UO$_2$-SIC COMPOSITE REACTOR FUELS WITH ENHANCED THERMAL AND MECHANICAL PROPERTIES PREPARED BY SPARK PLASMA SINTERING

By

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This work is dedicated to my parents, Inbae Yeo and Younsook Jeong, and my sister, Seungmi Yeo for their love, and support.
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LIST OF ABBREVIATIONS

ASTM American Society for Testing and Materials
BET Brunauer–Emmett–Teller
CNT Carbon nano tube
CTE Coefficient of thermal expansion
DC Direct current
EDS Energy dispersive X-ray spectroscopy
FAST Field assisted sintering technique
LOCA Lost of coolant accident
LWR Light water reactor
MOX Mixed oxide fuel
NRC Nuclear Regulatory Commission
PNNL Pacific Northwest National Laboratory
PyC Pyrolytic carbon
SEM Scanning electron microscopy
SiC Silicon carbide
SiCp Silicon carbide spherical particles
SiCw Silicon carbide whiskers
SPS Spark plasma sintering
TD Theoretical density
TO Transverse optical
TRISO Tristructural isotropic
UHP Ultra high purity
UO₂ Uranium dioxide
XRD X-ray diffraction
The primary ceramic fuel used in nuclear reactors, Uranium Dioxide (UO₂), has a low thermal conductivity which results in a decrease in both the energy output and the safety of a nuclear reactor. The introduction of high thermal conductivity fuel pellets enables a nuclear reactor to produce more thermal energy while maintaining plant safety due to lower pellet centerline temperature and thermal gradient, resulting in a lower level of fission gas release and thermal cracking.

The main objective of this research is to increase the thermal conductivity of UO₂ by the incorporation of Silicon Carbide (SiC) particles or whiskers. Oxidative sintering and Spark Plasma Sintering (SPS) techniques have been used to produce UO₂-SiC composite pellets. While oxidative sintering failed to achieve enhanced thermal conductivity, the SPS sintered pellet contained promising features such as higher density, better interfacial contact, and reduced chemical reaction, and hence, the enhanced thermal conductivity was obtained.

The influence of SiC particle size (0.6-55μm) and volume fraction (5-20%) on the thermal conductivity of spark plasma sintered UO₂-SiC composites was investigated. The composites containing a larger volume of SiC particles where size is less than 16.9μm showed higher
thermal conductivity. The measured thermal conductivity was in excellent agreement with calculated effective thermal conductivity based on a theoretical model.

The mechanical properties, such as hardness and Young's modulus, and the internal stress of SiC particles of UO$_2$-SiC composites containing different sizes and volume fractions of SiC particles were examined. Hardness and Young's modulus showed increases up to 53% and 18% with 20vol% of 1μm SiC addition, respectively. The compression stress of SiC particles up to 1.65GPa was successfully measured using Raman spectroscopy.

Lastly, thermal aging was performed at 1000°C and 1500°C for 12hours on fabricated UO$_2$-SiC composites to investigate the performance of the composites in the operational conditions of nuclear reactor. Microstructural defects such as microcracking and interfacial debonding, and SiC particles and whiskers removing from the polished surface were observed after the 1500°C thermal aging probably due to a chemical reaction between UO$_2$ and SiC. The thermal conductivity of composites was found to be decreased by 5-10% after the aging test.
CHAPTER 1
INTRODUCTION

Over the last few years, there have been enormous changes in the energy sector. Energy consumption has been increasing dramatically. Oil and gas prices have doubled over the last two years. We are experiencing exhausting fossil energy resources, environmental pollution and climate change which threatens us with diminishing green house gases. Therefore, many countries are meeting these issues by seeking sustainable and competitive energy sources. Nuclear fuel has been a well known candidate for an ecological and high energy density fuel in response to these challenges. As a result, nearly 20% of electricity in the USA is produced by nuclear reactors, and this power source is growing year by year.

Despite the availability of numerous types of nuclear fuels (metals, MOX, nitrides, etc) commercial reactors in the world are fueled by Uranium Dioxide (UO$_2$). It is the fuel of choice for several reasons such as high melting point (transient accident resistance [1-2]) and enhanced oxidation resistance. Also, UO$_2$ behavior has been studied in much more depth throughout different power cycles than other fuel types. Its major disadvantage is a low level of thermal conductivity, which causes both a steep temperature gradient and a high centerline temperature of uranium dioxide pellets during a reactor’s operation.

Owing to the steep temperature gradient and high centerline temperature, a variety of expected phenomena are induced. Important components of the fuel, such as pores, oxygen, and fission products, are redistributed from a uniform condition [1]. Thermal stress caused by a large temperature gradient results in either cracking in a low temperature region or plastic deformation in the high temperature region. Moreover, in the loss of coolant accident (LOCA), the Zircaloy cladding temperature is rapidly increased due to the high centerline temperature of the fuel pellet leading to significant Zircaloy and water reactions [2] (ex: $\text{Zr}+2\text{H}_2\text{O}=\text{ZrO}_2+\text{H}_2$). ZrO$_2$ is produced on the cladding surface, decreasing heat conduction and causing a cladding rupture.
Hydrogen gases, produced by the reaction, increase the internal pressure of the reactor and may cause an explosion.

Increasing the thermal conductivity of nuclear fuel not only decreases these harmful phenomena, but it allows for the output of a reactor to be increased and enhance the safety of a reactor during normal operation and short-term excursions. The maximum heat output from the reactor core could be increased by the high thermal conductivity of the fuel pellet enabling the reactor to produce more thermal energy while maintaining the plant safety. Moreover, with a decrease in centerline temperature caused by the increased thermal conductivity of the fuel pellet, the temperature gradient in the fuel is decreased causing reduced fission gas release and reduced cracked or broken pellets due to thermal stresses while maintaining the desired fuel and cladding temperatures.

Because the development of the thermal performance of UO₂ fuel has been regarded as a major priority in the research of nuclear power technology, other ideas and efforts has been reported. Tristructural-isotropic (TRISO) fuel [3] is a micro-sized high density UO₂ particles coated with four different layers such as porous buffer layer made of carbon, a dense pyrolytic carbon (PyC) layer, a fission product retainable Silicon Carbide layer, and a dense outer layer of PyC. Various researches [4-7] regarding TRISO fuel and its constituents are currently being conducted. A more simple and cost-efficient idea is to fabricate composite fuels containing UO₂ matrix and high thermal conducting secondary material.

The idea of UO₂ composite fuels containing a secondary material can be approached in few ways forming either a high heat conducting percolation pathway or a high thermal conductivity secondary particles distributed homogeneously in the matrix material (UO₂). While most thermal energy can be conducted through a percolation pathway, the thermal energy must pass through both higher thermal conducting secondary particles and lower thermal conducting UO₂ matrix in
the composite containing dispersed secondary particles. Therefore, forming a high heat conducting percolation pathway can lead to more efficiently conducting heat because less thermal energy is conducted through the lower thermal conducting UO$_2$ matrix. However, the manufacture of composite fuel containing such a percolation pathway is quite difficult. Sarma et al. [8] and Singh et al. [9] attempted to produce UO$_2$-SiC composites with a percolation pathways. Their method involved fabrication of a UO$_2$ pellets with open porosity followed by polymer infiltration and pyrolysis of a silicon carbide pre-ceramic polymer to form a percolation pathway. The result, however, was a pellet with degraded thermal conductivity compared to a pure UO$_2$ pellet because the formed SiC in the composite pellet had much lower density and thermal conductivity than pure SiC. In our work, we fabricated UO$_2$ based composite fuels containing homogeneously dispersed high thermal conducting SiC particles.

This concept of incorporating high thermal conductivity material into a UO$_2$ pellet has been studied [10], and silicon carbide has been considered a prime candidate for the high thermal conducting secondary particles. This is due to its low neutron cross section, high thermal conductivity, chemical stability (strong resistance to oxidation in air and air-moisture environments), and high melting temperature (~ 2973°C) [11]. Silicon carbide (β-SiC) also has the advantage of being non-toxic and isotropic over alternatives such as beryllium oxide [12]. Hunt et al. [13] stated that incorporation of at least 4mol% SiC in UO$_2$ fuel has a benefit of maintaining O to M ratio near two during irradiation. Allen et al. [14] however, found that chemical reactions occur between UO$_2$ and SiC around 1370°C which may severely degrade the thermal conductivity of the composite. Solomon and associates [15] investigated reaction products and suggested the formation of USi$_{1.88}$, U$_{20}$Si$_{16}$C$_3$, UC, CO, and SiO. Originally, it was believed that a continuous phase of SiC throughout the pellet would lead to significantly higher thermal conductivity. However, simulations performed by Latta et al. [16] revealed that
discontinuous SiC fibers produced nearly the same increase in thermal conductivity as that of a continuous phase. This result is in part due to the higher density and crystallinity of the SiC whiskers compared to that formed by the pre-ceramic polymer. Jiwei Wang [17] researched the incorporation of whisker type silicon carbide by powder mixing. SiC whiskers are configurationally preferable to prevent fission gas swelling during the irradiation, and more conductive for heat to disperse from UO₂ pellets. However, he did not measure the thermal conductivity values of the UO₂-SiC pellets, and only obtained relatively low density pellets by pressureless sintering at 1650°C. Hence, supplementary researches for the development of competent sintering methods, and the thermal conductivity characterization of UO₂-SiC composite pellets, are required.

Besides SiC, diamond is a potentially possible candidate as the incorporating secondary material because of its superior thermal conductivity (~500 W/mK). Diamond is already a hot research topic material used as a high heat conducting secondary material in ceramic composites used for a heat sink in semi-conductor devices [18, 19]. Hanada et. al. [18] increased the thermal conductivity of Cu-diamond composite up to 18% compared to pure Cu by adding diamond only 1vol%. Abdel et. al. [20] increased the thermal conductivity of Cu based composite up to 21% by adding 20vol% diamond coated Cu particles. Although several researchers are proceeding in that field, to the authors’ knowledge, no reported literature exists for the fabrication of composite fuel using diamond particles. Because a research project of UO₂-diamond composite fuel is now under active development, only preliminary results of UO₂-diamond composites will be introduced in this dissertation.

The main objective of this work is an experimental exploration of the properties of UO₂-SiC composite fuel pellets. The objective are achieved by successful outcomes for the following goals.
First, fabricate high density and high thermal conductivity UO$_2$-SiC composite pellets using a Spark Plasma Sintering (SPS) technique. We have observed that simply mixing and conventional sintering of both UO$_2$ and SiC powders leads to poor sintering behavior hampering the densification as shown in Figure 1. The relative density of UO$_2$-SiC composite pellets decreases with increasing SiC volume fraction. Similar trends were observed in various composites [21-23]. It was found that the increase in volume fraction of secondary particles hinders the consolidation of matrix grains. Maekawa et al. [23] suggested that pores remain locked around particles and eventually form pore channels decreasing the three dimensional connectivity of a matrix material to lower relative density. In this dissertation, SPS was performed to overcome this hindrance. SPS is an advanced sintering technique in which localized heat and uniaxial pressure are generated for the consolidation of ceramic powders. Nevertheless, in light of advantages, such as rapid sintering, uniform sintering, and low running cost, the effect of SPS on the sintering of nuclear fuel has not been empirically demonstrated. Thermal conductivity measurements was conducted to reveal the resulting thermal conductivity of the composite fuel pellets.

Second, investigate the influence of SiC particle size and volume fraction on thermal properties of UO$_2$-SiC composites. In general, it was found that ceramic composites containing second phase particles with larger size (low surface to volume ratio) reduce the interfacial area, inducing thermal resistance and hence, increase the thermal conductivity of ceramic composites [24-26]. The relationship between the thermal conductivity of a two phase mixture and the volume fraction of particles was introduced by Maxwell J.C. [27] and Bruggeman and Johnson [28]. According to their theoretical works, the thermal conductivity increases with increasing the volume fraction of SiC in UO$_2$-SiC composite pellets. Thus, we speculate that, for UO$_2$-SiC composites, higher thermal conductivity composite fuel would be expected with larger size and
higher volume fraction of SiC particles. In our study, a series of UO$_2$-SiC composites with different sizes and volume fractions of SiC particles was fabricated and their thermal conductivities are examined and compared with theoretically calculated thermal conductivities.

Third, identify the mechanical property of UO$_2$-SiC composites. Sustainable mechanical properties of a nuclear fuel is required to prevent fuel failures [29] during long operating cycles of a nuclear reactor. Because of its excellent mechanical properties, SiC have often added in a composite to increase mechanical properties [30, 31]. Therefore, UO$_2$-SiC composites are expected to have better mechanical properties then those of UO$_2$. Harness and Young's modulus of various composites containing different sizes and volume fractions of SiC were examined in this study.

Fourth, test UO$_2$-SiC composite fuels under the temperature similar to a reactor core to investigate changes in their properties and microstructures. Even if UO$_2$-SiC composites exhibited outstanding properties, it would be critical to examine the sustainability of their properties and sound microstructures under the operating condition of a nuclear reactor. It is difficult to imitate the exact same condition as a nuclear reactor core, and hence, fabricated UO$_2$-SiC composites were thermal aged at an expected maximum fuel centerline temperature to reveal the influence of extreme temperature on the composites. Microstructures and thermal conductivity of UO$_2$-SiC composites were examined and compared before and after the thermal aging test.
Figure 1-1. The densities of sintered pellets with various vol% of SiC at 1650°C for 4 hours under the conventional sintering process.
CHAPTER 2  
LITERATURE AND METHODOLOGY REVIEWS

Literature Review

Thermal Conductivity of UO₂

As reported in many other papers [32-36], the thermal conductivity of UO₂ is very low when compared with other ceramic materials. Fink [36] reported that the thermal conductivity of 95% relative density UO₂ can be calculated by Equation 2-1, where \( t = \frac{T}{1000} \) and \( \lambda \) is the thermal conductivity of 95% dense UO₂ in W/m. Figure 2-1 shows the results and Figure 2-2 compares it with the thermal conductivity values of single crystal beta silicon carbide [37].

\[
\lambda = \frac{100}{7.5408 + 17.692t + 3.6142t^2} + \frac{6400}{t^{5/2}} \exp\left(-\frac{16.35}{t}\right)
\]  

(2-1)

The low thermal conductivity of UO₂, compared with other ionic materials, is mainly due to the anharmonic components of crystal vibrations [1]. Since ionic-covalent bonding of ceramic materials doesn’t form free electrons, heat transport in ceramic materials occurs through the quantum of Young’s vibration of the lattice called a phonon. It is obvious that phonon-phonon scattering rapidly decreases thermal conductivity, considering its value at high temperature, as shown in Figure 2-2. In UO₂, the phonon-phonon scattering is maintained to a relatively high level throughout the temperature range by lattice anharmonicity which increases with the mass difference between the anions and the cations in the ionic solid. Because UO₂ has nearly the greatest mass difference, thermal conductivity of UO₂ is considerably lower than that of other ionic materials. Along with the inevitable factors of lattice anharmonicity and bonding structure, specific conditions of UO₂ also impact thermal conductivity. Two conditions are essential to this concept.

First, UO₂ stoichiometry influences thermal conductivity. The uranium oxide with an O/U ratio greater than 2.0 is called hyper-stoichiometric UO₂; the uranium oxide with an O/U ratio
less than 2.0 is called hypo-stoichiometric UO\(_2\). The stoichiometric UO\(_2\) and the intermediate oxidation products, U\(_4\)O\(_9\) and U\(_3\)O\(_7\), are the fluorite structures in which uranium atoms are in a face centered pattern contained in a cube of oxygen atoms [1]. Compared with stoichiometric UO\(_2\), U\(_4\)O\(_9\) and U\(_3\)O\(_7\) have clustered interstitial oxygen atoms at unoccupied cubic sites, accompanied by the displacement of neighboring U atoms [38]. On the other hand, a completely oxidized state, U\(_3\)O\(_8\), has an orthorhombic lattice structure [39], and its density is 8.38 g/cm\(^3\), which is 24\% less than UO\(_2\). The thermal conductivity of hyper and hypostoichiometric UO\(_2\) is shown in Figure 2-3 [40, 41]. The excessive oxygen atoms and the strain field in the matrix surrounding the vacancy act as phonon scattering centers so that thermal conductivity for both hyper- and hypo-stoichiometric UO\(_2\) is decreased.

Second, the increase in volume porosity significantly decreases the thermal conductivity of UO\(_2\) pellets. Since the thermal conductivity of air corresponds to an extremely small value, 0.026 W/m-K, it follows that as a pellet has more porosity its thermal conductivity decreases. According to Orlander’s “Fundamental aspects of nuclear reactor materials” [1], if all pores are of equal size and dispersed randomly, the thermal conductivity of UO\(_2\) pellets with porosity can be obtained by Equation 2-2. In the equation, \(K\) is the effective thermal conductivity, \(K_s\) is the thermal conductivity of the fully dense pellet, \(P\) is the volume porosity defined by the volume of pores divided by the entire volume, and \(\alpha\) is a coefficient with a function of temperature.

\[
\frac{K}{K_s} = \frac{1 - P}{1 + (\alpha - 1)P}
\]  

(2-2)

Van Craeynest and Stora [42] found that Equation 2-3 fits their empirical data from 50\(^\circ\)C to 1000\(^\circ\)C.

\[
\frac{K}{K_s} = 1 - \left(2.58 - 0.58 \times 10^{-3} T\right)P
\]  

(2-3)
Figure 2-5 reveals the calculated \( K/K_S \), relative thermal conductivity, at 100°C with different volume porosity. This figure predicts that the UO\(_2\) pellet presents a linear decrease in thermal conductivity values in proportion to an increase in the degree of porosity.

**Oxidative (Hyper-stoichiometric) Sintering**

Uranium dioxide pellets are generally made by a four hour sintering process at 1700°C in a hydrogen containing gaseous atmosphere to achieve at least 95% relative density. However, due to this high temperature, the energy and maintenance of furnace operation are costly.

For decades, oxidative sintering has been cited by many researchers as a strategy for the lower temperature sintering of UO\(_2\). In 1959, Williams et al. [43] studied sintering UO\(_2\) with different O/U ratio and atmospheres. He found that hyper-stoichiometric UO\(_{2+x}\) sintering in nitrogen and argon atmosphere lower the temperature to 1400°C. In 1960, Langrod [44] attained 95% density UO\(_2\) pellets by sintering hyper-stoichiometric powder with the O/U ratio of 2.3 at 1300°C in a nitrogen atmosphere for 2 hours followed by reduction in a hydrogen atmosphere. Chevron [45] reported in 1992 that the most appropriate O/U ratio for sintering is 2.25. Dehaudt [46], in 2001, found that the activation energy of hyper-stoichiometric UO\(_{2.25}\) for diffusion at grain boundary is lower than that of stoichiometric UO\(_2\).

Numerous authors agree that excessive oxygen atoms are the key for enhanced densification [47-49]. In the high temperature sintering process, where uranium ions are heaviest and slowest, the diffusion rate of uranium ions controls the entire densification rate. Since uranium ions are displaced in the hyper-stoichiometric UO\(_{2+x}\) fluorite structure due to the penetration of oxygen atoms, there is more space for uranium ions to diffuse. The higher diffusivity of uranium ions improves the total diffusion rate so that hyper-stoichiometric UO\(_{2+x}\) performs higher sinterability.
The experimental methods for the oxidation and reduction of UO$_2$ have been investigated by researchers. In order to create hyper-stoichiometric UO$_{2+x}$, the initial UO$_2$ powder needs to be oxidized in air. The inverse process, reduction, is also necessary after sintering since stoichiometric UO$_2$ has a much higher degree of thermal conductivity, as shown in Figure 2-4. Ohashi’s empirical result [50] showed that the ultimate oxidized state U$_3$O$_8$ is achieved by heating the UO$_2$ powder in dry air at 350°C for 27 hours. Blackburn [51] reported that U$_3$O$_8$ is obtained by heating the UO$_2$ powder in dry air, at 800°C, for 3 hours. According to ASTM C 1430-07, the reduction can be achieved by heating the hyper-stoichiometric UO$_{2+x}$ pellets at 800°C for 4 hours, in a 4%H$_2$-N gas, with water vapour atmosphere maintained at 35°C, using a water bath system.

Methodology Review

Spark Plasma Sintering (SPS)

SPS is distinguished from the typical sintering method by the use of spark discharge. Figure 2-5 shows our Dr. Sinter® SPS-1030 system which is utilized to perform the SPS process. According to the most frequently accepted micro-spark, or plasma theory [52], while DC current pass through the compact powder in a graphite die, the high energy pulse current induces a spark discharges between the fine particles. The plasma momentarily generates intense heat, bonding the particles together. The plasma of SPS, however, has not been identified directly, but electric noise was observed and is considered to correspond to plasma generation [53].

A rapid densification process with high diffusivity of SPS is achieved by three factors; 1) mechanical pressure, 2) rapid heating rates, and 3) electric field and pulsed direct current [54]. Firstly, it is obvious that the application of mechanical pressure during the sintering improves the pore removing process from compacts and enhances diffusion. Secondly, the fast heating rate, caused by localized spark discharges, facilitates rapid and uniform densification. Lastly, the
electric field and pulsed direct current induce spark discharges at the inter-particle contacts and remove surface contaminants and absorbed species such as CO$_2$ and H$_2$O from the particle surface, thus improving the grain-boundary diffusion processes [54].

**Laser Flash Instrument**

The Laser Flash Method is one of the most common methods to measure the thermal conductivity derived by Equation 2-4, where $K$ is the thermal conductivity in W/m-K, $\alpha$ is the thermal diffusivity in m$^2$/s, $C_p$ is the specific heat capacity in J/kg-K, and $\rho$ is the density in kg/m$^3$.

$$K = \alpha \cdot C_p \cdot \rho$$  \hspace{1cm} (2-4)

The derivations of thermal diffusivity, $\alpha$, and specific heat capacity, $C_p$, are 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. As shown in Figure 2-6, induced heat from a pulsed laser beam travels through a sample, and the heat increase on the rear surface of the sample is measured by an IR detector. The thermal diffusivity $\alpha$ in m$^2$/s is calculated by Equation 2-5, 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. On the other hand, the specific heat capacity $C_p$ is calculated by Equation 2-6, where $Q$ represents the energy of the pulsed laser beam, which can be determined by a reference sample, $m$ is the mass of the specimen, and $\Delta T$ is the maximum value of the temperature rise. In the Laser Flash Machine, shown in Figure 2-8, this value is obtained by comparing the maximum value of the temperature rise with that of a reference.

$$\alpha = \frac{0.1388 \ L^2}{t_{1/2}}$$  \hspace{1cm} (2-5)

$$C_p = \frac{Q}{m \cdot \Delta T}$$  \hspace{1cm} (2-6)
Figure 2-1. Thermal conductivity of 95% relative density UO$_2$ pellet [36].
Figure 2-2. Comparison of thermal conductivities between $\text{UO}_2$ and beta SiC [36, 55].
Figure 2-3. Thermal conductivity of UO$_2$. A) hyper stoichiometric UO$_2$. B) hypo stoichiometric UO$_2$ [40, 41].
Figure 2-4. Thermal conductivity of UO$_2$ with different volume porosity [42].
Figure 2-5. Spark Plasma Sintering system (Dr. Sinter® SPS-1030) in Particle Engineering Research Center (PERC). Photo courtesy of Sunghwan Yeo.
Figure 2-6. Flashline 3000 made by Anter in New Engineering Building (NEB) and its schematic apparatus. Photo courtesy of Sunghwan Yeo.
CHAPTER 3
PREDICTIVE THERMAL CONDUCTIVITY MODELS FOR CERAMIC COMPOSITES

Heat can be conducted by both lattice vibration waves (phonon) and free electrons in solid materials [56]. Because non-metallic materials such as UO$_2$ or SiC lack free electrons, phonons are primary responsible for thermal conduction. Transport by phonons is not as effective as free electrons because phonon scattering frequently occurs due to microstructure defects and lattice imperfections [57]. Since our research materials are ceramic composites containing two constituents, it is reasonable to consider factors that could lead to the phonon scattering, and hence, have influence on the effective thermal conductivity of composites. These include the thermal conductivity of individual constituents and the crystallinity of the second phase materials (monocrystalline SiC has higher thermal conductivity than polycrystalline SiC). The second phase particle shape, size, volume fraction, degree of mixing, and orientation in a matrix material also have effects on the thermal conductivity of a ceramic composite.

The interfacial characteristics such as bonding between UO$_2$ and SiC also greatly affect the thermal conductivity. Because a void at the interface scatters thermal energy and hinders the thermal energy transport to the high thermal conducting second phase particles, a physically well bonded interface between UO$_2$ and SiC is essential for high thermal conductivity. However, even though the interface is atomically perfect, some portion of the phonon is scattered due to the difference in physical and vibrational properties of the composites' constituents. This is well known as Kapitza resistance. Kapitza [58] researched the heat transfer of liquid helium to capillaries and suggested that temperature change at the interface is proportional to the normal component of the heat flux.

$$\Delta T_{\text{out-in}} = -R_k \times q_{\text{interface}}$$

(3-1)

Where $\Delta T_{\text{out-in}}$ is a change in temperature between the matrix and second-phase particle at the interface, $q_{\text{interface}}$ is the heat flow at the interface, and $R_k$ is Kapitza resistance. $R_k$
depends on how different and similar in thermal and physical properties of materials that composed of composites.

Maxwell Model

Since 1950s, various researches have reported the predictive models of the effective thermal conductivity of composites. The Maxwell theoretical model [27] is a basis for many theoretical models. Maxwell originally derived an equation to obtain the electrical conductivity of composites. However, the physical concepts and governing equations could be easily adopted to the effective thermal conductivity of composites. Maxwell assumed a composite containing non-interacted spherical second-phase particles in a matrix material. The spatial distribution of temperature outside and inside a spherical particle can be obtained by Laplace equation when the particle is placed in an infinite medium and subjected to an uniform heat flux as illustrated in Figure 3-1 [59].

\[
T_{out} = Ar \left(1 + \frac{B}{r^3}\right) \cos \theta = Az \left(1 + \frac{B}{r^3}\right) \quad (3-2)
\]

\[
T_{in} = Cr \cos \theta = Cz \quad (3-3)
\]

Where \(r\) and \(z\) are the directions of heat flux as shown in Figure 3-1, \(A\), \(B\), and \(C\) are unknown coefficients, and \(\theta\) is the angle between \(r\) and \(z\) axes. Outside a spherical particle, \(T_{out}\), the spatial temperature can be expressed using both the linear temperature change along the direction of heat flux (first term in 3.2) and the temperature fluctuation due to the existence of a second-phase particle (second term in 3.2). As \(r \rightarrow \infty\), the second term, the temperature fluctuation is disappeared in this equation. The temperature inside a spherical particle, \(T_{in}\), is linear along the \(z\)-axis. The following conditions are necessary to obtain the unknown values \(A\) and \(B\) [27].

\[
T_{out} = T_{in} \quad (3-4)
\]

\[
-k_m \left(\frac{\partial T_{out}}{\partial r}\right) = -k_p \left(\frac{\partial T_{in}}{\partial r}\right) \quad (3-5)
\]
Where $k_m$ and $k_p$ are the thermal conductivities of matrix and second-phase particles, respectively. While Equation 3-4 refers to no existence of interfacial resistance, Equation 3-5 means there is no thermal energy accumulation at the interface. Solving these equations using Equation 3-2 and 3-3 leading to [27],

$$B = \frac{R^3(1-k_p/k_m)}{2+k_p/k_m}$$ (3-6)

$$C = \frac{3A}{2+k_p/k_m}$$ (3-7)

Where $R$ is the radius of a particle as shown in Figure 3-1. Equation 3-2 can be reformed using Equation 3-6 as [27],

$$T_{out} = Az \left(1 + \frac{R_0^3(1-k_p/k_m)}{r^3\frac{1}{2+k_p/k_m}}\right)$$ (3-8)

If the boundary conditions of particle are given by the continuity of temperature and components of heat flux, the distribution of heat at any point inside and outside a second-phase particle can be calculated [27]. When total $N$ identical second-phase particles with $R_o$ radius are dispersed homogeneously without any particle-particle interaction in an infinite medium, a single particle can be treated as a sphere in an infinite medium. Then, the temperature at some distance from a particle can be expressed as [27].

$$T = \sum_{i=1}^{N} Az \left(1 + n \frac{R_0^3(1-k_p/k_m)}{r_i^3\frac{1}{2+k_p/k_m}}\right) \approx Az \left(1 + N \frac{R_0^3(1-k_p/k_m)}{r^3\frac{1}{2+k_p/k_m}}\right)$$ (3-9)

Where $N$ is the number of spheres and $R_0$ is the radius of a sphere. Let us assume that all particles are in a large circle area of the medium with a radius of $R_1$. Then, the temperature outside the large circle can be expressed [27].

$$T = Az \left(1 + \frac{R_1^3(1-k_p/k_m)}{r^3\frac{1}{2+k_p/k_m}}\right)$$ (3-10)
Where \( k_e \) is the effective thermal conductivity of the composite. Because the temperature at some distance from a particle and the temperature outside a large circle of medium are thermally equivalent, Equation 3-9 and Equation 3-10 are same [27].

\[
T = Az \left( 1 + N \frac{R_0^3}{r^3} \frac{1-k_p/k_m}{2+k_p/k_m} \right) = Az \left( 1 + \frac{r^3}{R_1^3} \frac{1-k_e/k_m}{2+k_e/k_m} \right) \tag{3-11}
\]

Solving this equation, we can obtain the Maxwell equation for the effective thermal conductivity of a composite [27].

\[
k_c = k_m \frac{k_p + 2k_m + 2\phi (k_p - k_m)}{k_p + 2k_m - \phi (k_p - k_m)} \tag{3-12}
\]

Where \( \phi \) is \( N \frac{R_0^3}{R_1^3} \) and same as the volume fraction of particles in the composite.

This equation is derived under several assumptions including that only spherical shaped particles are distributed and the interaction between particles does not exist [27]. The volume fraction of second-phase particles has to be small enough to be isolated from each other. The thermal conductivity of composites containing non-spherical shaped second-phase particles such as whisker or plate types can't be applied to Maxwell equation. Above all, the interfacial thermal resistance is not considered in the calculation. As a result of assumptions, the size of the particles is also not considered in the equation. In an actual case, because different dispersed particle sizes changes the area of interface, the effective thermal conductivity is modified. However, there is quite a few experimental reports that have confirmed the validity of Maxwell equation. Wong et. al. [60] found that experimentally determined thermal conductivity of epoxy based composite filled with silica is in good agreement with the calculated value using Maxwell equation when the composite contains less than 40vol% of silica filler. Boey et. al. [61] fabricated Aluminum Nitride (AlN) - Yttrium Oxide (Y\(_2\)O\(_3\)) composite and found that its thermal conductivity is closer to the calculated value using Maxwell equation when the lower volume fraction of Y\(_2\)O\(_3\) is added.
According to various experimental studies, composites containing second-phase particles less than approximately 10-20vol% and when there is large difference in the thermal conductivities between particle and matrix follow the Maxwell equation.

**Hasselman and Johnson Model**

Because of the limitations of the Maxwell model, Hasselman and Johnson [62] modified Maxwell’s calculation to derive a new expression for the effective thermal conductivity of composites containing spherical, cylindrical, and flat plate second-phase particles. They found that the effective thermal conductivity is not only dependant on the volume fraction of second-phase particles but also on the size of dispersed particles. This result is because the interfacial thermal resistance increases with the decreasing size of the dispersed particles due to the larger interfacial area. They obtained expressions for composites containing spherical and cylindrical dispersed particles by modifying the original Maxwell equation. For flat plate dispersed particles, they utilized the series-circuit approach. Here, we will briefly describe only the expression for the composite containing spherical dispersed particles which is applicable to our UO$_2$-SiC composites. The effective thermal conductivity of composites is expressed as [62],

$$k_{eff} = k_m \frac{2(k_p + k_p - 1)\theta + k_p + 2k_p + 2}{(k_p - k_m)\theta + k_p + 2k_p + 2}$$  \hspace{1cm} (3-13)

Where $a$ is the radius of particle and $h_c$ is the interfacial thermal conductance. Hasselman and Johnson introduced the interfacial thermal conductance and considered the effect of particle size on the effective thermal conductivity. The interfacial thermal conductance is a measure of thermal flow at the interface and the inverse form of the interfacial thermal resistance, $R_k$, which is also known as Kapitza resistance. If $h_c \to \infty$, Hasselman and Johnson model, Equation 3-13, and Maxwell model, Equation 3-12 become identical.
Nan's Effective Thermal Conductivity Model

Nan et. al. [63] also used an effective medium approximation for calculating the effective thermal conductivity where the interfacial thermal resistance and dispersed particle size are included. They developed this theory further than Hasselman and Johnson model by calculating interfacial thermal resistance based on multiple scattering theory [64]. Nan obtained several formulations for composites containing spherical particles, randomly oriented ellipsoidal particles, aligned continuous fibers, and flat plates. Here, we will describe the calculations for spherical, and randomly oriented and aligned ellipsoidal particles.

For spherical particles, the effective thermal conductivity is given by [65],

\[ k_c = k_m \frac{k_p (1+2\alpha)+2k_m+2\phi[k_p(1-\alpha)-k_m]}{k_p (1+2\alpha)+2k_m-2\phi[k_p(1-\alpha)-k_m]} \]  \hspace{1cm} (3-14)

Where \( \alpha \) is a dimensionless parameter and defined as,

\[ \alpha = \frac{R_k k_m}{a} \]  \hspace{1cm} (3-15)

Where \( R_k \) and \( a \) are the interfacial thermal resistance and the radius of dispersed particles, respectively. Considering the interfacial thermal resistance is the inverse form of the interfacial thermal conductance, \( R_k = 1/h_c \), the Nan's model, Equation 3-14, and the Hasselman and Johnson model, Equation 3-13, are identical.

For the formulation of aligned ellipsoidal particles, the structure model of particle in a composite is illustrated in Figure 3-2. An ellipsoidal particle with the thermal conductivity of \( k_p \) and semi-axes \( a_1 \) and \( a_3 \) is incorporated in a matrix with the thermal conductivity of \( k_m \). The directions of thermal conductivity according to the particle geometry and interfacial thermal conductance are also shown in the figure. The thermal conductivity of composite with specific direction is expressed as [65],

\[ k_{ii} = k_m \frac{1+\phi \beta_{ii}(1-L_{ii})}{1-\phi \beta_{ii}L_{ii}}, \,(i = 1,2,3) \]  \hspace{1cm} (3-16)
Where $L_{ii}$ is geometrical factor and $\beta_{ii}$ is defined as,

$$\beta_{ii} = \frac{k_{ii}^c - k_m}{k_m + L_{ii}(k_{ii}^c - k_m)}$$ \hspace{1cm} (3-17)

Where $k_{ii}^c$ is expressed as,

$$k_{ii}^c = k_{ii} \frac{k_p}{(2+p)L_{ii}k_{ii}^p}, (i = 1,2,3)$$ \hspace{1cm} (3-18)

Geometrical factors $L_{ii}$ is expressed as,

$$L_{11} = L_{22} = \frac{p^2}{2(p^2-1)} - \frac{p}{2(p^2-1)^{3/2}} \cosh^{-1} P$$ \hspace{1cm} (3-19)

$$L_{33} = 1 - L_{22}$$ \hspace{1cm} (3-20)

Where $P$ is the aspect ratio of ellipsoidal particle and expressed as,

$$P = \frac{a_3}{a_1}$$ \hspace{1cm} (3-21)

The above equations are practical for the composite fuel containing aligned ellipsoidal particles such as SiC whiskers. Several experiments using the SPS consolidation technique revealed that most ellipsoidal particles in a composite are aligned along a sample plane due to the pressure applied perpendicular to the plane [66-68].

Nan also predicted a calculation for a composite containing completely random oriented ellipsoidal particles. With random orientation, the effective thermal conductivity becomes in simpler form than that of aligned orientation,

$$k_e = k_m \frac{3+\phi[\beta_{11}(1-L_{11})+\beta_{33}(1-L_{33})]}{3-\phi(2\beta_{11}L_{11}+\beta_{33}L_{33})}$$ \hspace{1cm} (3-22)

Where $L_{ii}$ and $\beta_{ii}$ are expressed in Equation 3-13 and Equation 3-14, respectively. This formulation is also useful to calculate theoretical thermal conductivity of $\text{UO}_2$-$\text{SiC}$ whiskers composites fabricated by conventional furnace method.
Figure 3-1. Spherical particle is subjected to uniform heat flux in an infinite medium.
Figure 3-2. Model of ellipsoidal particles in a composite.
CHAPTER 4
ENHANCED THERMAL CONDUCTIVITY OF UO₂-SiC COMPOSITE FUEL PREPARED BY BOTH OXIDATIVE AND SPARK PLASMA SINTERING (SPS)

Background

As mentioned in chapter 1, increasing the thermal conductivity of nuclear fuel would allow for the output of a reactor to be increased and enhance the safety of a reactor during normal operation and short-term accidents. Moreover, with a decrease in centerline temperature caused by the increased thermal conductivity of the fuel pellet, the temperature gradient in the fuel is decreased allowing reduced fission gas release and number of cracked or broken pellets due to thermal stresses while maintaining the desired fuel and cladding temperatures.

Building on a previous study performed by Wang [17], we concluded that incorporating β-SiC into UO₂ may increase the thermal conductivity of nuclear fuel. This study has focused on the utilization of an advanced technique to fabricate fully dense UO₂-SiC composite pellets with excellent thermal properties. Both low-temperature oxidative sintering [69] and SPS techniques were employed to fabricate UO₂-SiC composite pellets and compare the resulting microstructures and properties. As described in chapter 2, in the oxidative low-temperature sintering, the UO₂ powder is co-sintered with SiC powder or whiskers by increasing the O to M ratio of the starting powder [43, 46] to an optimum value of 2.25 [45]. 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 [70-72]. In recent years, spark plasma sintering (SPS) has evolved as a promising sintering technique for rapid fabrication of UO₂ pellets of required shape and size [73]. However, to the authors’ knowledge, no reported literature exists for the fabrication of UO₂ composite fuels. As mentioned in chapter 2, in SPS, 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 controversy in the literature whether or not plasma is created due to this spark discharge between the particles [53]. Regardless, intense heat is generated at the particle contacts which bonds them together in a very short time. With the application of pressure, high density compacts can be produced.

**Experiment**

**Powder Preparation**

The uranium dioxide (UO$_{2.11}$) powder was obtained from Areva, Hanford, WA. The powder was reported to have a bulk density of 2.3g/cm$^3$, tap density of 2.65g/cm$^3$, mean diameter of 2.4µm, and a surface area from gas absorption method [74] (BET surface area) of 3.11m$^2$/g. Hyper-stoichiometric UO$_{2.25}$ was produced by heating the starting powder in air at 350°C for 27 hours to produce U$_3$O$_8$ and then mixing it back with the starting powder (UO$_{2.11}$) at 30:70 weight ratio.

Both SiC whiskers (SiC$_w$) and SiC particles (SiC$_p$) were used in this investigation to produce UO$_2$-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 4-1 reveals SEM images of as received β-SiC whisker and powder morphologies.

The UO$_2$ and 10vol% (~3.24wt%) 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 homogeneous dispersion of SiC whiskers and powder particles in UO$_2$ matrix as will be discussed later.
Sintering

Both oxidative sintering and spark plasma sintering (SPS) processes were employed. For oxidative sintering green body pellets were made by compressing the blended 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 taken out. The die and pellet diameters were 12.7mm. The green body pellets were then sintered in an alumina tube furnace with a ramp rate of 2.6°C/min until the temperature reached 1600°C where it was held for 4 hours. To maintain a hyper-stoichiometric state, an ultra high purity (UHP) Ar gas atmosphere, with a continuous flowing rate of 2 liter/min, was created in the furnace during the sintering process.

Spark plasma sintering was performed in a Dr. Sinter$^\text{®}$ SPS-1030 system, see Figure 4-2. 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 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 hold time. The maximum sintering temperature was set at 1400°C, 1500°C, and 1600°C for different pellets.

After the pellets were sintered by both oxidative sintering and SPS techniques, they were reduced to stoichiometric 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%H$_2$-N gas, with a water vapor atmosphere using a water bath maintained at 35°C. The UO$_2$-SiC composite pellets were fabricated with 10vol% SiC at hold temperatures of 1400°C, 1500°C, and 1600°C.
For a comparison of properties between UO$_2$-SiC composite pellets with those of UO$_2$ pellets, sintering of UO$_2$ pellets was also conducted using both 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 by the SPS process at 1500°C and 1600°C yielded 96% theoretical density and were used for comparison of grain size and thermal conductivity.

**Characterization Methods**

The characterization of 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 chemical products using XRD, and thermal conductivity measurements.

The density of the 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 Archimedean 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 UO$_2$-SiC pellets were taken and the average grain size was measured in each micrograph by the line intercept method [75]. To determine elemental diffusion ranges, penetration curves of U and Si along a line normal to the interface of 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 (XRD, 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 UO$_2$-70vol% (~41.27wt%) SiC pellets were same as those for UO$_2$-10vol%SiC pellets.

The thermal conductivity of the pellets was measured using an Anter Flashline® 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 m$^2$/s is given by, $0.1388 \frac{L^2}{t_{1/2}}$, 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, $\frac{Q}{dT \cdot m}$, 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 conductivity as UO$_2$. By multiplying density with $\alpha$ and $C_p$, thermal conductivity was calculated.

**Result**

Typical UO$_2$ pellets were produced via oxidative sintering and SPS and are shown in Figure 4-3. Each pellet was 12.5 mm in diameter and 2-4mm thick. The pellets were cut and prepared for various characterization methods discussed in the previous section and the results are presented in the following section.

**Density**

Porous structures are expected to have lower thermal conductivity compared to fully dense
pellets, and therefore, obtaining high density UO$_2$-SiC pellets is critical for enhanced thermal conductivity fuel. The measured relative density of the oxidative and SPS sintered UO$_2$-SiC pellets at various sintering temperatures are shown in Figure 4-4. The density of sintered UO$_2$-10vol% SiC pellets increased with an increase in sintering temperature. However, the highest density among oxidative sintered pellets was still low at 88.91%. On the other hand, all SPS pellets sintered at higher than 1400$^\circ$C had higher density between 91.25 and 97.78%. Interestingly, in each of the sintering methods both SiC whiskers and particle additions yielded almost the same overall densities of the composite pellets at 1600$^\circ$C.

**UO$_2$-SiC Microstructure and Interface Characterization**

**Microstructure of UO$_2$-SiC composite pellets**

Figure 4-5 reveals the distributions of SiCw and SiCp in the composite pellets. Both the whiskers and particles are seen to be uniformly distributed without any agglomeration. This was accomplished with the use of a 2,3-Dihydroperfluoropentane dispersing agent during green compact preparation.

UO$_2$-10vol%SiC pellets sintered at 1500$^\circ$C by both processing methods and their micro-morphologies are shown in Figure 4-6. It is noted that, in general, a higher level of porosity and poor interfacial contact were observed in oxidative sintered pellet compared to SPS sintered pellet. 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 for high thermal conductivity fuel. The higher level of porosity in the oxidative sintered pellet shown in Figure 4-6 (a) and (c) also leads to lower density of these pellets shown earlier in Figure 4-4. Conversely, both density and the interfacial contact have improved in the same composition pellets sintered by SPS, see Figure 4-6 (b) and (d). The improved interfacial contact illustrates the
advantage of SPS for sintering high thermal conductivity UO$_2$-SiC pellets as will be shown later.

**Diffusion at the UO$_2$-SiC interface**

Figure 4-7 reveals a high magnification of the UO$_2$-SiC interface of a SPS sintered pellet processed at 1600°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 4-7, revealed approximately 3µm interpenetration of the two elements. This interaction width measurement could be different depending on the electron beam diameter of an instrument.

These profiles also illustrate that uranium penetration depth into SiC is around 1.17µm, where as Si penetration into UO$_2$ is around 1.83µm. 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 would be expected to be greater into UO$_2$ than that of uranium into SiC.

**Chemical reaction**

Controlling chemical reactions between SiC and UO$_2$ during high temperature sintering process is critical to the fabrication of dense UO$_2$-SiC pellets, because the formation of various reaction products at the UO$_2$ and SiC interface may lead to poor thermal properties. A study by Sarma et al. [8] found 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 4-8 shows two XRD spectra obtained from UO$_2$-70vol%SiC pellets sintered at 1600°C for 4 hours and at the same temperature by SPS for 5 minutes hold time. A USi$_{1.88}$ 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$_2$. Both could significantly reduce the thermal conductivity of the composite pellet as will be seen in a later section.

**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 4-9. In each pellet, the average grain size was determined from three micrographs from different regions. It is seen that UO$_2$ without any additives has the highest grain size. The grain size decreased with silicon carbide additions in both sintering methods. This is because when insoluble second-phase particles are dispersed randomly in a polycrystalline solid, the grain boundary movement will be pinned by the inclusions resulting in smaller grain size of the matrix. As a result, UO$_2$-SiC$_p$ pellets processed via oxidative and SPS sintering have 62% and 68.5% smaller grains, respectively, than those of the UO$_2$ pellet.

In general, SPS pellets revealed smaller UO$_2$ grain size than the oxidative sintered pellets. This result is because of 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$_2$ pellet made by SPS than in oxidative sintered UO$_2$ pellet.

While the addition of SiC reduces the grain size of UO$_2$, 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$_2$ grain size results with SiC powder.
Thermal Conductivity

Figure 4-10 shows the thermal conductivity measurements on UO$_2$-SiC pellets sintered at different temperatures by SPS and oxidative sintering. The measurements are 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$_2$ from the literature [76] 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$_2$-SiC composite pellets have higher measured thermal conductivity than UO$_2$ pellets. In general, 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 previously measured value of pure UO$_2$ pellets. A maximum thermal conductivity enhancement was observed in UO$_2$-SiC composites sintered by SPS at 1600°C and the increases are 54.9%, 57.4%, 62.1% at 100°C, 500°C and 900°C, respectively, compared to the literature UO$_2$ value. The SPS sintered composite pellets show a trend similar to that of UO$_2$ with respect to temperature, i.e., a gradual decrease in conductivity with increase in temperature. This trend in thermal conductivity is due to the well known phonon-phonon scattering phenomena in many ceramic materials [77]. Finally, there was no significant difference in the thermal conductivity values of both UO$_2$-SiC whisker composites and UO$_2$-SiC powder particle composites at all temperatures considered in this study.

Discussion

The sintered pellets by the SPS technique show higher density than oxidative sintered pellets as shown in Figure 4-4. These higher densities indicate that features in SPS such as mechanical pressure and rapid heating can result in fabrication of high density UO$_2$-SiC composites even with significant shorter hold times compared to oxidative sintering method.
In the case of oxidative sintering, the poor interfacial contact (Figure 4-6) and the presence of voids result in low density composites and lead to reduced thermal conductivity. Conversely, the physical contact between UO$_2$ and SiC grains along the interface is better in the pellets sintered by SPS. The presence of voids at the interface scatter conducted heat in a pellet and therefore, less heat reaches the interior SiC particles. Therefore, thermal conductivity is dramatically reduced in an oxidative sintered pellet.

As revealed in Figure 4-5, USi$_{1.88}$ peak was clearly seen in the oxidative sintered pellet where as the SPS pellet sintered at the same temperature didn’t show a similar reaction product. In the SPS, the pellet stays above 1370°C only for 9.6 minutes which is a significantly shorter time when compared to the 6.9 hours in oxidative sintering. The longer exposure time in oxidative sintering allows for diffusion of chemical species and formation of intermetallics (USi$_{1.88}$) and gas phases such as CO or CO$_2$. While intermetallics increase phonon scattering sites at the interfaces, gas phases may hinder the interfacial contact of UO$_2$-SiC by forming voids or causing separation. Both these factors could significantly reduce the thermal conductivity of the oxidative sintered pellet as seen in Figure 4-10.

It is clear from the results presented in this study that SPS not only offers significantly a shorter sintering time, but also provides a denser UO$_2$-SiC composite with reduced formation of chemical products, better interfacial properties, and above all, significantly better thermal conductivity than pellets obtained from oxidative sintering. It has been noted in the literature that a smaller grain size yields a lower thermal conductivity [78, 79]. However, for reactor applications a larger grain size of UO$_2$ is preferred due to the potential high diffusivity of fission products along grain boundaries. While the oxidative sintering method provides a larger grain size than SPS, one can increase the UO$_2$ grain size easily in SPS by simply increasing the hold time for an additional few minutes. Nevertheless, the current results indicate that when SiC is
added to UO₂, the effect of small grain size is not a significant factor when pellets with good density, good interfacial contact and no extraneous chemical products (such as intermetallics) are produced. In the current work SPS seems to produce UO₂-SiC composite pellets with all the above beneficial features.

**Conclusion**

UO₂-SiC pellets fabricated by SPS revealed higher density, better restraint of chemical reaction to form uranium silicide, superior interfacial contact, and smaller grain size compared to those fabricated by oxidative sintering. The SPS technique not only gives higher sintering rate, approximately 30 minutes operating time per pellet, but also allows up to 10% higher density of fabricated pellets compared to pellets prepared by the other method. XRD analysis on UO₂-SiC pellets revealed that the SPS sintering alleviates the concerns of reactions between the two phases that have been reported above 1370°C. Better interfacial contact between UO₂ and SiC were observed in SEM micrographs. Higher density, restriction on chemical reactions, and good interfacial contact are promising features for enhanced thermal conductivity UO₂ composite pellets.

Consequently, despite the small grains, the UO₂-SiC pellets made by SPS revealed enhanced thermal conductivity up to 62.1% compared to UO₂ pellets. On the other hand, the oxidative sintered pellets had lower thermal conductivity than UO₂ pellets and failed to achieve desired density above 95%. These experimental results suggest that SPS technique is more suitable for sintering of enhanced thermal conductivity UO₂-SiC nuclear fuel.
Figure 4-1. Morphologies of SiC whiskers and powder from manufacturers.

Figure 4-2. Dr. Sinter® SPS-1030 system and schematic drawing of the sintering chamber. Photo courtesy of Sunghwan Yeo.
Figure 4-3. Fabricated UO₂-SiC composite pellets. A) oxidative sintered composite. B) fabricated by SPS technique. Photos courtesy of Sunghwan Yeo.

Figure 4-4. Relative density of UO₂-10vol%SiC composite pellets sintered by SPS and oxidative sintering at various temperatures.
Figure 4-5. Polished surfaces of high density UO$_2$-10vol%SiC composites sintered by SPS showing uniform dispersion of SiC. A) SiCw and B) SiCp.

Figure 4-6. Microstructure of UO$_2$-10vol%SiC composites. A) and C) sintered by oxidative sintering method at 1500°C for 4 hours. B) and D) sintered by SPS at 1500°C and 5 minutes hold time.
Figure 4-7. EDS line scan across the interface of UO$_2$-SiC grains in a composite pellet fabricated by SPS at 1600°C.
Figure 4-8. Comparison of XRD spectra of UO$_2$-70vol%SiC pellets sintered by SPS and oxidative sintering at 1600°C. The peaks contained in dotted circles refer to USi$_{1.88}$ phase.
Figure 4-9. UO$_2$ grain size in composite pellets resulting from the addition of SiC powder particles and SiC whiskers.
Figure 4-10. The measured thermal conductivity values of UO$_2$ and UO$_2$-SiC composite pellets sintered by SPS and by oxidative sintering.
CHAPTER 5
THE INFLUENCE OF SIC PARTICLE SIZE AND VOLUME FRACTION ON THE THERMAL CONDUCTIVITY OF UO$_2$-SIC COMPOSITES

Background

In chapter 4, it has been shown that enhanced thermal conductivity of UO$_2$-10vol%SiC composite fuel pellets can be fabricated by the Spark Plasma Sintering (SPS) technique. In that study, SPS provided higher density composites, better interfacial contact, and reduced chemical reaction between UO$_2$ and SiC particles, compared to conventional sintering. SPS pellets also revealed a thermal conductivity increase of up to 62.1% at 900$^\circ$C compared to the literature value of UO$_2$ [76]. Because of its unique and superior properties such as high thermal conductivity, low neutron cross section, high melting point, and great chemical stability, Silicon Carbide (SiC) was chosen as the secondary phase in the UO$_2$ matrix to form heat conducting paths in the ceramic composites.

The thermal conductivity of a composite depends on the volume fraction, size, shape, and distribution of second phase particles, as well as the thermal resistance between its constituents [80]. The effective thermal conductivity depends on mechanical interfacial contact and interfacial phonon scattering phenomenon which is well known as Kapitza resistance [58] which was discussed in chapter 3. Kapitza resistance is always present in a composite even when the interfacial contact is atomically perfect. The influence of particle size and volume fraction of second phase particles on the effective thermal conductivity and its association with the interfacial thermal resistance have been well documented in literature. However, these principles and models have not been applied to nuclear fuels. Hanada et al., [18] determined that diamond particle size and volume fraction had a significant influence on the effective thermal conductivity of copper-diamond composites. They found that the composites containing larger diamond particles up to 7.7 µm and smaller volume fraction near 1% show higher thermal conductivity.
Hasselman et al., [81] investigated SiC reinforced alumina composites and found that composites containing larger SiC particles show higher thermal conductivity than that of alumina without SiC. Every et al., [19] observed that the thermal conductivity of zinc-sulphide could be increased by adding large diamond particles and decreased by adding sub-micrometer diamond particles due to increased interfacial thermal resistance. Bai et al., [24] fabricated MoSi$_2$-SiC composites containing 10, 20, and 30vol% of 0.5μm and 100nm SiC particles and found that the composite showed lower thermal conductivity with decreasing SiC particle size and increasing volume fraction due to the interfacial thermal resistance. Chu et al., [82] sintered Cu-Carbon Nanotube (CNT) composites and found that these composites had much lower thermal conductivity than calculated thermal conductivity value based on the rule of mixture which ignored the interfacial resistance. In general, it is found that ceramic composites containing larger particles (low surface to volume ratio) with high thermal conductivity reduce the interfacial thermal resistance, and hence, increase the effective thermal conductivity of ceramic composites.

In the current study, a series of UO$_2$- SiC composite fuel pellets with different sizes and volume fractions of SiC particles was fabricated using the SPS technique. The thermal conductivities of these composites were measured and compared to the values determined from theoretical formulations available in the literature. During the fabrication process, the sintering parameters such as hold time, ramp up/down rate, and pressure were kept constant so as to investigate only the effects of SiC particle size and volume fraction on the resulting thermal conductivity of the composite pellets.

**Experiments**

**Fabrication of UO$_2$-SiC Composite Pellets**

UO$_2$-SiC pellet fabrication procedure using SPS was described in detail in the previous chapter. Therefore, only a brief description is provided here. The uranium dioxide (UO$_{2.11}$)
powder was obtained from AREVA NP, Richland, WA and the SiC powder was obtained from Superior Graphite, Inc., Chicago, IL. The reported SiC particle mean diameters were 0.6, 1.0, 9.0, 16.9, and 55µm. The UO₂ and SiC powders were mixed in a ceramic vial with stainless steel balls and a blending aid, 2,3-Dihydroperfluoropentane, and blended in a SPEX 8000 shaker for 1 hour. For each mixing run the SiC mean particle size and the volume fraction of SiC powder in the mixture with UO₂ were varied as shown in Table 5-1 to investigate their effect on the thermal conductivity of the resulting UO₂-SiC composite pellet. The SiC particle sizes used in this study are most widely used in various applications and are also available as high purity (>98%) powders, and hence were obvious choice in our study. SiC particles with 1µm size at 5, 10, 15, and 20vol% were chosen to fabricate UO₂-SiC composite pellets. This volume range was selected because 20vol% is the maximum range where the available models are valid (to be described in the next section) so that we can compare the resulting thermal conductivity of the composites with model prediction. Also, excessive addition of SiC in nuclear fuel is unrealistic due to the exorbitant cost and stringent regulation of U-235 enrichment process which is necessary to compensate reduced fissile isotope in UO₂-SiC composite fuel. SiC particles dispersed in UO₂ powders were then sintered using a Dr. Sinter® SPS-1030 system at 1350°C and 1450°C for 5min in a vacuum (~30mTorr). The ramp up/down rate and mechanical pressure at the maximum sintering temperature were held constant at 100°C/min and 36MPa, respectively.

The heat treatment procedure described in ASTM C 1430-07 was conducted on the sintered composite pellet to reduce UO₂-x to stoichiometric UO₂,0, which is known to have the optimum thermal properties [1]. The ramp up/down rate and maximum temperature were set at 2.6°C/min and 800°C, respectively. The heat treatment was performed in a Lindberg® alumina tube furnace using 4%H₂-N₂ gas with a dew point maintained at 35°C.
Characterization Methods

The weight of each pellet in air and water was measured and the average density was calculated from three weight measurements per pellet using the Archimedes principle. The measured density of the composite was then compared with theoretical density obtained from the rule of mixture [83].

\[
\rho_c = \rho_{UO_2}(1 - V_p) + \rho_{SiC}V_p
\]  \hspace{1cm} (5-1)

Where \(\rho_{UO_2}\), \(\rho_{SiC}\), and \(V_p\) are the densities of UO\(_2\) and SiC, and the SiC volume fraction, respectively.

The microstructure of the fabricated composite pellets were observed using a scanning electron microscope (SEM, JEOL JSM-6335F). The pellets were metallographically polished with successively smaller grit SiC abrasive paper and finally with 0.06\(\mu\)m colloidal silica. The surface was thermally etched at 1340\(^\circ\)C in Ar atmosphere for 4 hours to reveal the grain boundaries of UO\(_2\) matrix in the composite pellets.

The measurement of thermal diffusivity was carried out at 100, 500, and 900\(^\circ\)C using a laser flash instrument (AnterFlashline\(^{\circledR}\)3000) with a Xenon discharge pulse for 1\(\mu\)s duration. Three measurements were performed at each temperature on each pellet and the average diffusivity was obtained. The specific heat capacity of UO\(_2\)-SiC composite pellet was calculated using the Neumann-Kopp rule [84], i. e.,

\[
C_p = C_{UO_2}(1 - f_p) + C_{SiC}f_p
\]  \hspace{1cm} (5-2)

Where \(C_{UO_2}\), \(C_{SiC}\), and \(f_p\) are theoretical specific heat capacities of UO\(_2\) and SiC, and weight fraction of SiC particles, respectively, at a specific temperature. \(C_{UO_2}\) and \(C_{SiC}\) at 100\(^\circ\)C, 500\(^\circ\)C, and 900\(^\circ\)C are listed in Table 5-2. The thermal conductivity, \(K\), of composite pellets was then determined from the relation.

\[
K = DC_p\rho_c
\]  \hspace{1cm} (5-3)
Where, $D$ and $\rho_C$ are the thermal diffusivity and density of the composite, respectively.

**Results and discussion**

*Size Effect of SiC Particles on UO$_2$-5vol$\%$ SiC Composite Properties*

The micro-morphologies and thermal properties of UO$_2$-5vol$\%$SiC composite fuel pellets containing SiC particles with five different sizes (Table 5-1) were examined. Figure 5-1 shows the microstructures of these composites where the SiC particles appear black and the brighter area indicates the UO$_2$ matrix. The SiC particles appear to be homogeneously dispersed in the UO$_2$ matrix in all the composites. However, as shown in Figure 5-1(e), in the composite containing 55µm SiC particles, distinct radial micro-cracks were observed originating at the interface between a SiC particle and UO$_2$ matrix and propagating towards another SiC particle.

The interfaces between the UO$_2$ matrix and SiC particles in UO$_2$-5vol$\%$SiC composite pellets with different sized SiC grains are shown in Figure 5-2. The micro-cracks emanating from the SiC particles are clearly seen in Figure 5-2 (c), (d), and (e) indicating that micro-cracks evolve in composites with SiC particles larger than 9µm in size. However, the micro cracking is less severe in composites with SiC particles of size 9µm and 16.9µm compared to the composite containing 55µm diameter SiC particles. No visible cracks in the micro structure was seen in the composite pellets with smaller size SiC particles.

It is also seen that with increasing particle size there is a larger separation between the SiC particle and the UO$_2$ matrix. Figure 5-3 shows the interfacial debonding between UO$_2$ and SiC particles in each composite with the three largest size SiC particles. While the interfacial contact between UO$_2$ grains and 9µm SiC particle is fairly good, a visible gap is observed at the interface between UO$_2$ grains and SiC particle when the particle size is 16.9µm or greater.

Micro-cracking and interfacial debonding occur in various composites during the sintering process due to a mismatch in coefficients of thermal expansion (CTE) between the matrix and
the second phase particles [85-91]. Lu et al., [90] studied thermal matrix cracking in various intermetallic composites and concluded that a critical particle size exists under which microcracking was suppressed. Todd et al., [85] investigated alumina-20% SiC composites and found thermal cracks in only the composites containing SiC particles larger than 9µm. Fu et al., [91] fabricated polypropylene (PP) -calcium carbonate (CaCO₃) composites and found interfacial debonding in composites containing larger than 0.1µm diameter CaCO₃ particles.

The relevant thermal properties for UO₂ and β-SiC are shown in Table 5-2. The thermal expansion coefficient of UO₂ is more than twice that of SiC so that the matrix expands into the particles during the cooling process forcing the SiC particles into compression. The larger the particle size, the more will be the induced compressive stress due to the lower surface area-to-volume ratio of the larger particles. When the stress intensity at the interface exceeds the grain boundary toughness of matrix material, spontaneous microcracking is initiated from the interface into the matrix in a ceramic composite [85]. The induced internal stress caused by a mismatch in CTE of constituents in a composite also leads to a partial interfacial debonding [92]. The degree of interfacial debonding is dependent on the level of mismatch in CTE, elastic properties of the constituents, the temperature range of cooling process, and the energy required to create a new surface [93]. Because these thermal cracks and the interfacial debonding in composite pellets obstruct the pathway for heat conduction, extensive cracking and poor interfacial contact obviously lead to lower thermal conductivity.

The measured density of UO₂-SiC composite fuel pellets containing 5vol% SiC particles but of different sizes are shown in Table 5-1. The densities of all composite pellets are near 95%TD and appear to not be dependent on the SiC particle size. Because the thermal conductivity is directly proportional to the density as seen in Equation 5-3, and the density of the composite pellet is not dependent on the SiC particle size, the measured pellet thermal
conductivity will mostly depend on the size of SiC particles as will be discussed in the following paragraph.

Figure 5-4 shows the temperature dependence of the measured thermal diffusivity for UO$_2$-5vol% SiC composite pellets containing various sizes of SiC particles. The red line refers to the literature value [76] of 95% dense UO$_2$. In general, the UO$_2$ thermal diffusivity decreases with temperature due to increased phonon-phonon scattering at higher temperatures [94]. This trend is maintained in the thermal diffusivity of UO$_2$-5vol%SiC composite pellets as well. In general, the larger the SiC particle size the lower the thermal diffusivity. However, the thermal diffusivity of the composite pellets containing 55µm SiC particle shows a significantly lower thermal diffusivity than the literature UO$_2$ value due to extensive micro-cracks and severe interfacial debonding as shown in Figure 5-2 and Figure 5-3.

Figure 5-5 shows the thermal conductivity determined by Equation 5-3 using the measured thermal diffusivity (Figure 5-4), calculated specific heat capacity, and the measured density (Table 5-1) for composites with different SiC size particles at three temperatures. The specific heat capacities of UO$_2$ and β-SiC are shown in Table 5-2 and were utilized to determine that of the UO$_2$-5vol% SiC composite. Using Equation 5-2, the specific heat capacities at 100, 500, and 900°C were calculated to be 266.5, 317.5, and 328.5 J/kg·K, respectively. While the composite pellets containing 0.6, 1.0, and 9.0µm diameter SiC particles showed enhanced thermal conductivity, the composite pellets containing 16.9 and 55µm diameter SiC particles revealed lower thermal conductivity than a UO$_2$ pellet. The SiC particle size dependence of thermal conductivity at various temperatures is shown in Figure 5-5. While marginal reduction in thermal conductivity in the pellets containing 16.9µm SiC particles is noted, the reduction in pellets containing 55µm diameter SiC particles is particularly large; a decrease of 21~28.3% depending on the testing temperature. These composite pellets with poor thermal conductivity and
containing large SiC particles are the same pellets which exhibited micro-cracks and interfacial debonding next to the large SiC particles as shown in Figure 5-2 and Figure 5-3. These observations support the hypothesis that micro-cracking and interfacial debonding are responsible for the reduction in thermal conductivity of UO_2-SiC composite containing large SiC particles. The 55µm diameter SiC particle composite pellet has the most severe micro-cracks and the largest interfacial debonding resulting in a greatly reduced thermal conductivity. Based on these observations, a composite pellet with SiC particles smaller than 16.9µm diameter is recommended for enhanced thermal conductivity.

The Effect of Volume Fraction of SiC Particles

To understand of the influence of volume fraction of SiC particles on the thermal properties of UO_2-SiC composite pellets, we have chosen one SiC particle size (1µm) and varied the volume fraction (Table 5-1) at 5, 10, 15, and 20%. All the other variables were kept constant during the sintering process. Micro-structures of the four composite pellets revealing homogeneously dispersed 1µm SiC particles are shown in Figure 5-6. With increase in volume fraction, particle-particle interaction is noted as seen in Figure 5-6 (c) and (d).

Figure 5-7 reveals a decrease in the relative density of UO_2-SiC composite pellets with increasing SiC volume fraction. This trend has been reported in literature for many composites [21-23]. It is rationalized that increase in particle volume fraction hinders the consolidation of matrix grains. Maekawa et al., [23] suggested that with increasing volume fraction of particles pores remain locked around particles and eventually lead to form pore channels decreasing the three dimensional connectivity of a matrix material to lower relative density.

The measured thermal diffusivity of the composite pellets containing various volume fractions of 1µm size SiC particles is shown in Figure 5-8. It is seen that the higher the volume fraction of SiC particles, the higher the thermal diffusivity of the composite. This trend indicates
that inclusion of higher thermal conducting particles into UO$_2$ matrix increases the diffusion of heat energy in the composite provided good interfacial bonding is maintained.

Figure 5-9 reveals the calculated (Equation 5-2) specific heat capacity ($C_p$) of UO$_2$-SiC composites containing various volume fractions of SiC particles at 100, 500, and 900°C. As the SiC volume fraction and temperature increase the specific heat capacity also increases. This is because larger number of molecular energy states are available at higher temperature and the specific heat capacity follows Neumann-Kopp rule (Equation 5-2) [84]. Also note that initially there is a significant increase in specific heat from 100°C to 500°C but this increase in $C_p$ is lower from 500°C to 900°C.

Hasselman and Johnson [62], and recently Nan et al., [65], provided an expression for calculating the effective thermal conductivity of a composite. Their model is based on the effective medium approximation [95] which includes the influence of size, volume fraction, and shape of second phase particles, as well as interfacial thermal resistance. For a composite containing spherical shaped particles dispersed homogeneously in a matrix material, the effective thermal conductivity is given by,

\[ k_{\text{eff}} = k_m \left( 1 + \frac{k_p}{k_m} \frac{V_p}{V_m} + \frac{k_p}{k_m} \frac{V_p}{V_m} \right) \]

(5-4)

Where $k_{\text{eff}}$ is the effective thermal conductivity, subscripts $p$ and $m$ are particle and matrix, respectively, $V_p$ is the volume fraction of particles, $a$ is the radius of particle, and $h_c$ is the interfacial thermal conductance. The reported interfacial thermal conductance $h_c$ for Al and SiC covers the range of $2.8 \times 10^8 \text{ W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$ [26]. So far, the value of $h_c$ accounting for the UO$_2$-SiC interface has not been reported to our knowledge. However, it can be estimated using the acoustic mismatch model of Swartz and Pohl [25] where the interfacial thermal conductance is given by,
\[ h_c \approx \frac{1}{2} \rho_m \cdot C_p \cdot \frac{v_m^3}{v_p^3} \cdot \frac{\rho_m \rho_p v_m v_p}{\rho_m v_m + \rho_p v_p} \]  \quad (5-5)

Where \( \rho \) is density, \( C_p \) is the specific heat capacity of matrix, \( v \) is phonon velocity, and subscripts \( p \) and \( m \) refer to particle and matrix, respectively. The phonon velocities of UO\(_2\) matrix and SiC particle can be estimated using the following equation [96].

\[ \frac{1}{v_l^2} + \frac{2}{v_t^2} = \frac{3}{v} \]  \quad (5-6)

Where \( v_l \) and \( v_t \) are the longitudinal and transverse phonon velocities. The referenced UO\(_2\) longitudinal and transverse phonon velocities are 5552.7 and 2841.8m/s [97], respectively, and those of SiC are 11800 and 7600m/s [98], respectively. The estimated phonon velocities of UO\(_2\) and SiC using Equation 5-6 are 3272.8 and 8470.9m/s, respectively. Utilizing these values for \( v_m \) and \( v_p \), \( \rho_m = 10960 \text{ kg/m}^3 \), \( \rho_p = 3200 \text{ kg/m}^3 \), \( C_p \) of UO\(_2\) at three different temperatures as listed in Table 5-2 and using Equation 5-5, we obtain \( h_c = 1.69 \times 10^8 \) at 100\(^o\)C, \( 2 \times 10^8 \) at 500\(^o\)C, and \( 2.06 \times 10^8 \text{ W/m}^2\text{K} \) at 900\(^o\)C, respectively.

Given these input parameters with particle volume fraction (0.05-0.2), radius (0.5\( \mu \)m), and \( k_m \) and \( k_p \) as listed in Table 5-1 into Hasselman and Johnson model (Equation 5-4), the comparison between experimentally obtained and theoretically calculated effective thermal conductivity is shown in Figure 5-10. Experimentally measured density (Figure 5-7), thermal diffusivity (Figure 5-8), and the calculated specific heat (Figure 5-9) were utilized to determine the experimental effective thermal conductivity using Equation 5-3. The higher the volume fraction of SiC particles, the higher the thermal conductivity of the composite. The average increase in thermal conductivity with the addition of 5, 10, 15, and 20vol\% of SiC particles are 14.23, 26.44, 43.22, and 49.84\%, respectively. Considering the error bar, great agreement between experimentally determined and theoretically calculated effective thermal conductivities
is seen for the composite pellets containing 5, 10, and 15 vol% of SiC particles. The agreement is also much better at higher temperature (900°C) than at lower temperature (100°C).

The lower experimental thermal conductivities of 20 vol% SiC can reflect the relatively lower densification and the abundance of particle-particle interactions of the composite containing higher volume fraction of SiC particles. As shown in Figure 5-7, the composite containing 20 vol% of SiC has only 94.41% relative density and seemed to be responsible for decreasing the thermal conductivity (Equation 5-3). The interaction between SiC particles is seen in Figure 5-6 and it is more abundant with increasing SiC volume fraction. The particle-particle interaction is not accounted for in Hasselman and Johnson model due to the complexity of the phenomena [65]. Observation of the interfacial contact between SiC particles (Figure 5-11) indicates that pores are predominantly located at the interface reducing the overall thermal conductivity due to the phonon scattering.

Non-ideal shape of SiC particles and thermal diffusivity measurement error also can reflect the difference between experimental and theoretical effective thermal conductivities. The irregularities in SiC particle shape can be clearly seen in Figure 5-1 and Figure 5-2. Because the Hasselman and Johnson model (Equation 5-4) only accounts for spherical shaped secondary particles, a discrepancy between theoretical model and experimental measurement is expected. Thermal diffusivity measurement error also may contribute to the difference between experimental and theoretical effective thermal conductivities. The difference between actual measurement temperature and the set up temperature and change in the density value of pellet at different temperatures may cause some error to the experimental thermal conductivity.

Regardless, we observed relatively good agreement between the experimental and theoretical effective thermal conductivities of UO₂-SiC composites. This result supports that UO₂ matrix and 1μm SiC particles are mechanically well contacted in UO₂-SiC composites thus
improving the effective thermal conductivity. Moreover, both experiments and the theoretical model revealed that higher effective thermal conductivity is obtained with increasing SiC volume fraction. However, the utilized powder blending procedure and SPS process conditions, see Table 5-1, are only valid for fabrication of UO$_2$-SiC composites containing up to 15% SiC particles by volume. More acceptable powder mixing procedure such as a longer time blending and better consolidation process such as SPS sintering at higher temperature, pressure, or longer hold time may be required to produce UO$_2$-SiC composite containing more than 15vol% of SiC at high densities. If the composite possesses reduced particle-particle interactions and higher density by doing so, probably higher effective thermal conductivity close to the predictions of Hasselman and Johnson model [62] could be obtained even in composites with larger particle sizes and at higher volume fractions.

### Conclusion

The microstructure and thermal properties such as thermal diffusivity, specific heat capacity, and thermal conductivity of UO$_2$-SiC composite fuel containing various SiC particle sizes and volume fractions were investigated. The SPS technique was utilized to fabricated high density composite pellets in a relatively short time of 5mins at 1350-1450°C. While the composite pellets containing 0.6, 1.0, 9.0µm diameter SiC particles showed higher thermal conductivity, those pellets containing 16.9 and 55µm diameter particles exhibited lower thermal conductivity than the literature UO$_2$ values. In the latter two composite pellets, extensive micro-cracks and interfacial debonding formed due to the mismatch in CTE between UO$_2$ and SiC and were attributed to be responsible for the observed low thermal conductivity of the composites. The composite pellets containing higher volume fraction of SiC particles revealed lower density, higher diffusivity and specific heat, and higher thermal conductivity. Good agreement was observed between experimentally determined thermal conductivity of the composites containing
5, 10, and 15vol% of 1μm size SiC and theoretically calculated thermal conductivity based on Hasselman and Johnson model [62]. However, the composite containing 20vol% of 1μm size SiC showed lower thermal conductivity than theoretical value due to the lower density and particle-particle interaction recognized in microstructure observation. Irregular shape of SiC particles and thermal diffusivity measurement error also possibly contributed to the difference between experimental and calculated thermal conductivities. Consequently, it is concluded that SiC particles smaller than 16.9μm to suppress micro-cracking and higher SiC volume fraction to form enough heat conducting paths are required to increase thermal conductivity of UO₂-SiC composite fuel pellets.
### Table 5-1. Details of SiC particle size, volume fraction, and sintering conditions in the SPS.*

<table>
<thead>
<tr>
<th>SiC particle mean diameter (µm)</th>
<th>SiC volume fraction (%)</th>
<th>Maximum sintering temperature (°C)</th>
<th>% TD of the composite pellet ±SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>5</td>
<td>1350</td>
<td>95.25 ± 0.24</td>
</tr>
<tr>
<td>1</td>
<td>5</td>
<td>1350</td>
<td>95.27 ± 0.3</td>
</tr>
<tr>
<td>1</td>
<td>5</td>
<td>1450</td>
<td>96.81 ± 0.39</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>1450</td>
<td>96.63 ± 0.35</td>
</tr>
<tr>
<td>1</td>
<td>15</td>
<td>1450</td>
<td>95.14 ± 0.23</td>
</tr>
<tr>
<td>1</td>
<td>20</td>
<td>1450</td>
<td>94.41 ± 0.3</td>
</tr>
<tr>
<td>9</td>
<td>5</td>
<td>1350</td>
<td>95.15 ± 0.09</td>
</tr>
<tr>
<td>16.9</td>
<td>5</td>
<td>1350</td>
<td>94.75 ± 0.17</td>
</tr>
<tr>
<td>55</td>
<td>5</td>
<td>1350</td>
<td>95.1 ± 0.13</td>
</tr>
</tbody>
</table>

* Hold time=5mins; ramp up/down rate=100°C/min; pressure=36MPa.

### Table 5-2. Thermal properties of UO₂ and SiC.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Thermal expansion coefficient (K⁻¹) [76, 99] at 25°C</th>
<th>Specific heat, Cₚ (J/kg·K) [55, 76]</th>
<th>Thermal Conductivity, K (W/m·K) [55, 76]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100°C</td>
<td>500°C</td>
<td>900°C</td>
</tr>
<tr>
<td>UO₂</td>
<td>9.93 x 10⁻⁶</td>
<td>258.17</td>
<td>304.62</td>
</tr>
<tr>
<td>β-SiC</td>
<td>4.4 x 10⁻⁵</td>
<td>815.88</td>
<td>1125.5</td>
</tr>
</tbody>
</table>
Figure 5-1. Microstructure of UO$_2$-5vol%SiC composite pellets containing various diameters of SiC particle. A) 0.6µm. B) 1µm. C) 9µm. D) 16.9µm. E) 55µm. Note microcracks originating from large size SiC particles in E.
Figure 5-2. SiC particles in UO$_2$-5vol%SiC composite pellets with various mean diameters. A) 0.6µm. B) 1µm. C) 9µm. D) 16.9µm. E) 55µm. The micro-cracks in matrix and between two SiC particles are identified by arrows.
Figure 5-3. Interfacial debonding in UO$_2$-SiC composites with various sizes of SiC particle. A) 9µm. B) 16.9µm. C) 55µm.
Figure 5-4. Thermal diffusivity of UO$_2$-5vol%SiC composite pellets with various SiC particle sizes as a function of temperature.
Figure 5-5. Thermal conductivity of UO$_2$-5vol%SiC pellets with various sizes of SiC particles at the selected temperatures. The dotted lines refer to UO$_2$ literature values at each temperature.
Figure 5-6. Microstructures of UO₂-SiC composites containing 1μm SiC particles with various volume fractions. A) 5%. B) 10%. C) 15%. D) 20vol%. Bright and dark areas refer to UO2 matrix and SiC particles, respectively. The red circles indicate particle-particle interactions.
Figure 5-7. Relative density of UO$_2$-SiC composite pellets containing various fractions of 1μm size SiC particles.
Figure 5-8. Thermal diffusivity of UO₂-SiC composite pellets containing various volume fractions of 1μm size SiC particles as a function of temperature.
Figure 5-9. Temperature dependence of specific heat capacities of UO$_2$-SiC composite pellets containing various volume fraction of 1μm size SiC particles.
Figure 5-10. Calculated and experimentally determined thermal conductivities of UO$_2$-SiC composites at the selected temperatures with various volume fraction of 1μm SiC particles. The UO$_2$ literature values at each temperature are indicated at Vf =0.

Figure 5-11. Interfacial contact between 1μm SiC particles in a UO$_2$-20vol%SiC composite. Interfacial porosities are indicated by arrows.
CHAPTER 6
MECHANICAL PROPERTIES AND INTERNAL STRESS MEASUREMENT OF UO₂-SIC COMPOSITES

Background

In the previous chapter, when the SiC volume fraction was maintained at 5vol%, the influence of five different mean diameters of SiC spherical particles (0.6, 1, 9, 16.9, and 55μm) on the thermal conductivity of composites were investigated. The extensive UO₂ microcracking and UO₂-SiC interfacial debonding were clearly observed in composites containing large SiC particles (16.9 and 55μm) due to the difference in CTEs (Figure 5-2). The microstructure of composite containing 9μm SiC particles showed relatively good interfacial bonding (Figure 5-3) and a few little microcracks (Figure 5-2). While the resulting thermal properties of the composite containing 16.9 and 55μm SiC particles decreased, the thermal properties of composite containing 9μm SiC particles showed similar to those of other composites containing 0.6 and 1μm SiC particles (Figure 5-4 and 5-5). Therefore, it is difficult to address the feasibility of 9μm SiC particles to produce UO₂-SiC composite fuels obtaining sound microstructure.

Microstructural flaws such as microcracks in a nuclear fuel can be a significant problem releasing fission gases during the operation of a nuclear reactor. The production of inert gases such as Helium (³He), Krypton (³⁶Kr), and Xenon (⁵⁴Xe) by the fission process of Uranium constituents about 15% of total fission product [100]. These gas atoms may form bubbles in the nuclear fuel or be released from the fuel when they reach any open porosity that is connected to a free volume. The microcrack is one of major open porosities and the large amount of fission gas can be released through microcracks. Once the gas is released to a free space in fuel pin, the pressure inside fuel pin increases leading to higher degree of cladding rupture and hence a reduced safety margin. Therefore, more detailed investigation on UO₂-SiC composites
containing various sized SiC particles to verify the onset of micro-cracking and the SiC particle critical size where micro-cracks can be suppressed.

Because microcracks are not always revealed in a polished surface and the thermal property measurements are not very sensitive to microcracking, the onset of microcracking can be monitored by the measurement of mechanical properties and internal stress. Pan et al. [101] investigated SiC-TiB₂ composites and found a decrease in Young's modulus due to the microcracking of a composite containing 4.7μm sized TiB₂ particles. Green [102] fabricated Al₂O₃-ZrO₂ composites and measured Young's modulus and hardness to find the critical ZrO₂ particle size where microcracking can be suppressed. In another study, Watts et al. [31] examined microcracking in hot pressing sintered ZrB₂-SiC composites. They showed that the strength, modulus, and hardness of composites decreased abruptly due to microcracking when the incorporated maximum SiC particle size exceeded 11.5μm. Todd and Derby [85] investigated Al₂O₃-20% SiC composites and found microcracks in only the composites containing SiC particles larger than 9μm. They especially measured the internal stress of SiC particles in composites and showed that matrix microcracking originating from the interface between Al₂O₃ and SiC released the compressive stress of SiC particles.

In addition to the observation of microcracking, the investigation of mechanical properties of UO₂-SiC composites is necessary to find additional benefits of SiC inclusion and clarify the values of UO₂-SiC composite fuel. Even though sound mechanical properties of nuclear fuel are essential for successful operation of nuclear reactor [1], no reported literature exists for the investigation of UO₂-SiC composites due to the manufacturing difficulty of such composites. Since we have successfully fabricated high density UO₂-SiC composites using SPS technique, it is rationalized to exam their mechanical properties.
Most mechanical properties of UO$_2$ fuel are expected to be increased by SiC addition based on other research publications regarding enhanced mechanical properties of composites by adding SiC particles. SiC has excellent mechanical properties such as hardness (20-30GPa), young’s modulus (400-500GPa) and shear modulus (160-190GPa) [103] due to its high bonding strength and unique lattice structure. Therefore, SiC is often utilized to the fabrication of composites to fulfill required mechanical properties. Chamberlain et al., [104] increased the strength and toughness of ZrB$_2$ from 565MPa to more than 1000MPa and from 3.5MPa to 5.3MPa, respectively, by adding 20-30vol% SiC particles. Chou et al., [30] found that alumina increased young’s modulus by near 20% by adding 30vol% SiC platelets.

In this study, we investigated mechanical properties of UO$_2$-SiC composites containing various sizes and volume fractions of SiC particles. The mechanical properties consist of Vickers and Knoop hardness, and Young's modulus. The internal stress of different sized SiC particles in UO$_2$ matrix was measured using a Raman-spectroscopy.

**Experiments**

**Sample Preparation**

The uranium dioxide (UO$_{2.11}$) powder was obtained from AREVA NP, Richland, WA and the SiC powder was obtained from Superior Graphite, Inc., Chicago, IL. Reported mean diameters of the obtained SiC powders were 0.6, 1, 9, 16.9, and 55μm. To ensure the particle mean diameters and size distribution, Laser Diffraction Particle Size Analyzer (LS 13 320, Beckmen Coulter, Inc., Brea, CA) was performed. This analysis was conducted three times per SiC powder. Particle mean size and particle size distribution were determined using volume distribution as shown in Table 1.

In this study, we utilized previously fabricated seven UO$_2$-SiC composites described in chapter 5 containing the five different sized SiC particles (0.6, 1, 9, 16.9, and 55μm) with 5vol%
and two different volume fractions (5 and 10%) of 1μm SiC. The composites containing 15 and 20vol% of 1μm SiC particles utilized in chapter 5 were found to have interactions between SiC particles (Figure 5-11) and lower density than other composites (Table 5-2). Because mechanical properties are sensitive to the density of composite and SiC particle interaction, it was required to produce higher density composites with reduced interaction between SiC particles. Basic SPS fabrication method is same as previous chapters except the blending procedure and the sintering temperatures. Hence, only these modifications are briefly described here. The UO₂ and SiC powder mixing was performed for 2hours which is 1hour longer than that of previous chapter to reduce the interaction between SiC particles in the composites. After mixing, higher SPS sintering temperatures than those of previous chapter were set at 1510 and 1550°C, respectively for fabricating higher density composites. The resulting average densities of these composites containing 15 and 20vol% of 1μm SiC particles increased to 96.54 and 96.51%TD, respectively. In addition to that, UO₂ pellets without any SiC addition were also fabricated using SPS at 1350 and 1450°C to compare the mechanical properties of UO₂ with UO₂-SiC composites. Table 2 lists the composition of fabricated composites and UO₂ with sintering conditions, SiC particle size and volume fraction, and relative density. While SPS processing conditions such as mechanical pressure, hold time, and ramp up/down rates were set at 36MPa, 5mins, and 100°C/min, respectively, during all fabrication processes, only sintering temperature was varied at each sample to maintain similar resulting densities. Relative densities of the listed composite and UO₂ cover the range of 95~97%.

The fabricated composites and UO₂ were mechanically polished with successively smaller grit SiC abrasive paper, Diamond particles, and finally 0.06μm colloidal silica. Thermal etching at 1350°C for 4hours in UHP Ar atmosphere was performed using a furnace (Lindberg 1700°C tube furnace) to reveal grain boundaries of composites. The microstructure of composites was
observed using Scanning Electron Microscopy (SEM, JEOL JSM-6335F). The UO$_2$ grain size was measured three times at different locations for each composite using the line intercept method [75].

**Mechanical Testing**

The hardness of the composites was measured using both Vickers and Knoop indentations (Model Tukon2100B, Instron, Jacksonville, FL). The measurements were conducted at 500g applied load with a dwell time of 12 seconds. At least 10 measurements were performed at each indentation with different locations and the average hardness values were obtained and utilized in this study. Ultrasonic measurement system (Model 5072PR, Olympus, Waltham, MA) was performed on each composite to measure both longitudinal and shear velocities to determine Young's modulus, respectively. Five measurements were performed on each composite and the average value was utilized in this study.

**Raman Spectroscopy**

Raman spectroscopy (InVia Raman Microscope System, Renishaw, Hoffman Estates, IL) was performed on the composites containing different size SiC particles to measure the internal stress of the SiC particles as a function of particle size. The Raman spectrometer consisted of a Si laser (532 nm) to excite samples, a single spectrograph, and optical microscope (a Leica microscope with a XYZ mapping stage). The spectrometer was initially calibrated with a Si(100) standard using a Si band position at 520cm$^{-1}$. The desired scattering area within SiC grains or at the interface between UO$_2$ and SiC were selected using a 100x objective lens. A maximum power of the laser was set at 25mW. Raman spectra were corrected from five different SiC particles in each composite and the average peak position was used in this study.
Results and Discussion

Mechanical Properties

Hardness of UO$_2$-SiC composites

Both Vickers and Knoop hardness, and Young's modulus were measured for all composites and are summarized in Table 6-2. Figure 6-2 shows the hardness as a function of the particle size and volume fraction of SiC. In Figure 6-2 (a), in general the hardness decreased with increasing SiC particle size and exhibited a discontinuous change, once the SiC particle size exceeds 1μm. From 1μm to 9μm SiC, the Vickers hardness decreased by almost 23% (6.9 to 5.3GPa). A similar trend can be seen in the Knoop hardness; the Knoop hardness decreased by 13% (5.6 to 4.7GPa) from 1μm to 9μm SiC. In Figure 6-2 (b), with increasing the volume fraction of SiC particles, both Vickers and Knoop hardness values increases. While the Vickers hardness increased up to 9.2GPa with 20vol% of 1μm SiC particles, the Knoop hardness increased up to 8.1GPa. When compared to pure UO$_2$, these enhancements are 53 and 58%, respectively.

Figure 6-3 (a) and (b) show typical shapes of the Vickers and Knoop indentations, respectively. The Vickers indentation is a square-pyramidal diamond with an included angle of 135° in both direction. The Knoop indentation is a elongated-pyramidal diamond along one diagonal with an included angle of 170° on the long axis and 130° on the short axis. The sharper Vickers indentation more effectively opens the pre-existing microcracks or interfacial debonding in the composite than the Knoop indentation. Therefore, Vickers hardness decreases more abruptly than that of the Knoop hardness when UO$_2$-SiC composites contain microcracks. A similar behavior has been reported in Al$_2$O$_3$-ZrO$_2$ and ZrB$_2$-SiC systems [31, 102]. Greater than ~10vol% of ZrO$_2$ addition in Al$_2$O$_3$-ZrO$_2$ composite resulted in decreased hardness due to microcracks [102]. The Vickers hardness of ZrB$_2$-30vol%SiC composites containing larger SiC particles than 11.5μm decreased more than that of Knoop hardness due to the sharper indentation geometry [31].

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In Figure 6-2, the relatively larger error bars of the composites containing large sized SiC particles (9, 16.9, and 55μm) in the Vickers hardness values may be caused by the limit of the Vickers indentation area. As shown in Figure 6-3, while the average diagonal length Vickers indentation covers the 15~20μm, that of the Knoop indentation covers 60~80μm in the long axis and 5~9μm in the short axis. The average covered area of Vickers indentation is 160~180μm² and that of Knoop indentation is 270~280μm². The average length between SiC particles in the composite containing 1μm SiC particles is less than 5μm, that of composite containing 9, 16.9, and 55μm are around 10, 15, and 27μm, respectively. Because the Vickers indentation covers a relatively small area, the indentation area may not include any SiC particles in the composites containing large SiC particles. Then, only UO₂ hardness values can be obtained decreasing the average hardness value and increasing the error bars.

**Bulk, shear, and Young's moduli of UO₂-SiC composites**

Hashin and Shtrikman [105] derived an expression for calculating the effective bulk and shear moduli of a composite. In fact, the Young's modulus of composites containing finite concentration of second phase spherical particles is very difficult to calculate because detailed elastic field analysis considering interface continuity condition is required [106]. Therefore, they had to assume the composite material was statistically isotropic and obtained homogeneous interfacial boundary conditions. Based on variational principles in terms of the elastic polarization tensor described in [107], they obtained upper and lower bounds on the effective bulk and shear moduli of a composite containing two phases [105].

\[
K_U^* = K_p + \frac{V_m}{1/(K_m - K_p) + 3V_p(3K_p - 4G_p)}
\]

\[
K_L^* = K_m + \frac{V_p}{1/(K_p - K_m) + 3V_m(3K_m - 4G_m)}
\]
Where $K$ is bulk modulus, $K^*_U$ and $K^*_L$ are upper and lower effective bulk moduli, respectively, $V$ is volume fraction, $G$ is shear modulus, and subscripts $p$ and $m$ refer to second-phase particle and matrix, respectively.

$$G^*_U = G_p + \frac{V_m}{1/(G_m - G_p) + 6V_p(K_p + 2G_p)/(5G_p(3K_p + 4G_p))} \quad (6-3)$$

$$G^*_L = G_m + \frac{V_p}{1/(G_p - G_m) + 6V_m(K_m + 2G_m)/(5G_m(3K_m + 4G_m))} \quad (6-4)$$

Where $G^*_U$ and $G^*_L$ are upper and lower effective shear moduli, respectively. These bounds follow typical relation of Young’s modulus of $E$ to $K$ and $G$.

$$E^*_U = \frac{9K^*_U G^*_U}{3K^*_U + G^*_U} \quad (6-5)$$

$$E^*_L = \frac{9K^*_L G^*_L}{3K^*_L + G^*_L} \quad (6-6)$$

Where $E^*_U$ and $E^*_L$ are upper and lower effective Young's moduli, respectively. The referenced UO$_2$ bulk and shear moduli are 184 and 76.3GPa [108], respectively, and those of SiC are 308.6 and 179GPa [109], respectively. The estimated upper and lower bounds on the effective bulk, shear, and Young's moduli of UO$_2$-SiC composite using equations above with different volume fractions (5-20%) are listed in Table 3.

To further investigate the influence of SiC addition on the Young's modulus and verify whether the experimentally determined values are in agreement with the calculated values using the Hashin and Shtrikman model, the Young's modulus values were examined using measured longitudinal and shear velocities. The following equations were utilized to determine Poisson's ratio, $\nu$, and Young's modulus, $E$ [110].

$$\nu = \frac{1-2(V_S/V_L)^2}{2-2(V_S/V_L)^2} \quad (6-7)$$

$$E = \frac{V_L^2 \rho(1+\nu)(1-2\nu)}{1-\nu} \quad (6-8)$$
Where $V_s$ and $V_L$ are shear and longitudinal velocities, and $\rho$ is the density of composite. With measured density of composite, the Poisson's ratio and Young's modulus of composites were determined.

Experimentally measured and theoretically calculated Young's moduli as a function of SiC particle size and volume fraction followed similar pattern as the hardness as shown in Figure 6-4 (a) and (b), respectively. The upper and lower bounds of calculated Young's moduli using Hashin and Shtrikman model [105] are presented as blue and red dash lines in Figure 6-4. For small SiC particle sizes (0.6 and 1μm), the Young's modulus remained constant at 209GPa which value is in an excellent agreement with upper and lower bounds of calculated Young's moduls as shown in Figure 6-4 (a). In contrast, with increasing SiC particle size, the elastic modulus markedly decreases to 130GPa when the mean SiC particle size is 55μm. Because the volume fraction of SiC particles is maintained at 5vol%, if there were a change in SiC particle size alone without microstructural defects, the resulting Young's modulus would not be changed. However, the decrease in Young's modulus for the composite containing 55μm particles is almost 39% when compared to composites containing 0.6 and 1μm particles. The starting point where the Young's modulus decreased is consistent with what has previously been observed in Vickers and Knoop hardnesses. These observations support the hypothesis that microstructural defects such as microcracks and interfacial debonding take place in the composites containing larger SiC particles than 1μm.

Figure 6-4 (b) shows the comparison between experimentally obtained and theoretically calculated effective Young's moduli with different SiC volume fractions. It is clearly seen that the experimentally determined Young's modulus increases linearly with increasing 1μm SiC volume fraction in UO$_2$-SiC composites. With 20vol% SiC particles, the Young's modulus is increased to 236.5GPa which is 18% higher than that of pure UO$_2$. The difference in effective
Young's moduli between upper and lower bounds of theoretical calculations increases with increasing SiC volume fraction. Average values of experimentally determined Young’s moduli are fallen into the range between upper and lower bounds of calculated effective Young’s moduli. This supports that 1μm SiC particles are homogeneously dispersed in UO₂ matrix and both phases are mechanically well contacted increasing the effective Young’s modulus of UO₂ by SiC addition.

Because the grain size effects mechanical properties, it is reasonable to investigate a change of UO₂ grain size in UO₂-SiC composites with different SiC particle sizes and volume fractions. The average grain size of UO₂ matrix in composites containing 5vol% SiC increases slowly from 1.45μm to 1.65μm with increasing SiC particle size from 0.6μm to 55μm as shown in Figure 6-5 (a). This moderate increase in grain size is probably due to the decreased surface area to volume ratio of larger SiC particle. The intensity of the pinning effect of embedded SiC particles in UO₂ matrix decreases with higher surface to volume ratio. In chapter 4, we observed larger UO₂ grain size in a UO₂-10vol%SiC composite containing SiC whiskers due to decreased surface to volume ratio (Figure 4-9).

Meanwhile, the average grain size of UO₂ and UO₂-SiC composites decreases with increasing 1μm SiC volume fractions as seen in Figure 6-5 (b). The grain size is dramatically decreased from UO₂ to UO₂-5vol%SiC by almost 74%, gradually decreased from UO₂-5vol%SiC to UO₂-15vol%SiC, and the value is preserved until UO₂-20vol%SiC. While the initial pinning effect of SiC particles has significantly influence on the reduction in UO₂ grain size, only moderate change in grain size exists by different SiC particle sizes or volume fractions.

Residue Stress Measurement

Figure 6-6 shows Raman spectra collected from a SiC particle in stress free SiC powder and the SiC particles with different sizes, 0.6, 1, 9, 16.9, and 55μm in UO₂-5vol%SiC composite
pellets. As shown in Figure 6-6, the Raman spectrum from a stress free SiC particle include a transverse optical (TO) peak at 796 cm\(^{-1}\). This peak has been reported \cite{111,112} as a standard TO peak in 3C-SiC thin film and directly correspond to Raman peak in free SiC particle without stress. However, changes in TO peaks are observed in various SiC particles in UO\(_2\)-5vol\%SiC composite pellets as shown in Figure 6-6.

While the largest particle size SiC (55\(\mu\)m) exhibit similar TO peak (795.7 cm\(^{-1}\)), the other composites SiC particles containing 0.6, 1, 9, and 16.9\(\mu\)m SiC particles show higher number of TO peaks (800~-803 cm\(^{-1}\)) than that of stress free 3C-SiC particle. Figure 6-6 also shows a decrease in TO peak Raman shift with increase in SiC particle size. The result suggests that small particle size SiC in UO\(_2\)-5vol\%SiC composite attain compression stress due to the mismatch of thermal expansion coefficient between UO\(_2\) and SiC. This compression stress appears during the cooling process when the UO\(_2\) matrix shrinks into the SiC particles as mentioned in chapter 5. With an increase of the SiC size, the compression stress of SiC particles decreased and reach a stress free TO position at 55\(\mu\)m size SiC particle. The first compression stress release is observed in 9\(\mu\)m SiC particle and the big drop of stress occurs from 9 to 16.9\(\mu\)m SiC particles. This SiC particle size where the initial stress release occurs is consistent with what has previously been observed in both Vickers and Knoop hardnesses, and Young's modulus. These observations support that microstructural defects at the interface such as microcracks and interfacial debonding release the concentrated stress and eventually produce stress free 55\(\mu\)m SiC particles.

Figure 6-7 (a) shows the measured TO-peak positions as a function of various SiC size in UO\(_2\)-5vol\%SiC composite pellets. Figure 6-7 (b) shows the shift in TO-peaks compared with the same peak in a stress free SiC particle (796 cm\(^{-1}\)). In each composite pellet, the Raman TO-peaks of three different size SiC particles were observed and the average value was presented in the
plots. For the composite containing 55µm SiC particles, an additional three TO-peaks were measured on different areas in a 55µm SiC particle from near the interface to the center of a particle and the average value was regarded as the measured TO peak of the particle. The averaged TO-peak of 1µm SiC particle represent the largest positive TO shift corresponding to the highest compression stress. This compression stress is released as the SiC particle size increases from 1µm to 9, 16.9, and 55µm. Micro-cracking (Figure 3(d) and (e)) represents the compression stress release. Although micro-cracks were not detected in the microstructure observation of the UO$_2$-5vol%SiC composite pellet containing 9µm SiC particle, there must be substantial cracks. This is supported by the compression stress release observed in the pellet containing 9µm SiC particles.

One can calculate the value of thermal residual stress using the changes in TO-peak positions [113].

$$\sigma = \frac{2W_0}{(S_{12}(p+q)+S_{11}q)} \Delta W_{to}$$  \hspace{1cm} (6-9)

Where $W_0$ is position of TO peak in a stress free SiC particle (796cm$^{-1}$), $S_{12}$ and $S_{11}$ are stress tensor components, $p$ and $q$ are the phonon deformation potentials, and $\Delta W_{to}$ is the shift in TO peak position. $p=-0.623 \times 10^6$cm$^2$ and $q=-2.634 \times 10^6$cm$^2$ are obtained from the mode Gruneisen parameters [114] for the hydrostatic ($\gamma_o$) and uniaxial stresses ($\gamma_s$).

$$p + 2q = -6\gamma_o W_0^2$$  \hspace{1cm} (6-10)
$$p - q = 2\gamma_s W_0^2$$  \hspace{1cm} (6-11)

The hydrostatic stress ($\gamma_o$) and uniaxial stress ($\gamma_s$) can have different value. However, they were assumed to be same as 1.56 [114] to calculate $p$ and $q$. $S_{11}=3.7 \times 10^{-13}$ and $S_{12}=-1.05 \times 10^{-13}$ were utilized to calculate residual stress [115]. Thus, Equation 6-9 reduces to

$$\sigma = -251.66 \Delta W_{to}$$  \hspace{1cm} (6-12)
Figure 6-8 shows thermal residual stress within SiC particles in UO₂-5vol%SiC pellets calculated from Equation 6-12 as a function of SiC particle sizes. The maximum average compression stress, 649MPa, is found in the composite containing 1µm SiC particles. As the SiC particle size increases, the compression stress is released and the 16µm SiC becomes almost a stress-free particle. Micro-cracks were directly observed by SEM in the pellet containing larger SiC particles (16 and 55µm) that coincides with the particle size in which stress relaxation is obvious. Therefore, micro-cracking is responsible for the stress relaxation. The critical SiC size to suppress the microcracking exists between 1 and 9µm. The compression stress is slightly reduced in the middle size SiC particle (9µm) from that of 1µm particle. In this plot, however, the reduction is too negligible to say there must be micro-cracks in the composite pellet.

**Conclusion**

The hardness and Young's modulus of UO₂-SiC composites were investigated with different SiC spherical particle sizes and volume fractions. Microcracking and interfacial debonding were monitored by the decrease in mechanical properties. The compression stress of embedded SiC particles with different sizes was estimated using Raman spectroscopy. The measured compression stress was up to 1.65GPa in 1µm SiC particle and decreased rapidly to 0Gpa with increasing particle size to 55µm because microcracking and interfacial debonding released the accumulated stress. The hardness and Young's modulus increased linearly with increasing 1µm SiC particle volume fraction. With 20vol% of 1µm SiC particles, while the Vickers hardness increased up to 53% , Young's modulus increased up to 18% when compared to that of UO₂ without any SiC addition. Upper and lower bounds of theoretical Young’s modulus of composites containing 0-20vol% SiC particles were calculated using Hashin and Shtrikman model [105]. The measured Young's modulus were in excellent agreement with these calculated upper and lower bounds.
Table 6-1. SiC powder used to produce UO₂-SiC composites. *

<table>
<thead>
<tr>
<th>SiC particle size (µm)</th>
<th>Maximum particle size (µm)</th>
<th>Mean size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>d10</td>
<td>d50</td>
<td>d90</td>
</tr>
<tr>
<td>0.13</td>
<td>0.48</td>
<td>1.54</td>
</tr>
<tr>
<td>0.32</td>
<td>0.89</td>
<td>1.98</td>
</tr>
<tr>
<td>1.94</td>
<td>7.27</td>
<td>22.75</td>
</tr>
<tr>
<td>3.07</td>
<td>13.06</td>
<td>31.56</td>
</tr>
<tr>
<td>30.07</td>
<td>54.75</td>
<td>89.00</td>
</tr>
</tbody>
</table>

* Grade; SiC=99.5% (SiO₂=0.2%, C=0.1, Si=0.03...)

Table 6-2. Details of SiC particle size, volume fraction, and sintering conditions in the SPS. *

<table>
<thead>
<tr>
<th>SiC particle maximum diameter (µm)</th>
<th>SiC volume fraction (%)</th>
<th>Maximum sintering temperature (°C)</th>
<th>% TD of the composite pellet ±SD</th>
<th>Young's modulus (GPa)</th>
<th>Vickers hardness (GPa)</th>
<th>Knoop hardness (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N/A</td>
<td>0</td>
<td>1450</td>
<td>96.5 ± 0.0</td>
<td>200.2</td>
<td>6±0.5</td>
<td>5.1±0.3</td>
</tr>
<tr>
<td>0.6</td>
<td>5</td>
<td>1350</td>
<td>95.25 ± 0.4</td>
<td>212.6</td>
<td>7.24±0.2</td>
<td>6.2±0.2</td>
</tr>
<tr>
<td>1</td>
<td>5</td>
<td>1350</td>
<td>95.27 ± 0.3</td>
<td>214.9</td>
<td>6.72±0.2</td>
<td>5.9±0.1</td>
</tr>
<tr>
<td>1</td>
<td>5</td>
<td>1450</td>
<td>96.81 ± 0.39</td>
<td>216.1</td>
<td>6.98±0.5</td>
<td>6.1</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>1450</td>
<td>96.63 ± 0.35</td>
<td>225.6</td>
<td>7.84±0.6</td>
<td>6.9</td>
</tr>
<tr>
<td>1</td>
<td>15</td>
<td>1510</td>
<td>96.54 ± 0.23</td>
<td>236.0</td>
<td>8.52±0.9</td>
<td>7.5</td>
</tr>
<tr>
<td>1</td>
<td>20</td>
<td>1550</td>
<td>96.51 ± 0.3</td>
<td>249.1</td>
<td>9.2±1.3</td>
<td>8.1</td>
</tr>
<tr>
<td>9</td>
<td>5</td>
<td>1350</td>
<td>95.15 ± 0.09</td>
<td>189.2</td>
<td>5.34±0.9</td>
<td>4.7±0.2</td>
</tr>
<tr>
<td>16.9</td>
<td>5</td>
<td>1350</td>
<td>94.75 ± 0.17</td>
<td>180.2</td>
<td>5.73±1</td>
<td>4.8±0.1</td>
</tr>
<tr>
<td>55</td>
<td>5</td>
<td>1350</td>
<td>95.1 ± 0.13</td>
<td>131.1</td>
<td>5.49±0.86</td>
<td>4.4±0.2</td>
</tr>
</tbody>
</table>

* Hold time=5mins; ramp up/down rate=100°C/min; pressure=36MPa.
Table 6-3. Calculated upper and lower bounds of bulk(K), shear(G), and Young's(E) moduli of UO$_2$-SiC composites using Hashin and Shtrikman model [105].

<table>
<thead>
<tr>
<th>SiC volume fraction (%)</th>
<th>Upper bound K (GPa)</th>
<th>Lower bound K (GPa)</th>
<th>Upper bound G (GPa)</th>
<th>Lower bound G (GPa)</th>
<th>Upper bound E (GPa)</th>
<th>Lower bound G (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>183.98</td>
<td>183.98</td>
<td>76.3</td>
<td>76.3</td>
<td>201.1</td>
<td>201.1</td>
</tr>
<tr>
<td>5</td>
<td>188.84</td>
<td>188.38</td>
<td>80.05</td>
<td>79.50</td>
<td>210.42</td>
<td>209.09</td>
</tr>
<tr>
<td>10</td>
<td>193.82</td>
<td>192.93</td>
<td>83.91</td>
<td>82.83</td>
<td>219.99</td>
<td>217.39</td>
</tr>
<tr>
<td>15</td>
<td>198.92</td>
<td>197.61</td>
<td>87.88</td>
<td>86.30</td>
<td>229.81</td>
<td>226.02</td>
</tr>
<tr>
<td>20</td>
<td>204.14</td>
<td>202.45</td>
<td>91.97</td>
<td>89.92</td>
<td>239.89</td>
<td>234.98</td>
</tr>
</tbody>
</table>

* UO$_2$: K=184GPa, G=76.3GPa [108]; SiC: K=308.6GPa, G=179GPa [109].
Figure 6-1. Selected SEM micrographs of UO$_2$ and UO$_2$-SiC composites showing the transition in SiC particle volume fractions and sizes. A) pure UO$_2$. B) 10% 1μm SiC. C) 20% 1μm SiC. D) 5% 9μm SiC. E) 5% 16.9μm SiC.
Figure 6-2. Vickers and Knoop hardness of UO$_2$-SiC composites. A) with different mean SiC particle sizes. B) with various volume fractions of SiC addition.
Figure 6-3. Optical microscopy pictures of Vickers and Knoop indents from the composite containing 5vol% 55μm sized SiC particles.
Figure 6-4. Young’s modulus of UO$_2$-SiC composites. A) with different mean SiC particle sizes. B) with various volume fractions of SiC addition. Note that blue and red dot lines refer to calculated Young’s modulus based on Hashin and Shtrikman model [105].
Figure 6-5. Grain size of UO$_2$-SiC composites. A) with different mean SiC particle sizes. B) with different volume fractions of SiC addition.
Figure 6-6. Raman spectra collected from within SiC particles with different sizes in each UO$_2$ 5vol%SiC composite.
Figure 6-7. TO-peaks in Raman shift and changes in TO-peak position compared to that of stress free SiC particles as a function of SiC particle size.
Figure 6-8. Evolution of internal stress as a function of SiC particle size in UO$_2$-5vol%SiC composites.
CHAPTER 7
EFFECTS OF THERMAL AGING ON THE MICROSTRUCTURE AND THERMAL CONDUCTIVITY OF UO$_2$-SiC COMPOSITES

Background

In previous three chapters, we successfully fabricated UO$_2$-SiC composite fuels and examined their improved thermal and mechanical properties. Because the final operational environment for the UO$_2$-SiC composite fuel pellet is a nuclear reactor core, it is appropriate to discuss the potential ramifications of using such fuel pellets. The reaction between UO$_2$ and SiC could be accelerated during plant operation because the current reactor core temperature is higher than the reaction temperature to form USi$_{1.88}$ and the irradiation is known to increase the diffusion of both chemical species. Moreover, a mismatch in CTE between UO$_2$ and SiC may cause microstructural defects such as interfacial debonding and thermal cracks leading to poor nuclear fuel performance during cooling process in a nuclear reactor.

It is difficult to induce similar environments as a nuclear reactor core such as steep temperature gradient and high radiation level due to facility restrictions. In this study, therefore, only the influence of reactor core temperature for a particular duration on UO$_2$-SiC composites was investigated. For this thermal aging, the expected fuel centerline temperature of UO$_2$-10vol%SiC composite fuel was obtained using the nuclear fuel performance code, FRAPCON. Then, thermal aging was performed at the predicted centerline temperature for fabricated high density UO$_2$-10vol%SiC composites containing SiC whiskers and 1μm SiC particles. Finally, changes in the microstructure and thermal conductivity of the composites after thermal aging were investigated.

Experiments and Results

Predicted Centerline Temperature of UO$_2$-10vol%SiC Composite Fuel

A fuel performance code FRAPCON 3.4 [116, 117] was developed by The Pacific Northwest National Laboratory (PNNL) for The Nuclear Regulatory Commission (NRC) to
calculate thermal and mechanical behaviors of Light Water Reactor (LWR) fuel rods during long-term burnup [118]. The centerline temperatures of pure UO\(_2\) and UO\(_2\)-10vol%SiC composite fuels can be calculated based on the following equation.

\[
K_S = \frac{1}{A+Bt+f(Bu)+(1-0.9\exp(-0.4Bu))g(Bu)h(T)} + \frac{E}{T^2} \exp\left(-\frac{F}{T}\right)
\]

(7-1)

Where \(T\) = Temperature (K)

\(Bu\) = Burnup (GWD/MTU)

\(f(Bu) = 0.00187 \cdot Bu\)

\(g(Bu) = 0.038 \cdot Bu^{0.28}\)

\(h(T) = [1+396e^{-Q/T}]^{-1}\)

\(Q = 6380\) K

\(A = 0.0452\) m·K/W for UO\(_2\)

\(A = 0.038646\) m·K/W for UO\(_2\)-10vol%SiC

\(B = 2.46E-4\) m·K/W/K for UO\(_2\)

\(B = 2.10E-4\) m·K/W/K for UO\(_2\)-10vol%SiC

\(E = 3.5E9\) W·K/m

\(F = 16361\) K

For this calculation, the measured thermal conductivity of SPS sintered UO\(_2\) and UO\(_2\)-10vol%SiC composite fabricated at 1600°C was utilized (Figure 4-10). The calculated centerline temperature of UO\(_2\) and UO\(_2\)-10vol%SiC composite fuels as a function of burnup rate is seen in Figure 7-1. The centerline temperatures rapidly increase with increasing burn up rate and reach to a maximum value in a range of burn up between 3 and 12 MWD/kgU. While the predicted maximum centerline temperature of UO\(_2\) is almost 1650°C, that of UO\(_2\)-10vol%SiC composite is only near 1500°C. The 60% increased thermal conductivity by 10vol%SiC addition leads to near 150°C decrease in the maximum fuel centerline temperature.
Thermal Aging of UO$_2$-10vol%SiC Composites

Both UO$_2$-10vol%SiC composites containing SiC particles and SiC whiskers were fabricated using SPS technique. While the 1µm β-SiC particles (3C-SiC) was obtained from Alfa Aesar Inc, Ward Hill, MA, 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, 0.65µm, and 10µm, respectively. Because SPS sintering procedures for UO$_2$-SiC composites are described in both chapter 4 and chapter 5, it is not described in this chapter. Both composites were sintered at 1600°C for 5mins with a mechanical pressure of 36MPa and ramp up/down rate of 100°C/min. Each sintered composite was cut in half horizontally yielding two disks for 1000°C and 1500°C thermal agings. Thermal agings were performed in a Lindberg blue M tube furnace with flowing UHP-Ar gas at 1500°C and 1000°C for 12hours. The thermal aging temperature, 1500°C, was chosen because it was the maximum predicted centerline temperature for UO$_2$-10vol%SiC composite fuel. For a moderate thermal aging, 1000°C was selected to compare the resulting microstructures and thermal conductivities of 1500°C and 1000°C aged composites.

Table 7-1 shows the composition of aged composites, their relative densities before and after thermal aging, and thermal aging temperatures and duration. While the relative density of composites increased by 1.5-2% after 1500°C thermal aging for 12hours, the relative density of 1000°C aged composites maintained at similar value. This is because the additional sintering of UO$_2$ takes place during the thermal aging at 1500°C, which is in a typical range of UO$_2$ sintering temperature (1400-1600°C) [119].

Figure 7-2 shows SEM micrographs of 1000°C and 1500°C aged UO$_2$-10vol%SiC composites containing 1µm SiC particles. While embedded SiC particles in the UO$_2$ matrix are clearly seen in the 1000°C aged composite, only traces for SiC particles embedded before
thermal aging are observed in the 1500°C aged composite as shown in Figure 7-2 (a) and (b), respectively. In addition to that, broader and more distinct grain boundaries are found in the 1500°C aged composite when compared to those of 1000°C aged composite.

These phenomena are also observed in the UO$_2$-10vol%SiC composites containing SiC whiskers. While embedded SiC whiskers are observed in 1000°C aged composite, all SiC whiskers are removed and only traces for whiskers are observed in 1500°C aged composite as seen in Figure 7-3 (a) and (b), respectively. Broad and distinct grain boundaries are seen only in the 1500°C aged composite.

A possible explanation for the removed SiC particles and whiskers in the surface of 1500°C aged composites is that brittle and fragile chemical reaction products arised at the interface between UO$_2$ and SiC during the thermal aging led to interfacial debonding and particle removing. 1370°C is a well known chemical reaction starting temperature [120] between UO$_2$ and SiC, and hence, chemical reaction should occur during the 1500°C thermal aging. In chapter 4, Figure 4-8 showed a reaction product, USi$_{1.88}$, in a XRD spectra of UO$_2$-70vol%SiC composite sintered at 1600°C for 4hours. This chemical reaction product at the interface between UO$_2$ and SiC may play a significant role removing embedded SiC particles and whiskers during the thermal aging.

The broader and more distinct grain boundary in 1500°C aged composites is because the grain boundary thermal etching occurred by small oxygen content (~1ppm) in UHP-Ar atmosphere during thermal aging. Higher temperature and longer duration than typical thermal etching procedure for UO$_2$ fuel (1340°C for 3-4hours in UHP-Ar) led to extensive grain boundary etching, and hence, broader and distinct UO$_2$ grain boundaries. Meanwhile, the grain boundary of 1000°C aged composite is much more vague compared to that of 1500°C aged composite because this temperature is lower than the typical thermal etching temperature.
Figure 7-4 shows the micrographs of 1500°C aged composites containing 10vol% SiC particles and whiskers. Yellow circles indicate particular areas containing large abnormal UO₂ grains. These grains are 4-5 times bigger than typical UO₂ grains in other areas as shown in Figure 7-4. These areas containing bigger UO₂ grains are only found in 1500°C aged composites due to the UO₂ grain growth during such high temperature thermal aging for 12 hours. Given the fact that traces for SiC particles and whiskers are not found in the particular areas containing large UO₂ grains, the reduced pinning effect of embedded SiC seemed like a motivation for the bigger grains. In other areas containing much smaller UO₂ grains, the pinning effect of SiC particles and whiskers hindered the grain growth of UO₂ matrix maintaining UO₂ grains with small size even after thermal aging.

Another distinct feature, microcracking, due to the 1500°C thermal aging is seen in Figure 7-5 and Figure 7-6. A microcrack in the aged UO₂-10vol% SiC composite containing 1µm SiC particles is clearly observed in Figure 7-5. A broader microcrack, which width is almost 1µm, is observed in the aged UO₂-10vol% SiC composite containing SiC whiskers as shown in Figure 7-6. These cracks were only found in 1500°C aged composites. They look very similar as thermal microcracks which were observed in UO₂-5vol% SiC composites containing large SiC particles (16.9 and 55µm) as shown in Figure 5-2. As mentioned in chapter 5, thermal microcracks occurred during the cooling process of SPS sintering due to the difference in CTE between UO₂ and SiC. However, this is not the same case for the 1500°C aged UO₂-10vol% SiC composites. 1µm SiC particles are small enough to suppress the microcracking based on the results in chapter 5. Moreover, before thermal aging, we had not found any similar microcracks in same composites sintered at 1600°C by SPS. If the difference in CTE between UO₂ and SiC were the only cause for microcracking, we would observe similar cracks before thermal aging because the
microcracking only happens during the cooling process and same composites cooled from 1600°C and 1500°C during sintering and thermal aging processes, respectively.

A possible reason for the microcracking during 12hours thermal aging at 1500°C is chemical reaction between UO$_2$ and SiC. If reaction products formed during the thermal aging at the interface had relatively low fracture toughness, they might not be able to endure the accumulated thermal stress due to the difference in CTE between UO$_2$ and SiC. In chapter 6, the accumulated compression stress in SiC particles was measured using Raman spectroscopy (Figure 6-9). The measured compression stress of 1µm SiC particles in UO$_2$-SiC composites was up to 1.7GPa. If this compression stress exceeded the fracture toughness of chemical reaction products at the interface, microcracks nucleate at the interface and propagate spontaneously into UO$_2$ matrix.

Figure 7-7 and Figure 7-8 show the thermal conductivity of UO$_2$-10vol%SiC composites containing SiC whiskers and 1µm SiC particles, respectively, before and after thermal aging at 1500°C for 12hours. While the enhanced densities of both composites after the thermal aging as listed in Table 7-1 could increase the thermal conductivity (Equation 5-3), the observed microcracks shown in Figure 7-5 and Figure 7-6 could decrease the thermal conductivity due to the significant phonon scattering. The measured thermal conductivities of the composites containing SiC whiskers and particles after thermal aging were reduced by 9.5% and 4.5% in average, respectively, when compared to those of same composites before thermal aging. The higher level of reduction in thermal conductivity in the composite containing SiC whiskers is probably due to more severe cracks as shown in Figure 7-6.

**Conclusion**

Thermal aging at 1000°C and 1500°C for 12hours were performed on two UO$_2$-SiC composites containing 1µm SiC spherical particles and SiC whiskers with an aspect ratio, a
diameter, and a length exceeding 10:1, 0.65µm, and 10µm, respectively. While 1000°C aging didn’t change microstructures and properties, the composite aged at 1500°C showed various modifications such as increased density, SiC particles and whiskers removing, microcracking, particular areas containing abnormally large grains, and moderately reduced thermal conductivity. The density increased because the 1500°C is within a UO₂ sintering temperature range. The removed SiC particles and whiskers and microcracking after thermal aging was probably because brittle chemical reaction product at the interface formed interfacial debonding and microcracks. The abnormally large grains were formulated due to UO₂ grain growth caused by reduced SiC pinning effect on particular areas. Nevertheless of many microstructural changes, we observed relatively good measured thermal conductivity of the composites after thermal aging when compared to that of same composites before aging. The average decrease in thermal conductivity of the composites containing SiC particles and whiskers were only 4.5% and 9.5%, respectively.
Table 7-1. Details of composition, thermal aging temperature and duration, and relative densities before and after thermal aging of UO$_2$-10vol%SiC composites.

<table>
<thead>
<tr>
<th>Composition</th>
<th>% TD of the composite before aging ±SD</th>
<th>Aging temperature (°C)</th>
<th>Aging duration (hours)</th>
<th>% TD of the composite pellet after aging ±SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC particles</td>
<td>96.81 ±0.39</td>
<td>1000</td>
<td>12</td>
<td>96.95 ±0.27</td>
</tr>
<tr>
<td>SiC whiskers</td>
<td>96.63 ±0.35</td>
<td>1000</td>
<td>12</td>
<td>96.78 ±0.33</td>
</tr>
<tr>
<td>SiC particles</td>
<td>96.81 ±0.39</td>
<td>1500</td>
<td>12</td>
<td>98.14 ±0.23</td>
</tr>
<tr>
<td>SiC whiskers</td>
<td>96.63 ±0.35</td>
<td>1500</td>
<td>12</td>
<td>98.41 ±0.3</td>
</tr>
</tbody>
</table>
Figure 7-1. Expected centerline temperature of UO$_2$ and UO$_2$-10vol%SiC composite fuels as a function of reactor burnup rate.
Figure 7-2. Microstructures of UO$_2$-10vol%SiC composites containing 1μm SiC spherical particles after thermal aging for 12 hours. A) thermal etched at 1000°C. B) thermal etched at 1500°C.
Figure 7-3. Microstructures of UO$_2$-10vol%SiC composites containing SiC whiskers after thermal aging for 12 hours at A) 1000°C and B) 1500°C.
Figure 7-4. Microstructures of UO$_2$-10vol%SIC composites after thermal aging for 12hours at 1500°C. A) SiC particles B) SiC whiskers. Note that yellow circles refer to particular areas containing large UO$_2$ grains.
Figure 7-5. Microstructures of UO$_2$-10vol%SiC composites containing 1μm SiC particles after thermal aging for 12 hours at 1500°C.
Figure 7-6. Microstructures of UO$_2$-10vol%SiC composites containing SiC whiskers after thermal aging for 12 hours at 1500°C.
Figure 7-7. Thermal conductivity of UO$_2$-10vol%SiC composites containing SiC whiskers before and after thermal aging at 1500$^\circ$C for 12 hours.
Figure 7-8. Thermal conductivity of UO$_2$-10vol%SiC composites containing 1μm SiC particles before and after thermal aging at 1500°C for 12 hours.
CHAPTER 8
CONCLUSIONS AND FUTURE WORK

Conclusions

Uranium dioxide (UO$_2$)- Silicon carbide (SiC) composite fuel pellets were produced by oxidative sintering and spark plasma sintering (SPS) at a range of temperatures from 1400 to 1600$^\circ$C. Both SiC whiskers and SiC powder particles were utilized. Oxidative sintering was employed over 4 hours and the SPS sintering was employed only for 5 minutes at the highest hold temperature. It was noted that composite pellets sintered by SPS process revealed smaller grain size, reduced formation of chemical products, higher density, and enhanced interfacial contact compared to the pellets made by oxidative sintering. Thermal conductivity measurements at 100$^\circ$C, 500$^\circ$C, and 900$^\circ$C revealed that SPS sintered UO$_2$-10vol%SiC composites exhibited an increase of up to 62% in thermal conductivity compared to UO$_2$ pellets, while the oxidative sintered composite pellets revealed significantly inferior thermal conductivity values.

The particle size (0.6-55µm diameter) and volume fraction (5-20%) of SiC were systematically varied to investigate their influence on the resulting UO$_2$-SiC composite pellet microstructure and the thermal properties. It was found that SiC particle size less than 16.9µm with a larger volume fraction is more effective for improving the thermal conductivity of the fuel pellets. Scanning Electron Microscopy examination revealed micro-cracking and interfacial debonding in the composites containing larger size SiC particles (16.9 and 55µm) which resulted in reduced thermal conductivity up to 26.5% compared to that of a UO$_2$ pellet. For the UO$_2$-SiC composites containing 1µm diameter SiC particles, the thermal conductivity increased almost linearly with volume fraction of particles. The experimental thermal conductivity values of the UO$_2$-SiC composite pellets containing 5, 10, and 15vol% are in good agreement with the theoretical values based on the available model in the literature. In the composite pellet
containing 20vol% of SiC particles, the experimental value is lower than the theoretical value by almost 9.9% due to both lower density and particle-particle interaction.

The influence of SiC particle size (0.6-55µm diameter) and volume fraction (5-20%) on the mechanical properties such as hardness and Young's modulus of UO₂-SiC composites were examined. Microcracking and interfacial debonding were monitored by the decrease in mechanical properties. Internal stress measurement using Raman spectroscopy revealed that 1µm SiC particle exhibited 1.65GPa compression stress. This stress decreased rapidly with increasing particle size until stress free 55µm SiC particle. The hardness and Young's modulus increased linearly with increasing the volume fraction of 1µm SiC particles. With 20vol% SiC particles, Vickers hardness and Young's modulus increased up to 53% and 18%, respectively, compared to those of UO₂. The measured Young's modulus were in excellent agreement with theoretically calculated upper and lower bounds of Young's modulus.

The influence of 1000°C and 1500°C thermal aging for 12hours on the microstructure and thermal conductivity of UO₂-10vol%SiC composites containing SiC particles and SiC whiskers was investigated. While no changes in microstructure or thermal conductivity were observed in 1000°C aged composites, SEM revealed removed SiC particles and whiskers from UO₂ matrix, microcracks, and particular areas containing 4-5times larger grains in the 1500°C aged composites. We observed the measured thermal conductivity of the 1500°C aged composites was reduced 5-10% compared to that of same composites before thermal aging.

**Future Work**

**Challenges in UO₂-Diamond Composites**

Since we have successfully increased the thermal conductivity of UO₂ with SiC additions, the potential benefit of a diamond addition to the UO₂ drew our research group's attention. The measured thermal conductivity of diamond at room temperature is about 22
W/cm·K [121] which is the highest of any solid material. Unlike any sp² structure material such as Carbon Nano Tube (CNT), Diamond is composed of sp³ carbon bonds to be resistant to the radiation environment [122, 123]. Therefore, it was expected for UO₂-diamond composites to provide an even higher thermal conductivity than that of UO₂-SiC composites. In preliminary experiment, UO₂-10vol%diamond composites were fabricated using SPS at 1400°C, 1450°C, and 1500°C for 5mins. The utilized diamond powder was obtained from Advanced Abrasives, Pennsauken, NJ and had a mean diameter of 25μm. Figure 8-1 reveals a SEM image of as received diamond powder morphology. The ramp up/down rate and mechanical pressure were set at 100°C/min and 36MPa, respectively in the SPS process. The utilized sample preparation and SPS procedure for UO₂-diamond composites are same as those of UO₂-SiC composites, and hence, it is not described here. The thermal conductivity of fabricated composites was measured before ASTM standard heating to obtain the stoichiometric UO₂. The thermal conductivity measurement procedure used for UO₂-SiC composites and described in chapter 5 was utilized here.

The resulting measured densities and thermal conductivities at 100°C, 500°C, and 900°C of the three fabricated composites were shown in Figure 8-2. Both relative densities and thermal conductivities were increased with increasing sintering temperature. The average increase in thermal conductivity of the highest density composite at those three temperatures were 30.9%, 52.1%, and 55.8%, respectively, when compared to a UO₂ literature value. ASTM C 1430-07 procedure was performed to further increase the thermal conductivity of composites by reducing hyper-stoichiometric UO₂+x to stoichiometric UO₂. As described in chapter 4 and 5, sintered composites were reduced in a furnace at 800°C for 6 hours, in a 4%H₂-N gas, with a water vapor atmosphere using a water bath maintained at 35°C. The thermal conductivity of three composites was measured again after reduction.
Figure 8-3 shows the thermal conductivity of same UO₂-diamond composites after the reduction process. Thermal conductivities of all composites were reduced dramatically, almost 20-30%, at three temperatures. The thermal conductivity of the diamond composites and UO₂ measured and literature values acquired a similar level. In other words, the benefit of diamond addition for enhanced thermal conductivity almost disappeared. The thermal conductivity of the highest density UO₂-diamond composite (96.2%TD) was measured again after thermal etching procedure at 1340°C for 4hours in UHP-Ar atmosphere. Figure 8-4 reveals that the thermal conductivity of the UO₂-diamond composite was again significantly reduced, by almost 30-35%, leading to much a lower thermal conductivity than the UO₂ literature value.

We investigated microstructures of UO₂-diamond composites before and after heat processing such as reduction (800°C, 6hours) and thermal etching (1340°C, 4hours). Figure 8-5 shows micrographs of diamond particles in as sintered UO₂-diamond composite (96.2%TD) ((a) and (c)) and same composite after reduction and thermal etching ((b) and (d)). Microcracking and interfacial debonding are clearly seen in the composite after heat processes as indicated by red arrows. We observed similar microstructural defects in UO₂-SiC composites containing large SiC particles (16.9 and 55μm) or small SiC particles after thermal aging (1500°C, 12hours) due to the difference in CTE between UO₂ and SiC (chapter 5 and 7). The microcracking and interfacial debonding in UO₂-diamond composite can occur more readily because the difference in CTE between UO₂ and diamond is almost five times that of UO₂-SiC (UO₂: 9.93x10⁻⁶ K⁻¹, diamond: 1.1x10⁻⁶ K⁻¹ [55]). Unknown features on the surface of diamond particles are observed only in the UO₂-diamond composite after heat processes as indicated by red circles in Figure 8-5. EDS elemental mapping and line scanning were performed on these features to investigate their elemental concentrations.
Figure 8-6 shows the SEM micrograph of the unknown features (a) and their EDS elemental counts of carbon Kα (b), oxygen Kα (c), and uranium Mα (d). While unknown features appearing brighter areas indicated by blue and red circles, the darker background refers to the surface of a diamond particle in the SEM micrograph. The carbon was found in almost the entire area while the background had higher concentration than that of the unknown features. The number of oxygen Kα counts in unknown features is more than that of background. The red circled unknown feature contains more uranium Mα counts than that of blue circled unknown features and background. Given these elemental concentrations, the red circled feature is probably UO₂ matrix and blue circled features are reaction products between UO₂ and diamond, possibly uranium oxy-carbide (UCₓOᵧ) or oxidized diamond. Evan and Phaal [124] found that the oxidation of diamond can occur at the temperature higher than 650°C even at the partial pressure of oxygen as low as 5x10⁻² mm. Hg. Zhou et. al. [125] found that uranium oxy-carbide (UCₓOᵧ) was formed on uranium surface after heat treatment at 500°C for 1 hour in vacuum (7 Pa) atmosphere. Therefore, utilized temperatures, heating durations, and oxygen potentials in both reduction and thermal etching processes are able to form both oxidized diamond and uranium oxy-carbide (UCₓOᵧ).

Figure 8-7 shows the SEM micrograph of a chemical reaction product and EDS elemental counts of carbon Kα, oxygen Kα, and uranium Mα along scanned line across the reaction product. The reaction product has a spherical shape probably because of melting during reduction or thermal etching processes. This reaction product seems to have a lower melting temperature than 1340°C. All selected signals such as carbon Kα, oxygen Kα, and uranium Mα are counted in the chemical reaction product, and hence, its chemical compound is probably uranium oxy-carbide (UCₓOᵧ).
In this preliminary study on UO₂-diamond composites, we have observed chemical reaction products between UO₂ and diamond, and microstructural defects such as microcracking and interfacial debonding. These significantly accelerate phonon scattering and can be major disadvantages for enhance thermal conductivity composite fuels. We revealed that the thermal conductivity of UO₂-diamond composites decreased dramatically during required heating processes such as reduction and thermal etching. Similar reduction in thermal conductivity is inevitable in the final operational environment, a nuclear reactor core, because its temperature, duration, and oxygen potential are extreme. Therefore, the microstructural defects and chemical reaction are essential challenges to be prevented. As we used smaller sized SiC particles to suppress microcracking and interfacial debonding in UO₂-SiC composites in chapter 5 and 6, similar microstructural defects in UO₂-diamond composites also can be reduced simply by utilizing small diamond particles. Further research is necessary, however, to prevent the chemical reaction between UO₂ and diamond which take place at a temperature as low as 650°C [124].

**Potential Ramifications of UO₂-SiC Composites**

As mentioned in chapter 7, the severe environment of nuclear core may have negative influence on nuclear composite fuels. The high centerline temperature of nuclear fuel (up to ~1500°C), steep temperature gradient (2000-3000°C/cm), and high dose radiation could accelerate the chemical reaction between UO₂ and SiC. Further research is needed to quantify the reaction products in an irradiation environment at appropriate temperatures. Reaction products, fission gas, and fission products could be precipitated along the interface severely affecting thermal thermal conductivity of the pellet. Therefore, it is important to investigate interfacial characteristics and the influence of reaction products after irradiation of the pellet. Radiation defects of SiC also have influence on conductivity of the pellet. However, studies [126, 127]
have shown that there is a reduction in defect concentrations caused by the irradiation damage and the thermal conductivity value is often recovered in the temperature range between 650 to 1400°C. Further study is needed to verify the recovery of thermal conductivity of irradiated UO₂-SiC composites in a temperature range of reactor core. Addition of SiC into a pellet reduces the amount of fissile isotope and hence a higher U-235 enrichment may be required to maintain neutron population sustaining fission process in a reactor core. The exorbitant cost and stringent regulation of U-235 enrichment process have to be considered to reveal the cost detriment of using UO₂-SiC composites.
Figure 8-1. Morphologies of diamond particles with 25μm diameter.
Figure 8-2. Thermal conductivity of as sintered UO$_2$-10vol% diamond composites sintered at different temperatures at 100$^\circ$C, 500$^\circ$C, and 900$^\circ$C. Grey and black lines refer to UO$_2$ measured and literature values.
Figure 8-3. Thermal conductivity of UO$_2$-10vol% diamond composites after reduction process performed at 800°C for 6 hours in 4%H$_2$-N$_2$+moisture atmosphere.
Figure 8-4. Thermal conductivity of UO$_2$-10vol% diamond composites after reduction process. The highest density composite (96.2% TD) was reduced and thermal etched.
Figure 8-5. SEM micrographs of a high density UO$_2$-diamond composite. A) and C) as sintered composite. B) and D) same composite after reduction and thermal etching processes. The micro-cracks and interfacial debonds are identified by arrows. Unknown features on the surface of a diamond particle are identified by circles.
Figure 8-6. SEM and EDS elemental maps of a diamond particle surface in the UO$_2$-diamond composite after reduction and thermal etching. A) SEM image of a diamond particle surface. B) EDS map of carbon Kα. C) EDS map of oxygen Kα. D) EDS map of uranium Mα. Unknown features are identified by circles.
Figure 8-7. SEM and EDS elemental spectra of carbon $K\alpha$, oxygen $K\alpha$, and uranium $M\alpha$ along scanned line across a chemical reaction product on the surface of a diamond particle in the UO$_2$-diamond composite.
LIST OF REFERENCES


BIOGRAPHICAL SKETCH

Sunghwan Yeo was born in Seoul, Republic of Korea. His parents are Inbae Yeo and Younsook Jeong. He has an younger sister, Seongmi Yeo. Sunghwan graduated with a Bachelor of Science in materials science and engineering from Illinois Institute of Technology in May, 2009. After that, he enrolled in materials science and engineering’s graduate program at the University of Florida in August of 2009. He received a non-thesis Master of Science degree in May of 2012, and is scheduled to graduate with a Doctor of Philosophy degree in August, 2013.