Project No. 10-917

Development of Innovative High Thermal Conductivity UO_2 Ceramic Composites Fuel Pellets with Carbon Nano-Tubes Using Spark Plasma Sintering

Fuel Cycle R&D

Dr. Ghatu Subhash
University of Florida

In collaboration with:
Florida International University

Frank Goldner, Federal POC
Kemal Pasamehmetoglu, Technical POC

NEUP Nuclear Energy University Programs
U.S. Department of Energy

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Abstract

The University of Florida has successfully completed the task of fabricating high thermal conductivity UO_2-CNT fuel pellets using spark plasma sintering. Traditionally uranium oxide powder is sintered at 1600 ^oC with a hold time of about 4 hours. The ramp rate to reach this temperature is around 10 ^oC/min and so the total time for a sintering cycle is around 10 hours. In the current research, a new technique called spark plasma sintering (SPS) is used to sinter UO_2 powders to 96% of theoretical density at temperatures as low as 1050 ^oC within 30 second hold time. The heating rate is at 200 ^oC/min leading to a total sintering run time of only 40 min. The influence of processing variables, microstructural development, mechanical properties and thermal properties were systematically studied by fabricating numerous pellets of various densities and grain sizes. UO_2 pellets with grain size as large of 90 microns were produced without addition of any dopants by increasing time and temperature during sintering. The thermal conductivity of SPS processed pellets were slightly higher than that of the conventionally sintered pellets at similar densities. Finally, net-shaped full size fuel pellets with chamfer and dimple were also fabricated using SPS process.

In the second step, 5 vol% and 10 vol% carbon nanotubes (CNTs) were dispersed in UO_2 powder using a two-step mixing process consisting of sonication and homogenization in organic solvents. The liquid was then evaporated and the dried powder was sintered using SPS to fabricate a high quality, high thermal conductivity UO_2-CNT ceramic matrix composite (CMC). It was found that the composite pellet with 5vol%CNT provided an improvement in thermal conductivity of about 30% over conventional UO_2 pellet. Interestingly, the grain size of the matrix phase (UO_2) in the composite pellet remained the same as the starting powder due to the pinning effect caused by the second phase particles (CNTs).

The project also identified numerous differences and advantages of SPS processing over conventional sintering of UO_2 pellets and documented these results in several papers. The project successfully completed all the proposed tasks and met all of its goals. The project supported 4 graduate students and resulted in four journal papers (two more pending manuscripts), six conference proceedings and numerous presentations at national and international conferences. Three invention disclosures and a provisional patent were filed. The students participating in this research also received 'Innovations in Fuel Cycle Research' Award and 'Best Paper' award at the *American Nuclear Society 2013 Student Conference – Massachusetts Institute of Technology*, and First Place- Graduate Design Competition 2013 ANS Winter Meeting and Nuclear Technology Expo, Washington DC.

Project Description

The purpose of the project was to explore the feasibility of fabricating full size nuclear fuel pellets using a novel processing technique called spark plasma sintering (SPS), also referred to as Field Assisted Sintering Technique (FAST). In this method, the powder to be processed is placed in a graphite die and sintered using a low voltage (5V) and high amperage (3000 A) pulsating current. Due to the rapid pulsating current, rapid Joule heating occurs at the contact surfaces of the powder particles and local temperature reaches close to the melting point of the powder. Upon application of pressure, the powder particles fuse together forming a sintered compact. SPS is a relatively newer technique and in recent years it has become increasingly a popular method for processing of difficult-to-sinter powders, such as uranium oxide.

The proposed project identified the following Milestones and Deliverables in the original proposal.

1. Milestone: Sintering of UO_2 pellets and determination of processing parameters in SPS.
   Outcome→ (i) SPS processing conditions for UO_2 pellets with optimal microstructure and mechanical properties.
   (ii) Comparison of microstructure and mechanical properties of SPS sintered UO_2 pellets with UO_2 produced by traditional methods. The data for the latter will be taken from the literature.
2. Milestone: Sintering of UO_2 and CNT mixtures from ball milling and in-situ growth processes.
   Outcome→ (i) UO_2-CNT composite pellets with uniformly disbursed CNTs in a UO_2 matrix
   (ii) SPS processing conditions for successful sintering of UO_2-CNT composites with desired microstructures (grain size and porosity) and uniform distribution of CNTs
   (iii) Mechanical and microstructural data for the UO_2-CNT composites as a function of volume fraction of CNTs
3. Milestone: Thermal conductivity measurements on selected UO_2-CNT composite pellets at temperatures up to 600 ^{o}C.
   Outcome→ (i) Thermal conductivity data for UO_2-CNT composite pellets as a function of temperature and volume fraction of CNTs.
   (ii) Establish relationship between microstructure, volume fraction of CNT, distribution of CNT, thermal conductivity values and mechanical properties.

All of the above milestones have been met successfully. In the following, a brief discussion of the tasks undertaken, research conducted, and the results are presented.

Task 1: SPS Processing of UO_2 Pellets

Sintering of the UO2 powder was performed in a graphite die using a Dr. Sinter® SPS-1030 system, see Fig.1. A systematic study of processing variables was performed by varying heating rate, maximum temperature, hold time, and axial pressure to investigate the evolution of grain size and density. These details are provided in Ge et al., (2013, 2014). A typical process parameter profile, pellets produced for characterization, and their microstructure are shown in Fig.2. The processing profile in Fig.2(a) reveals that the desired maximum sintering temperature is reached in 10 min and held for 30 sec at that temperature when the axial pressure is applied. The temperature is then turned off

to allow cooling of the pellet in the die. Upon cooling, the pellet is removed (Fig.2(b)) and the surfaces were polished and thermally etched to reveal the grain boundaries and intra granular porosity as shown in Fig. 2(c).

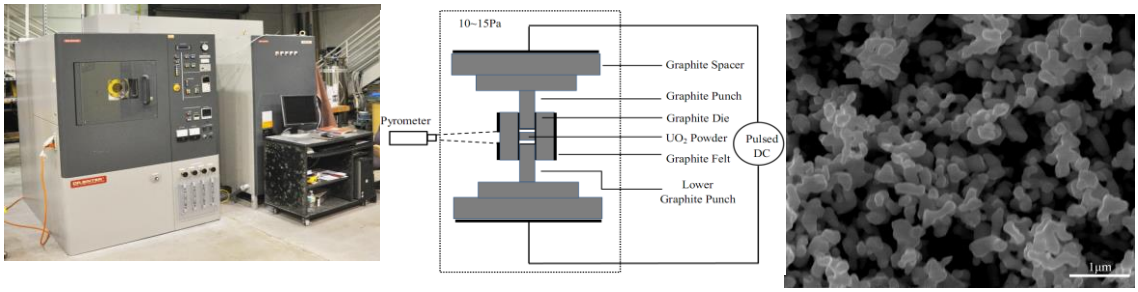
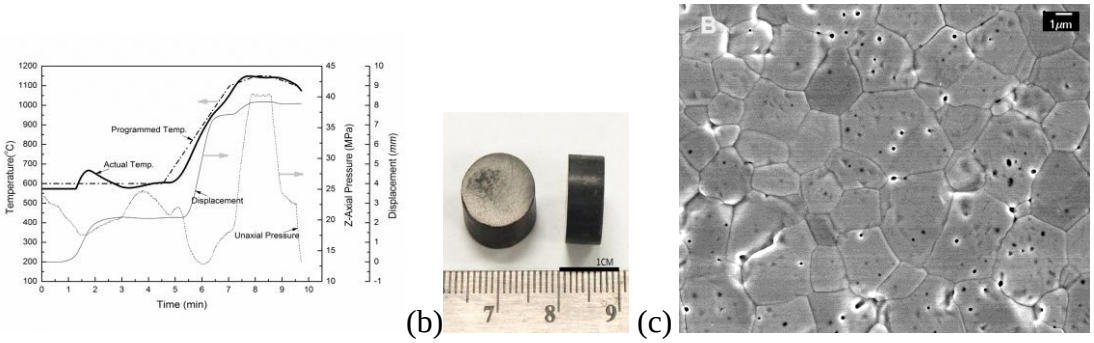


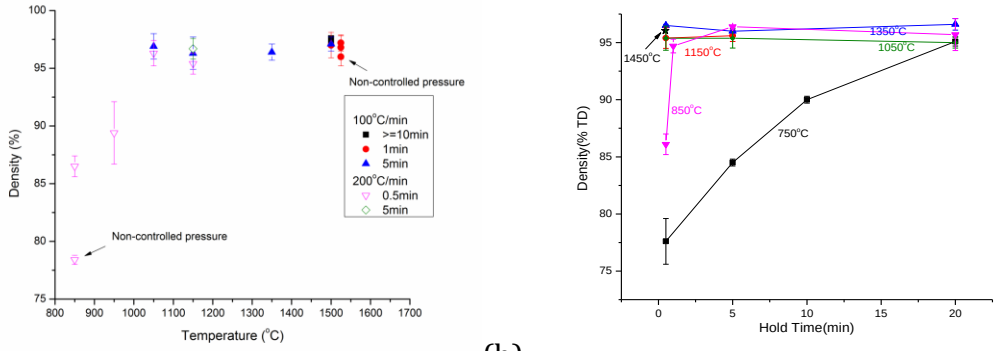
Fig.1. SPS machine, schematic of the graphite die assembly, and the starting UO_2 powder.



(a) (b) (c)

Fig.2. (a) Typical sintering profile, (b) pellets produced, and (c) microstructure revealing intragranular porosity.

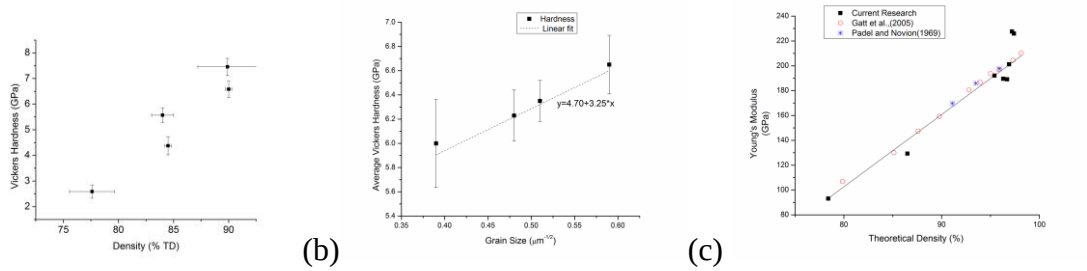
The dependence of pellet density on heating rate (100 °C/ min and 200 °C/min), maximum sintering temperature (between 850-1100 °C), and hold time (0.5 - 5 minutes) was investigated by fabricating pellets with a range of densities and grain sizes. It was found that higher temperatures provide the desired 96% density more rapidly than lower temperatures at longer hold times, see Fig.3. High density pellets can be produced at a temperature as low as 1050 °C with a hold time of only 0.5 min.



(a) (b)

Fig. 3. (a) Evolution of density as a function of temperature and (b) hold time. Note that at even at 1050 °C with only 0.5 min hold time, a density of 95% is achieved.

Vickers hardness as well as density and ultrasonic wave velocities (to determine Young's modules) were measured on each pellet. From Fig. 4, it is clear that the modulus of the SPS processed pellets is the same as those reported in the literature.



(a) (b) (c)

Fig.4. Vickers hardness and Young's modulus increase with density of pellets. Modulus values are the same as those reported in literature.

The mechanism for formation of intragranular porosity was investigated by sintering a pellet at low temperatures. The micrograph in Fig.5 reveals various steps during SPS processing. Initially, neck formation occurs (step#1) between two adjacent particles. The neck grows larger (step#2) as they come closure. As the densification advances, neighboring particles come closure but the porosity between the particles remains as intergranular porosity (step#3). As the grain coarsening occurs, these pores get trapped within a grain and remain as intragraular porosity (step#4).

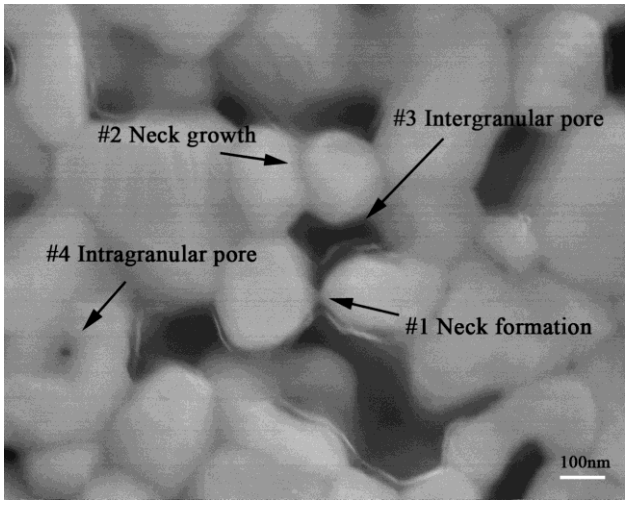
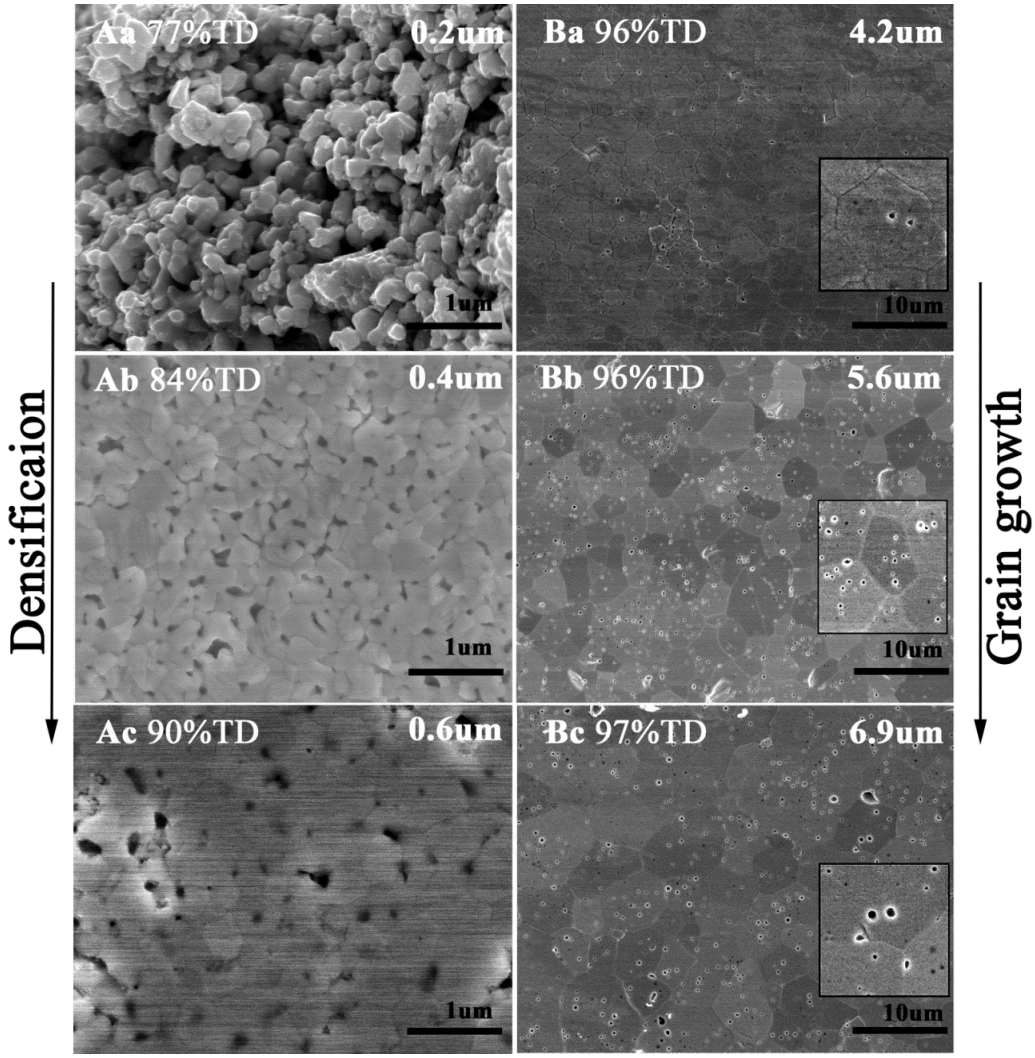
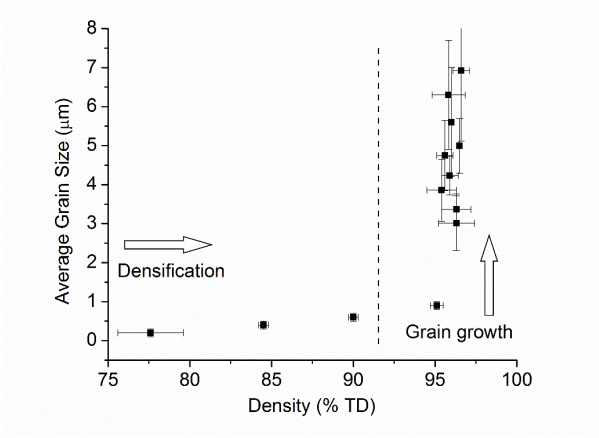


Fig.5. Micrograph illustrating the formation of intragranular porosity during sintering.

Our systematic investigations also revealed that the gran size in the pellet is intimately related to instantaneous density. With increase in density the grain coarsening occurs but not until a density of 95% reached. Until this phase, the grain growth is only marginal, i.e., from 400 nm (original powder particle size) to around 1 micron. Upon reaching a critical density of around 95%, rapid grain growth occurs to around 9 microns and results in the formation of intragranular porosity. These results illustrated in Fig. 6.



(a)



(b)

Fig.6 (a) Images of selected pellets revealing the grain size – density relationship during SPS. Images Aa – Ac reveal densification with limited grain growth and high porosity, whereas images Ba – Bc reveal grain growth at high densities. (b) Grain size and density relationship reveals that no significant grain growth occurs until almost 95% density is reached and rapid grain growth occurs after 95% density is reached.

In the next step, full scale pellets with dimple and chamfer were produced to illustrate the feasibility of the method to manufacture commercial scale pellets. Figure 7, shows a typical pellet with the desired features.

Fig.7. Near-net-shape UO_2 fuel pellet made by SPS

Finally, the ability of SPS to manufacture large grain size pellets was also investigated by varying the processing parameters. Figure 8 shows that pellets with grain sizes as large as 80 microns can be fabricated using this technique.

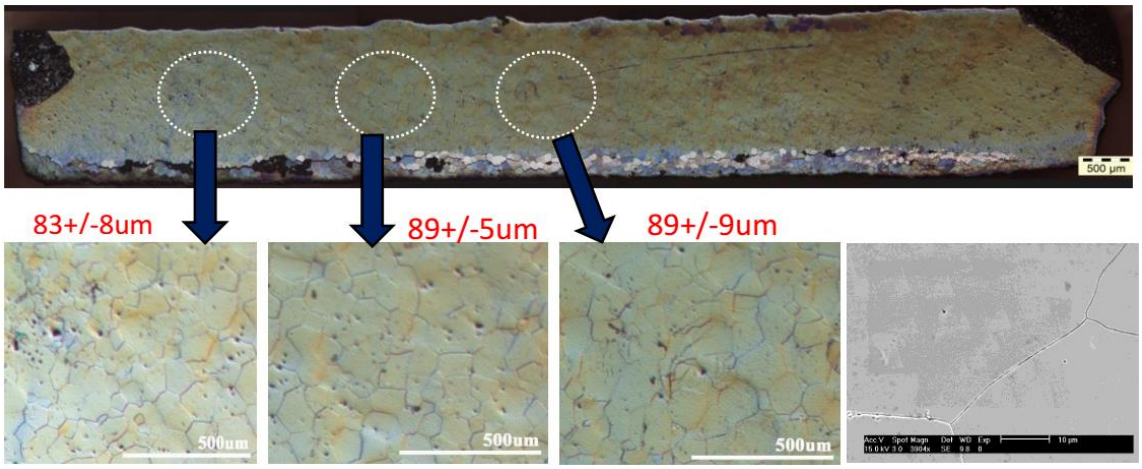


Fig.8. Microstructure of UO2 pellet revealing large grain size with interior porosity. The grain size is indicated at the top of each image. Interior porosity is seen in the SEM image.

Thermal Conductivity Measurements on UO_2 pellets

Thermal conductivity measurements were performed on a large number of pellets produced by SPS using. Thermal conductivity was calculated using the relationship $k = C_p\, \rho\, \alpha$, where k is thermal conductivity (W/m·K), C_p is constant-pressure specific heat (J/kg·K), ρ is density (g/cm^3), and α is thermal diffusivity

(cm^2/s). The thermal diffusivity was measured at three temperatures 100°C, 500°C and 900°C under N_2 atmosphere using laser flash method (Anter Flashline™ 3000). The results are shown in Fig. 9. In general, pellets processed by SPS have shown slightly higher conductivity compared to the values reported in the literature. This is because the literature values are for 95% density and the pellets produced by SPS are at higher density.

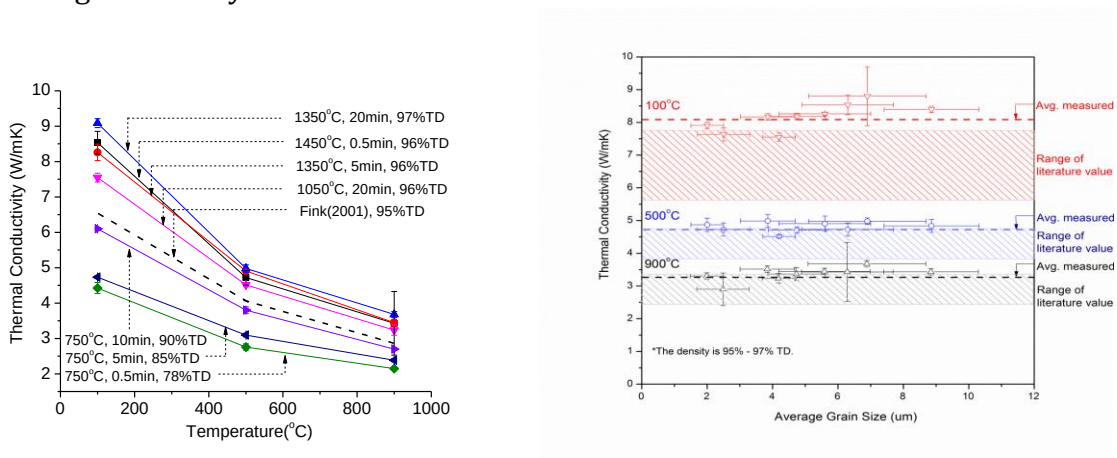


Fig. 9 Measured thermal conductivity of the pellets at 100°C, 500°C and 900°C as a function of temperature and grain size. The processing conditions and densities of the pellets are listed in the legend.

Clearly, it is shown that spark plasma sintering is capable of producing high density pellets with desired shape and size. In the next task we will illustrate our efforts to produce UO_2-CNT composite pellets.

Task 2: Sintering of UO_2-CNT Composite Pellets

The main challenge in this task was to obtain a homogeneous mixture of UO_2 powder and carbon nanotubes (CNTs). Both single wall nanotubes (SWNT) and multiwall carbon nanotubes (MWNT) tend to agglomerate and so dispersing them homogeneously into UO_2 powder is a non-trivial task. Our original research plan called for ball milling and in-situ growth of CNTs on UO_2 powder. However, it was quickly determined that simple ball milling was an inefficient means of dispersing CNTs. Decaflouropentane was used as a dispersing agent during mixing process. The powder was then sintered using SPS at 1500°C with a 5 min hold time and 40MPa pressure. Figure 10 shows scanning electron micrographs of the sintered specimen from ball milled powder revealing large CNT agglomerations characterized by black regions (Fig. 10(a)) and no discernible tubular structure on the agglomerate surfaces (Fig. 10(b)); this microstructure indicates the formation of amorphous carbon which is known to form during ball milling. Therefore, attempts using ball milling were abandoned and other mixing methods were explored.

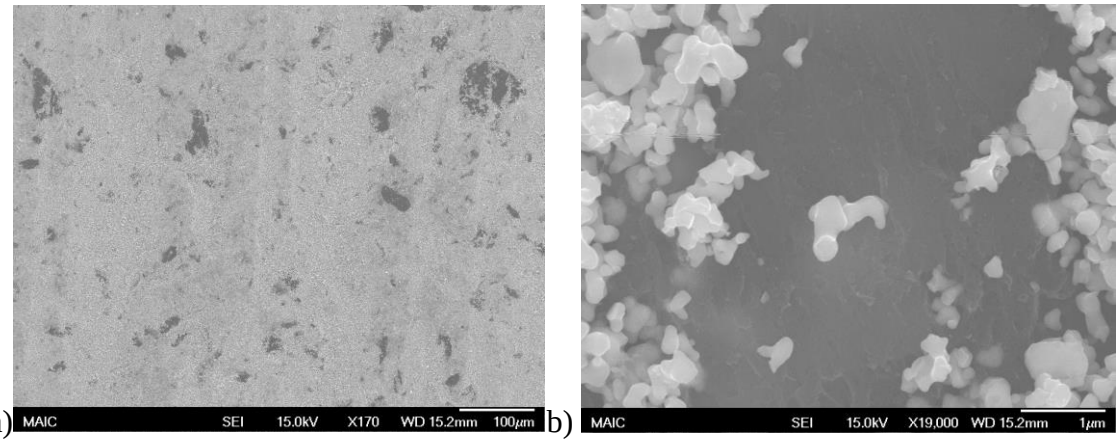


Fig. 10. Micrographs of UO_2-SWNT composite specimens revealing (a) clusters of carbon in the microstructures and (b) high magnification image revealing no discernable CNT structure (amorphous carbon)

The major factors that affect uniform dispersion of CNTs into a matrix are the mixing liquid and the means of physical dispersion. A two-step mixing process was developed in this study: sonication and homogenization. Two mixing liquids were explored: Ortho-dichlorobenzene (ODCB)- an organic solvent that has been shown to aid in the dispersion of CNTs, and ethanol- used extensively in CNT distribution studies. For the homogenization process, either 5 vol% or 10 vol% of CNTs (either SWNT or MWNT) were added to 200mL of solvent that is homogenized using a commercial homogenizer rotating at approximately 7000 rpm. The suspension was then sonicated with a Qsonica3000® Sonicator for 10 minutes. This process has shown to yield a stable dispersion of solvent and CNTs. The UO_2 powder was then added slowly while the solvent is sonicated for an additional five minutes. The liquid was evaporated over 24 hours at 60°C. The mixed powder was observed under microscope to verify if CNTs survived the mixing process intact; Figure 11 shows that the CNTs did indeed survive the mixing process both in ethanol (Fig. 11a) and ODCB (Fig. 11b).

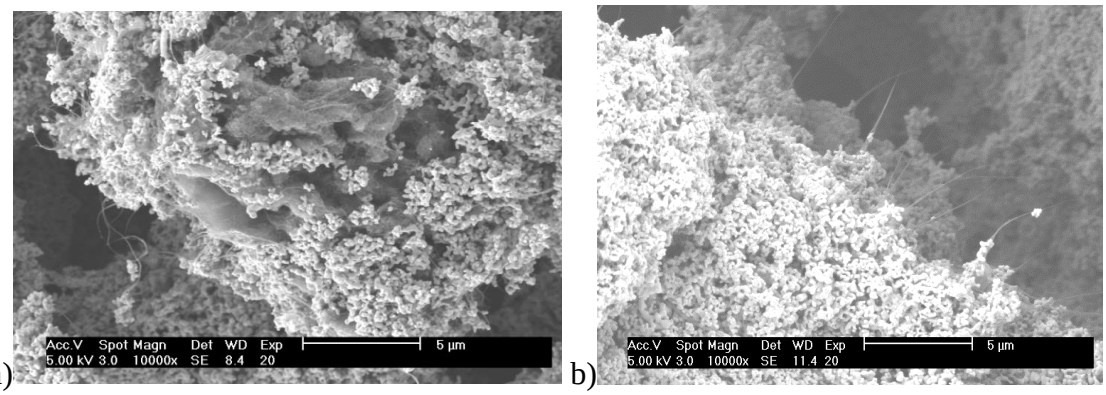


Fig. 11 SEM images revealing good dispersion in UO_2 powder after homogenization and sonication.

The homogenized powders were sintered in SPS at 1400 ^{o}C for 5 min. Figure 12 shows the distribution of CNTs in the sintered pellet and the resulting microstructure

when ethanol was used as a mixing agent. Figures 13 and 14 show the same type of samples mixed with ODCB. These images reveal that ODCB was more effective in achieving enhanced dispersion. Samples produced using ethanol (Fig.12) show incomplete sintering (little to no clear grain structure), and a large bi-modal grain size distribution, see Figs. 12(c) and 12(d). The large difference in grain size is indicative of poor mixing and lack of distribution of CNTs. Uncontrolled grain growth is evident in areas without CNTs or CNT clusters, and tiny grains of the size of the starting powder around CNT clusters.

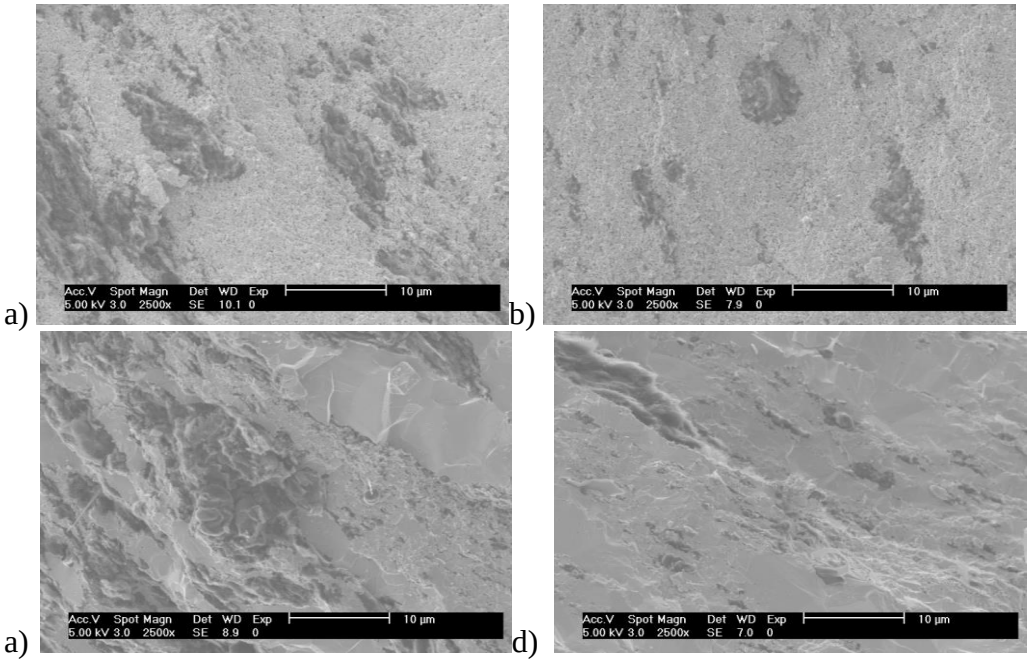


Fig.12 Microstructure and distribution of CNTs utilizing ethanol as a mixing agent where a) 5vol% SWNT b) 10vl% SWNT c) 5vol% MWNT d) 10vol% MWNT

On the contrary, specimens prepared using ODCB as the mixing agent showed smaller grain size differences in Fig. 13. Grain growth beyond the initial starting powder can be seen in all of the images. The homogeneity in grain size can be associated with the increased pinning effect caused by the more homogeneously dispersed CNTs, as seen in Fig.14. In Fig.13(a) the microstructure consists of large grains (up to 10 micron in size) surrounded by small grains of size 500nm – 2micron. The large grains are the result of a lack of CNTs in the vicinity, which allowed grain growth to occur freely. On the other hand, the distributed CNTs in other regions limited the UO_2 grain growth due to their pinning effect. In Fig.13(b) the size of the larger grains was smaller than in Fig. 13(a) due to a better dispersion of SWNT. In both cases, a bi-modal grain size distribution was achieved. Similarly in Fig. 13(c) and 13(d), the grain size distribution is again bi-modal, however, for 10vol% MWNT, the gradient between larger and smaller grains is the lowest. This clearly indicates a better dispersion of MWNTs than the SWNTs in the microstructure. A high magnification image in Fig. 14 reveals that CNTs are present in the regions containing small grains and these CNTs have indeed pinned the grain growth. The typical size of grains in this region is similar to the starting powder size, which is 300-500nm.

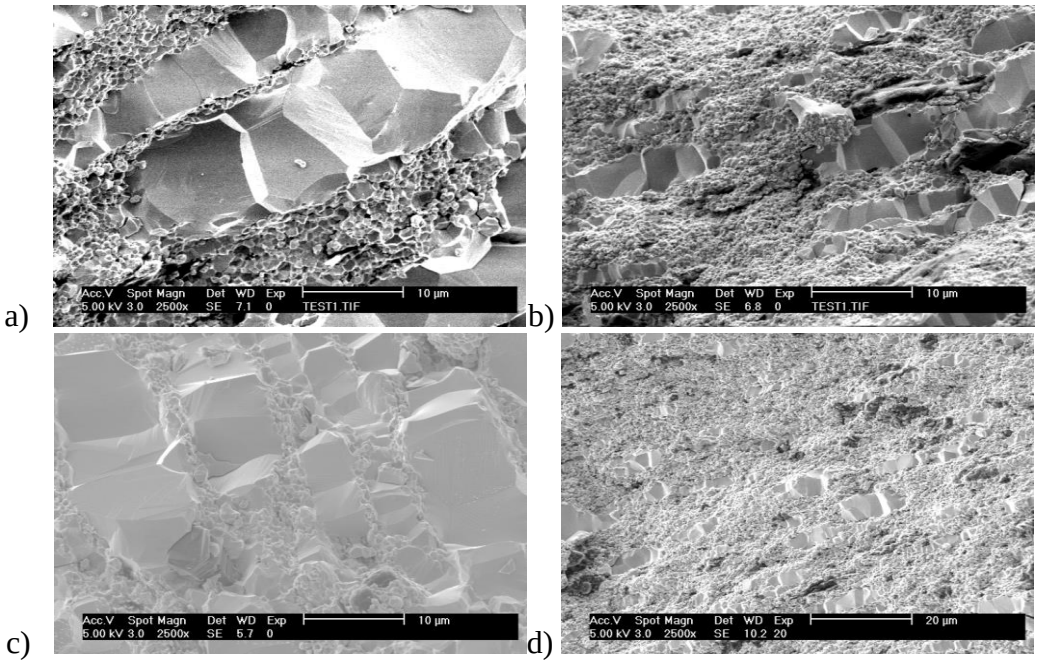


Fig. 13 Microstructure revealing distribution of CNTs utilizing ODCB as a mixing agent with a) 5vol% SWNT, b) 10vl% SWNT, c) 5vol% MWNT, and d) 10vol% MWNT.

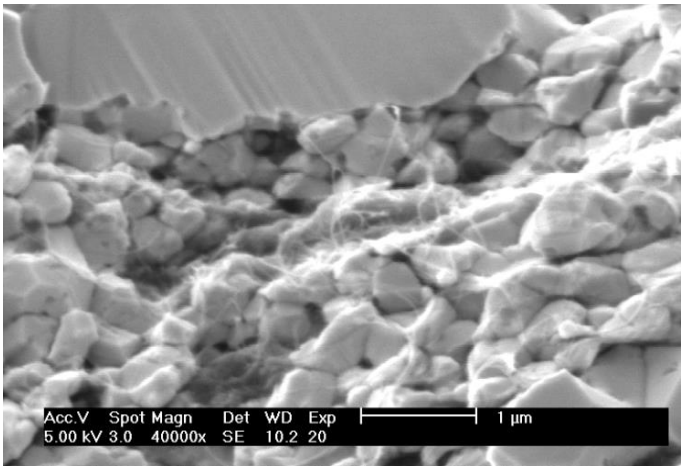
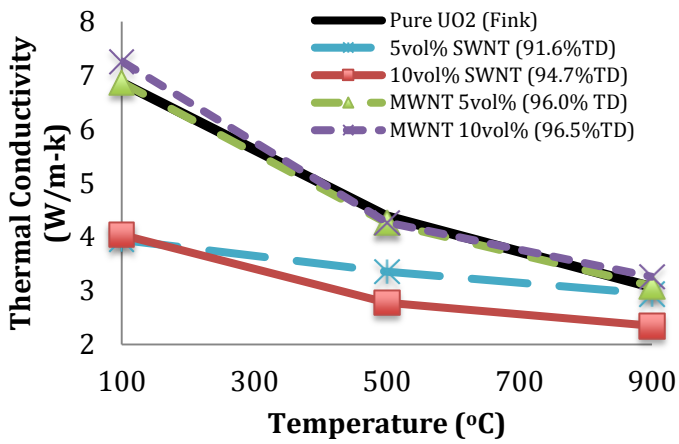


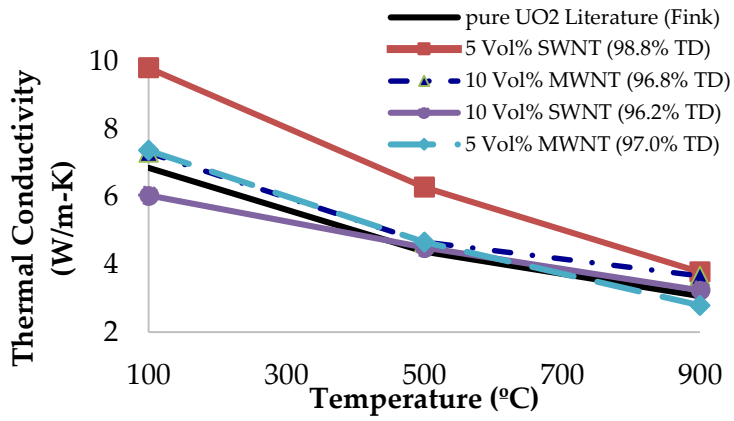
Fig. 14 Image of fracture surface of UO_2 + 5vol% SWNTs revealing CNTs on the smaller grain surfaces

Task 3: UO_2-CNT Pellet Thermal Conductivity

Thermal conductivity values for sintered pellets were measured utilizing an Anter Flashline3000® unit. Conductivity values were recorded for three times at three temperatures (100°C, 500°C, and 900°C). The thermal conductivity for pure UO_2, found in literature, was also plotted for comparison. The thermal conductivity values for pellets made utilizing ethanol and ODCB are provided in Fig. 15. Note that the sintered UO_2-CNT composites show a trend similar to pure UO_2 with respect to temperature, i.e., a gradual decrease in thermal conductivity as temperature increases.



(a)



(b)

Figure 15: (a) Thermal conductivity values of (a) ethanol mixed samples revealing a lower value than pure UO_2 conductivity and (b) ODCB Mixed Samples revealing a higher thermal conductivity than UO_2.

As explained previously, a more homogeneous CNT distribution, as seen in Fig. 14, helps reduce the probability of CNT-CNT interactions and provides better thermal properties in the composite. The ethanol mixed samples had clusters of CNTs present in the microstructure and revealed a lower thermal conductivity, see Fig 15(a). Another factor that contributed to the low thermal conductivity values of ethanol mixed samples was low density (below 95%TD with SWNTs). MWNT samples mixed with ethanol showed densities greater than 95% TD, however, poor distribution and the presence of large clusters, prevented the thermal conductivity from increasing beyond that of pure UO_2. Since thermal conductivity is linearly correlated to density, maximizing density is key to ensuring a high quality composites. Utilizing ODCB as a mixing agent and 5 vol% SWNT, a 29.7% increase in thermal conductivity of the composite, relative to UO_2 literature value, is observed, see Fig.15(b). This can be attributed to a relatively more uniform microstructure and higher density (98.8% TD), which is indicative of better CNT distribution and fewer CNT-CNT interaction sites.

Summary

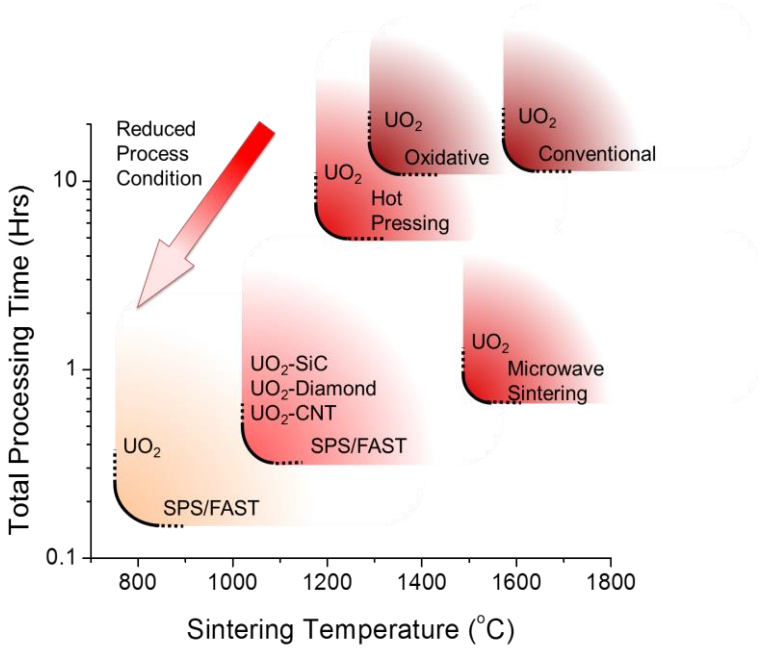
Processing of UO_2 using SPS offers numerous advantages over conventional sintering: significantly reduced processing time, lower sintering temperature, as well as good mechanical properties and thermal conductivity similar to those of conventionally sintered pellets. It can also provide control of grain size and porosity distribution. Near net-shaped pellets can be produced in a short duration. The advantages of SPS extend to all three stages of the sintering process as summarized in Table 1.

A mixing procedure for uniformly distributing CNTs in UO_2 powder has been developed. The sintered pellet clearly reveals uniform UO2 grain size (with occasional large grains) and well distributed CNTs. The thermal conductivity of the UO_2-5vol% CNT composite is higher than the UO_2 pellet. In our other on-going studies difficult-to-sinter powder mixtures such as UO_2-SiC and UO_2-Diamond have also been processed successfully.

Table: Comparison of SPS and conventional sintering techniques

Sintering stage	Feature	SPS	Conventional
Pre-sintering	Modification to starting powder	Not required	Required
	Cold compaction of green body	Not required	Required
Sintering	Temperature ramp rate	50-200℃/min	2-10℃/min
	Maximum sintering temperature	750-1450℃	1600-1700℃(H_2) 1200-1400℃(Oxidative)
	Hold time	0.5-20 min	1-10 hrs
	Total sintering run time	<1hr	~15 hrs.
	Pressure	20-80 MPa	No
	Sintering environment	Vacuum (~10Pa)	Gaseous environment
	Dimensional control	Yes	Limited
	Pellet stoichiometry during sintering	Changed	Unchanged
	Control of Grain growth	High	Low
	Ability to produce near net shape pellets	Yes	Limited
	Ability to sinter difficult-to-sinter materials	Yes	Limited
Post-sintering	Requires reduction of sintered pellet to desired stoichiometry	No (if initial powder is at the right stoichiometry)	Yes
	Pellet requires additional machining to obtain desired final dimensions	May not be required	Yes

Finally, a survey of the literature on processing times and temperatures of SPS with other sintering techniques such as microwave sintering, hot pressing and conventional sintering was conducted. Once again, SPS offers significant advantages over the other methods as illustrated in the Fig. 16 below.



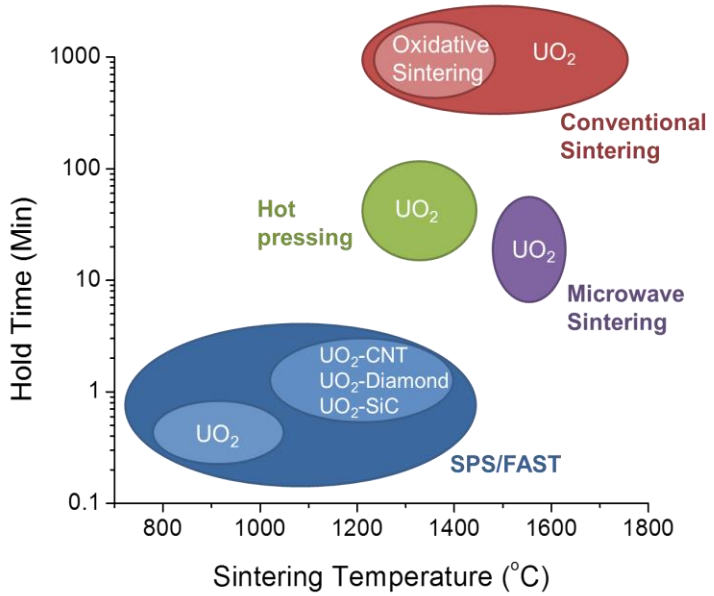


Fig.16 Comparison of total processing time (on the top) and hold time (on the bottom) for sintering of high-density UO_2 related nuclear fuel pellets between various sintering techniques.

Peer-reviewed Journal Articles

1. L. Ge, G. Subhash, R.H. Baney, J. Tulenko, "Influence of processing parameters on thermal conductivity of uranium dioxide pellets prepared by spark plasma sintering" *Journal of European Ceramic Society* 34 (2014) 1791-1801.
2. L. Ge, G. Subhash, J. Tulenko, R. Bane, and E. McKinna, "Densification of Uranium Dioxide Fuel Pellets Prepared by Spark Plasma Sintering (SPS)" *Journal of Nuclear Materials*, 435(2013) 1-9.
3. S. Yeo[+], E. McKenna, R. Baney, G. Subhash* and J. Tulenko, "Enhanced Thermal Conductivity of Uranium Dioxide-Silicon Carbide Composite Fuel Pellets Prepared by Spark Plasma Sintering (SPS)" *Journal of Nuclear Materials*, 433 (2013) 66-73.
4. S. Yeo[+], R. Baney, G. Subhash* and J. Tulenko, "The influence of SiC particle size and volume fraction on the thermal conductivity of spark plasma sintered UO2-SiC composites, *Journal of Nuclear Materials* 442 (2013) 245-252
5. A. Cartas, H. Wang, R. Baney, G. Subhash, J. Tulenko, "Influence of Carbon Nano-tube (CNT) Dispersion in UO2-CNT Ceramic Matrix Composites Utilizing Spark Plasma Sintering" *Journal of Nuclear Technology (*Submitted, Dec 2013)
6. L. Ge, G. Subhash, J. Tulenko, "Processing of large grain size UO2 pellets using Cr2O3 and ZrB2 dopants" (in preparation)

Conference Proceedings

1. G. Subhash, S. Yeo, and L. Ge, J. Tulenko, R. Baney, "Comparison of SPS versus Conventional Sintering of Accident Tolerant UO2-Composite Fuel Pellets" Transactions of the ENS Conference "LWR Fuel Performance/Top Fuel" Charlette, NC, 15-19, Sept 2013.
2. D. Permar, A Cartas, S. Yeo, L. Ge, J. Tulenko, R. Baney, G. Subhash, "FRAPCON 3.4 to determine enhanced performance of UO2 composite fuel fabricated by spark plasma sintering" *American Nuclear Society 2013 Student Conference – Massachusetts Institute of Technology* Boston, Massachusetts, USA, April 4-6, 2013, on CD-ROM, American Nuclear Society, LaGrange Park, IL (2013) [This paper received 'Innovations in Fuel Cycle Research' Award].
3. A. Cartas, D. Permar, J. Kuntawala ,J. Tulenko "An Innovative Accident Tolerant UO2 Composite Fuel for Use in LWRs" 2013 ANS Winter Meeting and Nuclear Technology Expo, Washington DC, Nov. 2013. Received First Place- Graduate Design Competition
4. A. Cartas, D. Permar, S. Yeo, L. Ge, J. Tulenko, G. Subhash, R. Baney "Fabricating the Next Generation of Nuclar Fuels" Conference Paper, ANS Student Conference at M.I.T, April 4-6, Boston, MA (2013). Received Best Paper Award.
5. A. Cartas, J. Tulenko, R. Bane, G. Subhash "Processing of UO2-CNT Ceramic Matrix Composites Utilizing Spark Plasma Sintering" 2013 ANS Winter Meeting and Nuclear Technology Expo, Washington DC, Nov. 2013.
6. S. Yeo, E. Mckenna, R. Baney, G. Subhash, J. Tulenko, "Fabrication Strategies and Thermal Conductivity Assessment of High Density UO2 Pellet Incorporated with SiC", 2012 MRS Spring meeting proceedings
7. G. Subhash, J. Tulenko, R. Baney, S. Yeo, A Cartas and L. Ge, "Development of Innovative High-Thermal Conductivity UO2-Ceramic Composite Fuel pellets with Silicon Carbide Whiskers using Spark Plasma Sinternig" Transactions of the ENS Conference "Top Fuel-Reactor Fuel Performance 2012" Manchester, UK 2-6 Sept 2012.

8. L. Ge, G. Subhash, J. Tulenko and R. Baney, “Rapid Denisfication of UO2 Pellts using Spark Plasma Sintering” Transactions of the ENS Conference, Top Fuel-Reactor Fuel Performance 2012, Manchester, UK 2-6 Sept 2012.

Technical Presentations

1 "Fabrication and Properties of High Thermal Conductivity UO2, UO2-SiC, UO2-Diamond, and UO2-CNT composites using Spark Plasma Sintering" 2014 TMS Annual Meeting & Exhibition, San Diego, CA Feb 16-20, 2014.

2 "Processing of High Thermal Conductivity UO2-Composites using Spark Plasma Sintering (SPS)" 38th International Conference on Advanced Ceramics and Composites, Daytona Beach, FL, January 26-29, 2014

3 “Comparison of SPS versus Conventional Sintering of Accident Tolerant UO2-Composite Fuel Pellets” “LWR Fuel Performance/Top Fuel” Charlette, NC, 15-19, Sept 2013.

4 Spark Plasma Sintering of UO_2: An investigation of densification and microstructure evolution” Presentation, 2013 ICACC meeting, Daytona Beach, USA 28-31st Jan 2013.

5 ASME-IMECE2012-85558“Processing-Structure-Property Relationships in SPS Sintered High Thermal Conductivity UO2-SiC Pellets” Nov 11-15, 2012, Houston, TX

6 "Structure and Property Relationship in Spark Plasma Sintered UO2 pellets" ICACC-S13-009-2012, Jan 22-27, 2012, 36th ICACC in Daytona Beach, FL

7 “Densification and microstructure characterization of UO_2 processed by spark plasma sintering” Presentation, 2012 MRS fall meeting, Boston, USA 25-28th Nov 2012.