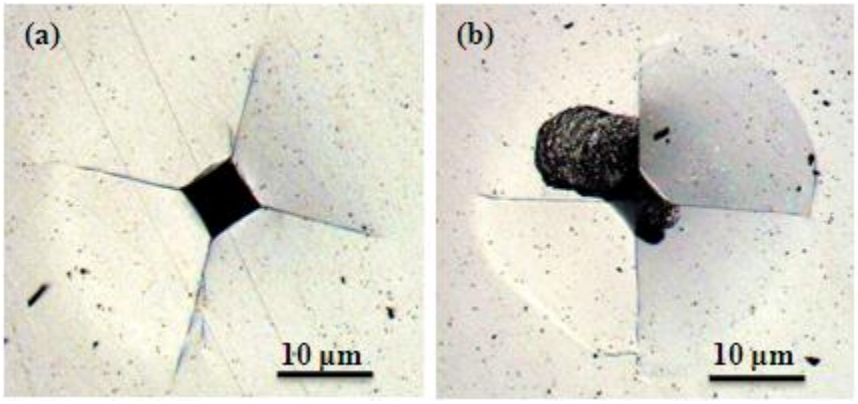

Figure 6: Representative tests performed on 8YZ samples at VT illustrating (a) Vickers indentation; (b) lateral chips coming out of the initial indentation after N number of cycles at constant load.

During this test, the applied load is kept constant and the number of cycles required to chip out the indentation at a particular load is recorded. This technique is repeated for different loads in order to obtain a relationship between the load and number of cycles required to chip the indentation. This method of predicting the fatigue behavior is relatively simple when compared to the conventional fatigue testing because it requires less material and is relatively quick to perform.

Fatigue Tests

The 8YZ pellets sintered at a temperature of 1500^{o}C for a soak time of 20 min were selected for the fatigue tests. Indentation fatigue testing was performed on two samples, one processed in a microwave hybrid system and the other in a conventional system. Both of these samples were polished down to 0.25 µm diamond paste. The results can be seen in Figure 7.

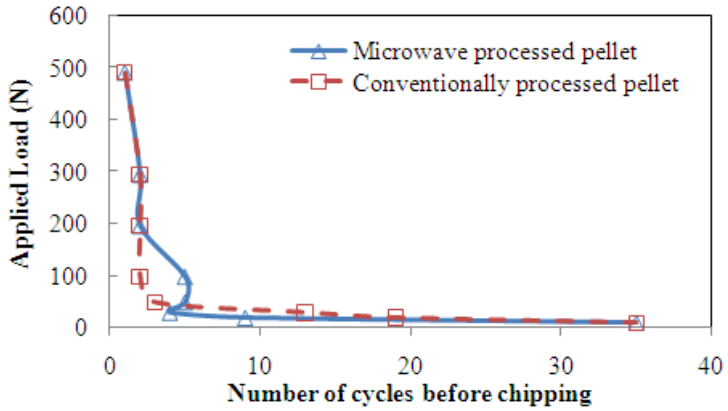

Figure 7: Fatigue curve for 8YZ: load vs. number of cycles before the formation of lateral chips.

It can be observed that the number of cycles required to cause chipping of the indentation increased as the indentation load decreased. At a load of 100N, the microwave processed sample survived a greater

number of cycles when compared to the conventionally processed pellet. In the above plot, a threshold indentation load level (fatigue limit) was not observed.

Strength Testing

Samples of the 1300°C 8YZ samples were halfed longitudinally using a diamond blade saw[1] and mounted into an epoxy resin which was allowed to cure for 9 hrs. These samples were subjected to series of coarse polishing through a standard progression of SiC papers (180, 320, 400, 600, and 1000 grits). Fine polishing was done using 15, 6 and 1 micron diamond suspensions in oil. The only problem that was encountered during polishing was the diamond suspensions which were in the size range of 15 to 1 μm. As the conventionally processed pellet had a porosity of ~ 30 %, the presence of these pores made polishing difficult. The microwave-processed pellet presented no problem during polishing as there was less porosity (~ 10 %). Vickers hardness testing was performed on the microwave-processed sample along several places across its cross section. The results can be shown in Figure 8.

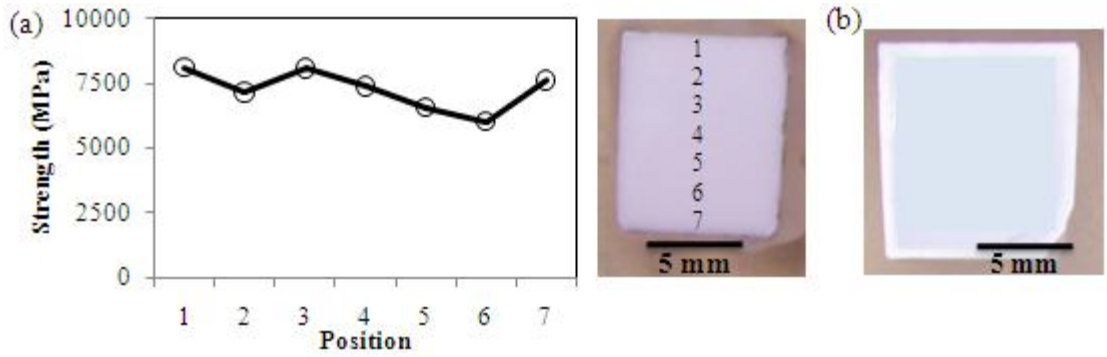

Figure 8: (a) Strength vs. position for a microwave-processed sample; (b) conventionally processed sample showing absorption of diamond paste (blue area).

Figure 8a is a plot between strength and position of indent across the sample surface. These positions are shown in photograph of the actual sample. The average hardness across the sample is 7260 MPa. Figure 8b is an image of a conventionally processed sample. Due to the presence of pores, the 15 μm diamond paste was absorbed into the sample surface and turned it blue. It can also be observed in Figure 8b that the diamond paste was absorbed all along the sample except the edges. This observation implies that the porosity is different on the edges from the interior of the sample. As fine polishing was unsuccessful for the conventionally processed sample, there was no perfect indentation measured during hardness testing; therefore, a one-to-one comparison between the pellets could not be performed.

A similar set of samples were sent to ASU for high-temperature compression testing. Compression testing was done on ~ 4 mm disks that were cut from the pellets using a diamond wafering saw. These disks were quartered using the same saw. These quarters were then ground into small rectangular parallelepipeds (~ 2.5 mm x 2.5 mm x 2.7 mm) using a 6 μm diamond-impregnated grinding disk followed by 600 grit SiC paper. Uniaxial compression testing was performed at ambient temperature using a servo-hydraulic load frame[2]. A custom made self-aligning fixture with a displacement rate of 0.002 in/min was used for testing. Compression testing was also performed at an intermediate temperature (800^{o}C) in a gettered ultra-high purity argon atmosphere. The results are presented in Figure 9.

[1] Buehler Isomet 1000

[2] Instron 1331

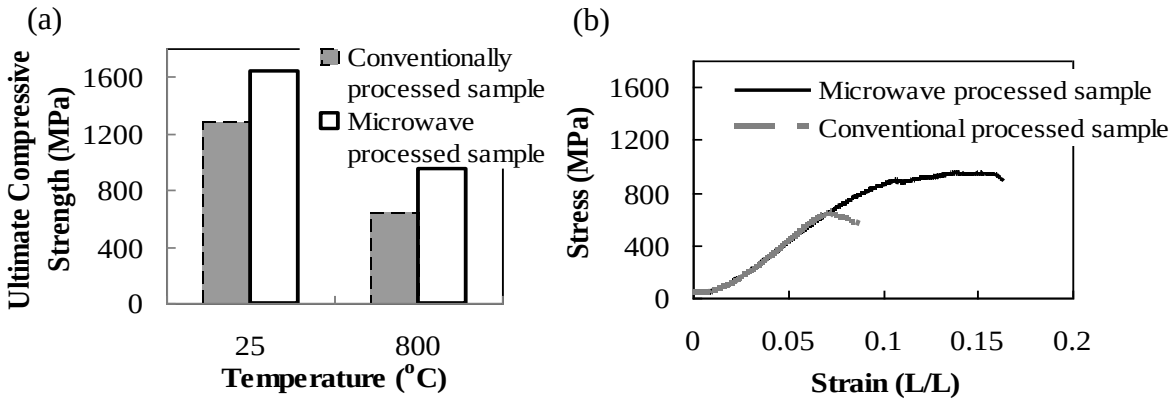

Figure 9: (a) Comparison of strength for 8YZ at 25°C and 800°C; (b) engineering stress-strain plot at 800°C.

At 25°C (Figure 9a), the microwave-processed sample showed a higher compressive strength (1600 MPa) then a conventionally processed sample (1300 MPa). Even at higher temperatures, the microwave-processed samples dominated in strength as compared to the samples processed conventionally. Figure 9b is the engineering stress and strain plots at 800°C. It can be observed that the microwave-sintered sample showed an increased capacity for damage accumulation. This data suggests that the mechanical behavior of the sample processed using microwave energy is different.

At Virginia Tech, microhardness testing was performed on two similarly dense pellets (~ 96 % TD) that were processed using different conditions to study the effect of processing technique on strength. The results can be seen in Figure 10.

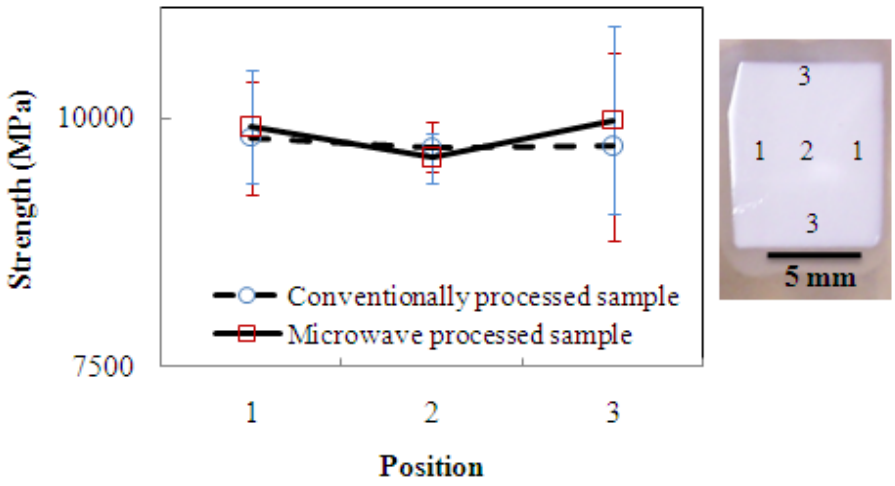

Figure 10: Strength vs. position for ~ 96 % TD samples.

Task 5: Identification of Optimum Processing Parameters

Work was proposed on the use of particle size control for increasing green density. This area was a significant research topic and was proposed in a NERI-C submission from Arizona State University, Georgia Tech, the University of Tennessee, and Virginia Tech as the lead organization. The proposal was

not granted and other options for funding the work was explored, including two pre-proposals with Los Alamos National Laboratory as the lead institution on one and Virginia Tech on the other. Neither of these pre-proposals resulted in an invitation to submit to the full proposal competition.

It was agreed upon with Dr. McClellan that the best way to proceed with optimizing processing parameters, not just for the 8YZ, but for a wide range of potential fuel compositions, was to continue to focus on the development of the MSC studies. This work was very promising and still is considered to be a viable area of research for the team. A new proposal will be submitted to further develop the MSC project when an appropriate solicitation is announced.

Task 6: Reports and Publications

All project reports were submitted. Additionally, short monthly reports were provided to Dr. McClellan to keep him up to date with the ongoing work.

No patents resulted from this project.

Publications and presentations included the following:

R.R. Thridandapani, D.C. Folz, and D.E. Clark, "Microwave Sintering of Simulated Inert matric Fuel for Generation IV Nuclear Reactors," **submitted for publication** to Ceramics International, July 2010.

R.R. Thridandapani, D.C. Folz, and D.E. Clark, "Effect of Direct Microwave Sintering on Structure and Properties of 8 mol% Y_2O_3-ZrO_2," **accepted for publication** in the *International Journal of Applied Ceramic Technology*, August 2010.

I. Alexeff and T. Meek, "The Effect of Electric Field Intensity on the Microwave Sintering of Zirconia," accepted for publication in *Journal of Materials Science Letters*, October 2010.

R.R. Thridandapani, C.E. Folgar, D.C. Folz, D.E. Clark, K. Wheeler and P. Peralta, "Microwave Sintering of 8 mol% Yttria-Zirconia (8YZ): An Inert Matrix Material for Nuclear Fuel Applications," **published** in the *Journal of Nuclear Materials*, 384 [2] 153-157 (2009).

R. Thridandapani, C. Folgar, D. Folz and D. Clark, "Versatile and Remote Processing of Inert Matrix Material using Microwave Energy," poster **presented** at the UNERI Annual Conference, Idaho Falls, ID, October 6-9, 2008.

R. Thridandapani, C. Folgar, D. Folz, D. Clark, "Sintering of Simulated Inert Matrix Fuels using Microwave Energy," **presented** at the American Nuclear Society Annual Meeting, Anaheim, CA, June 8-12, 2008.

R. Thridandapani, C. Folgar, D. Folz, D. Clark, "Microwave Sintering of Inert Matrix Fuels," **presented** at the American Nuclear Society Student Conference, College Station, TX, Feb. 28 - Mar. 1, 2008

T.T. Meek, K. Gwathney, C. Narula, and L.R. Walker, "High Density Green Pellets of ZrN Fabricated by Particle Processing," Advances in Sintering Science & Technology, Ceramic Transactions, Vol. 209, p. 21 (2010).

R. Thridandapani, C. Folgar, D. Folz, D. Clark, "Sintering of Simulated Inert Matrix Fuel by Microwave Hybrid Heating," **presented** at the American Nuclear Society Annual Conference, Anaheim, CA June 8-12, 2008.

D. Clark, D. Folz, C. Folgar, R. Thridandapani, "Effects of Microwave Processing on Porosity," **published** in the extended abstract book for the Microwave World Congress, Otsu, Japan, August 4-8, 2008.

R. Thridandapani, C. Folgar, B. Sandbrook, D. Folz, S. McGinnis, D. Clark, "Sintering of Inert Matrix Fuel (IMF) Using Microwave Energy," **presented** at the Materials Science & Technology Conference, Detroit, MI, September 2007.

C. Folgar, D. Folz, S. McGinnis, D. Clark, "Temperature Measurements In A Microwave Field," **presented** at the Materials Science & Technology Conference, Detroit, MI, September 2007.

R. Thridandapani, C. Folgar, B. Sandbrook, D. Folz, S. McGinnis, D. Clark, "Sintering of Inert Matrix Fuel (IMF) Using Microwave Energy," **awarded best poster** in fuels category at the GNEP Annual Review Meeting, Phoenix, AZ, October 2007.

C. Folgar, D. Folz, S. McGinnis, D. Clark, "Temperature Measurements in a Microwave Field," **presented** at the GNEP Annual Review Meeting, Phoenix, AZ, October 2007.

D.C. Folz, D.E. Clark, "Potential Advantages of Microwave Processing," **invited presentation** at the 31st Annual Conference on Composites, Materials and Structures, Daytona Beach, FL, January 2007.

D.C. Folz, D.E. Clark, "Potential Advantages of Microwave Processing," **invited presentation** at the Immediate Energy Savings via Microwave Usage in Major Materials Technologies, National Academy of Engineering Workshop, Penn State University, June 2006.