

Project No. 09-773

# Developing a High Thermal Conductivity Fuel with Silicon Carbide Additives

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Integrated University Programs

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**“Developing a High Thermal Conductivity Fuel with Silicon Carbide Additives.”**

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**1. Abstract**

Enhanced thermal conductivity oxide fuels offer increases in both safety and efficiency of commercial light water reactors. Prior to the beginning of this present research, work was attempted by Purdue researchers to produce thermally conducting fuel by incorporating a polymeric precursor of SiC into porous fuel by the SiC polymeric precursor route infiltration/pyrolysis (PIP). Also, prior to this present project, efforts at the University of Florida (UF) to incorporate SiC whiskers by pressure sintering had also failed to yield fully dense pellets. Early in this project, strategies to overcome the failure of the PIP process by vacuum infiltration and replace the pressure sintering by oxidative sintering in the SiC whisker composites by the UF research team also proved unsuccessful in producing fully dense fuel pellets. A new processing technique, Spark Plasma Sintering (SPS), became available and was tried with the UO<sub>2</sub>-SiC composites. Immediately, it was recognized that the SPS process yielded fully dense UO<sub>2</sub>-SiC composite pellets.

Low-temperature oxidative sintering and Spark Plasma Sintering (SPS) techniques with SiC powder and whiskers have been used to produce UO<sub>2</sub>-SiC composite pellets. In the UF research, oxidative sintering was performed for 4 hours at 1200~1600°C and SPS sintering was employed only for 5 min. at the same temperature. While oxidative sintering failed to achieve enhanced thermal conductivity, the SPS sintered pellets obtained promising features such as higher density, better interfacial contact, reduced chemical reaction and improved thermal conductivity. Thermal conductivity measurement at 100°C, 500°C, and 900°C for SPS sintered UO<sub>2</sub>-10vol% SiC composite pellets revealed a maximum 62% higher thermal conductivity value, when compared to UO<sub>2</sub> pellets. These results show that SPS processing is an effective technique to achieve high density, high thermal conducting UO<sub>2</sub> pellets.

**2. Introduction**

The development of enhanced thermal performance of UO<sub>2</sub> ceramic fuel has been regarded as a major priority in the research of nuclear power technology. Despite the

availability of numerous types of nuclear fuels (metals, MOX, nitrides, etc), commercial reactors globally are fueled by Uranium Dioxide ( $\text{UO}_2$ ). It is the fuel of choice for several reasons.  $\text{UO}_2$  has a high melting point and enhanced oxidation resistance<sup>[1]</sup>. Also,  $\text{UO}_2$  behavior has been studied in much more depth throughout different power cycles. A major disadvantage, however, is a low level of thermal conductivity for  $\text{UO}_2$  based fuels, which causes both a steep temperature gradient and a high centerline temperature for the fuel pellets during power operation.

Due to the steep pellet temperature gradient and resultant high centerline temperature, a variety of undesirable phenomena are induced. Important structural components of the fuel, such as pores, oxygen, and fission products, are redistributed from a uniform condition<sup>[2]</sup>. Thermal stress, caused by the large temperature gradient results in either cracking in a low temperature region or plastic deformation in the high temperature region. Fission gas release due to the steep temperature gradient diminishes the safety of a reactor during normal operation and short-term excursions.

The concept of incorporating high thermal conductivity material such as SiC, into a  $\text{UO}_2$  pellet has been reported<sup>[3-4]</sup>. Silicon carbide has sixty times the thermal conductivity of uranium dioxide at room temperature<sup>[5]</sup>. Moreover, it has a low thermal neutron absorption cross section, a high melting point, and good irradiation, as well as chemical stability.

Two approaches have been employed to enhance thermal conductivity. One is to incorporate a thermally conducting phase into a matrix in a way such that there is a continuous pathway of the highly conducting phase through the matrix. The point where the pathway is completed is referred to as the percolation threshold. Early work for enhancing the thermal conductivity of  $\text{UO}_2$  based fuels was largely directed at strategies to engineer open continuous porosity  $\text{UO}_2$  which was then backfilled with a gas or liquid precursor to the conducting phase<sup>[3]</sup>. This strategy proved to be a challenge because narrowing points into any pore structure would narrow further and eventually blocking the formation of a continuous percolation network of the conducting phase.

The second approach was to form a composite of a highly thermally conducting phase, such as SiC with the  $\text{UO}_2$ , and then depend on the “rule of mixtures” to increase the thermal conductivity. The rule of mixtures essentially states that the thermal conductivity of a mixture should be the mean of the volume percent of the thermal conductivities of the components if the two phase were in tight contact with each other.

During the early phase of this research, the ceramic sintering process, SPS, became

available at the University of Florida. In this research work, both low-temperature oxidative sintering<sup>[6]</sup> and the SPS techniques were employed to fabricate UO<sub>2</sub>-SiC composite pellets and compare the resulting microstructures and properties. The term oxidative sintering refers to sintering of hyper-stoichiometric uranium dioxide powder. In the oxidative low-temperature sintering, the UO<sub>2</sub> powder is co-sintered with SiC powder or whiskers by increasing the O to M ratio of the starting powder to an optimum value of 2.25<sup>[7]</sup>. This enhanced sinterability is due to the increased diffusivity of Uranium atoms through vacancies.

Spark Plasma Sintering (SPS) or Field Assisted Sintering Technique (FAST) has recently gained significant interest in numerous research fields<sup>[8-10]</sup>. Although many advanced features are achievable using this technique no reported literature exists for the fabrication of UO<sub>2</sub> fuel using SPS or its relevant composites. In SPS<sup>[11]</sup> a high amperage (up to 3000 Amp) pulsed DC current is passed through the powder compact resulting in joule heating at the inter-particle contact areas. There is a discussion in the literature whether or not plasma is created due to this spark discharge between the particles<sup>[12]</sup>. Regardless, intense heat is generated at the particle contacts, which bonds them together in a very short time. With application of pressure, high density compacts can be produced to a controlled outer diameter. Lastly, the electric field and pulsed direct current induce spark discharges at the inter-particle contacts that removes surface contaminants and absorbed species such as CO<sub>2</sub> and H<sub>2</sub>O from the particle surface, thus improving the grain-boundary diffusion processes<sup>[13]</sup>.

### 3. Powder Preparation

The uranium dioxide (UO<sub>2.11</sub>) powder used in our research was obtained from AREVA, Hanford, WA. The powder was reported to have a bulk density of 2.3g/cm<sup>3</sup>, tap density of 2.65g/cm<sup>3</sup>, mean diameter of 2.4µm, and a surface area from gas absorption method<sup>[14]</sup> (BET surface area) of 3.11m<sup>2</sup>/g. Hyper-stoichiometric UO<sub>2.25</sub> was produced by heating the starting powder in air at 350°C for 27 hours to produce U<sub>3</sub>O<sub>8</sub> and then mixing it back with the starting powder (UO<sub>2.11</sub>) at a 30:70 weight ratio.

Both SiC whiskers (SiCw) and SiC powders (SiCp) were used in this investigation to produce UO<sub>2</sub>-SiC composite pellets. The β-SiC whiskers (3C-SiC) were obtained from Advanced Composite Materials, Greer, SC (SC-9D, deagglomerated SiC whiskers) with an aspect ratio, a diameter, and a length exceeding 10:1, 0.65 µm, and 10 µm, respectively. The β-SiC powder (3C-SiC), with the mean diameter of 1µm, was obtained from Alfa Aesar Inc., Ward Hill, MA. Figure 1 shows SEM images of both as received β-SiC whisker and powder

morphologies.

The  $\text{UO}_2$  and SiC were blended with the aid of 2,3-Dihydroperfluoropentane in a SPEX 8000 shaker for 1 hour. After mixing, the blending aid was allowed to evaporate in a fume hood, leaving no residual contamination. This process resulted in a homogeneous dispersion of SiC whiskers and powder particles in the  $\text{UO}_2$  matrix, as will be further discussed later.

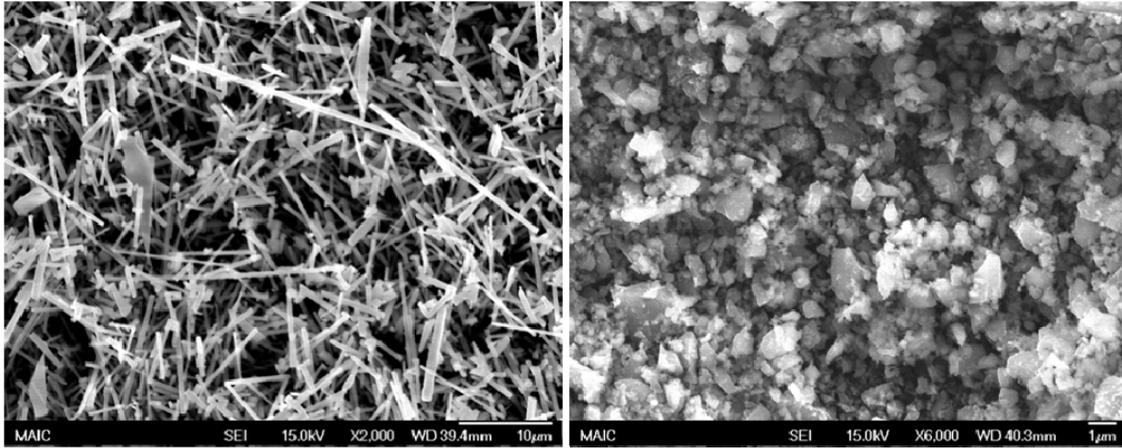


Figure 1. Morphologies of SiC whiskers and powder as procured from the manufacturers.

## 4. Experiments

### 4.1 Oxidative Sintering

For the oxidative sintering process, green body pellets were made by compressing the blended  $\text{UO}_2$ -SiC powder at 200 MPa for 10 minutes in a stainless steel die. The die walls were lubricated with a film of stearic acid to prevent fracture of the green body pellets while being removed from the die. The pellet diameters were 12.7mm. The green body pellets were then sintered in an alumina tube furnace with a ramp rate of  $2.6^\circ\text{C}/\text{min}$  until the temperature reached the maximum temperatures,  $1200\text{-}1600^\circ\text{C}$ , where they were then held for 4 hours. To maintain a hyper-stoichiometric state, an ultra high purity (UHP) Argon gas atmosphere, with a continuous flowing rate of 2 liter/min, was maintained in the furnace during the sintering process.

### 4.2 Spark Plasma Sintering

Spark plasma sintering was performed in a Dr. Sinter<sup>®</sup> SPS-1030 system, see Figure 2. For SPS, the blended material was loaded into a 12.7mm diameter graphite die. The inner die surface was covered by a thin graphite foil to prevent reaction of the  $\text{UO}_2$  powder with the die

wall. Cylindrical graphite plugs were inserted into both ends of the die. The end of each plug that contacts the powder was coated with an aerosol of graphite (ZYP Coatings, Inc., Oak Ridge, TN) to prevent reaction of the plug and the powder. The ramp up/down rate was set at 100°C/min and the hold time at the maximum temperature was set at 5 minutes. An axial pressure of 40 MPa was applied at the beginning of the hold time. The maximum sintering temperature was set at 1400°C, 1500°C, and 1600°C for the different pellets.

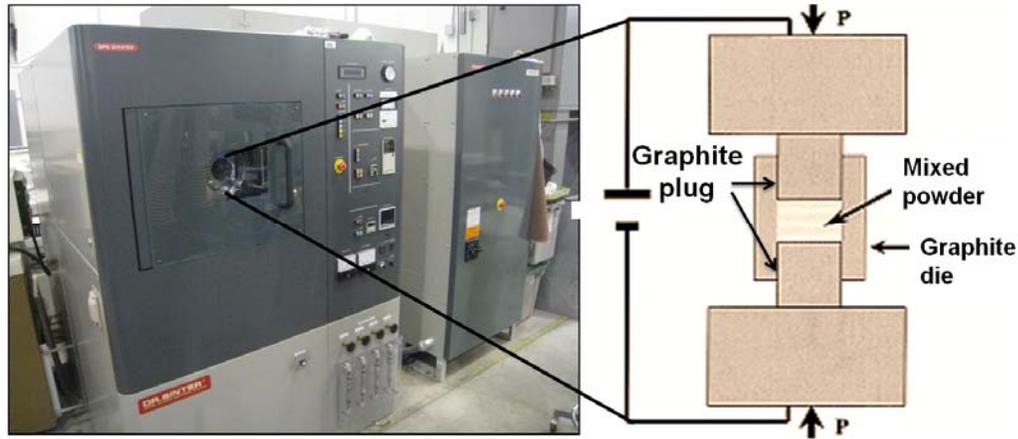


Figure 2. Dr. Sinter<sup>®</sup> SPS-1030 system and schematic drawing of the sintering chamber.

#### 4.3 Reduction Process

After the pellets were sintered by both oxidative sintering and SPS techniques, they were reduced to stoichiometric  $\text{UO}_2$  following the procedure outlined in ASTM C 1430-07. A thermal treatment for the reduction was conducted in a furnace at 800°C for 6 hours, in a 4% $\text{H}_2$ -N gas, with a water vapor atmosphere using a water bath maintained at 35°C. The  $\text{UO}_2$ -SiC composite pellets were fabricated with 10vol% SiC at hold temperatures of 1400°C, 1500°C, and 1600°C.

#### 4.4 $\text{UO}_2$ Sintering

To enable a comparison of properties between the  $\text{UO}_2$ -SiC composite pellets with those of  $\text{UO}_2$  pellets, sintering of  $\text{UO}_2$  pellets was also conducted using both the SPS and oxidative sintering at the same conditions as described before. While low-temperature sintering at 1200~1400°C yielded poor densities in both methods, the pellets sintered at 1500°C and 1600°C yielded the target 96% theoretical density and were used for a comparison of the grain size and the thermal conductivity.

#### 4.5 Thermal Conductivity Optimization

In order to optimize the thermal conductivity of the  $\text{UO}_2$ -SiC composite pellets, four sets of SiC powders with different volumes were mixed with the  $\text{UO}_2$  and the mixtures were sintered by the SPS technique. The volumes of the SiCp were set at 5%, 10%, 15%, and 20%. Sintering with various temperatures was conducted for each set to produce high density and good integrity pellets.

#### 4. Characterization Methods

The characterization of  $\text{UO}_2$ -SiC composite pellets consisted of density measurements, microstructural analysis using scanning electron microscopy (SEM), analysis of grain size and SiC distribution, and U and Si penetration curves along an interface using EDS, determination of the chemical products using XRD, and the thermal conductivity using an Anter Flashline<sup>®</sup> 3000 system...

The density of the  $\text{UO}_2$ -SiC composite pellets was measured by coating a thin layer of paraffin wax to take into account the open porosity and then using the Archimedeian immersion method. The paraffin coated pellet was weighed three times in water and the average density was calculated.

For the microstructural observations using SEM, the pellet surfaces were polished with successively smaller grinding medium down to 0.04 micron of colloidal silica. Grain boundary relief was produced by thermal etching at 1340°C for 4 hours in an Argon atmosphere. Using the secondary electron mode in SEM (JEOL 6335F), 3-5 micrographs of  $\text{UO}_2$ -SiC pellets were taken and the average grain size was measured in each micrograph by the line intercept method<sup>[15]</sup>. To determine elemental diffusion ranges, penetration curves of U and Si along a line normal to the interface of  $\text{UO}_2$ -SiC were obtained by Energy Dispersive X-ray Spectroscopy (EDS) coupled with high resolution FE-SEM.

To determine the reaction products after sintering, X-Ray Diffraction (Philips APD 3720) was performed on the pellets. To overcome the XRD detection limit of 2~5wt% of chemical compounds, pellets with higher SiC vol% were fabricated. Processing conditions for these  $\text{UO}_2$ - 70vol% (~41.27wt%) SiC pellets were same as those for  $\text{UO}_2$ -10vol%SiC pellets.

The thermal conductivity of the pellets was measured using an Anter Flashline<sup>®</sup> 3000 system. In this method, the derivation of thermal diffusivity,  $\alpha$ , and specific heat capacity,  $C_p$ ,

were based on the measurement of the rising temperature on the back surface of a sample caused by a pulsed laser beam on the sample's front surface. The measurement was performed three times each at 100°C, 500°C, and 900°C and the average conductivity at each temperature was calculated. The thermal diffusivity  $\alpha$  in  $\text{m}^2/\text{s}$  is given by  $0.1388 L^2/t_{1/2}$ , where  $L$  is the thickness of the specimen in m and  $t_{1/2}$  is the time in seconds for the rear surface temperature to reach 50% of its maximum value. The specific heat capacity  $C_p$  is given by  $Q/dT \cdot m$ , where  $Q$  represents the energy of the pulsed laser beam, which can be determined by comparing the maximum value of the temperature rise with that of a reference,  $m$  is the mass of the specimen and  $dT$  is the maximum value of the temperature rise. Pyroceram, a glass-ceramic material and certified reference, was used as a reference pellet due to its similar thermal conductivity to  $\text{UO}_2$ . By multiplying density with  $\alpha$  and  $C_p$ , the thermal conductivity was calculated.

## 5. Results and Discussion

Typical  $\text{UO}_2$  pellets produced via oxidative sintering and SPS are shown in Figure 3. Each pellet had a 12.5 mm diameter and was 2-4mm thick. A thin pellet was used to preserve the supply of depleted uranium oxide. Conventional sized pellets, with an L/D of 1, were produced to verify normal production parameters. Pellets were cut and prepared for various characterization methods discussed in the previous section and the results are presented in the following section.

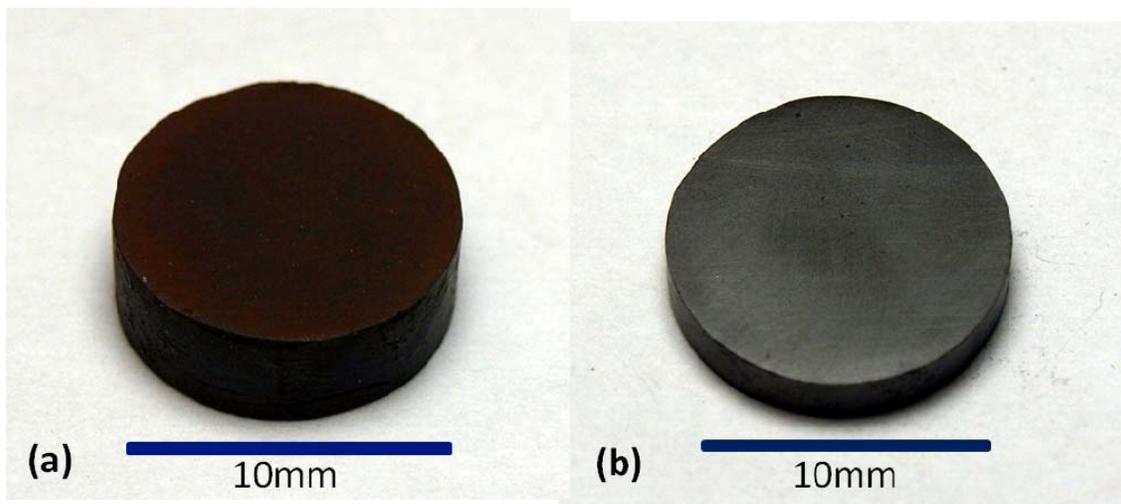


Figure 3. Fabricated  $\text{UO}_2$ -SiC composite pellets by (a) oxidative sintering and (b) SPS.

## 5.1 Comparison of oxidative and SPS sintering

### 5.1.1 Density

Porous structures have a lower thermal conductivity compared to fully dense pellets and therefore, obtaining high density  $\text{UO}_2\text{-SiC}$  pellets is critical for the production of a higher thermal conductivity fuel. The measured relative density of the oxidative and SPS sintered  $\text{UO}_2\text{-SiC}$  pellets at various sintering temperatures is shown in Figure 4. The density of the sintered  $\text{UO}_2\text{-10vol\% SiC}$  pellets increased with an increase in the sintering temperature. However, the highest density produced among the oxidative sintered pellets was low at 88.91%. On the other hand, all of the SPS processed pellets sintered at higher than  $1400^\circ\text{C}$  had higher densities between 91.25 and 97.78%.

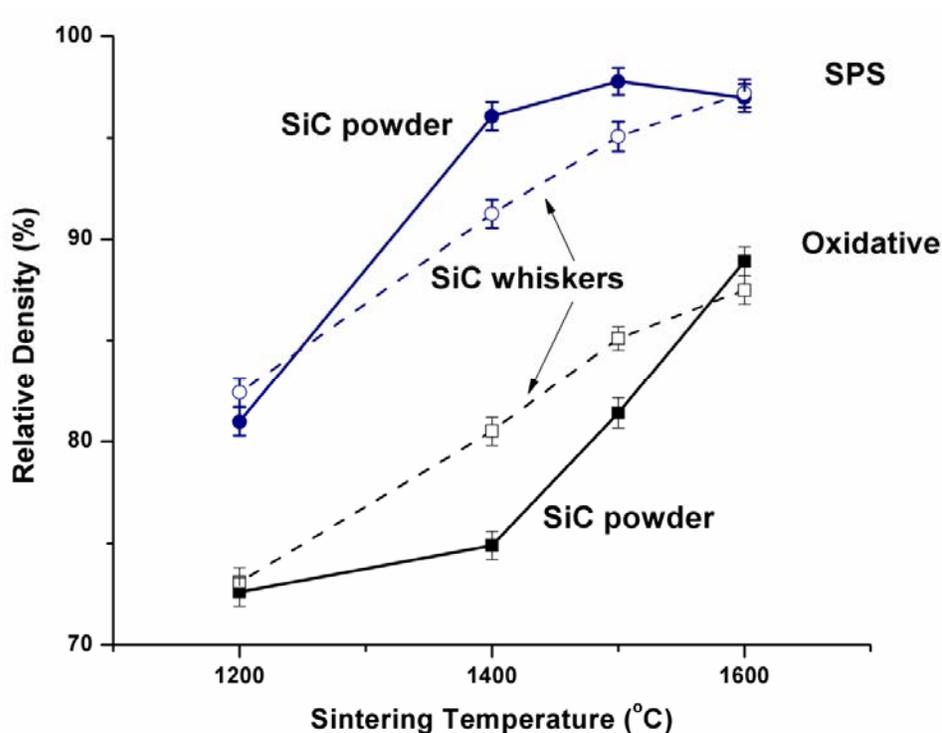


Figure 4. Relative density of  $\text{UO}_2\text{-10vol\%SiC}$  composite pellets sintered by SPS and oxidative sintering at various temperatures.

### 5.1.2 $\text{UO}_2\text{-SiC}$ Microstructure and Interface Characterization

Figure 5 shows the distributions of SiCw and SiCp in the composite pellets. Both the

whiskers and particles are seen to be uniformly distributed without any agglomeration. A improved distribution resulted from the use of a 2,3-Dihydroperfluoropentane dispersing agent during green compact preparation.

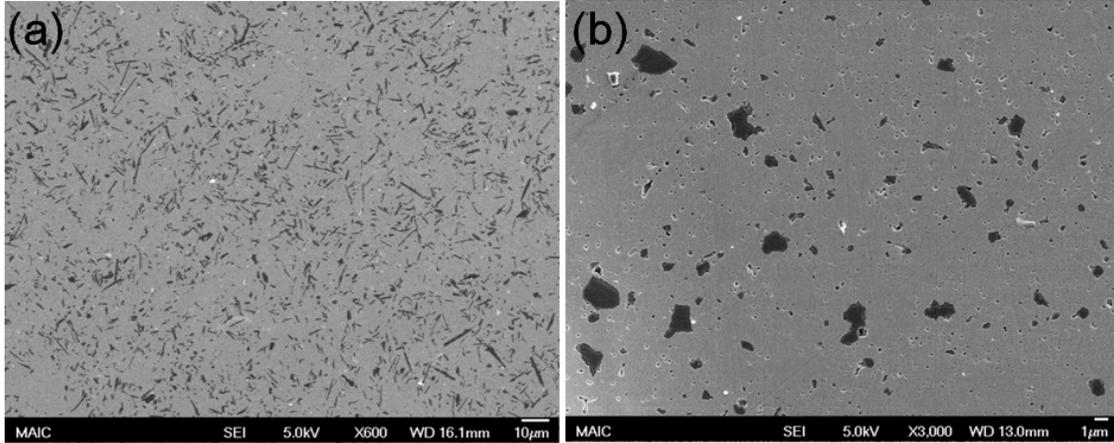


Figure 5. Polished surfaces of high density  $\text{UO}_2$ -10vol% (a) SiCw and (b) SiCp pellets sintered by SPS showing uniform dispersion of SiC.

$\text{UO}_2$ -10 vol % SiC pellets sintered at  $1500^\circ\text{C}$  by both processing methods and their micro-morphologies are shown in Figure 6. It is to be noted that, in general, a higher level of porosity and poor interfacial contact were observed in the oxidative sintered pellets compared to the SPS processed pellets. In light of the fact that the conducted heat in a pellet can be blocked by the presence of voids at the interface of two grains or poor interfacial contact between the two phases, it is beneficial to produce good interfacial contact in order to obtain a high thermal conductivity  $\text{UO}_2$ -SiC fuel. The higher level of porosity in the oxidative sintered pellet shown in Figure 6 (a) and (c) also leads to a lower density of these pellets shown earlier in Figure 4. Conversely, both the density and the interfacial contact have improved in the same  $\text{UO}_2$ -SiC composition pellets sintered by SPS, see Figure 6 (b) and (d). The improved interfacial contact illustrates the advantage of SPS for sintering high thermal conductivity  $\text{UO}_2$ -SiC pellets.

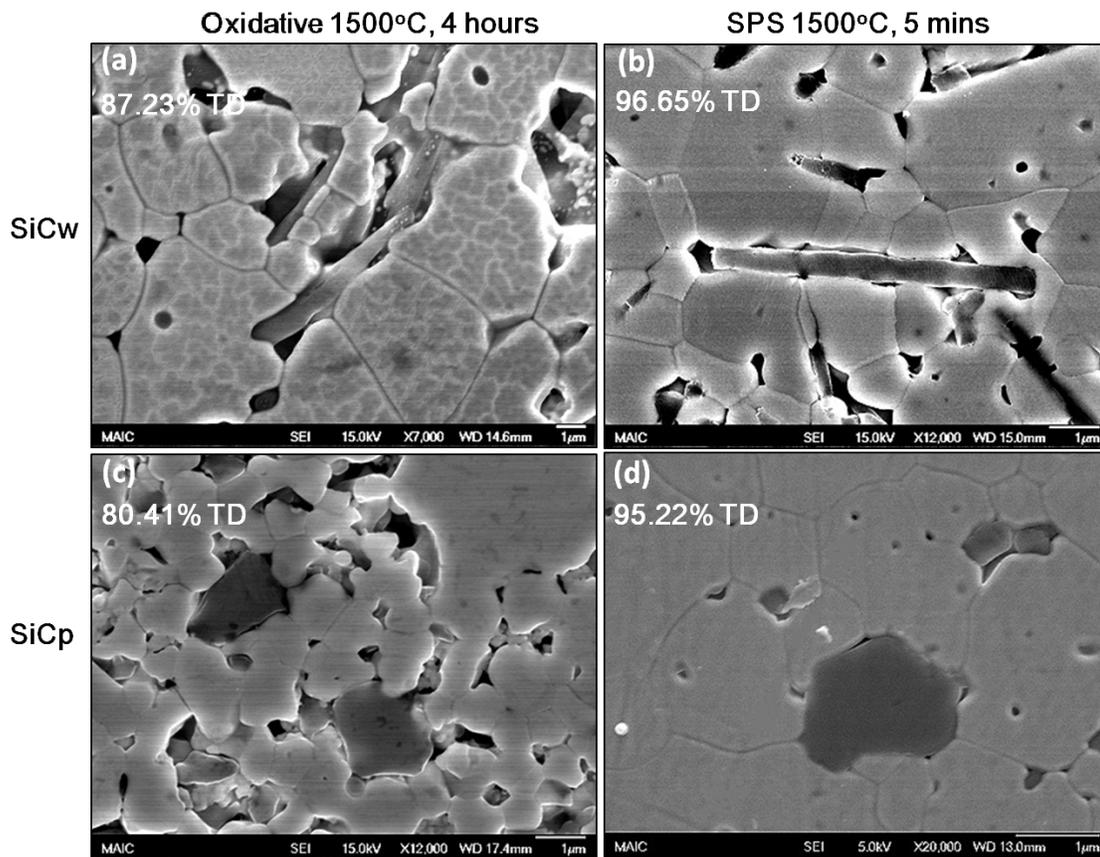


Figure 6. Microstructure of  $\text{UO}_2$ -10 vol % SiC pellets (a) and (c) sintered by oxidative sintering method at  $1500^\circ\text{C}$  for 4 hours; and (b) and (d) sintered by SPS at  $1500^\circ\text{C}$  for a 5 minutes hold time.

Figure 7 reveals a high magnification of the  $\text{UO}_2$ -SiC interface of a SPS processed pellet sintered at  $1600^\circ\text{C}$  for 5 minutes. The separation between the two phases is normally less than 100nm wide. EDS line scanning was performed to determine the uranium and silicon concentration profiles across the interface. The concentration profiles, shown in Figure 7, revealed approximately  $3\mu\text{m}$  interpenetration of the two elements. This interaction width measurement can be somewhat different, depending on the electron beam diameter of the instrument.

These profiles also illustrate that the uranium penetration depth into SiC is around  $1.17\mu\text{m}$ , where as the Si penetration into the  $\text{UO}_2$  is around  $1.83\mu\text{m}$ . Thus, uranium penetration depth is 36% less than that of silicon. If we assume both materials have similar number of vacancy defects in their lattice structures, since uranium has a greater atomic density and weight than those of silicon, the silicon transport is expected to be greater into the

UO<sub>2</sub> than that of the uranium into the SiC.

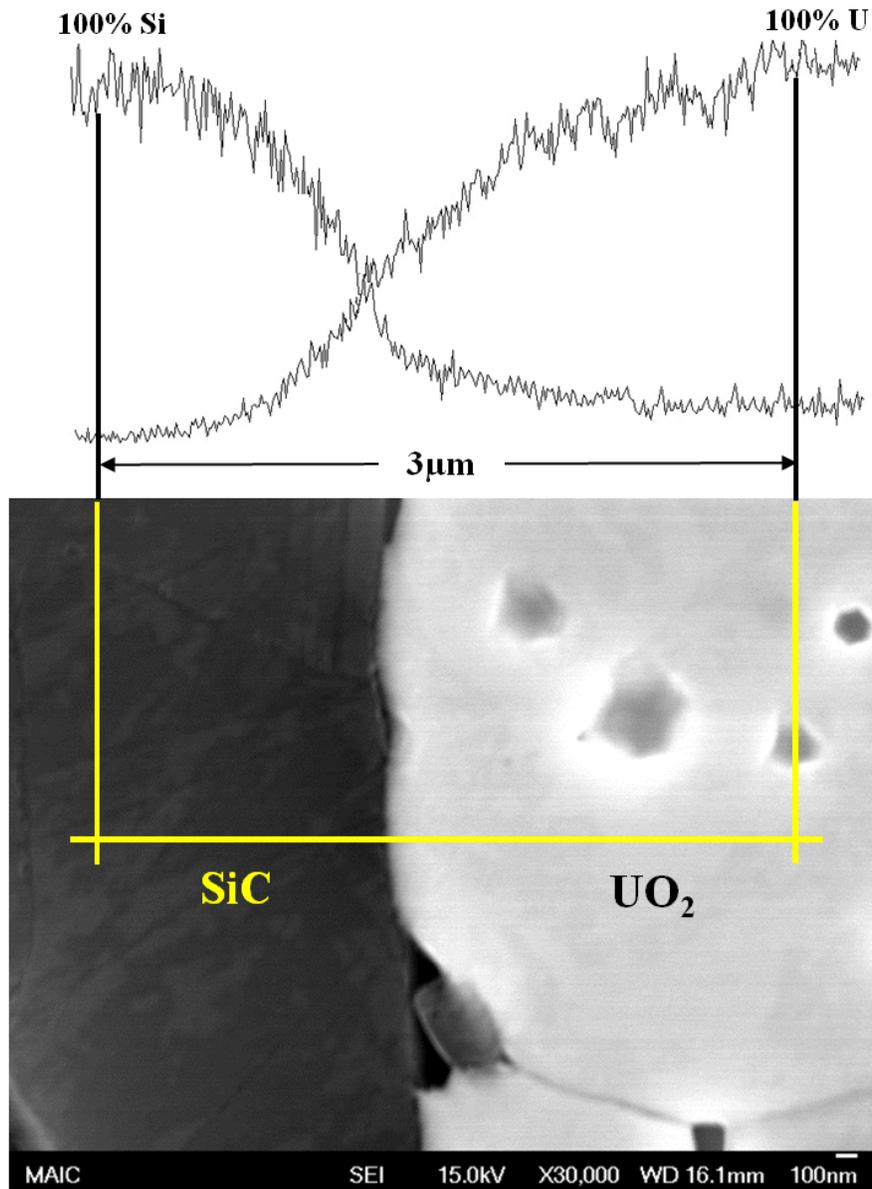


Figure 7. EDS line scan across the interface of UO<sub>2</sub>-SiC grains in a composite pellet fabricated by SPS at 1600°C.

### 5.1.3 Chemical Reaction

Controlling the chemical reactions between the SiC and the UO<sub>2</sub> during the high temperature sintering process is critical to the fabrication of dense UO<sub>2</sub>-SiC pellets, because the formation of various reaction products at the UO<sub>2</sub> and SiC interface may lead to poor

thermal properties. A report by Sarma et al. [16] suggested that reactions between the two materials could occur at temperature as low as 1370°C. In our study, XRD analysis was used to determine the reaction products at the interface. Figure 8 shows two XRD spectra obtained from UO<sub>2</sub>-70vol%SiC pellets sintered at 1600°C for 4 hours and at the same temperature by SPS for 5 minutes hold time. A USi<sub>1.88</sub> peak was clearly seen in the oxidative sintered pellet, and conversely, no such reaction product was detected on the pellet fabricated by SPS. The longer exposure time in oxidative sintering allows the formation of intermetallics and gas phases such as CO or CO<sub>2</sub>. Both could significantly reduce the thermal conductivity of the composite pellet as will be discussed in a later section.

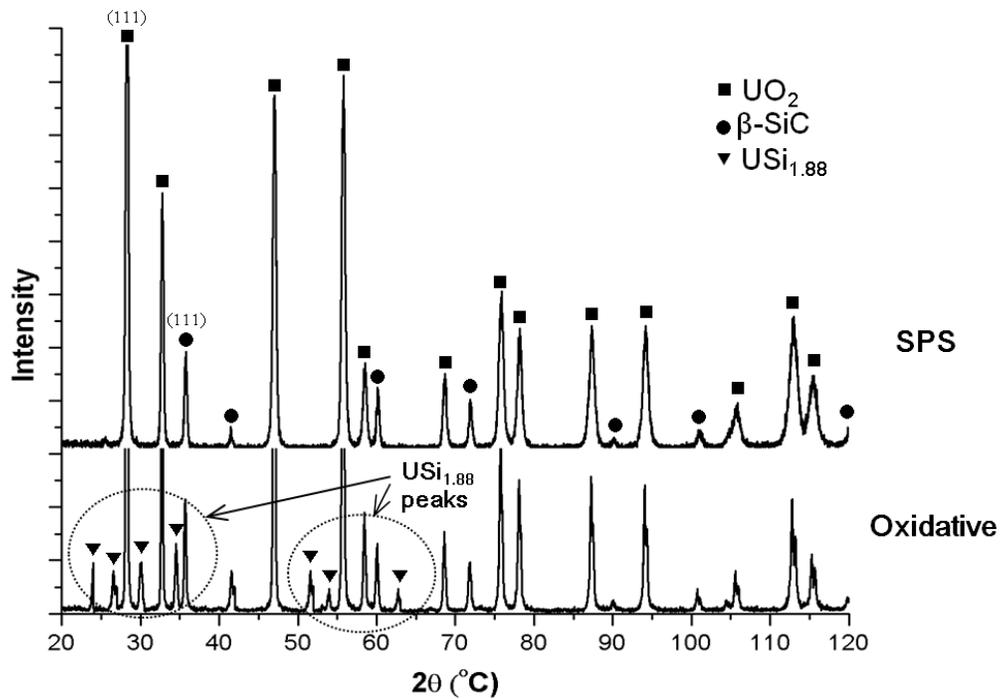


Figure 8. Comparison of XRD spectra of UO<sub>2</sub>-70vol%SiC pellets sintered by SPS and oxidative sintering at 1600°C. The peaks contained in dotted circles refer to USi<sub>1.88</sub> phase.

#### 5.1.4 Grain Size

The average grain size in various composite pellets sintered at 1500°C by both oxidative sintering and SPS according to their composition is plotted in Figure 9. In each pellet, the average grain size was determined from three micrographs from different regions. It is seen that UO<sub>2</sub> without any additives has the largest grain size. The grain size decreased with silicon carbide additions in both sintering methods. This can be expected when insoluble

second-phase particles are dispersed randomly in a polycrystalline solid. The grain boundary movement will be pinned by the inclusions, resulting in a smaller grain size of the matrix. As a result, UO<sub>2</sub>-SiCp pellets processed via oxidative and SPS sintering have 62% and 68.5% smaller grains, respectively, than those of the UO<sub>2</sub> pellet.

In general, SPS processed pellets revealed a smaller UO<sub>2</sub> grain size than the oxidative sintered pellets. This result can be explained by the rapid sintering in the SPS process, which provides shorter time for grain growth. A 53.3% reduction in average grain size is observed in the UO<sub>2</sub> pellet made by SPS than in oxidative sintered UO<sub>2</sub> pellet. It was found that increasing the sintering time led to increased grain size.

While the addition of SiC reduces the grain size of UO<sub>2</sub>, the SiC particle addition reduced the grain size more severely than the addition of SiC whiskers. The greater amounts of second phase particles increase the pinning effects resulting in the smaller grain size of a composite. While the surface-area-to-volume ratio for the SiC whisker is  $4a\pi$ , the ratio for the SiC powder is  $6/a$ , where  $a$  is the diameter of single particle. Thus, for the same 10vol% SiC, the composite with powder particles will have approximately 4.6 times more interface area than the whisker SiC and hence a small UO<sub>2</sub> grain size results with SiC powder.

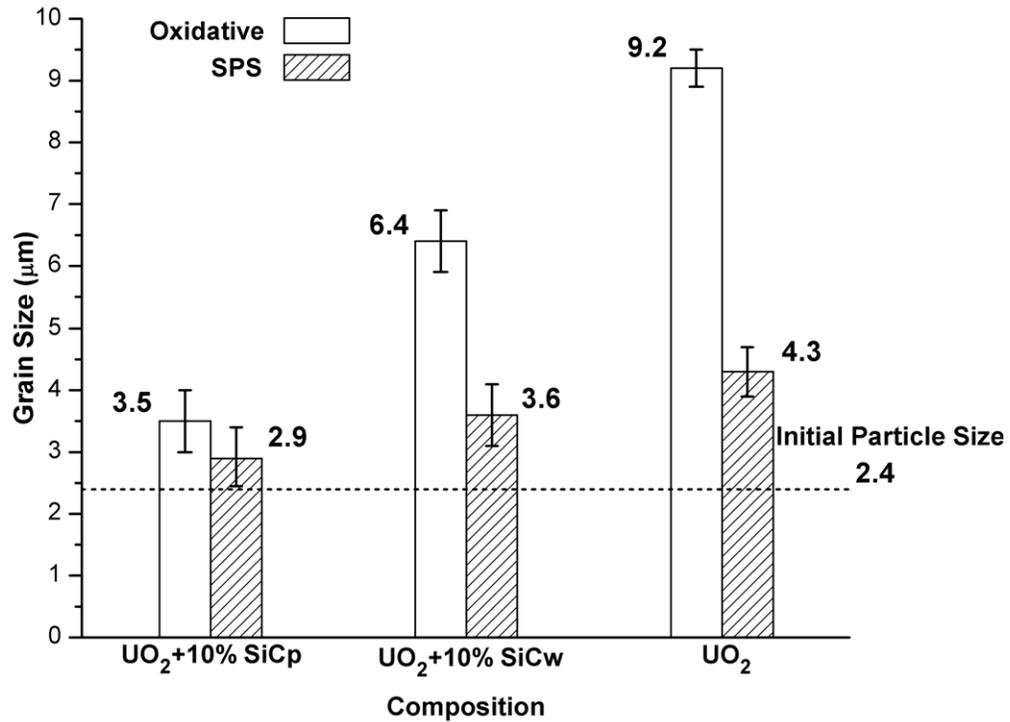


Figure 9. UO<sub>2</sub> grain size in composite pellets fabricated by the two processes with the addition of SiC powder particles and SiC whiskers.

### 5.1.5 Thermal Conductivity

Figure 10 shows the thermal conductivity measurements on UO<sub>2</sub>-SiC pellets sintered at different temperatures by both the SPS and oxidative sintering processes. The measurements were conducted three times each at 100°C, 500°C and 900°C and the average values were plotted. The average thermal conductivity values of UO<sub>2</sub> from the literature<sup>[17]</sup> at various temperatures and the measured values at the above three temperatures are also shown on the plot. Many observations can be made from this plot. The SPS sintered UO<sub>2</sub>-SiC composite pellets have higher measured thermal conductivity than the UO<sub>2</sub> pellets. In general, it can be stated that the higher the SPS sintering temperature, the higher the measured thermal conductivity. The oxidative sintered composite pellets at 1600°C exhibited significantly lower conductivity values than the previously measured value of pure UO<sub>2</sub> pellets because of their lower density. A maximum thermal conductivity enhancement was observed in UO<sub>2</sub>-SiC composites sintered by SPS at 1600°C. The increases are 54.9%, 57.4%, 62.1% at 100°C,

500°C and 900°C, respectively, compared to the literature  $\text{UO}_2$  value. The SPS sintered composite pellets show a trend similar to that of  $\text{UO}_2$  with respect to temperature, i.e., a decrease in conductivity with an increase in temperature. This trend in thermal conductivity is due to the well known phonon-phonon scattering phenomena in many ceramic materials [18]. Finally, there was no significant difference in the thermal conductivity values of both  $\text{UO}_2$ -SiC whisker composites and  $\text{UO}_2$ -SiC powder particle composites at all temperatures examined in this study.

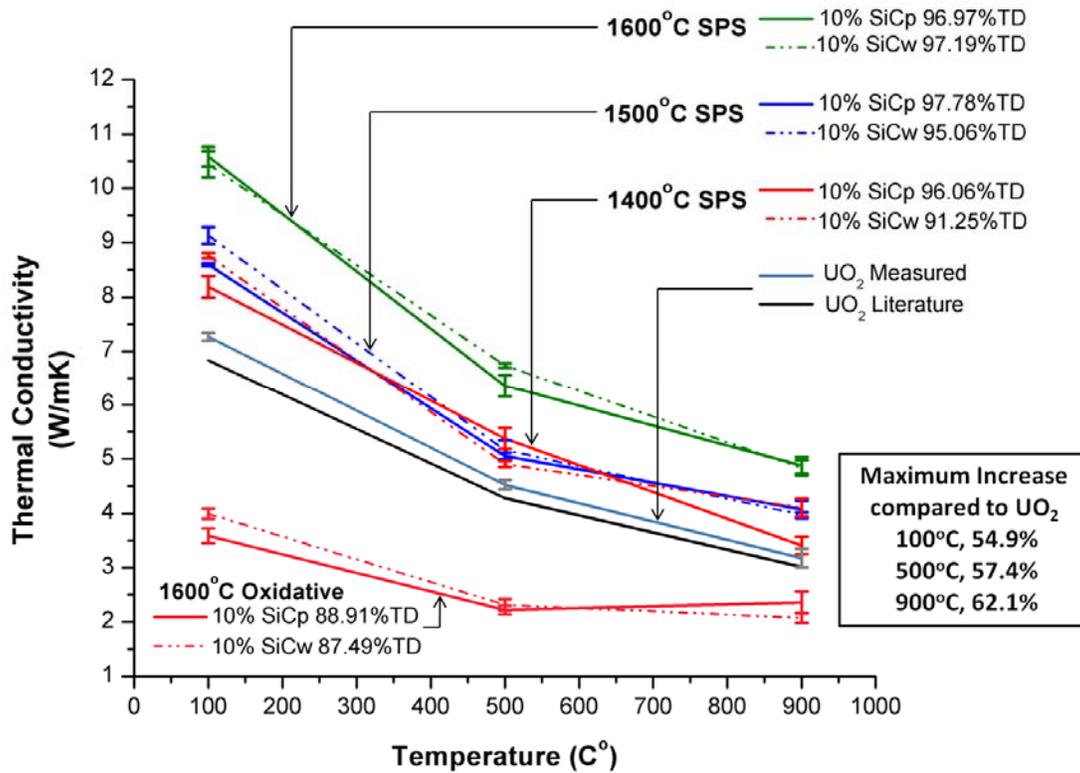


Figure 10. The measured thermal conductivity values of  $\text{UO}_2$  and  $\text{UO}_2$ -SiC composite pellets sintered by SPS and by oxidative sintering.

## 5.2 Thermal conductivity optimization

Figure 11 shows the thermal conductivity values of  $\text{UO}_2$ -SiC pellets with 5, 10, 15, and 20 vol% SiC powder. The thermal conductivity was found to increase with a higher SiC volume percent in the 5 to 15% range. However, difference in thermal conductivity between  $\text{UO}_2$ -15vol% SiC and  $\text{UO}_2$ -20vol% SiC pellets was found to be negligible.

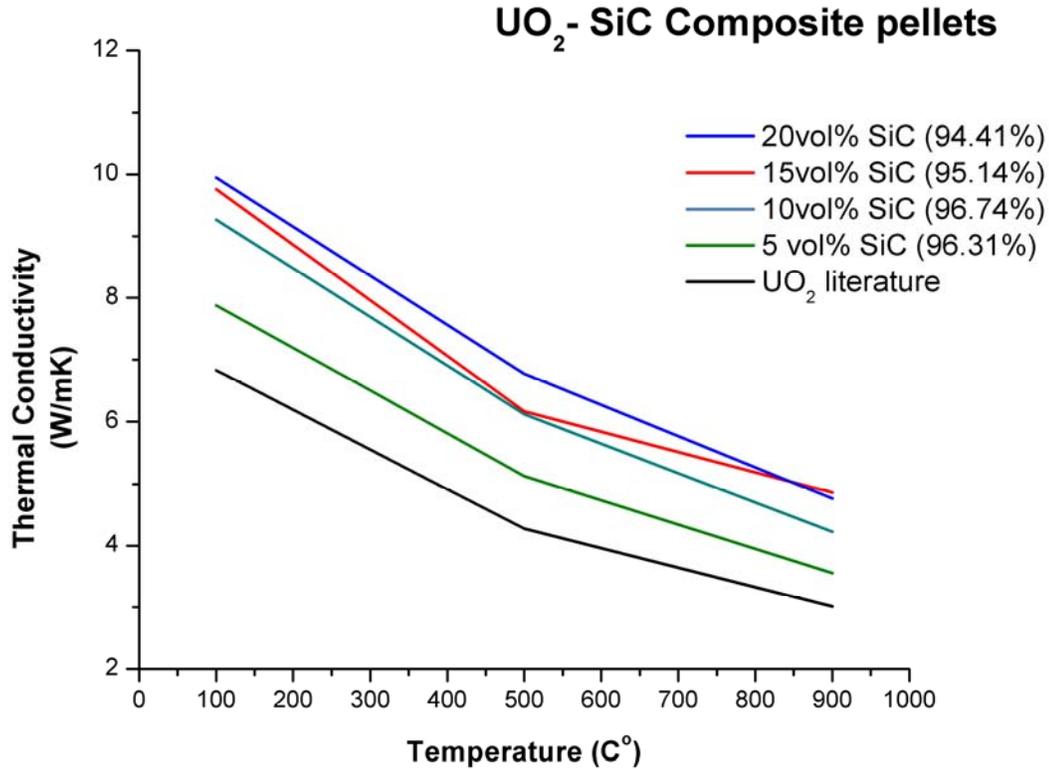


Figure 11. The measured thermal conductivity values of UO<sub>2</sub>-SiC composite pellets with 5, 10, 15, and 20vol % of SiC powder sintered by SPS.

## 6. Conclusion

UO<sub>2</sub>-SiC pellets fabricated by SPS revealed a higher density, an absence of chemical reaction forming uranium silicide, a superior interfacial contact, and a smaller grain size compared to those fabricated by oxidative sintering. The SPS technique was found to give a considerable higher sintering rate, i.e., approximately 30 minutes operating time per pellet compared to 8 hours. SPS sintering also yields up to a 10% higher density of fabricated pellets compared to pellets prepared by the oxidative sintering method. XRD analysis on UO<sub>2</sub>-SiC pellets revealed that the SPS sintering process eliminated the reaction between the uranium oxide and the silicon carbide that has been reported. SPS sintering was found to give better interfacial contact between UO<sub>2</sub> and SiC as were observed in SEM micrographs. The higher density, restriction on chemical reactions, and good interfacial contact resulting from SPS are promising features for enhanced thermal conductivity UO<sub>2</sub> composite pellets.

Consequently, despite the smaller grains, the UO<sub>2</sub>-SiC pellets made by SPS reveal

enhanced thermal conductivity up to 62.1% compared to  $\text{UO}_2$  pellets in the unirradiated state. On the other hand, the oxidative sintered process  $\text{UO}_2$ -SiC composite pellets with their resultant lower pellet density had a lower thermal conductivity than  $\text{UO}_2$  pellets and failed to achieve densities above 90%.

## **7. Technical Challenges Remaining**

### *7.1 Optimization of SPS Process Parameters*

By the end of the project, no detailed process optimization studies were able to be performed. The SPS processing parameters such as, ramp rate, hold time and pressure need to be determined for obtaining the optimum increase in  $\text{UO}_2$ -SiC thermal conductivity. The optimum loading of the SiC phase has to be finalized. The optimum size and size distribution of the SiC, as well as the aspect ratio, i.e., nano-particles, whiskers or fibers must be determined. An economic analysis of the SPS process needs to be completed. An analysis of enrichment requirements and influences of the SiC upon the neutronics has also to be conducted. Follow on contracts will be addressing these issues.

### *7.2 Analysis of Potential Failure Modes*

The reaction between  $\text{UO}_2$  and SiC to form  $\text{USi}_{1.88}$  was identified during the oxidative sintering studies. There is no evidence that this reaction will occur under reactor operating conditions with the expected reduced center line temperature of the SPS produced  $\text{UO}_2$ -SiC composites. It is necessary to irradiate  $\text{UO}_2$ -SiC composite pellets in order to be assured that the thermal conductivity advantages of the SPS produced  $\text{UO}_2$ -SiC composites would not be degraded with fuel burn-up. It is planned to propose  $\text{UO}_2$ -SiC pellet irradiation in the ATR reactor.

## **8. Publications, Patents and Oral Presentations**

### *8.1 Publications*

The following publications have been made under this contract:

- S. Yeo, E. McKenna, R. Baney, G. Subhash, 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

## 8.2 Patents

The following patents have been made under this contract:

- G. Subhash, J. Tulenko, R. Baney, E. McKenna, L. Ge, and S. Yeo, US Provisional Patent Application No. 61/683,384 entitled “High Density UO<sub>2</sub> and High Thermal Conductivity UO<sub>2</sub> Composites By Spark Plasma Sintering (SPS)” was filed on August 15, 2012.

## 8.2 Oral Presentations

The following oral presentations with resultant publication have been made under this contract:

- S. Yeo, E. McKenna, R. Baney, G. Subhash, J. Tulenko, , "Fabrication Strategies and Thermal Conductivity Assessment of High Density UO<sub>2</sub> Pellet Incorporated with SiC", 2012 MRS Spring Meeting proceedings, San Francisco CA, April 11
- J. Tulenko, G. Subhash, R. Baney, A. Cartas, S. Yeo, L. Ge, “Development of Innovative High Thermal Conductivity UO<sub>2</sub> Ceramic Composite Fuel Pellets with Silicon Carbide Whiskers Using Spark Plasma Sintering”, Top Fuel, 2012, Manchester, UK, September

## 9. References

- [1] M. Amaya, M. Hirai, H. Sakurai, K. Ito, M. Sasaki, T. Nomata, K. Kamimura and R. Iwasaki, *Journal of Nuclear Materials* **2002**, *300*, 57-64.
- [2] D. R. Olander, *Fundamental Aspects of Nuclear Reactor Fuel Elements, Vol. 1 (TID-26711-P1)*, NTIS, **1976**, p. 624 pp.
- [3] A. Solomon, S. Revankar and J. K. McCoy in *Enhanced Thermal Conductivity Oxide Fuels, Vol. 2006*, p. Medium: ED.
- [4] J. Wang in *Developing a high thermal conductivity nuclear fuel with silicon carbide additives, Vol. Copyright (C) 2011 American Chemical Society (ACS). All Rights Reserved. 2008*, p. 132 pp.
- [5] G. A. Slack, *J. Appl. Phys.* **1964**, *35*, 3460-3466.
- [6] H. Assmann, W. Dörr and M. Peehs, *Journal of Nuclear Materials* **1986**, *140*, 1-6.
- [7] H. Chevrel, P. Dehaut, B. Francois and J. F. Baumard, *Journal of Nuclear Materials* **1992**, *189*, 175-182.
- [8] J. Shen, F. M. Zhang, J. F. Sun, Y. Q. Zhu and D. G. McCartney, *Nanotechnology* **2006**, *17*, 2187-2191.
- [9] F. Zhang, C. Mihoc, F. Ahmed, C. Lathe and E. Burkel, *Chem. Phys. Lett.* **2011**, *510*, 109-114.
- [10] B. Cheng, Y. Lin, J. Lan, Y. Liu and C. Nan, *J. Mater. Sci. Technol. (Shenyang, China)* **2011**, *27*, 1165-1168.
- [11] Z. A. Munir, U. Anselmi-Tamburini and M. Ohyanagi, *J. Mater. Sci.* **2006**, *41*, 763-777.
- [12] M. Omori, *Materials Science and Engineering A* **2000**, *287*, 183-188.
- [13] S. Zhijian, M. Johnsson, Z. Zhe and M. Nygren, *Journal of the American Ceramic Society* **2002**, *85*, 1921.
- [14] N. Tang, *Guisuanyan Tongbao* **1988**, *7*, 16-18.
- [15] D. J. Willis and J. S. H. Lake, *Scripta Metallurgica* **1987**, *21*, 1733-1736.
- [16] K. H. Sarma, J. Fourcade, S. G. Lee and A. A. Solomon, *Journal of Nuclear Materials* **2006**, *352*, 324-333.
- [17] J. K. Fink, *J. Nucl. Mater.* **2000**, *279*, 1-18.
- [18] P. G. Klemens in *Phonon interactions in solids. Theoretical study, Vol.* Univ. Connecticut, **1971**, p. 14 pp.