PROCESSING OF URANIUM DIOXIDE NUCLEAR FUEL PELLETS USING SPARK PLASMA SINTERING

By

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To my parents, Cao Ge and fengchun Xu, for their love and support
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<td>DC</td>
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<td>EPMA</td>
<td>Electron probe microanalysis</td>
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<td>FAST</td>
<td>Field assisted sintering technique</td>
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<td>GWe</td>
<td>Giga watt electrical</td>
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<td>HREM/ARM</td>
<td>High and atomic resolution electron microscopy</td>
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<td>IEA</td>
<td>International Energy Agency</td>
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<td>LWR</td>
<td>Light water reactor</td>
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<td>O/U</td>
<td>Oxygen/Uranium</td>
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<td>OM</td>
<td>Optical microscope</td>
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<td>PAS</td>
<td>Plasma activated sintering</td>
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<td>PHWR</td>
<td>Heavy water reactor</td>
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<td>TD</td>
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<td>TEM</td>
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<td>UHTC</td>
<td>Ultra-high temperature ceramic</td>
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<td>WNA</td>
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PROCESSING OF URANIUM DIOXIDE NUCLEAR FUEL PELLETS USING SPARK PLASMA SINTERING

By

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Uranium dioxide (UO$_2$), one of the most common nuclear fuels, has been applied in most of the nuclear plant these days for electricity generation. The main objective of this research is to introduce a novel method for UO$_2$ processing using spark plasma sintering technique (SPS).

Firstly, an investigation into the influence of processing parameters on densification of UO$_2$ powder during SPS is presented. A broad range of sintering temperatures, hold time and heating rates have been systematically varied to investigate their influence on the sintered pellet densification process. The results revealed that up to 96% theoretical density (TD) pellets can be obtained at a sintering temperature of 1050$^\circ$C for 30s hold time and a total run time of only 10 minutes.

A systematic study is performed by varying the sintering temperature between 750$^\circ$C to 1450$^\circ$C and hold time between 0.5 min to 20 min to obtain UO$_2$ pellets with a range of densities and grain sizes. The microstructure development in terms of grain size, density and porosity distribution is investigated. The Oxygen/Uranium (O/U) ratio of the resulting pellets is found to decrease after SPS.
The mechanical and thermal properties of UO$_2$ are evaluated. For comparable density and grain size, Vickers hardness and Young’s modulus are in agreement with the literature value. The thermal conductivity of UO$_2$ increases with the density but the grain size in the investigated range has no significant influence. Overall, the mechanical and thermal properties of UO$_2$ are comparable with the one made using conventional sintering methods.

Lastly, the influence of chromium dioxide (Cr$_2$O$_3$) and zirconium diboride (ZrB$_2$) on the grain size of doped UO$_2$ fuel pellet is performed to investigate the feasibility of producing large-grain-size nuclear fuel using SPS. The benefits of using SPS over the conventional sintering of UO$_2$ are summarized. The future work of designing macro-porous UO$_2$ pellet and thorium dioxide (ThO$_2$) cored UO$_2$ pellet is also proposed.
CHAPTER 1
INTRODUCTION

Along with the development of human society, the demand for energy has increased substantially over the centuries. Energy normally comes from natural resources such as coal, natural gas and petroleum. However, due to the limited amount of these resources and the emission of greenhouse gases that cause environmental problems, it is of great importance to find alternatives of these traditional resources. Hydrogen energy, solar energy and wind energy are considered as the next generation of clean energy sources. In effect, great efforts have been paid over the decades to improve the power efficiency of these energy sources. However, up to now, these resources only take up a limited amount of the total energy demand. Nuclear energy has been used for power in society for decades. Although safety issues like radiation and waste disposal are still a concern, nuclear energy has many unique benefits. First, large reserves and high heat value of nuclear fuels makes it a sustainable resource available for centuries. Based on the data provided in the World Nuclear Association (WNA)[1], at the current consumption rate, the supply of uranium will be available for more than 190 years. Another merit of nuclear energy is its ability to provide electricity with zero emission of greenhouse gases. Nowadays, owing to human activity, more greenhouse gases, especially carbon dioxide (CO₂), are emitted into the natural environment. According to the International Energy Agency (IEA) [2], coal, oil and natural gas are the three major sources of emission and responsible for 99.6% of the CO₂ emissions in 2009, as seen in Figure 1-1 (a). The total amount of CO₂ emissions has also significantly increased from 14000 million tons in 1971 to 29000 million tons in 2009, as seen Figure 1-1 (b).

The public is now aware of the dangers of global warming and climate change by the excessive consumption of these fossil fuels. However, besides these fossil fuels, nuclear energy
is the only readily available large-scale alternative to decrease the greenhouse emission gases while keeping a continuous and adequate power supply for society. The importance of nuclear energy is revealed from the data of electricity generation in IEA. Figure 1-2 demonstrated the contribution of different energy source for electricity generation in 2009. It is noted that coal and natural gas ranked the highest and they together provided 62% of the total electricity. However, these fuels emit enormous CO₂. Although hydropower contributed 16.2% of energy, the development of hydropower is limited due to the environmental conditions. It is now still challenging to scale up electricity generation by hydropower without harming the environment. Nuclear energy accounts for 13.4% of the electricity and ranks 4th next to hydropower, which is much higher than oil and other powering sources including geothermal, solar and wind, etc. This makes it a good candidate for the major provider of green energy.

Currently, nuclear energy development has been emphasized in a lot of countries throughout the world. The proportion of electricity generated by nuclear energy[3] in 2012 in different countries is shown in Figure 1-3. It is seen that for the world’s average level, 11% of the electricity is generated using nuclear energy while most western countries and South Korea are above the average level. There are more than 10 European countries that have the proportion more than twice of the average value. In France, more than 75% of the electricity is based on nuclear energy. In developing countries, nuclear development is still behind the world’s pace where most countries have the proportion of nuclear energy below the world’s average level. However, some countries, like China and India, have realized the importance of nuclear energy since recent decades and have set up ambitious goals to build more nuclear plants. In 2007, China’s state Council set a goal of increasing its nuclear power capacity from 7 Giga watt electrical (GWe) to 40 Gwe by 2020, and the current trends even imply an actual more than 70
Gwe by 2020. In the long term, up to 2050, the total capacity is anticipated to be 300-500 Gwe [4]. India, expected to have 14.6 GWe nuclear capacity line by 2020 and aimed to supply 25% of electricity using nuclear energy by 2050[5]. In the United States, although only 20% of electricity is currently generated by nuclear power, Department of Energy (DoE) has invested over $233 million for nuclear research projects in addition to infrastructure investment since 2008 to promote a sustainable nuclear industry in the U.S. Therefore, it is becoming a worldwide trend to develop nuclear energy in these days.

In nuclear power plants, the heat is generated by burning nuclear fuels through nuclear fission. The most common fissile nuclear fuel is Uranium-235 ($^{235}\text{U}$). Despite different forms of nuclear fuels, e.g. uranium nitride and uranium carbide, the most commonly used fuel is uranium dioxide ($\text{UO}_2$). $\text{UO}_2$ has a calcium fluorite crystal structure with ionic bonding between $\text{U}^{4+}$ and $\text{O}^{2-}$. The structure belongs to the $Fm\bar{3}m$ group with $\text{U}^{4+}$ occupying $fcc$ positions and $\text{O}^{2-}$ taking the tetrahedral sites, see Figure 1-4. Ideally, the unit cell parameter for stoichiometric $\text{UO}_2$ is 0.547 nm[6]. However, a large non-stoichiometric range from $\text{UO}_{1.65}$ – $\text{UO}_{2.25}$ is achievable under different oxygen potentials[7]. When exposed in the oxidizing atmosphere, oxygen is easily dissolved into the fluorite structure and transforms to the hyper-stoichiometric phase $\text{UO}_{2+x}$, and the lattice parameter ($a$) is contracted subject to the equation $a=-0.132x + 5.4705$ by Teske, et al[8]. On the other hand, the hypo-stoichiometric phase $\text{UO}_{2-x}$ is also achievable in a reducing atmosphere[9]. The bonding of $\text{UO}_2$ makes it a high-temperature material with a melting point around 2400 - 2800°C in 1 standard atmosphere[10], which also makes it a perfect nuclear fuel for operating at high temperatures (900-1000°C). The harmonic thermal vibration of the $fcc$ structure provides $\text{UO}_2$ better thermal stability than other types of fuels. $\text{UO}_2$ also has better chemical stability, which can be easily compatible with different cladding materials such
as zirc alloy and stainless steels. However, there are still some drawbacks of using the current UO$_2$ fuel in the nuclear reactor. For example, the low thermal conductivity of UO$_2$ creates a great radial thermal gradient, and the centerline temperature can be as high as 1350°C[11] which would shorten the cycle life of nuclear fuel. Also, the brittle ceramic form of the fuel enables the easy formation and propagation of cracks during the manufacturing, transportation and service, which may cause the pellet crumbling, fission gas release and eventually may threaten the safe operation of the nuclear reactor.

Generally, there are three main stages involved in the manufacturing of UO$_2$ pellets used in light water reactors (LWR) and heavy water reactors (PHWR)[12].

1. Producing pure UO$_2$ from UF$_6$ or UO$_3$.
2. Producing high-density accurately shaped ceramic UO$_2$ pellets.
3. Producing the rigid metal framework for the fuel assembly (mainly zirconium alloy).

Of these, the critical stage that determines the fuel performance is stage 2. In another words, the fabrication of UO$_2$ pellet influences the final life cycle of fuel in the nuclear reactor.

To reach the mass production scale, a general processing procedure is introduced as follows[12]:

First, the powder needs to be blended to ensure its uniformity in terms of particle size distribution and specific surface area. Then, additives such as U$_3$O$_8$[13] and Cr$_2$O$_3$[14] may be added to either enhance the sinterability or modify the microstructure for better performance, such as enhanced fission gas retention and higher plasticity. Other ingredients, such as lubricants may also need to be included. After the powder preparation, the UO$_2$ powder is then fed into a die and biaxially pressed into a cylinder to form a green pellet with a density that is around 50% of the theoretical density (% TD). Then, these green pellets are sintered in a furnace at around 1750°C for 3-4 hours[9] with a controlled reducing atmosphere (argon-hydrogen). After sintering, the pellets are machined to about 1cm in height and diameter. In addition, for some
reactors, dimples and chamfers and also shaped on both ends of the pellet to cancel the effect of fission gas swelling and thermal expansion, see Figure 1-5. The flow chart of production of UO$_2$ fuel is provided in Figure 1-6.

As mentioned in the above paragraph, using the current processing procedure to produce nuclear fuel pellets, multiple steps are taken and hours of processing time are required. In this research, a novel fabrication method, spark plasma sintering (SPS), see Figure 1-7, is used to process UO$_2$ nuclear fuel pellets.

The objective of this research is to evaluate the feasibility of applying SPS on processing UO$_2$ pellets. Firstly, an investigation into the influence of processing parameters on densification of UO$_2$ powder during SPS is presented. The microstructure development in terms of grain size, density and porosity distribution is then investigated. The properties, such as Vickers hardness, Young’s modulus, and thermal conductivity are also evaluated. Finally, several different concepts of UO$_2$ composite fuels are investigated and the benefits of using SPS over the conventional sintering of UO$_2$ are summarized.
Figure 1-1. World CO$_2$ emissions [2]. A) 2009 fuel shares of CO$_2$ emissions. B) World CO$_2$ emission from 1971 to 2009.

*Other includes industrial waste and non-renewable municipal waste.
Figure 1-2. Shares of different energy source on the electricity generation in 2009 [2]

* Other includes geothermal, solar, wind, biofuels and waste and heat.

Figure 1-3. The percentage of nuclear electricity generation in different countries in 2012 [3].
Figure 1-4. The schematic of UO$_2$ fluorite structure

Figure 1-5. The schematic of UO$_2$ nuclear fuel pellet [15]
Figure 1-6. Steps of UO₂ pellet manufacturing

Figure 1-7. Spark plasma sintering system (Dr. Sinter® SPS-1030) in Particle Engineering Research Center (PERC).
CHAPTER 2
LITERATURE REVIEW

Introduction of Spark Plasma Sintering

Since 1990s[16], spark plasma sintering (SPS), also known as plasma activated sintering (PAS)[17] or field assisted sintering technique (FAST)[18], has become a popular sintering method for consolidation of powders in various fields[19]. As for a comparatively novel technique for sintering, SPS provides the possibility to sinter the material with better properties than conventional sintering methods and is capable of sintering what cannot be sintered in conventional methods[20]. Using the SPS, the finer grain sizes as well as the higher density can be achieved with the rapid heating rate. With such incredible features, great attentions have been drawn on SPS for both laboratory and industry applications. Figure 2-1 reveals the publications (on the left) and citations (on the right) of SPS listed from 1995 to 2014 in web of knowledge® citation index website. It is shown that within the past 18 years, the number of the publication has grown tremendous from 2 to more than 550 per year. And more than 7000 citations are recorded by the end of 2013. This rapid growing numbers of paper indicates the popularity of SPS among the scientific researchers. In industry, there are three major vendors supplying commercial SPS systems as listed in Table 2-1. Among them, there are at least two major vendors of SPS that have disclosed their ambition of making SPS system[21] that is capable of manufacturing massive products, large-size sample, near-net-shape sample with complex shape[22] as seen in Figure 2-2. All of these indicate a high demand of SPS in the industrial world.

The sintering mechanism in SPS is similar to the hot pressing and the green body is located in the graphite die with the uniaxial pressure applied to the powder using the graphite punch, as shown in Figure 2-3. Distinctively, instead of using external heating method, there is
pulsed direct current (DC), flows through the punches as well as the die, which means that the powders is heated from both outside and inside through Joule heating if the sample is electronically conductive. With the addition of the vacuum system, the whole set can provide the sinter period within 5 to 20 minutes and the sintering temperature 200 to 500 °C lower than the conventional counterparts, hot pressing.[23] Thus, it is of great importance for us to understand the intrinsic mechanism of SPS.

**Mechanism Development of Spark Plasma Sintering**

The mechanism of SPS was first described by M. Tokita[24] in 1993. In his paper, he introduced four major effects caused by large current pulse that result in the sintering characteristics, that is, spark plasma, spark impact pressure, Joule heating, and the electrical field diffusion effect. To illustrate all these effect, how the pulse current flows through the particles in SPS is schematized in Figure 2-4.

As shown in the figure, firstly, the powder surface are more easily purified and activated by passing the current through the die and powder particles directly, the Joule heat is then generated by the current, say $I^2R$, where $I$ is the current flowing through the powder and $R$ is the resistance of the powder. With the application of pressure, the high heating rate can be achieved due to the enhanced plastic flow of the powder. Secondly, the sintering stages in SPS includes the initial stage of spark discharging, generation of spark plasma and the vaporization and melting actions on the particle surfaces. Spark plasma generated the high temperature distribution and spark impact pressure eliminates the impurities on the particles surface. Then, high speed diffusion migration of ionized particles occurred under the electric field, and under the function of the pressure, the neck formed between the particles, following the conventional material transfer paths of sintering.
However, M. Tokita didn’t provide the evidence to prove the mechanism he claimed. Mamoru Omori[25] used SPS for the etching of organic fibers to claim the existence of plasma. In the experiment, discharge is applied to the fibers in the graphite die for 3s with the atmosphere choosing from air, N₂, Ar, and vacuum. The SEM images of the discharged fibers are displayed in Figure 2-5. By contrast, the points on the surface of the polyethylene implied the generation of the plasma and the etched areas are localized. The points where spark plasma is generated are near the place of contacting other particles and there is no new bonds made in the process that connects fibers. By illustrating, he said that it is seemly low energy plasma occurred with the energy higher than ultraviolet in the sintering by providing evidences that plasma cuts C-C bonds without generating carbon. [26]

In the research of Joanna R. Groza[27], the plasma hypothesis is proved by electrical discharge effects. She advocated that whereas the discharge hasn’t been completely disclosed, distinct surface effects of the current discharges have been noticed in FAST consolidated specimens in YBCO. And by sintering the AlN alloy and Si₃N₄ powder[28], she also directly observed the clean grain boundaries with direct grain to grain contact and concentrated Al₂O₃ pockets in AlN, see Figure 2-6, and she claimed that either a low-temperature gas plasma state or a contact point plasma may be created by “micro-discharges” at the contact points of powder particles and there is critical voltage for the plasma generation. The effect of the plasma cleaning particle surface is also investigated[29] by K.R. Anderson and Groza. The transmission electron microscopy (TEM) observation of the FAST sintered NiAl shows that there are no surface oxide layers and the high and atomic resolution electron microscopy (HREM/ARM) of the pure tungsten powder indicated the clean boundaries, both of which implied the cleaning function of the pulsed electrical filed.
Meanwhile, some researchers disagree with the concept of plasma formation in the pulsed discharge sintering process. Dustin M. Hulbert [30, 31] in UC-Davis conducted a series of experiments in SPS using several different powders e.g. Al, Al$_2$O$_3$, NaCl, etc. to prove there is no plasma occurred during the sintering process. He adopted three major methods in his investigation:

1. In situ atomic emission spectroscopy
2. Direct visual observation
3. Ultrafast in situ voltage measurement.

In the spectroscopy, he claimed no characteristic photons were detected from the result. And due to the sensitivity issue of the AES device and human eyes and to make it more persuasive, he did the additional voltage measurement, and still, no voltage anomalies for the evidence of plasma were observed. Thus, none of the experimental methods employed detecting the generation of the plasma or any sparking or arcing present in the whole stages of SPS process.

While Dr Hulbert made the comprehensive experiments to exclude the plasma generated between the particles, it’s still not safe to conclude that there are no plasmas since other factors that have not been well considered like the extent of the pressure and the size of the particles or there may occurs the arc in some small parts but not the whole sample that haven’t been detected. Thus, it seems premature for Dr Hulbert’s conclusion.

Apart from the direct discussion of the plasma generation, the researches turned to the current effect then. For the better understanding of role current played in the SPS, Umberto Anselmi-Tamburini’s team composed a series of fundamental investigations. First, by studying the effect of DC pulsing on the reactivity[32] of Mo/Si system, he concluded that, the RMS(root mean square) of current value between the die is steady when changing the pulse pattern,
indicating RMS is the dominant condition to the power and temperature. In addition, direction has no effect on the reactivity as well as the different on-off pulse pattern. In the successive research, the modeling of current and heat distribution is established by utilizing the conductive and non-conductive materials as samples.\[33\] The current effect on the reactivity was studied and basing on the previous experimental data of SPS for Mo/Si system, he found that when under the current, MoSi\(_2\) layer grows significantly faster than that without the current. And the presence of the current does not alter the original reaction mechanisms, \[34\] suggesting that the pulsing of DC, responsible for the activation of plasma, had no effect on the mass transport. For answering how the role of current on the mass transport, James M. Frei\[35\] sintered copper spheres to the copper plates by pulsed electric current method, see Figure 2-7. He said that volume diffusion mechanism is the dominant factor in absence of current on the neck growth. And under the current, the enhanced neck growth, see Figure 2-8, arises for the electromigration with void formation in the high density areas of the current. In addition, the formation and increase in defect mobility under the influence of a current was also proved by Javier E. Garay\[36\] in his research on Ni\(_3\)Ti intermetallics, who indicated that changes in the concentration of point defects or mobility would result in the changes of growth mechanism.

As for the effect of the pressure to the rapid densification rate, J. Reis and R. Chaim\[37\] made effort by using a HIP model to construct the densification maps for SPS of nano-MgO. In this model, plastic yield and diffusion process are the dominating factors in the densification of SPS and factors of particle coarsening and grain growth are added to the HIP model as well. The result shows that the densification rates are too slow when applying HIP model to describe the SPS experimental data, which indicates the additional faster kinetics in densification mechanisms in SPS, implying the current effects. Chaim\[38\] also introduced the effect of the particle size in
SPS. The nano-sized particles may possibly activate discharge due to the narrow gap and high surface area. He claimed that, morphological and material dependently, nanoparticles enable high electric charge accumulating even under low voltages in SPS, which may result in the surface plasma formation and particle surface heating, the densification driving factors. The example is, when sintering yttrium aluminum garnet (YAG) under 360MPa at 1785 °C, which has the high yield stress in high temperature, the plastic deformation caused by the pressure cannot account for the rapid densification rate, see Figure 2-9, while the only reason is the nano size of the particles, on which the heated particle surface may become liquid and the liquid can aid for the grain rotation and sliding, accelerating the sintering process. Besides, Chaim and Zhijian Shen[39] also studied to control the grain size by external pressure application regime during SPS of YAG, concluding that applying pressure before significant coarsening of the particles in SPS is beneficial for the suppression of further grain growth in the densification process.

By using the numerical methods, Eugene A. Olevsky[23] considered two major factors of densification which contribute to SPS mass transfer: grain-boundary diffusion and power-law creep. In these material transport factors, three driving sources are considered: externally applied load, sintering stress (surface tension) and steady-state electro-migration while omitting a number of factors including possible plasma effect. From above, he derived the constitutive model and the densification map for aluminum, see Figure 2-10, using a series of equations for the total shrinkage rate in SPS by combining the grain-boundary diffusion and power-law creep mechanisms. Additionally, to broaden the scope of mechanisms in the modeling framework, he also studied the thermal factors[40, 41] in SPS that enhance the densification during SPS, and introduced the temperature gradient-driven thermal diffusion into account as well. By combining
the constitutive model to the shrinkage rate, the equation has been obtained and the result for the contributions of different mass transport mechanisms to the overall shrinkage rate are also calculated using the alumina powders, which is shown in the below figure 9 and which also corresponds well with the experimental data. In addition, the shape effect of the die in the role of SPS is also concerned now by Olevsky[42]. By considering the different geometry of the die, different thermal and electrical distribution would occur and the additional model should be established to comply with the growing demand of the industry.

**Future and Challenge of Spark Plasma Sintering**

Whereas it has shown clearly improvement from processing condition to final product in SPS, there are still some challenges preventing it from substituting conventional sintering methods. First, the problem of reduction and carbon contamination due to the low oxygen partial pressure in the SPS chamber causes side effects on the final product. It is documented in the literature that the properties of some sintered product are changed due to the carbon contamination [43, 44]. In our work, when sintering UO$_2$ at 1450$^\circ$C in SPS, a thin layer of uranium carbide is detected which resulting in the crumbles of the resulting compact in most cases. Solving this problem may involve the improvement of the processing condition or changing the die materials. Noudem et al., [43] has managed to sinter the oxides under air atmosphere by using stainless steel/tungsten carbide dies. However, this modification can be only applied at low temperatures (<1000$^\circ$C). Alternative solution is yet to be developed for materials to sinter at high temperatures in SPS.

Another challenge for SPS is to fabricate large-scale, complicated-shape products. With the increase of the sample dimension, higher temperature gradient may occur within the sample. Also, the temperature distribution may become complicated when the complexity of the shape is increased. Both of them may have detrimental effect on the final product. As is mentioned in
[45], some efforts have been made to improve the situation. Additional heating element can be applied surrounding the die to decrease the temperature gradient. Also, a careful design of the die set makes it possible to sinter a relatively complex shape with identical microstructure [46].

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Figure 2-1. Scientific publication of SPS. A) Papers of SPS published from 1995 to 2014. B) Citations of SPS from 1995 to 2014.
Figure 2-2. Sintered SPS Samples [22]. A) SPS sample with diameter up to 400 mm. B) Complex near-net shape parts.
Figure 2-3. Schematic drawing illustrating the features of an SPS apparatus[47].
Figure 2-4. Effect of current on assisting densification of powder in SPS[16]
Figure 2-5. Image of polyethylene fiber revealing the effect of electrical discharge [25]. A) SEM image of polyethylene fiber. B) SEM image of the polyethylene fiber exposed to electrical discharge in air.
Figure 2-6. TEM micrograph of FAST-consolidated AlN. AlN polytypes and Al$_2$O$_3$ pockets are indicated by arrows [28].
Figure 2-7. Schematic of sample of sphere to plate sintering geometry[48].
Figure 2-8. Time dependence of neck growth between copper spheres and copper plates at 900 °C under different currents. The neck size at zero time refers to the value obtained during ramp up to temperature[48].
Figure 2-9. Relative density and grain size versus the SPS temperature of nc-YAG powder at 100MPa for 3min[38].
Figure 2-10. Densification map for aluminum powder in SPS, $T=673K$, Pressure=2.83MPa[23]
Figure 2-11. Contribution to shrinkage rate from different mechanisms of mass transport for an alumina powder, applied stress 30MPa, porosity 0.3 heating rate 200 K/min, grain size 0.5μm.[40]
CHAPTER 3
DENSIFICATION OF URANAIUM DIOXIDE PREPARED BY SPARK PLASMA SINTERING

Introduction

Uranium dioxide (UO$_2$) has been widely used as nuclear fuel in water cooled reactors since 1960s due to its excellent corrosion resistance in water-steam and satisfactory compatibility with the claddings [49]. However, UO$_2$ is a refractory oxide with a melting point in excess of 2800 °C [50, 51] and therefore, requires high sintering temperature around 1700 °C in a hydrogen atmosphere for several hours using conventional sintering methods [52]. Numerous efforts have been made over decades to lower the sintering temperature of UO$_2$. Williams et al., [53] first studied the effect of hyperstoichiometry and atmosphere on sinterability of UO$_2$ and claimed that high density pellets could be obtained at 1100-1400 °C in neutral atmosphere by sintering the oxide with an oxygen (O) to metal (M) ratio greater than 2.06 and then reducing in a hydrogen atmosphere. Carrea [52] achieved low temperature sintering by increasing the BET specific surface area of UO$_2$ during sintering. A two-step heating cycle was set up to sinter UO$_2$ at 1200 °C for 2 hours to achieve 97.6% theoretical density (TD) and the total run time was 8 hours. The significance of enhanced uranium diffusion coefficient which accounts for the improved sinterability in hyperstoichiometric UO$_{2+x}$ was discussed by Lay and Carter [54]. Stuart and Adams [55] sintered UO$_{2.20-2.28}$ in H$_2$-N$_2$-H$_2$O gas mixture at 1300°C and achieved 96% TD in a single-stage process. However, the total run time was more than 9 hours. Chevrel et al., [13] introduced hyperstoichiometric UO$_2$ sintering by mixing U$_3$O$_8$ with UO$_{2.08}$ to achieve O/U ratio of 2.25 and obtained 96.5% TD under a combined argon and oxygen atmosphere at 1100 °C for 3 hours. Kutty et al., [9] studied shrinkage behavior of UO$_2$ under six different atmospheres, from which they concluded that shrinkage may occur at a temperature 300-400 °C lower in an oxidizing atmosphere than in others, but the typical total run time was several hours. Although
progress has been achieved in improving sinterability of UO₂, sintering by these methods was still a diffusion controlled process, which means long processing time and high temperature are required.

Sintering by non-traditional methods has also been pursued by many researchers. Amato et al., [56] utilized inductive hot pressing while sintering reactor-grade UO₂ to achieve more than 95% TD at 1200 °C and 8000 psi (55MPa). However, the total processing cycle and quality of sintered pellet were not reported and hence, the validation for inductive hot pressing of UO₂ remains questionable. In recent years, increasing interest has been shown in sintering UO₂ by alternative sintering techniques. Microwave sintering of UO₂ has been attempted by Yang et al., [57] who obtained 96.4% TD at 1600 °C under H₂ atmosphere for more than 1 hour. However rapid sintering has not been achieved due to formation of cracks at high heating rates (20-30K/min). Later, Yang et al., [58] introduced pressureless induction heating for rapid UO₂ sintering within 5 minutes to produce crack-free 96% TD pellets. However, many critical issues such as crack formation during higher heating rates (442K/min) and density inhomogeneity continue to be major challenges in the field.

Since 1990s [16], spark plasma sintering (SPS), also known as plasma activated sintering (PAS) [17] or field assisted sintering technique (FAST) [29], has become a popular sintering method for consolidation of powders in various fields [19]. The merits of SPS include rapid processing, homogeneity of final product, low energy consumption, etc [17]. In SPS, the green body is placed in a graphite die and uniaxial pressure is applied to the powder through graphite punches, as shown schematically in Figure 3-1. Low voltage (3-5V) and high amperage (600-800A) pulse current are applied to the powder compact via the graphite punches. The current flows through the punches and the die, causing rapid heating. Numerous mechanisms for
sintering have been proposed, including resistive heating by dies and punches, direct Joule heating if the powder is electrically conductive, enhanced diffusion and electron migration by the electronic field [23, 35], particle surface cleaning by the plasma [29], surface plasma formation and particle surface heating [38], spark plasma and spark impact pressure [16, 27, 31, 59], power-law creep mechanism by external pressure [23], temperature gradient-driven thermal diffusion [40, 41], etc. There has been an intense debate on whether or not a plasma is created in the SPS process [31]. Regardless, it is now well accepted that pulsed current causes joule heating at the inter-particle contact areas and upon application of pressure, these particles fuse to form the final compact. In the case of dielectric materials, the microscopic level discharge caused by the electrical field is expected to occur and favor densification [47]. Typical sintering times are on the order of 1 to 10 minutes at significantly lower processing temperatures than those in conventional sintering method. More details of SPS process are available in reference reports [19, 23, 27, 35, 38, 47, 59, 60].

Although a variety of refractory materials have been successfully processed in SPS [19], to the authors knowledge, literature on processing of nuclear fuels by SPS is limited. In this manuscript, a systematic study of densification during processing of UO<sub>2</sub> in SPS is described. The main objectives of the investigation were (i) to successfully sinter UO<sub>2</sub> powder in to pellets with 96% theoretical density and (ii) to reduce the maximum sintering temperature and sintering duration. Pellets were produced under different heating rates, hold times, and maximum sintering temperatures. The microstructure evolution and densification process under each of these processing conditions are investigated.
Experimental Procedure

Starting Powder

The uranium dioxide powder was supplied by Areva Fuel System, Charlotte, NC. The powder was reported to have a bulk density of 2.3g/cm$^3$, tap density of 2.65g/cm$^3$, mean particle diameter of 2.4µm, and a BET surface area of 3.11m$^2$/g. The grain size was determined using high resolution SEM to be between 100-400 nm, see Figure 3-2. The O/U ratio for the starting powder was determined to be 2.11 by measuring the weight change before and after reducing the powder into stoichiometric UO$_2$ using ASTM equilibration method (C1430-07). Note that in conventional oxidative sintering [13], hyperstoichiometric powder UO$_{2.25}$($U_3O_8+UO_2.11$ in 30:70 wt. ratio) is often used. In the current SPS, this step was completely eliminated by using the as-received powders.

SPS Sintering

Sintering was performed using a Dr. Sinter® SPS-1030 system. The as-received starting powder was loaded into a graphite die of diameter 12.7mm. The inner die surface was covered by a thin (0.13mm) roll of graphite foil to prevent reaction of UO$_2$ with the die wall. Cylindrical graphite punches were inserted into both ends of the die. The surface of each punch that comes in contact with the powder was coated with an aerosol of graphite (ZYP Coatings, Inc., Oak Ridge, TN) for preventing undesirable reaction between the punch and the pellet as well as for easy release of the UO$_2$ pellet from the die after sintering. The die was then wrapped with a sheet of graphite felt to reduce the heat loss from the graphite surface, decrease the thermal gradient between the surface of the die and the pellet, and finally, protect the outer steel chamber from thermal radiation damage. A window was cut in the felt (appox. 10mm x 10mm) for temperature measurement on the surface of the die by using a radiation pyrometer during the sintering process.
The entire die assembly was placed in the sintering chamber of the SPS and the chamber was depressurized to 10 Pa. A pulsing current (600-800A) was supplied at an on-off ratio of 12:2. The applied uniaxial pressure, temperature, z-axis motion of the punch, the chamber atmosphere pressure, current, and voltage were continually recorded as a function of time. A typical plot of some of the processing parameters during a sintering run is provided in Figure 3-3. The pyrometer lower limit of detection was 600°C and hence the programmed heating schedule was initiated only after the temperature of the die surface (measured through the opening cut in the felt) reached this value. Beyond this temperature, the heating rate was programmed at either 100 °C/min or 200 °C/min up to a temperature slightly below (around 50 °C) the desired maximum sintering temperature, and then at 50 °C/min up to the set maximum sintering temperature which ranged between 850 °C to 1525 °C for various runs (e.g. 1150 °C in Figure 3-3). The hold time at the maximum temperature was varied between 0.5 minutes to 20 minutes for different sintering runs (e.g. 0.5 minutes in Figure 3-3). Initially no programmed pressure was applied on the powder compact, which is denoted as ‘non-controlled’ pressure. This non-controlled pressure, which ranges between 14 MPa to 24 MPa, is mainly used to maintain the contact between various surfaces of the assembly. When the temperature of the die reached a specified temperature (e.g. 1100°C in Figure 3-3), the additional uniaxial pressure of 40 MPa was applied. This applied pressure was designated as ‘controlled’ pressure in the reminder of the manuscript. Both pressure and temperature were held constant for desired times (e.g. about 0.5 minutes in Figure 3-3) and then the pressure was released immediately after the hold time is completed. Note in Figure 3-3 that the actual measured temperature by the pyrometer follows closely the programmed temperature profile. During this procedure, the Z-axis displacement of the punch provides the details of the densification process in the UO2 powder compact. It is seen that
significant displacement occurs during the period when temperature rises above 600°C. The displacement then remains constant until the controlled pressure is initialized. The final densification occurs upon application of the peak controlled pressure of 40 MPa just before the maximum sintering temperature. The entire processing period lasted for 10 minutes and the resultant UO₂ pellet product is shown in Figure 3-4. A typical pellet disc was 12.5 mm in diameter and 6 mm thick and all our sintered pellets were nearly of the same diameter. The as-sintered pellets (with graphite foil) had a diameter of 12.54±0.02mm. The thickness of the residual graphite foil on the circumference of the pellet is no more than 0.025mm. So the actual diameter of the pellet is around 12.51mm, which is 98.5% of the target diameter of 12.7 mm and is in agreement with the thermal contraction calculation according to Fink’s paper.[61] The pellet height (thickness) is determined by the total mass of the powder used and the density (% TD) of the sintered pellet, i.e., if the mass of the initial powder and processing condition are kept the same, the dimension of the resulting pellet would be almost identical. To accomplish the objective of reducing maximum sintering time and duration, we have utilized two heating rates (100°C/min and 200°C/min), a range of maximum sintering temperatures (850-1525°C) and hold times (0.5-20 minutes). The initial runs were made at high temperatures (1500-1525°C) and long hold time (10-20 minutes) at the lower ramp rate of 100°C/min. With each successful run, the above parameters were simultaneously varied to achieve the desired result of 95% theoretical density or higher.

**Characterization Methods**

After sintering, the chamber was allowed to cool for 1 hour and the graphite die with sintered compact was taken out of the SPS chamber. The pellets were ground using 240 grit sandpaper to remove the residual graphite foil and aero gel on the surface. The pellets were then reduced to stoichiometric UO₂ following the procedure described in ASTM C1430-07. For the
micro-indentation hardness measurements, the pellet surfaces were ground and polished down to 0.05\(\mu\)m colloidal silica using standard metallographic methods. The Archimedes’ method was used to determine the density of each pellet. The pellet surfaces were polished and thermally etched at 1400°C for 1 hour to reveal the grain boundaries. X-ray Diffraction (Philips APD 3720) was conducted to detect the possible presence/absence of residual carbon and formation of carbides (or intermetallic) after the sintering and reduction processes. Scanning electron microscopy (SEM) was conducted using an accelerating voltage of 15KV and electron beam current of 10-12 \(\mu\)A to image microstructural features. Grain size was measured by the line-intercept method using ASTM E112 method covering over 100 grains in each sample.

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**Result and Discussion**

**Starting Powder Results**

The XRD results in Figure 3-5 show that due to the hyper-stoichiometry of the starting \(\text{UO}_2.11\) powder, small peaks in addition to \(\text{UO}_2\) peaks are revealed. The reduction process completely reduces the starting powder into the stoichiometric \(\text{UO}_2\) powder. Also, the spark plasma sintered, polished and then reduced \(\text{UO}_2\) compact reveals identical peaks to those of reduced \(\text{UO}_2.00\) powder. This result implied that no residual carbon or formation of carbides (or intermetallic) occurs after the whole process.

**Densification**

As stated earlier, our objective was to reduce both the maximum sintering temperature, as well as the sintering time, while achieving the desired 95% TD. Several combinations of process parameters were employed during the sintering of various pellets to investigate the densification process. The results are listed in Table 3-1. The densification was measured by the reduction in
the length of the green body pellet during sintering. Figure 3-6 shows few selected plots of the
die surface temperature and densification ($\Delta L/L_o$) of UO$_2$ compacts for two heating rates,
different hold times, and various maximum temperatures during sintering. $\Delta L$ is the displacement
of the lower punch and $L_o$ is the original green body thickness before sintering. It is seen in
Figure 3-6 that the densification process is different for different process conditions. In general,
an s-shape profile was revealed in all cases except for the 850°C plot. When the furnace
temperature is below 720°C, only limited densification was observed. As the temperature
increased beyond 720°C, there was a rapid increase in densification until 1000°C was reached.
This temperature range, 720°C -1000°C, is referred to as the ‘densification range’ in the
subsequent discussions. Further increases in the temperature did not result in further increase in
densification, as revealed by the plateau of the s-shaped curve. These phenomena are in good
agreement with the three primary sintering stages in a conventional sintering process [62].
Further densification is now possible only by the application of controlled pressure (40 MPa), as
revealed by the steep rise at the end of each curve in Figure 3-6. When the temperature was
increased beyond 1350°C, even with the application of the controlled pressure, a slight decrease
in densification was noted. This behavior may imply that the thermal expansion of the punch was
greater than the shrinkage of the compact in this high temperature regime. Thus, for all the above
cases where the maximum sintering temperature was above 1000°C, the densification behavior
followed the s-shaped curve. However, when the maximum sintering temperature was only
850°C, the densification behavior was different. There was no plateau at the final sintering
temperature. This behavior will be discussed in more detail in Figure 3-9. Therefore, the effect of
the maximum sintering temperature on densification can be separated into two regimes: when the
set sintering temperature was below 1000°C, say 850°C, no s-shape densification curve was
observed. Once the set maximum sintering temperature was above 1000°C, say 1050°C, an s-shape curve was observed and further increases in temperature would only extend the length of the plateau. However, no effect of the heating rate and hold time was revealed in this plot. Regardless of the heating rate (200°C/min or 100°C/min), hold time (0.5–20 min) and maximum set temperature (1050°C-1500°C), the densification range in the s-curve remained the same and all sintering runs yielded the same degree of densification ($\Delta L/L_o$) and almost the same final density except for the case of sintering at the lowest set temperature (850°C), which would be further discussed in Figure 3-9.

Figure 3-7 illustrates the plot of pellet density as a function of maximum sintering temperature under various processing conditions. By adopting a rapid heating rate (200°C/min) and a short hold time (0.5min), when sintering was conducted at 850°C with the non-controlled pressure, the maximum density achieved in the pellet was only 78.4%. Upon application of the controlled pressure (40 MPa) at the same temperature, the density increased to 86.5%. Further increase in pellet density was achieved by increasing the maximum sintering temperature and application of the controlled pressure. At a maximum sintering temperature of 950°C, 89.4% TD was achieved and when the maximum sintering temperature was raised to 1050 °C, 96.3% TD was achieved. Beyond this temperature, varying the processing conditions revealed little influence on the final pellet density. The highest densities of 97%-97.6% were achieved by further increasing the maximum sintering temperature to 1500-1525 °C with the application of controlled pressure starting from 1350 °C. To further understand the effect of the controlled pressure on the final density at these higher temperatures, another pellet was sintered at 1525°C without the application of the controlled pressure. There was only marginal increase in the density (from 96% to 97%) under these conditions. It is obvious that the effect of pressure is
more significant when the controlled pressure was applied at the low temperature (850°C) than at the high temperature (1350°C). Recall in Figure 3-6 that the major densification started from 720°C and ended around 1000°C. When controlled pressure is applied at the low temperature, say 850°C, a number of the powder particles were still undergoing particle adhesion and rearrangement, which is described as the first stage of sintering [62]. With the help of the controlled pressure, more particles may contact each other, and the neck formation was much easier between the neighboring particles, thus contributing to the densification. If the controlled pressure was only applied at the high temperature, say 1350°C, when the final stage of sintering was attained and the densification was mainly controlled by diffusion, the effect of the controlled pressure becomes insignificant.

To better reveal and compare the effects of various sintering parameters on densification, the densification rate $d(\Delta L/L_0)/dt$ was plotted in Figure 3-8 as a function of die surface temperature during the sintering process at two heating rates (100°C/min and 200°C/min), different hold times and maximum temperatures. It can be seen that the densification rate increased rapidly at the temperature above 700°C, and reached the maximum rate between 800-900°C. When the maximum set sintering temperature was only 850°C, which is below the upper limit of the ‘densification range’ (e.g. 1000°C in Figure 3-6), the densification rate decreased rapidly to zero after the hold time. For higher sintering temperatures, the densification rate fell gradually to zero and there was little effect of varying the set maximum sintering temperature above the ‘densification range’ on the curves. Also, when the maximum sintering temperature was limited to 850°C, the final density of a sintered pellet would be less than 87% as shown in Figure 3-7. Therefore, a further increase in the sintering temperature is essential for continued densification and a positive densification rate as observed in Figure 3-8. The effect of the heating
rate on the densification rate can be clearly seen in this Figure. Increasing the heating rate to 200°C/min, compared to 100°C/min, caused almost the same initial densification rate. However, a significant increase in the maximum densification rate was observed for 200°C/min. As is shown in Figs.3-6 and 3-7, the final density of the pellets remained almost the same in both cases. The application of controlled pressure close to the end of the sintering phase (see Figure 3-6) provided the additional densification rate which could be seen as a hump at the end of each curve. Also, no effect on the densification rate was seen for various hold times. Finally, regardless of the differences in the above process conditions, the temperature range where the positive densification rate occurs is between 720 °C and 1000 °C, which is in good agreement with the ‘densification range’ observed in Figure 3-6.

The effect of the controlled pressure on densification and densification rate is demonstrated in Figure 3-9 by choosing the densification plot corresponding to a pellet sintered at a maximum temperature of 850°C. This plot was selected because at 850°C, the UO₂ compact was still in the major densification phase (Figure 3-6) with high densification rate (Figure 3-8) and the effect of controlled pressure can be better illustrated than at higher set sintering temperatures. In Figure 3-9, the die surface temperature versus the densification and the densification rate during sintering are presented. Recall that the non-controlled pressure provided the uniaxial pressure between 14-24MPa during the whole processing period while the controlled pressure (set by the user) was applied at 800°C and then reached a peak pressure of 40 MPa at 850 °C. The plot reveals that without the controlled pressure (dashed line), the densification increased from around 700°C up to the maximum sintering temperature and continued to increase even after 0.5 minutes hold time elapsed after which the temperature dropped to around 825°C due to cooling. The densification rate curve also revealed the same phenomena. The steep
drop of the curve at 850°C indicates that the densification has stopped. On the other hand, by applying additional controlled pressure (solid line), both higher densification and higher densification rate were achieved. The resulting final density was 86.5% with the controlled pressure and only 78.4% with non-controlled pressure as shown in Figure 3-7.

In conventional or oxidative sintering methods [9, 13, 52-58], the densification of UO₂ was controlled by the diffusion of uranium ions [9] at high sintering temperature and under long hold time (more than 3 hours) [9, 13, 52, 54]. Chevrel et al., [13] studied the effect of initial O/U ratio on densification, in which the onset of shrinkage of all compositions with different O/U ratio were observed from 800-900°C in vacuum (10ppm of O₂). The highest theoretical density was reported as 96.5% for sintering temperatures up to 1100°C at the total duration of more than three hours and with initial O to U ratio of 2.22. The influence of the atmosphere on the densification of UO₂ was studied by Kutty et al., [9] where it was reported that the lowest temperature for densification in oxidizing atmosphere (300-1000ppm of O₂) started around 700°C and reached 90% TD at 1350°C. The total run time was also above three hours. While in reducing atmosphere, the onset temperature for densification was between 1100°C and 1150°C, and a maximum sintering temperature of 1600°C was required to attain 90%TD. In our present work, the densification started at a temperature as low as 720°C and 96.3% TD was achieved at 1050°C for hold time of only 0.5 minutes at the maximum temperature (as shown Figure 3-7). The required total run time for the whole process in our research was only 10 minutes. This result is a significant improvement over the conventional sintering method [52] as well as other methods [9, 13] mentioned above. The result also implies that diffusion of uranium is not a major factor in densification because the entire sintering cycle was only 10 minutes and the duration above 720°C during sintering was only around 4 minutes. This result is consistent with the well
documented facts about SPS that the uniaxial pressure [38, 39, 47, 63] and the pulsed current [16, 27, 29, 38, 47] are the key factors favoring rapid densification of powders. The effect of the uniaxial pressure was apparent: by applying the controlled pressure, both densification and densification rate have been increased. The pulsed current also contributed to the densification. Although there is still uncertainty on the formation of the plasma, due to the dielectric nature of the oxide and only limited current passing through the particles, it is well accepted [47] that a microscopic discharge occurs on the surfaces of the particles which promotes the densification.

**Microstructure**

To evaluate the quality of the densification as well as the effect of sintering parameters, it is important to investigate the resulting microstructure of the sintered compacts. The microstructure of a sintered pellet at 1150°C for 5 minutes is shown in Figure 3-10, where Figure 3-10(a) shows the fracture surface and Figure 3-10(b) reveals the polished surface after thermal etching at 1400°C for 30 minutes. Both micrographs reveal significant inter- and intra-granular pores. The density of the pellet was 96.3% and the average grain size was 2.9± 0.3um. Comparison of the two micrographs reveals that the thermal etching process did not cause significant grain growth. Comparing the grain size to the starting particle size (2.4µm), it is noted that there was limited grain growth during the SPS process which is mainly due to the rapid heating rate and short hold time. With the help of rapid heating, coarsening-dominated region in the lower temperature range (below 700°C) has been bypassed rapidly [62] and the densification is favored in a very short time at higher temperature (above 700°C). Interestingly, the images in Figure 3-10 (a) and (b) reveal a large number of intra-granular pores. The appearance of these intra-granular pores is often a measure of over sintering in the traditional sintering process [62] where high temperatures or long sintering times are employed. Under these conditions, inter granular pores break away from grain boundaries and migrate to the interior of the grains. When
the pores were isolated from the grain boundary, it is difficult to eliminate them due to the low lattice diffusion rate [62]. However, in SPS, the powder compact was unlikely to get over-sintered within such a short time and at low temperature. An alternative explanation may be the effect of the high densification rate. It is likely that due to the high heating rate and application of the uniaxial pressure at the peak sintering temperature, neck formation occurs along the inter-particle contacts and closed pores are formed before the gas between the particles can escape. Inter-granular pores are more likely to diminish due to the grain boundary diffusion during the neck formation while most of the intra-granular pores remained locked-in. A similar phenomenon was also seen in Shen’s study on sintering alumina using SPS [47] where the porosity (both inter- and intra-granular porosity) was significantly increased with the increase in heating rate from 50°C/min to 580°C/min. This residual porosity may explain the limitation in final density achieved in the UO₂ pellets. It is seen in Figure 3-7 that the maximum density was 97%. The remaining 3% porosity is mostly intra-granular porosity and thus it is difficult to reduce the porosity over a short sintering time. Compared to the inter-granular porosity, the presence of the intra-granular porosity helps the fission gas retention, which may be beneficial during the in-pile operation. [64] In addition, as is mentioned in the reference [65], isolated pores and intra-granular fission-gas bubbles have less thermal resistance compared with the pores with the mutual interference for the same amount of the porosity. In our case, the SPS sintered pellets have a higher level of intra-granular pores compared to inter granular pores and may provide a higher thermal conductivity.

The hold time is shown to have little effect on densification as discussed previously. However, the influence of the hold time on the grain growth can be significant. The isothermal grain growth of UO₂ at 1500°C is shown in Figure 3-11 for various hold times. As the
temperature was held constant, the average grain sizes increased with an increase in hold time. It is seen that when the hold time was increased from 1min to 5min, there was only limited increase (13%) in grain size, while from 5min to 10min, a significant increase (53%) in grain size was observed, as seen in Figure 3-12. Similar phenomena have also been observed by researchers while sintering other ceramics in SPS [63], where a critical temperature or hold time existed for activation of the rapid grain growth. This phenomenon can be explained by the elimination of inter granular pores during hold time. With less pores along the grain boundaries, the force retarding the grain boundary migration is reduced, and hence a higher rate of grain growth is expected [62]. However, the increase in density over a 10 minutes period was not significant.

Conclusions

The investigation of the influence of processing parameters during spark plasma sintering of UO$_2$ powder revealed that 96.3% theoretical density can be achieved in SPS at a maximum sintering temperature of 1050°C for only 0.5 minutes hold time. As long as the sintering conditions are above these value, the variations in parameters such as the maximum sintering temperature (up to 1500°C), heating rate (200°C or 100°C/min) and hold time (0.5–20 min) exhibit little influence on the densification behavior when moderate pressure (40 MPa) is applied. Most densification occurs in the temperature range of 720°C-1000°C. Application of the controlled uniaxial pressure promotes the densification as well as the densification rate. The increase in hold time increases the grain size and reduces porosity.
<table>
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<tr>
<th>Sintering Temperature(°C)</th>
<th>Hold time(min)</th>
<th>Heating Rate (°C/min)</th>
<th>Controlled Pressure</th>
<th>Density (% TD)</th>
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</thead>
<tbody>
<tr>
<td>1525</td>
<td>1</td>
<td>100</td>
<td>N/A</td>
<td>96.8±1%</td>
</tr>
<tr>
<td>1525</td>
<td>1</td>
<td>100</td>
<td>N/A</td>
<td>96.0±0.8%</td>
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<tr>
<td>1500</td>
<td>1</td>
<td>100</td>
<td>Y</td>
<td>97.2±0.7%</td>
</tr>
<tr>
<td>1500</td>
<td>1</td>
<td>100</td>
<td>Y</td>
<td>97±1.1%</td>
</tr>
<tr>
<td>1500</td>
<td>5</td>
<td>100</td>
<td>Y</td>
<td>97.1±0.6%</td>
</tr>
<tr>
<td>1500</td>
<td>10</td>
<td>100</td>
<td>Y</td>
<td>97.4±0.4%</td>
</tr>
<tr>
<td>1500</td>
<td>20</td>
<td>100</td>
<td>Y</td>
<td>97.6±0.6%</td>
</tr>
<tr>
<td>1350</td>
<td>5</td>
<td>100</td>
<td>Y</td>
<td>96.4±0.7%</td>
</tr>
<tr>
<td>1150</td>
<td>5</td>
<td>100</td>
<td>Y</td>
<td>96.3±1.4%</td>
</tr>
<tr>
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<td>5</td>
<td>100</td>
<td>Y</td>
<td>96.9±1.1%</td>
</tr>
<tr>
<td>1150</td>
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<td>200</td>
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<td>96.7±0.9%</td>
</tr>
<tr>
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<td>200</td>
<td>Y</td>
<td>95.4±0.9%</td>
</tr>
<tr>
<td>1050</td>
<td>0.5</td>
<td>200</td>
<td>Y</td>
<td>96.3±1.1%</td>
</tr>
<tr>
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<td>200</td>
<td>Y</td>
<td>89.4±2.7%</td>
</tr>
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<td>200</td>
<td>Y</td>
<td>86.5±0.9%</td>
</tr>
<tr>
<td>850</td>
<td>0.5</td>
<td>200</td>
<td>N/A</td>
<td>78.4±0.4%</td>
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</table>
Figure 3-1. Schematic of die assembly and sintering chamber in SPS.
Figure 3-2. SEM image of the starting powder (UO$_{2.11}$)
Figure 3-3. SPS parameter profiles during a sintering run. The grey arrows indicate the direction of axes labels.
Figure 3-4. SPS sintered UO$_2$ Pellets of diameter 12.5mm X 6mm thickness
Figure 3-5. XRD pattern of the starting UO$_{2.11}$ powder, reduced UO$_{2.00}$ powder and the spark plasma sintered (SPSed), polished and reduced compact.
Figure 3-6. Densification profile for various heating rates during sintering. It is seen that the majority of the densification occurs between 720°C-1000°C and is shown in the plot as “densification range”. The controlled pressure was applied in all cases towards the end of the sintering phase. The arrows in the plot indicate the sharp increase in densification caused by the controlled uniaxial pressure of 40 MPa. The final density of each pellet is shown next to the sintering parameters.
Figure 3-7. Densities of UO$_2$ pellets versus sintering temperature for various hold times, pressures and heating rates. Note that all pellets were sintered with the controlled pressure (40 MPa) except those marked as “Non-controlled Pressure” which were sintered with non-controlled pressure.
Figure 3-8. Densification rate versus temperature during sintering for two heating rates, different hold time and different maximum temperature. Note that the controlled pressure of 40 MPa was applied towards the end of sintering in all cases and the arrows indicate the associated increase in densification rate.
Figure 3-9. Densification (thick line) and densification rate (thin line) versus temperature during sintering with controlled pressure (40 MPa) and non-controlled pressure (14-24 MPa) for maximum sintering temperature of 850°C and hold time of 0.5 minutes.
Figure 3-10. Microstructure of sintered pellets at 1150°C for 5min, and 96.3% TD revealing intra-granular pores. A) Microstructure of fracture surface before thermal etching. B) Microstructure of polished surface after thermal etching.
Figure 3-11. Micrographs revealing grain growth over different isothermal hold time at 1500°C. The hold time, relative density and average grain size are listed on each image.
Figure 3-12. Plot of average grain size with hold time revealing increased rate of grain growth with hold time. All pellets had almost the same (97%-97.4%) density.
CHAPTER 4
MICROSTRUCTURE DEVELOPMENT OF URANIUM DIOXIDE PREPARED BY SPARK PLASMA SINTERING

Introduction

The microstructural properties, such as porosity and grain size, of UO₂ pellets play an important role in their performance as an effective nuclear reactor fuel. The creep response, yield strength, thermal conductivity, fission gas retention, and swelling effect are all known to be influenced by the microstructure [49]. Thus, it is essential to control the microstructure of the nuclear fuel during the fabrication process. The influences of microstructure on the properties of conventionally sintered UO₂ have been studied extensively [49, 50, 66]. In the conventional methods, a preformed UO₂ powder compact is sintered at 1600-1700°C for several hours without the application of any pressure. It usually takes more than 10 hours to fabricate a UO₂ pellet [67]. This time includes the rise time (2-4 hrs) to desired high temperature, hold time (2-4 hrs) at that temperature to cause sintering and cooling time (2-4 hrs) to room temperature. Sintering atmosphere and powder characteristics are the key parameters that influence the sinterability of UO₂ in conventional sintering methods. By modifying the surface conditions of the starting powder[13, 67] or changing the sintering condition into a properly oxidized atmosphere [9, 13], lower sintering temperature (1200-1400°C) could be achieved. However, in both methods, the enhanced sinterability is still controlled by the diffusion process, which means that the long processing time (several hours) is needed to achieve the desired high density. Recently, a new technique called spark plasma sintering (SPS) or field assisted sintering technique (FAST) has been gaining popularity in the fabrication of UO₂ nuclear fuels [68, 69]. It has been shown that high-density (>95% TD) UO₂ fuel pellets can be produced at a significantly lower sintering temperature (1050°C) within a hold time of only 30 seconds [69]. Due to this short processing time, the microstructure of the spark plasma sintered UO₂ pellets is quite different from the
pellets made by conventional sintering methods. For example, the grain size in SPS may be smaller and may consequently influence the thermal properties of the resulting fuel pellets. Systematic studies on the influence of processing conditions on microstructure evolution and the thermal properties are still needed to evaluate the suitability of pellets made by SPS process in nuclear reactor environment. In this manuscript, the O/U stoichiometry and microstructure evolution during SPS of UO₂ pellets were investigated by varying the processing conditions such as hold time, heating rate, and maximum sintering temperature.

**Experimental Procedure**

**Starting Powder**

The uranium dioxide powder was supplied by Areva Fuel System, Hanford, WA. The powder was reported to have a bulk density of 2.3 g/cm³, tap density of 2.65 g/cm³, and BET surface area of 3.11 m²/g. The powder particle grain size was determined using high resolution SEM to be around 100-400nm as shown in Figure 4-1(a). The stoichiometry of the starting powder was determined to be UO₂.₁₆ by measuring the weight change before and after reducing the powder to stoichiometric UO₂ using ASTM equilibration method (C1430-07).

**SPS Processing Conditions**

Sintering was performed using a Dr. Sinter® SPS-1030 system. The starting powder was loaded into a 12.5mm inner diameter graphite die with a die wall thickness of 9.5mm. The die was covered with a graphite felt to limit the heat loss from the die. A small window was cut in the felt to focus the pyrometer for monitoring the temperature of the die surface during the sintering process. The above die assembly was placed in the sintering chamber of the SPS which was depressurized to 10 Pa. Two heating rates of 50 and 200°C/min were used and a uniaxial pressure of 40 MPa was applied when the maximum sintering temperature was reached and held for desired duration of time to achieve different grain sizes in the microstructures. The detailed
sintering cycle was described in a previous publication [69]. The maximum sintering temperature was varied from 750°C to 1450°C and the hold time was varied from 0.5min to 20min. Pellets of size 12.5mm in diameter and 6mm in height were fabricated.

**Characterization Methods**

All the sintered pellets were reduced to UO$_{2.00}$ as described in [68]. The O/U ratio of the resulting pellets were estimated by measuring the weight change before and after the reduction process. The density of the reduced pellets was measured using the Archimedes method by immersing the pellets into the distilled water. X-ray Diffraction (XRD) was conducted on the starting powders and each sintered pellet to measure the lattice parameter of UO$_2$ and detect the possible formation of intermetallics and other reaction products. The diffraction patterns were recorded at a temperature of 25°C by PANalytical X’Pert Powder® diffractometer with a Cu tube (Cu$_{k\alpha}$=1.5406 Å). The 2θ angle was scanned from 20-80° with a step size of 0.0082° and a scanning time of 10s per step. The lattice parameter was calculated using Bragg’s Law: $n\lambda=2dsin\theta$. The software X’Pert HighScore Plus® was used to fit the peak profile. The resulting diffractogram of the starting powder UO$_{2.16}$ and the reduced powder UO$_{2.00}$ is plotted in Figure 4-2. It is seen that both UO$_{2.00}$ and UO$_{2.16}$ show typical peaks of the cubic crystal structure. The lattice parameter of UO$_{2.00}$ is 5.472±0.0096Å, calculated by averaging the all the peaks in the plot. This value is consistent with the 5.4711±0.001Å reported in literature [6, 70]. The lattice parameter for UO$_{2.16}$ is 5.455±0.008Å, which shows contraction of the lattice. The inset in the plot shows that with a higher O/U ratio, the $111$ peak of UO$_{2.16}$ shifted to higher diffraction angle indicating a smaller lattice parameter. The contraction of the lattice parameter of UO$_{2+x}$ can be attributed to the formation of U$^{5+}$ and U$^{6+}$, which have a smaller ionic radius and a higher
specific charge. Detailed discussion on the influence of oxygen on the lattice parameter of UO$_2$ can be obtained in the literature [71].

A field emission scanning electron microscopy was used to image microstructural features. Grain size was measured from several micrographs of the polished pellet surface using the mean linear intercept method and observation of the fracture surfaces in SEM.

**Result and Discussion**

**Density and Grain Size**

A typical pellet sintered at 1050°C, 0.5 min hold time, and 40 MPa pressure is shown in Figure 4-1 (b). The pellet was 96.3% of the TD. A fracture surface micrograph is shown in Figure 4-1 (c) to reveal the typical microstructure. The estimated average grain size is about 3 µm.

The influence of hold time at different maximum sintering temperatures on the density of the sintered pellets is plotted in Figure 4-3. It is seen that below 95% of the TD, densification can be enhanced either by increasing the maximum sintering temperature or hold time. At 750°C, the pellet reached only 76% of the TD when the hold time was 0.5 min. By increasing the hold time to 20 min, the density increased to 95% of the TD. The density can also be increased to 96% of the TD by increasing the temperature to 1050°C with only a 0.5 min hold time. Thus, one can increase the density of the pellets either by increasing the hold time at a lower sintering temperature or by increasing the maximum sintering temperature but for a shorter hold time. However, after reaching 95% of the TD, increasing either the maximum sintering temperature or hold time will result in little further densification. As a result, all the densities achieved in this study were below 98% of the TD.
The influence of hold time and maximum sintering temperature on grain size is plotted in Figure 4-4. At 750°C with a hold time of 0.5 min, the resulting average grain size is only 0.2 µm which is the same range as the starting powder (0.1-0.4 µm). Even after increasing the hold time to 20 min at this temperature, the average grain size is increased to only 0.9 µm. On the other hand, by increasing the maximum sintering temperature to 1050°C for a 0.5 min hold time, the average grain size increases to 3µm and with further increase in maximum sintering temperature to 1450°C, the average grain size increased significantly to 6.3µm with a hold time of only 0.5 min. However, at a slightly lower temperature of 1350°C, the maximum average grain size of 7µm was achieved with a hold time of 20 min. Thus, the effect of maximum sintering temperature and the hold time are clearly evident in this figure, i.e., at a given maximum sintering temperature, an increase in hold time has a marginal effect on the grain size. On the other hand, for a given hold time, an increase in sintering temperature has a dramatic effect. Further increase in the maximum sintering temperature or hold time beyond 1450°C causes large cracks and eventual crumbling of pellets. This may be due to the excessive thermal expansion and potential chemical interaction between the graphite dies and UO₂ powder. A summary of processing conditions and the resulting density and grain size of the pellets is given in Table 4-1.

The correlation between the grain size and density of the sintered UO₂ pellets for all the sintering runs with different hold times and maximum sintering temperatures is plotted in Figure 4-5. It is seen that the grain size of UO₂ appears to be a function of the pellet theoretical density, regardless of the hold time and maximum sintering temperature. The plot reveals that during the early stage of densification, until around 90% of the TD, there is only limited grain growth; the average grain size remains below 0.6µm until the density reaches 95% of the TD where it increases to 0.9µm. Beyond this density, the grain size increases dramatically to 3 µm while
there is only a slight increase in the density. The grain size reaches to almost 7 µm when the
density reaches close to 97% of the TD. Thus, most of the dramatic increase in grain size occurs
between 95% to 97% of the TD. The possible mechanism associated with this delay in the grain
growth and densification process can be explained with the help of microstructure evolution at
various processing conditions as discussed below.

**Microstructure Development**

From Figure 4-5, it appears that the final microstructure of the sintered pellet is a function
of the level of densification and grain growth behavior during the sintering process. Also, the
grain size appears to be only a function of the density regardless of the hold time and maximum
sintering temperature. This grain size-density relationship was also observed in other materials
[72-74] sintered in conventional sintering methods as well as in SPS, which implies that the
microstructure development of UO$_2$ in SPS is similar to those of other materials sintered using
conventional methods. The lack of the grain growth at low density (<95% of the TD) can be
rationalized based on the intergranular porosity that exists in the starting powder compact. As the
sintering process continues under the applied pressure, the powder particles get closer but the
grain growth is limited by the pinning effect of the intergranular pores present along the grain
boundaries as revealed in Figure 4-6 (Aa-Ac). These microstructures show that the grain size is
constant at about 0.4µm, but the density values increase from 77% to 90% of the TD. Large
porosity levels are clearly seen in these low-density pellets. The pores surrounding each grain
inhibit the grain boundary migration, thus limiting the densification process. With increasing
temperature or hold time along with the applied pressure, grains get closer and the densification
process continues where most pores shrink due to the grain boundary diffusion. Some pores
remain attached to the grain boundary with the boundary migration and grain growth. As the
grain gets larger, a small portion of the pores are left within the grain, forming intragranular pores as shown in Figure 4-6 (Ba-Bc). Once the density reaches around 95% of the TD, the grain size increases rapidly. The residual porosity now mainly consisted of intragranular porosity as seen in the high-magnification images on Ba-Bc of Figure 4-6. The elimination of intragranular porosity is possible by lattice diffusion which requires longer processing time [75]. Thus, the presence of intragranular porosity limits the final density of the pellet to 97% of the TD under the current processing conditions.

The mechanism for formation of intragranular porosity during densification can be clearly observed in the high magnification SEM image of a pellet, shown in Figure 4-7, sintered at 750°C with a density of 77% of the TD. As indicated by the arrows in the image, the sequence of mechanisms which are operative during grain growth and subsequent densification are shown. Initially, neck formation occurs between two adjacent grains (Step#1). With the surrounding grains simultaneously forming similar necks (Step#2), grain growth occurs and intergranular pores were formed (Step#3). As the densification and grain growth-induced grain boundary migration continues, some pores shrank and closed while some others separated from the grain boundaries were left inside the grain, forming intragranular pores (Step#4). Based on these sequence of observations, it is now possible to rationalize the relationship between the grain size and densification in Figure 4-5. During the early stage, the starting powder particles cannot grow into large grains as they are farther apart. With application of the pressure and increase in temperature, the grains get closer and start to grow due to the neck formation. This process eventually reduces porosity and allows densification to occur beyond 95% of the TD with simultaneous rapid grain growth as illustrated in Figure 4-5. Thereafter, a majority of the intragranular porosity remains due to the short duration of the sintering period.
The ability to fabricate pellets with a controlled intragranular porosity is of significant value during reactor operation. The released fission gases can be captured in these intragranular pores. On the other hand, if only intergranular pores are present, the fission gas trapped in these pores can cause grain boundary cracking which eventually leads to pellet cracking. Thus, SPS offers the benefit of control of the porosity in the UO$_2$ pellet.

**O/U Ratio**

Recall that the starting O/U ratio of the UO$_2$ powder is 2.16. However, it has been observed in our experiments that, depending on the process conditions, the stoichiometry of the sintered pellet changed, see Figure 4-8. The O/U ratio decreased moderately with an increase in hold time but more severely with the maximum sintering temperature. At a low sintering temperature of 750°C, only a moderate decrease in O/U ratio is obtained when extending the hold time from 0.5 min to 20 min. However, with an increase in the maximum sintering temperature to 850°C, the O/U ratio dropped more rapidly, and at 1450°C, only a 0.5 min hold time was needed for the O/U ratio to reach the desired 2.00. No further decrease in O/U ratio was observed in the range of processing conditions. These results implied that chemical reactions may occur during sintering to reduce the oxygen level in the powder.

Stoichiometry of UO$_2$ (i.e. O/U ratio) plays a critical role in thermal conductivity. A slight deviation in the O/U ratio from 2.00 may result in significant decrease in thermal conductivity [76]. Thus, for efficient operation of UO$_2$ pellet in reactor environment, the O/U ratio of 2.00 must be maintained in a pellet. In conventional sintering methods, there are two major ways to maintain this optimal O/U ratio [13, 67]. One method is to sinter the starting powder in a H$_2$ atmosphere, which results in the O/U ratio of the final pellet at 2.00. However, due to the low sinterability of UO$_{2.00}$, high temperature in the range of 1600-1700°C is required.
for sintering high density pellets [67]. Another way is to sinter the hyper stoichiometric powder (O/U=2.25) to promote the sinterability [13] and thus decrease the sintering temperature to 1200-1400°C. However, this method usually requires the pre-sintering step of mixing UO₂ and U₃O₈ powder to get O/U of 2.25 and the subsequent post-sintering step, i.e. reduction in H₂ atmosphere as per ASTM (C1430-07) to reduce the pellet to UO₂.00. On the contrary, the pellets produced in SPS revealed an O/U ratio lower than that of the starting powder, see Figure 4-8. Additionally, it is noted that, at a maximum sintering temperature of 1350°C and hold time of 5 min, the O/U ratio of 2.00 is automatically achieved in the pellet. This result indicated that by manipulating the processing conditions in SPS, the O/U ratio of the starting powder can be reduced into the stoichiometric form of UO₂.00 without any need for post-sintering reduction step. The reduction of UO₂ may occur from the chemical reaction between graphite punch and the powder. XRD was performed to analyze the reaction products in the sintered pellet. The reaction between graphite and UO₂ is usually used for the preparation of uranium carbides. Depending on the atmosphere and starting powder conditions, the reaction begins at 1000-1300°C [77-79]. The most common reaction products are UC, UC₂ [78] or UC₁₋ₓOₓ [80] depending on the amount of the residual oxygen in the UC lattice. According to a mass spectrometry study carried by Gosse et al [79], for hyper-stoichiometric UO₂ powder, the reaction starting temperature could be as low as ~700°C and in this reaction, UO₂ₓ⁺ is reduced into UO₂.00 without the formation of carbides. In our work, UO₂ powder was enclosed in a graphite die, and heated up to 1450°C, which allowed the reaction between graphite and UO₂ to form carbides. The decrease of the O/U ratio even at 750°C in our study also confirms the result by Gosse et al[79]. The carbide was detected by XRD on the surface of the as-sintered pellet. It is seen in Figure 4-9 that the formation of UC was revealed on the surface of the pellet sintered at 1450°C and 0.5min hold time. The six peaks clearly reveal the
cubic structure of UC and all the peak positions match the UC reference based on Powder Diffraction File (PDF), the official database for phase identification. The slight derivation from the reference may be due to the residual oxygen in the UC lattice or thermally induced residual stress. The graphite detected at around 26° is attributed to the residual graphite foil on the pellet surface. The rest of the peaks remained unknown. These unknown peaks may be attributed to the tetragonal UC\(_2\) phase. However, due to the low intensity of these peaks, no exact matches could be detected. All the identified peaks in Figure 4-9 are listed in Table 4-2.

After hand-grinding the surface layer on the pellet with 400 grit SiC paper for two minutes, only the UO\(_2\) peaks were detected. This result suggests that only a layer of reaction product between the graphite punch and UO\(_2\) powder was formed on the pellet surface. The reaction between graphite and UO\(_2\) is more likely to happen on the surface because of the higher temperature on this region. During SPS, graphite punches act as a heating source where a large amount of Joule heat is generated by the high density of electric current flowing through the punch [33]. Thus, the following sequence of reactions [79, 81] are possible in the surface layer:

\[
\begin{align*}
\text{UO}_2^+ + x\text{C} &\rightarrow \text{UO}_2 + x\text{CO} \\
\text{UO}_2 + 4\text{C} &\rightarrow \text{UC}_2 + 2\text{CO} \\
3\text{UC}_2 + \text{UO}_2 &\rightarrow 4\text{UC} + 2\text{CO}
\end{align*}
\]

However, once the surface layer is removed, carbon can no longer be detected in the UO\(_2\) pellet when observed in SEM. Due to the trace amount of carbon and limited resolution in SEM, no evidence of carbon was found in EDS either. WDS analysis was not successful due to the overlapping peak positions between uranium and carbon. Therefore, it is assumed that the reaction products between graphite and UO\(_2\) only appeared on the surface of the pellet. Thus, SPS offers the benefit of reducing the stoichiometry of UO\(_2\) powder into 2.00 and eliminating the additional post-sintering steps by employing suitable processing conditions.
Conclusions

High density UO$_2$ pellets with grain sizes between 0.9 - 9μm were fabricated by spark plasma sintering. It was found that high-density pellets (up to 97% of the TD) can be fabricated either at moderate sintering temperature with short hold time (1050°C, 0.5min) or at low sintering temperature with relatively long hold time (750°C, 20min). An increase in sintering temperature has a significant influence on grain growth than an increase in hold time. The O/U ratio of the resulting pellets was found to decrease under SPS, which is possibly due to a chemical reaction between graphite punch and the UO$_2$ powder.

The mechanisms of densification and grain growth are similar to those found in traditional oxidative sintering process. Two main phases of densification and grain growth are observed. When the density of pellet is low (<95% of the TD), the grain growth is marginal and the porosity is mainly intergranular. When the density is high (>95% of the TD), grain growth occurs rapidly and intragranular porosity evolves. The ability to control the intragranular porosity in SPS can benefit in-reactor performance by trapping the fission gases and limit pellet cracking.
Table 4-1. SPS processing parameters and the resulting properties of UO$_2$ pellets

<table>
<thead>
<tr>
<th>Max.Temp. (°C)</th>
<th>Heating rate (°C/min)</th>
<th>Hold time (min)</th>
<th>Density (% of TD)</th>
<th>Grain size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>750</td>
<td>200</td>
<td>0.5</td>
<td>77.6+/-2.0</td>
<td>0.2+/-0.1</td>
</tr>
<tr>
<td>750</td>
<td>200</td>
<td>5</td>
<td>84.5+/-0.3</td>
<td>0.4+/-0.1</td>
</tr>
<tr>
<td>750</td>
<td>200</td>
<td>10</td>
<td>90.0+/-0.3</td>
<td>0.6+/-0.1</td>
</tr>
<tr>
<td>750</td>
<td>200</td>
<td>20</td>
<td>95.1+/-0.4</td>
<td>0.9+/-0.1</td>
</tr>
<tr>
<td>850</td>
<td>200</td>
<td>0.5</td>
<td>86.1+/-0.9</td>
<td>n/a</td>
</tr>
<tr>
<td>850</td>
<td>200</td>
<td>1</td>
<td>94.7+/-0.6</td>
<td>n/a</td>
</tr>
<tr>
<td>850</td>
<td>200</td>
<td>5</td>
<td>96.4+/-0.1</td>
<td>n/a</td>
</tr>
<tr>
<td>850</td>
<td>200</td>
<td>20</td>
<td>95.7+/-1.4</td>
<td>2+/-0.5</td>
</tr>
<tr>
<td>1050</td>
<td>200</td>
<td>0.5</td>
<td>96.3+/-1.1</td>
<td>3.0+/-0.7</td>
</tr>
<tr>
<td>1050</td>
<td>200</td>
<td>5</td>
<td>96.3+/-0.9</td>
<td>3.4+/-0.4</td>
</tr>
<tr>
<td>1050</td>
<td>200</td>
<td>20</td>
<td>95.9+/-0.5</td>
<td>4.2+/-0.5</td>
</tr>
<tr>
<td>1150</td>
<td>200</td>
<td>0.5</td>
<td>95.4+/-0.9</td>
<td>3.9+/-0.8</td>
</tr>
<tr>
<td>1150</td>
<td>200</td>
<td>5</td>
<td>95.6+/-0.5</td>
<td>4.7+/-0.9</td>
</tr>
<tr>
<td>1350</td>
<td>200</td>
<td>0.5</td>
<td>96.5+/-0.1</td>
<td>5.0+/-0.7</td>
</tr>
<tr>
<td>1350</td>
<td>200</td>
<td>5</td>
<td>96.0+/-0.1</td>
<td>5.6+/-1.4</td>
</tr>
<tr>
<td>1350</td>
<td>200</td>
<td>20</td>
<td>96.6+/-0.5</td>
<td>6.9+/-1.8</td>
</tr>
<tr>
<td>1450</td>
<td>200</td>
<td>0.5</td>
<td>95.8+/-1.0</td>
<td>6.3+/-1.4</td>
</tr>
<tr>
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<td>20</td>
<td>96.9+/-0.2</td>
<td>2.5+/-0.8</td>
</tr>
<tr>
<td>1350</td>
<td>50</td>
<td>20</td>
<td>96.9+/-1.0</td>
<td>8.9+/-1.4</td>
</tr>
</tbody>
</table>
Table 4-2. XRD peak positions of the phases on the surface of the as-sintered (1450°C, 0.5min) pellet

<table>
<thead>
<tr>
<th>Phase</th>
<th>hkl</th>
<th>Peak position in this study (°)</th>
<th>Reference peak position (°)</th>
<th>PDF code</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>002</td>
<td>26.47</td>
<td>26.43</td>
<td>00-001-0646</td>
</tr>
<tr>
<td></td>
<td>111</td>
<td>31.16</td>
<td>31.14</td>
<td></td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>36.15</td>
<td>36.24</td>
<td></td>
</tr>
<tr>
<td></td>
<td>220</td>
<td>52.13</td>
<td>52.17</td>
<td></td>
</tr>
<tr>
<td></td>
<td>311</td>
<td>62.06</td>
<td>61.98</td>
<td>00-009-0214</td>
</tr>
<tr>
<td></td>
<td>222</td>
<td>65.02</td>
<td>65.03</td>
<td></td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>76.71</td>
<td>76.81</td>
<td></td>
</tr>
<tr>
<td>UC</td>
<td>111</td>
<td>28.22</td>
<td>28.23</td>
<td></td>
</tr>
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<td></td>
<td>200</td>
<td>32.71</td>
<td>32.71</td>
<td></td>
</tr>
<tr>
<td></td>
<td>220</td>
<td>46.93</td>
<td>46.94</td>
<td></td>
</tr>
<tr>
<td>UO₂</td>
<td>311</td>
<td>55.68</td>
<td>55.68</td>
<td>03-065-0285</td>
</tr>
<tr>
<td></td>
<td>222</td>
<td>58.38</td>
<td>58.38</td>
<td></td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>68.56</td>
<td>68.55</td>
<td></td>
</tr>
<tr>
<td></td>
<td>331</td>
<td>75.73</td>
<td>75.72</td>
<td></td>
</tr>
<tr>
<td></td>
<td>420</td>
<td>78.06</td>
<td>78.05</td>
<td></td>
</tr>
</tbody>
</table>
Figure 4-1. Typical UO$_2$ images. A) Typical UO$_2$ starting powder particles. B) UO$_2$ bulk pellet sintered at 1050°C for 0.5min. C) Fracture surface of the sintered pellet revealing its typical microstructure and grain size.
Figure 4-2. XRD patterns of the starting powder (UO$_{2.16}$) and the reduced powder (UO$_{2.00}$) indicate the fcc structure of UO$_2$ and its peak shift to higher 2θ region due to the excessive oxygen.
Figure 4-3. The influence of hold time on the density of the sintered pellets at different maximum sintering temperatures. Note that above 1050°C, even 30 second hold time can provide a pellet with 95% of the TD.
Figure 4-4. The influence of hold time and maximum sintering temperature on the average grain size of the sintered pellets. Note that the influence of maximum sintering temperature at a given hold time on the grain size is more dramatic than the influence of hold time at a given temperature.
Figure 4-5. The evolution of average grain size with theoretical density of the samples sintered using a heating rate of 200°C/min. Until almost 95% of the TD is reached, there is only marginal change in grain size and then it increases rapidly.
Figure 4-6. Images of selected pellets revealing the grain size-density relationship. Images Aa-Ac reveal densification with limited grain growth and high porosity, whereas images Ba-Bc reveal grain growth at high densities.
Figure 4-7. SEM image revealing the formation of the intragranular pores during densification. The density of the pellet is 77% of the TD. The arrows indicated the steps that lead to intragranular pores during the sintering process.
Figure 4-8. The influence of hold time and maximum sintering temperature on the resulting O/U ratio of the sintered pellets. The upper dash line indicates the initial O/U ratio of 2.16. Note that at higher maximum sintering temperatures, the O/U ratio can be decreased to 2.00 within 30 seconds.
Figure 4-9. Comparison of XRD patterns of the surface of the as-sintered (1450°C, 0.5min) pellet before/after surface grinding indicates the formation of UC. The lines show the reference peak position and intensity for different planes of UC.
CHAPTER 5
HARDNESS, YOUNGS MODULUS AND THERMAL CONDUCTIVITY OF URANIUM DIOXIDE PREPARED BY SPARK PLASMA SINTERING

Introduction

The properties of sintered uranium dioxide (UO$_2$) nuclear fuel pellets play an important role in the reactor. The mechanical properties determine the stress induced crack formation during service and the thermal properties influences the temperature gradient inside the fuel pellet. Sound mechanical and thermal properties of fuels provide the reactor with a higher safety level and longer life of the nuclear fuel.

In literature, several publications have been reported regarding to mechanical and thermal response of UO$_2$ by using different techniques [61, 82-85]. However, little literature has been reported by applying mechanical and thermal tests on UO$_2$ sintered by spark plasma sintering (SPS). The objective of this study is to evaluate the mechanical and thermal properties of UO$_2$ processed by SPS and compare the results to the literature values of UO$_2$ processed using conventional sintering methods. In this study, UO$_2$ was sintered in SPS under different processing conditions to achieve different microstructures; Vickers indentation was made to measure the hardness regarding to different densities and grain sizes; Ultrasonic measurement was made to measure the elastic properties of UO$_2$ and detect the possible internal cracks; Flash method was used to measure the thermal diffusivity of UO$_2$ and investigate the influence of temperature, densities, and grain size on the thermal properties of UO$_2$.

Experimental Procedure

Sample Preparation

The uranium dioxide powder was supplied by Areva Fuel System, Charlotte, NC. The powder was reported to have a bulk density of 2.3g/cm$^3$, tap density of 2.65g/cm$^3$, mean particle diameter of 2.4µm, and a BET surface area of 3.11m$^2$/g. The grain size was determined using
high resolution SEM. The density is measured by Archimedes method. The details of density and grain size measurements can be referred to the experimental part in Chapter 3 or Chapter 4. The processing conditions and resulting density and grain size of UO$_2$ can be referred to Table 3-1 and Table 4-1.

**Mechanical Property Measurement**

Indentation hardness measures the resistance of a sample to deformation due to a constant compression load without destructing the sample. Ultrasonic measurement is a non-destructive method by applying ultrasonic waves to the sample body and measuring Young’s modulus, a measure of the stiffness of a material. It is also easy to detect the internal defects of the material by ultrasonic measurement, e.g. porosity and internal cracks.

For the micro-indentation hardness measurements, the pellet surfaces were ground and polished down to 0.05µm colloidal silica using standard metallographic methods. Vickers hardness measurements were conducted at 200g, 500g, and 1Kg applied load for 11 seconds. At least five measurements were performed at each load and at different locations on each pellet. Ultrasonic measurements (both longitudinal and shear wave velocity) were conducted on each pellet to determine Young’s modules.

**Thermal Conductivity Measurement**

Thermal conductivity is a key factor that influences UO$_2$ fuel performance in a reactor. With higher thermal conductivity, the thermal gradient can be reduced inside the fuel pellet to prevent pellet cracking due to high thermal stresses. Thermal conductivity measurement was calculated using the relationship $k = C_p \rho \alpha$, where $k$ is thermal conductivity (W/m-K), $C_p$ is constant-pressure specific heat (J/kg·K), $\rho$ is density (g/cm$^3$), and $\alpha$ is thermal diffusivity (cm$^2$/s). The thermal diffusivity was measured at three temperatures 100°C, 500°C and 900°C under N$_2$
atmosphere using laser flash method (Anter Flashline™ 3000), see Figure 5-1. Before the measurement, the sintered pellets were sectioned into disks of 3mm thickness. Both surfaces of the disks were coated with a colloidal graphite spray to ensure constant heat absorption during the measurement. The laser flash method utilizes a xenon pulse to generate heat on the front surface of the disc specimen and the temperature rise on the rear surface is recorded [86]. The thermal diffusivity (\( \alpha \)) is calculated by measuring the specimen thickness (\( L \)) and the time (\( t_{0.5} \)) for the temperature of the rear face of the disk to rise to half of its maximum value (\( \alpha = \frac{1.38L^2}{\pi t_{0.5}} \)).

Due to the difficulty in directly measuring the specific heat, the theoretical specific heat for UO\(_2\) is used for the calculation, which is 258 (J/kg·K), 305 (J/kg·K) and 314 (J/kg·K) at 100°C, 500°C and 900°C, respectively [61].

**Result and Discussion**

**Mechanical Property**

Sound mechanical properties of UO\(_2\) are essential for successful application of nuclear fuels. As discussed in Chapter 4, the microstructure of UO\(_2\) in SPS can be divided into densification region and grain growth region. When the density is below 95 %TD, densification dominates and there is only limited grain growth while when the density is higher than 95% TD, grain growth is dominant and densification is limited. Thus, the results of the Vickers hardness measurements are investigated by separating the effect of porosity (or density) and grain size. Figure 5-2 reveals the influence of porosity on the hardness below 95% TD when the grain size of all the sample is around 0.4-0.9μm. It is seen that with increasing density, the hardness is increased significantly. The increase of hardness is mainly due to the decrease of the porosity in the bulk and the sample is more resistant to the deformation when the density increased. Vickers hardness versus the inverse of average grain size is plotted in Figure 5-3. All of the pellets
measured in this plot have the comparable density of 96 %TD. It is seen that the hardness values increased linearly with decrease in the grain size and this correlation is in good agreement with the Hall–Petch relation [62]. The average hardness value was around 6.4±0.4GPa which is in agreement with reference value 6.4±0.5GPa at comparative load level [82, 87].

The Young’s modulus $E$ and Poisson’s ratio $\nu$ were determined using ultrasonic measurement. The correlation between the longitudinal velocity $V_L$, shear velocity $V_S$ and density $\rho$ are given by [83]:

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

$$E = \frac{V_L^2 \rho (1+\nu)(1-2\nu)}{1-\nu} \quad (2)$$

With the known density of the pellets, the Young’s modulus was calculated using equations (1) and (2) and the value are plotted in Figure 5-4 which revealed a linear relationship between the Young’s modulus and the relative density of the pellets. The Young’s modulus is affected by the porosity (or density) of the pellets [83]. In Figure 5-4, the results of Gatt et al., [85] and Padel and Novion [88] are also plotted. These results show good agreement with our work. The average Young’s modulus for pellets of density above 95% in our work is around 204±18GPa, which is in good agreement with the reference data [83, 85, 88]. This result reveals that using SPS, intact high-density pellet can be sintered without detectable crack formation.

**Thermal Property**

The results of the thermal diffusivity measurements of the sintered pellets are plotted in Figure 5-5 at three different temperatures. For all the pellets, the thermal diffusivity decreased with the increase in operating temperature. However, a significant difference is seen among the pellets with different processing conditions at each operating temperature. The pellets sintered at
750°C for hold times of 0.5min and 5min have the lowest diffusivity values of only 0.02cm²/s at
100°C while the one sintered at 1350°C for 20min hold time showed a diffusivity of 0.033cm²/s, an increase of 65%. With the increase in operating temperature, this difference tended to
decrease. At 900°C, the lowest value was 0.008 cm²/s and the highest value was 0.011 cm²/s, an
increase of only 38%. For comparison, the diffusivity values of conventionally sintered UO₂ are
referenced from a review paper by Fink [61]. By comparing the literature value with the ones in
this study, it is noted that the pellets with the comparable densities showed similar diffusivity
values, indicating the validity of the current measurements. Using these values presented in
Figure 5-5, we calculated thermal conductivity and plotted these values in Figure 5-6 as a
function of temperature. The thermal conductivity versus temperature revealed a trend similar to
that of diffusivity in Figure 5-5. In general, a higher sintering temperature and a longer hold time
appear to be more favorable to yield a higher thermal diffusivity and conductivity in a pellet.
This result may be due to the improved microstructure development (i.e., higher density and
larger grain size). Thus, the microstructure plays an important role in the resulting thermal
properties.

The low thermal conductivity of UO₂ has been a major concern while operating as a
nuclear fuel in a reactor environment. From this perspective, it is essential to understand the
dependence of thermal conductivity on properties such as density, grain size and other
microstructural features such as porosity distributions as well as the operating temperature. From
Figure 5-5 and Figure 5-6, it is clear that operating temperature influences the thermal
conductivity of UO₂. The heat transport in UO₂ at the low temperature (<1700°C) generally
occurs through the motion of phonons in the crystal lattice [61]. With the increase in
temperature, the mean free path of phonon is decreased because of the stronger phonon-phonon
scattering. The higher level of scattering leads to a higher resistance to heat transfer and thus the thermal conductivity is reduced at the higher temperatures.

The microstructure also has an important role in influencing the thermal conductivity. Recall from Figure 4-5 that there are two distinct mechanisms that are operative during the sintering process: densification dominated regime below 95% TD and grain growth dominated regime above 95% TD. The pellets with the same grain size in the densification phase (<95% TD) are chosen to study the influence of density on thermal conductivity. Figure 5-7 shows the thermal conductivity of pellets as a function of density. The conductivity value increased with increase in density at all three operating temperatures. Due to the existence of a high level of porosity at these densities in the microstructure, the phonon scattering is much more severe at the gas-solid interfaces. The poor thermal conductivity of the gas inside the pores further impedes the heat transfer in the solid. This relationship between density and thermal conductivity is also in agreement with the reported literature [61, 66] for conventionally sintered UO2 pellets.

The relationship between grain size and thermal conductivity for all the pellets is plotted in Figure 5-8. In order to get a more comprehensive understanding of the influence of the grain size, additional SPS runs with slower heating rate (50°C/min) have also been conducted and the processing conditions for these pellets are also listed in Table 4-1. As seen in Figure 5-8, by varying the grain size from 2 to 9μm, no significant difference in thermal conductivity was noted at all three temperatures. Although the grain size in our study is as small as 2μm, compared with 10-15μm in conventional sintering methods [64], the thermal conductivity of pellets prepared by SPS appears to be either in the upper range or slightly above the reported values in literature as indicated. Also at larger grain size, a higher value of thermal conductivity is seen, especially at lower temperatures (~100°C). This dependence of thermal conductivity on grain size can be
explained from the interfacial resistance, which is measured in terms of Kapitza length [89]. It is well noted that when the grain size is smaller than or comparable to the Kapitza length, which is \( \sim 100\text{nm} \) at \( 100^\circ\text{C} \) for \( \text{UO}_2 \) [89], the grain itself offers the same thermal resistance as the interface. Thus, the thermal conductivity is mainly dominated by grain size in this regime. Further decrease of the grain size may strongly decrease the thermal conductivity. On the other hand, when the grain size is larger than the Kapitza length, only the interfacial resistance at the grain boundaries affects the thermal conductivity. With larger grain size, there is less volume of grain boundaries that can act as the barrier to heat transport. Thus, higher thermal conductivity is expected for larger grain size. In our case, the typical grain size is more than 10 times larger than the Kapitza length, which indicates that the increase in thermal conductivity is mainly due to the decreased volume of grain boundaries (or larger grain size). According to the simulation work by Watanabe et al [89], there is only a marginal increase in thermal conductivity of \( \text{UO}_2 \) at 300K when the grain size is larger than 1\( \mu \)m. This conclusion is in agreement with the result presented in our study. In addition, the average values of thermal conductivity for these pellets are 8.2W/mK, 4.7W/mK and 3.4W/mK at three operating temperatures as indicated by the dashed lines in Fig.13, which is also comparable with the values reported in the literature for conventionally sintered \( \text{UO}_2 \) pellets [61] as indicated by the shaded areas.

**Conclusion**

The resulting \( \text{UO}_2 \) pellets had an average Vickers hardness of \( 6.4\pm0.4\text{GPa} \) and Young’s modulus of \( 204\pm18\text{GPa} \), which are in excellent agreement with values reported in literature for \( \text{UO}_2 \) processed by other methods. The Vickers hardness is increased with density for pellet with density below 95\% TD and Hall-Petch relationship is revealed for the pellet with density (~96\% TD). No internal crack formation is detected for all \( \text{UO}_2 \) pellets. The thermal conductivity of \( \text{UO}_2 \) pellets increased with density but the grain size in the investigated range had no significant
influence. The measured thermal conductivity values up to 900°C were consistent with the reported literature for conventionally sintered UO\textsubscript{2} pellets. This research reveals that the mechanical and thermal properties of UO\textsubscript{2} are comparable with the literature and SPS is a feasible tool to process UO\textsubscript{2} fuel pellets with reliable properties.
Figure 5-1. Image of laser flash machine (Anter Flashline™ 3000) located in New Engineering Building (NEB)
Figure 5-2. Influence of density on Vickers hardness of UO$_2$ pellet in SPS. The grain sizes of all measured pellets are between 0.4-0.9 µm.
Figure 5-3. Plot of Vickers hardness versus inverse of the grain size revealing the conformity with the Hall-Petch relationship. Note that the data presents the mean grain size and standard deviation measured at all loads of 0.2kg, 0.5kg and 1kg.
Figure 5-4. Comparison of Young’s modulus of SPS sintered pellets with those available in literature
Figure 5-5. The measured thermal diffusivity of the pellets at 100°C, 500°C and 900°C. The processing conditions and densities of the pellets are listed in the legend.
Figure 5-6. The thermal conductivity of the pellets at the temperatures of 100°C, 500°C and 900°C. The processing conditions and the resulting densities are listed in the legend.
Figure 5-7. The thermal conductivity of the low-density (<90% of the TD) pellets at the temperatures of 100°C, 500°C and 900°C. With increasing density, there is a significant increase in thermal conductivity, especially at the low temperature.

*The grain size is 0.2-0.6μm.
Figure 5-8. The thermal conductivity of the high density (95%-97% of the TD) pellets versus the average grain size at the temperatures of 100°C, 500°C and 900°C. The dashed lines indicate the average value of thermal conductivity in our work while the shaded areas indicate the literature values by Fink [61].
CHAPTER 6
GRAIN GROWTH OF DOPED URANIUM DIOXIDE PREPARED BY SPARK PLASMA SINTERING

Introduction

Considerable attention has been drawn on the development of large-grain-size UO₂ fuel pellets in nuclear industry. UO₂ with large grain sizes (e.g. 50 µm) is expected to exhibit better in-pile performance including high fission gas retention capacity, high creep resistance, delay of high burn-up structure formation, and increased thermal conductivity [90]. These benefits may reduce the fuel cycle costs and increase the accident tolerance during operation. Currently, doping small amount of additives (usually less than ~1 wt%) has been proven an effective way to increase the grain sizes [91]. Among which, Cr₂O₃ is been most intensively investigated. It is revealed that by using conventional sintering methods, the grain size of Cr₂O₃ doped UO₂ can be successfully increased by 700% from 10µm to 73µm [14]. Although the mechanism is not thoroughly understood, some experimental [14, 92] and simulation[93] works indicated that Chromium prefers staying in the grain boundary of UO₂ and forming (Cr, U, O) solid solution with low melting temperature. The high mobility of the liquid phase facilitates the mass transport between the two grains and achieves the large grain size. However, in order to achieve the large grain size, at least 6-hour hold time is required to fulfill the grain growth kinetics [14]. Recently, spark plasma sintering (SPS) has been applied in sintering UO₂ fuel pellets [68, 69]. The merits of SPS include rapid processing cycle and reduced energy consumption. It is revealed that only 10 minutes total processing time is required to sinter high-density UO₂ pellets via SPS [69]. However, the grain size of UO₂ made in SPS is usually from 1~10 µm [94]. In literature, SPS is generally used for processing materials with fine grain size [95]. Very limited publications are considering of developing a microstructure with large grain size. In order to develop large grain
size UO₂ pellets using SPS, one strategy is to follow the traditional processing method by doping Cr₂O₃ into UO₂ and process the mixed powder by SPS.

Another strategy is to change the electrical properties of UO₂ by adding Zirconium diboride (ZrB₂) into the starting powder. It is known that during SPS, electric current has great effect in mass transport by electromigration and Joule heating [23, 48]. ZrB₂ is a promising ultra-high temperature ceramic (UHTC) with its high melting point of 3200°C [96], excellent corrosion resistance[97] as well as high electrical (9.2×10⁻⁶Ω·cm)[98] and thermal conductivities (60–140 W·m⁻¹K⁻¹)[98]. By adding ZrB₂ into UO₂, a better electrical conductivity and power dissipation in UO₂ powder is expected in SPS, which may possibly enhance the mass transport in UO₂ during grain growth.

In addition, ZrB₂ has also been applied in nuclear industry for years. ZrB₂ has been used as an integral fuel burnable absorber (IFBA) by applying it on the outer surface of UO₂ fuel as a thin coating layer [99]. During the operation of a nuclear reactor, boron compensates the reactivity effect of fuel burn up. A flattening of reactivity-to-time curve can be then achieved by balancing the reactivity loss due to the burn up of fuel and the reactivity gain due to the burn up of the fuel poison, boron[100]. Thus, it is reasonable to study the effect of ZrB₂ on UO₂ grain size.

The present work describes the result of a preliminary study on enhancing the grain growth of UO₂ in SPS in a short period of time by adding Cr₂O₃ and ZrB₂ into UO₂ matrix. In this study, Cr₂O₃ was doped in UO₂ (Cr₂O₃-UO₂) with different concentrations and ZrB₂ was doped in UO₂ (ZrB₂-UO₂) with one concentration in SPS. The grain size distributions were examined for all the doped pellets. To better understand the grain growth development of UO₂ in
SPS, pure UO₂ pellet was also sintered at the same sintering temperature with different hold times for comparison.

**Experimental Procedure**

The grain size of the powder particle was determined using high resolution SEM as shown in Figure 6-1. The UO₂ and Cr₂O₃ powders had the grain size around 300-600nm and the grain size of ZrB₂ powder was about 3-5μm.

The UO₂ were blended with 1000 ppm (1000μg Cr₂O₃ / 1g UO₂), 1500 ppm and 2000 ppm Cr₂O₃, 1500 ppm ZrB₂ with the aid of 2,3-Dihydroperfluoropentane in a SPEX 8000 shaker for 1 hour. After mixing, the residual contamination was eliminated by evaporation in a fume hood. This process resulted in homogeneous dispersion of Cr₂O₃ or ZrB₂ powder in UO₂ matrix as will be discussed in the following section.

Sintering was performed using a Dr. Sinter® SPS-1030 system. The mixed powder was loaded in a graphite die so that a UO₂ pellet of about 6 mm in thickness could be achieved after SPS. The heating rate was fixed at 200°C/min and the uniaxial pressure of 40 MPa was applied at the sintering temperature for all the pellets. The maximum sintering temperatures of 1450°C and 1600°C and the hold times of 0.5min and 40min were set for different pellets, the detailed sintering procedures can be referred to our earlier publications[68, 69]. It is known that sintering temperature and hold time control the activation and development of grain growth during sintering. Thus, to achieve large grain size, the highest possible temperature 1600°C and longest practical hold time of 20 min were used. To prevent the chemical reaction between graphite punch and UO₂ powder above 1450°C[94], 1600°C was used only for 0.5 min hold time and at 1450°C, 20 min hold time was used so as to obtain the intact pellets. For pure UO₂, hold times of 0.5 min, 10 min, and 20 min were used to reveal the development of grain growth at 1600°C. All
pure UO₂, Cr₂O₃-UO₂ and ZrB₂-UO₂ pellets were produced into the length of 6 mm and diameter of 12.7 mm. In addition, a full size ZrB₂-UO₂ pellet of 10 mm thickness was also made to reveal the influence of thickness on grain size distribution in SPS. The details of processing conditions in SPS was revealed in Table 6-1.

After sintering, residual graphite foil was polished off the pellets and Archimedes method was used to determine the density of the pellets. The results are listed in Table 6-1. The pellets were then longitudinally cross-sectioned and polished, see Figure 6-2. Thermal etching was conducted using CO₂ gas at 1290°C for 10-30 minutes to reveal the grain size of the polished pellets while minimizing the grain growth. Optical microscope (OM) and scanning electron microscope (SEM) were used to observe the grain size. The grain size distribution was measured by observing the polished surface of the pellet in OM over a sequence of steps. Linear intercept method was applied to determine the grain size.

Homogeneity of the dopant in the UO₂ matrix was determined by electron probe microanalysis (EPMA) using JEOL Superprobe 733. The elemental composition of the pellets was measured by wavelength dispersive X-ray analysis (WDS). Peaks for CrKα and UMα were measured using Lithium Fluoride (LIF) crystal and Pentaerythritol (PET) crystal respectively on each pellet. The chromium and uranium contents were determined by scanning the polished cross section of the pellet, see Figure 6-2. Two scan modes were used during analysis: the coarse scan mode with a 20 μm diameter electron beam and a 100 μm step size and the fine scan mode with 1μm diameter electron beam and a 1μm step size. The examined area was scanned from the surface to the interior of the pellet as indicated in Figure 6-2. ρφz procedure was applied to convert the measured intensities to concentrations.
Result and Discussion

Density

The densities of all sintered pellets were revealed in Table 6-1. It was seen that by sintering either at 1450°C for 20 min or 1600°C for 0.5 min, high density (>95% TD) was achieved for all UO₂, Cr₂O₃-UO₂ and ZrB₂-UO₂ pellets. For pure UO₂ pellets, increasing hold time significantly increased the final density. When hold time was equal or more than 10 min, ultra-high density of 99% was reached. However, due to the longer hold time at 1600°C, these pellets came out crumbled. Therefore, only 0.5 min hold time was applied at 1600°C to process the rest of the pellets. Meanwhile, for the doped pellet, the effect of doping concentration on the resulting density was revealed in Figure 6-3. It was seen that for all concentrations, the pellets sintered at 1450°C for 20 min had densities slightly higher than 1600°C for 0.5 min. However in both processing conditions, the density was decreased by increasing the doping amount. This result might due to the excessive addition of Cr₂O₃ segregated on the grain boundaries [14] and prevented the densification of the UO₂. The undissolved and segregated Cr₂O₃ was also revealed in EMPA which would be discussed in the following section. For ZrB₂-UO₂ pellet, a slightly lower density was revealed on the 10 mm pellet than 6 mm pellet.

Dopant Dispersion

To realize the homogeneity of dopant mixing procedure, EMPA was used on the polished 2000 ppm Cr₂O₃-UO₂ pellet. The concentration of uranium and chromium were plotted as a function of the depth from surface to the interior of the pellet. The depth was normalized as the ratio of the total pellet length. It was seen in Figure 6-4 that the measured average concentration of chromium (0.16 wt%) was close to the calculated theoretical concentration (0.14 wt%). In most depths, chromium concentrations were relatively consistent. No significant chromium concentration gradient was revealed from the pellet surface to the center. However, chromium
peaks of high concentration were shown in the interior of the pellet, especially in the depth between 0.35 and 0.42 of the total length. This high-intensity peak stands for the Cr$_2$O$_3$ particles that didn’t dissolved into the UO$_2$ matrix. As seen in Figure 6-5, a fine WDS scan with a spot size of 1 μm was done across this region to better reveal the segregation of chromium. Note that Figure 6-5 (A) is a secondary electron image showing the pores and segregated Cr$_2$O$_3$ particle as black spots in the image. Figure 6-5 (B) is an X-ray mapping image, in which chromium was distinguished from the pores on the surface as the white spot in the figure. By applying WDS line scan (red dash line) on the white spot in Figure 6-5 (B), a high concentration (14 wt%) of Cr was revealed, see Figure 6-5 (C). This indicated a large volume of undissolved chromium with the size about 2-3 μm.

**Grain Size Distribution**

The grain size distribution of pure UO$_2$ under different hold times was revealed in Figure 6-6. Against the conventional grain growth, the large grain region of UO$_2$ at 1600°C was expanded from the surface to the interior of the pellet. There existed an exaggerated grain growth region originated from the surface of the pellet. As seen in Figure 6-6 (A), when the hold time was 0.5 min, large grains (around 40μm) only existed at 0.01 (1%) of the thickness. Below this region, the grain size was evenly distributed throughout the depth and the average grain size was below 10 μm. When the hold time was extended to 10 min, the exaggerated grain growth region with grain size larger than 60 μm expanded to the depth 25% of the thickness. Below this region, the grain size sharply decreased to around 25 μm at the depth 35% of the thickness. This transformation of the grain size was also revealed in the OM image in Figure 6-6 (B). It was seen that a region containing the exaggerated large grains of 60-80 μm were on the top half of the image while on the bottom half, the grain size was only less than 20 μm. However, in spite of the
large grain size, a wide-gap crack propagated along several grain boundaries was also revealed in
the exaggerated grain growth region. This crack might be a cause of the pellet crumbling.

Between these two regions, an interface region was marked by two white dash lines in the image.
In this region, the intermediate grain size of 30-40 μm was shown within the width of only about
80 μm, which implied a rapid grain size transformation during SPS. With the increase of the hold
time, the exaggerated grain growth region continually expanded to the interior area. When the
hold time reached 20 min, the exaggerated grain growth region expanded to the entire half of the
pellet (45% of the thickness) with the grain size of around 45-60 μm and there was no normal
grain growth region throughout the pellet cross section.

The grain size distribution of Cr₂O₃-UO₂ was revealed in Figure 6-7. It was seen that for
both processing conditions and all concentrations, largest grain size appeared on the surface of
all pellets. Below the surface, different concentrations exhibited different influences on the grain
size distribution. For 2000 ppm Cr₂O₃-UO₂, the distribution was comparable with pure UO₂. In
both processing conditions, the grain size was sharply decreased to less than 10μm on the depth
10% of the thickness. Below that, the grain size maintained the same and averaged about 10 μm
in the rest of the interior areas. However, 1000 and 1500 ppm Cr₂O₃ increased the grain size of
UO₂. In the condition of 1450°C and 20 min, the grain size of 1000 ppm pellet was larger than
pure UO₂ until it decreased to around 10 μm on the depth 20% of the thickness, see Figure 6-7
(A). Similar distribution was also in 1500 ppm pellet. The grain size was larger than the pure
UO₂ in all the depths until it reaching 43% of the thickness.

In another word, 1000 ppm and 1500 ppm Cr₂O₃ helped increasing the grain size of UO₂
in a way that the grain size was larger on the surface and decreased with a lower rate than pure
UO₂ from the surface to the interior of the pellet. The grain size distribution of pellets made in
1600°C and 0.5 min was also consistent with these results. It was seen in Figure 6-7 (B) that 2000 ppm pellet exhibited the same grain size distribution with pure UO$_2$. The grain size in 1000 ppm pellet was decreased with a slower rate than pure UO$_2$ and in 1500 ppm pellet, an even much slower rate was observed.

Additionally, processing conditions also influenced the grain size distributions. For example, at 1600°C, the grain size in the interior area of the pellet was larger than 1450°C. At 1450°C, the grain size of 1000 ppm pellet reached 10 μm at the depth 20% of the thickness while at 1600°C it was at the depth 40% of the thickness. In the case of 1500 ppm, the smallest grain size at 40% of the thickness was 17 μm at 1600°C, which is much larger than the one at 1450°C. Difference of hold times also accounted for the difference of the grain size on the surface of the pellet. By holding 20 min, large variation of the surface grain size was observed. 1000 and 1500 ppm Cr increased the grain size to about 50 μm while in pure and 2000 ppm pellets, the surface grain size was only 30 μm. By contrast, using 0.5 min hold time with an even higher temperature of 1600°C showed almost no difference of surface grain size. Instead, consistent grain size of around 35-40 μm was observed for all concentrations.

The grain size distribution of 1500 ppm ZrB$_2$-UO$_2$ was revealed from one surface to the other surface (bottom) of the pellet as seen in Figure 6-8. Unlike pure UO$_2$ and Cr$_2$O$_3$-UO$_2$ pellets, for ZrB$_2$-UO$_2$ pellets, the surface grain size was not the largest throughout the thickness. Instead, lowest grain size of around 25-28 μm was revealed on both surface and bottom of the pellet. The highest grain size of around 31-36 μm appeared on the depth 20% or 79% of the thickness from both ends, forming a double-hump distribution through the entire thickness. The average grain size of around 30 μm was indicated by a dash line in the plot.
In nuclear reactor, a real fuel pellet has the length of around 10 mm. Thus, a full size ZrB\(_2\)-UO\(_2\) pellet of 10 mm thickness was made by SPS to compare its grain size distribution with the 6 mm-thick pellet. Figure 6-9 (A) showed its distribution in the radial direction from one edge of the pellet to the other. The highest grain size of around 27 \(\mu m\) appeared at the center of the pellet and was gradually deceased when the position was derivate from the center. The smallest grain size of around 18 \(\mu m\) was reached on the one edge of the pellet. The average grain size was around 23 \(\mu m\) and was indicated by a dash line in the plot. This result indicated a thermal gradient from the pellet center to the edges causing the distribution of the grain size, where the die worked as a heat sink and temperature on the edge of the pellet was therefore lower than on the center. In the longitudinal direction, see Figure 6-9 (B), the grain size was very similar with the 6 mm pellet in Figure 6-8. A double-hump grain size distribution was revealed with the smallest grains of on the surface, center (32\% of the thickness) and the bottom and the largest gains on the depths of around 17\% or 83\% of the thickness. The highest grain size was about 47\(\mu m\) while the lowest was about 25 \(\mu m\). The average grain size was about 33 \(\mu m\).

Comparing with 6 mm and 10 mm ZrB\(_2\) doped pellets with other UO\(_2\) pellets, it is easy to conclude that 1500 ppm ZrB\(_2\) increased the average grain size of UO\(_2\) to the scale of 30 \(\mu m\) in both cases. Distinguished from pure UO\(_2\) and Cr\(_2\)O\(_3\)-UO\(_2\) pellets, 6 mm and 10 mm ZrB\(_2\)-UO\(_2\) pellets had the same longitudinal double-hump grain size distribution with largest grain size on the certain depth underneath the surface and the smallest grains on the surfaces. However, larger difference between the largest and smallest grain size was revealed in 10 mm pellet, which may be possibly due to the larger thermal gradient within the 10 mm pellet. The detailed microstructure of 10 mm ZrB\(_2\)-UO\(_2\) was revealed in Figure 6-10.
This was known in SPS, if the powder in the die was electrically insolated, the electrical current would bypass the powder and only flows through the die, which was indicated as the blue arrows Figure 6-11 (A). The heat used to sinter the pellet was generated through Joule heating and transferred to the powder from the graphite punch [33, 94]. In the case of pure UO$_2$ sintered at 1600°C for 0.5 min, it was revealed that there was a thin layer of grains possessed the large grain size of around 36 μm on the pellet surface. Meanwhile, after a closer observation, the exaggerated grain growth was also found at the four corners of the pellet as seen in Figure 6-11 (B). It was seen that, in the corner, this affected area with the exaggerated grain growth had the grain size of around 40-60 μm. Below the corner, the grain size became unaffected and remained 5-10 μm. Thus, a model describes the affected areas was presented in Figure 6-11 (C) where the exaggerated grain growth regions were located on the four corners and both surfaces of the pellet as well. Comparing with the electrical current flow path and the location of the affected regions, it appears that the rapid grain growth was affected by the flow of electrical current close to the UO$_2$ powder, which was indicated as the red lines in Figure 6-11 (A). Most of the affected regions were in contact with the punches and the die where the current was flowing through. The following effects of the current might facilitate the grain growth: 1) Increased Joule heating due to the contact resistance between the punch, die and the powder helped increased the local temperature and thus accelerated the diffusion process in grain boundary migration in the local area. 2) Increased ion mobility as well as defect densities due to the current flow and the electrical field between the electrodes (punches), which also promoted the mass transport in these regions. UO$_2$ has very low thermal and electrical conductivities. Due to a lack of power dissipation, excessive input power enabled the localized exaggerated grain growth, forming the affected area as indicated in Figure 6-11 (C). By increasing the hold time to 10 and 20 min, the
localized power gradually dissipated into the further depth of the pellet and thus, the exaggerated grain growth region expanded into the interior until reaching the entire pellet.

The effect of Cr$_2$O$_3$ is generally considered to be the formation of solid solutions with high mobility on the UO$_2$ grain boundaries. This solid solution has a lower melting point and forms a thin film of liquid phase wetting the grain boundaries, which accelerate the mass transport between the grain boundaries [14, 92, 93]. However, no trace of liquid phase was observed and there was only limited acceleration of grain growth on certain depths of the pellet. This result might be attributed to the shorter processing time, which prevents the complete formation of (Cr, U, O) solid solution. Thus, only moderate increase of the grain size was observed in 1000 ppm and 1500 ppm Cr$_2$O$_3$-UO$_2$ pellets. No influence of 2000 ppm Cr$_2$O$_3$ was revealed in this research. This may because of the excessive doping materials segregating on the UO$_2$ grain boundary, which impaired the grain boundary migration of UO$_2$.

However, by doping ZrB$_2$ into UO$_2$ pellet, there was no exaggerated grain growth region on the surfaces. Instead, a double-hump grain size distribution was revealed across the longitudinal direction of the pellet. The smallest grains were on both surfaces and the largest were on certain depths underneath the surface of the pellet. However, on all four corners of the pellet, large grain size regions were still observed by examining its entire cross section. Figure 6-12 (A) showed the image of the fracture cross section of a ZrB$_2$-UO$_2$ sintered at 1600°C with 0.5 min hold time. It was seen that on all four corners of the pellet, the color turned from black into silver. The color change of these areas implied the affected regions where the exaggerated grain growth happened during SPS. The grain size in these affected regions was much bigger than on the rest of the regions, thus reflecting as sliver rather than black under the light. Figure 6-12 (B) was a fracture SEM image of the location pointed out with a white dash rectangular in Figure 6-
12 (A). It was clearly seen in the image that there was no abrupt grain size decrease from the surface to the interior of the pellet. The grain size on the surface was around 20-30 μm, which was even slightly smaller than the interior grain size (top left part of the image). This result was consistent with the plot in Figure 6-8. The grain size on the corner of the pellet was revealed in a fracture SEM image in Figure 6-12 (C). As seen in the image, the grain size on the pellet was about 60-80 μm which was much larger than the grains in unaffected areas as seen in Figure 6-12 (B) and could be viewed as the exaggerated grain growth region.

Comparing with the grain size distribution in pure UO₂, the disappearance of the surface exaggerated grain growth region and the enhanced interior grain size in ZrB₂-UO₂ is much likely attributed to the unique properties of ZrB₂. Apart from the high electrical conductivity of ZrB₂ itself, boron anion is also possible to increase the electrical conductivity of UO₂. As a semiconductor, doping boron with the concentration of 10¹⁹ atom/cc by ion implantation can increase the electrical conductivity of UO₂ four orders of magnitude larger than the undoped single crystal UO₂ from 1.5×10⁻³ S/cm to 6 S/cm[101]. It is also known that the electrical conductivity of amorphous carbon is 10⁻²⁰ S/cm[102], which means the electrical conductivity of boron doped UO₂ could be comparable with amorphous carbon. In our work, assuming boron is evenly distributed in the UO₂ matrix, 1500 ppm ZrB₂ could be equivalent with the concentration of 2×10¹⁹ atom/cc. Thus, an increasing amount of electrical current is expected to directly flow through the UO₂ powder during SPS. This increase in electrical current density could lead to the grain growth in UO₂ pellet. The effect of current density on the microstructure development was also studied in the field of flash sintering. In some recent papers, it were clearly revealed that a higher electric current density enhanced both densification and grain growth of ceramic powders [103, 104]. Under the electrical field and the electric current, Frenkel
defect pairs (vacancy and interstitial pairs) can be created [103]. These increased defects promoted the diffusion process. Meanwhile, the mobility of these charged carriers were also promoted under the electrical field, leading to a higher rate of mass transport and grain growth. Additionally, due to the increased electrical conductivity, the contact resistance between the punch and pellet surface was decreased, the input power was thus better dissipated into the interior of the pellet, eliminating the exaggerated grain growth area on the surface of the pellet.

Therefore, the result of grain size distribution of pure UO\(_2\), Cr\(_2\)O\(_3\)-UO\(_2\) and ZrB\(_2\)-UO\(_2\) were summarized in Figure 6-13. Although pure UO\(_2\) sintered at 1600°C with 20 min hold time provided the highest grain size, the pellet was crumbled after SPS. Therefore, doping ZrB\(_2\) into UO\(_2\) provides the most feasible way of rapidly increasing the grain size of UO\(_2\) in SPS. However, some issues, such as the reason for the double-hump longitudinal grain size distribution, have still not been fully understood yet. To further investigate, emphasis on optimizing the dopant concentration and SPS processing conditions are still undergoing to better understand the effect of ZrB\(_2\) on UO\(_2\) microstructure development.

**Conclusion**

Grain growth development was investigated in pure UO\(_2\). An exaggerated grain growth region with large grains (>50μm) was observed on the surfaces and corners of the pellet sintered at 1600°C. By extending the hold time from 0.5min to 20min, this exaggerated grain growth region expanded from the surface to the entire pellet interior.

Large-grain pellet was partially achieved in Cr\(_2\)O\(_3\)-UO\(_2\) pellets. The grain size distribution of 2000ppm Cr\(_2\)O\(_3\)-UO\(_2\) pellet was similar with pure UO\(_2\). 1000ppm and 1500ppm Cr\(_2\)O\(_3\)-UO\(_2\) increased the grain size in a way that grain size decreased with a lower rate than pure UO\(_2\) from surface (∼40μm) to the interior (∼15μm) of the pellet.
Large-grain pellet with average grain size of around 30 μm was achieved in ZrB$_2$-UO$_2$ pellets. No exaggerated grain growth region was appeared on the surface of ZrB$_2$-UO$_2$ pellets. Radially, the grain size was increased from edge to the center of the pellet. Longitudinally, 6 mm and 10 mm pellets exhibit similar grain size distribution where a double-hump grain size distribution was revealed in both pellets.
Table 6-1. The processing conditions in SPS and the resulting density of different pellets

<table>
<thead>
<tr>
<th>Doping type</th>
<th>Maximum sintering temperature (°C)</th>
<th>Hold time (min)</th>
<th>Density (% TD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure</td>
<td>1600</td>
<td>0.5</td>
<td>97.6±0.4</td>
</tr>
<tr>
<td></td>
<td>1600</td>
<td>10</td>
<td>99.4±0.3(Crumbled)</td>
</tr>
<tr>
<td></td>
<td>1600</td>
<td>20</td>
<td>99.1±0.3(Crumbled)</td>
</tr>
<tr>
<td></td>
<td>1450</td>
<td>20</td>
<td>98.7±0.4</td>
</tr>
<tr>
<td>1000 ppm Cr₂O₃</td>
<td>1600</td>
<td>0.5</td>
<td>97.5±0.3</td>
</tr>
<tr>
<td></td>
<td>1450</td>
<td>20</td>
<td>97.5±0.1</td>
</tr>
<tr>
<td>1500 ppm Cr₂O₃</td>
<td>1600</td>
<td>0.5</td>
<td>96.7±0.2</td>
</tr>
<tr>
<td></td>
<td>1450</td>
<td>20</td>
<td>97.3±0.1</td>
</tr>
<tr>
<td>2000 ppm Cr₂O₃</td>
<td>1600</td>
<td>0.5</td>
<td>95.8±0.4</td>
</tr>
<tr>
<td></td>
<td>1450</td>
<td>20</td>
<td>97.3±0.2</td>
</tr>
<tr>
<td>1500 ppm ZrB₂</td>
<td>1600</td>
<td>0.5</td>
<td>98.2±0.4</td>
</tr>
<tr>
<td>(6 mm in length)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>1500 ppm ZrB₂</td>
<td>1600</td>
<td>0.5</td>
<td>97.9±0.4</td>
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<tr>
<td>(10 mm in length)</td>
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</table>
Figure 6-1. SEM image of starting powders. A) UO$_2$. B) Cr$_2$O$_3$. C) ZrB$_2$. 
Figure 6-2. The schematic of how the pellet was half cut. The blue area showed the examined cross section. The arrow pointed out the line scan direction in EMPA.
Figure 6-3. Influence of doping concentration on final densities of doped UO₂ pellets.
Figure 6-4. WDS scan across the cross section from pellet surface to its interior. It was seen that the measured average Cr concentration was consistent with the theoretical concentration (2000 ppm or 0.14 wt %).
Figure 6-5. EMPA of the polished cross section of 2000 ppm Cr$_2$O$_3$-UO$_2$ pellet. A) Secondary electron image revealing the dark spots on the examined cross section. B) X-ray mapping image of the same location revealing the spots were undissolved chromium. The red dash line demonstrated a WDS line scan path. C) The plot of the fine WDS line scan quantitatively indicated 14 wt % of Cr which was revealed as a white spot in (B).
Figure 6-6. Grain size distribution of pure UO$_2$ from pellet surface to the interior. A) Grain size distribution of pellets sintered at 1600°C with 0.5min, 10min, and 20min hold times. B) OM image of pellet with 10min hold time indicating the normal grain growth region and exaggerated grain growth region on the depth 25% of the thickness. The dash lines on indicated the interface between two regions. The schematic of examined cross section of 3mm thickness is shown on the right top position in the plot.
Figure 6-7. Influence of Cr$_2$O$_3$ doping concentration of pure, 1000 ppm, 1500 ppm and 2000 ppm on grain size distribution of Cr$_2$O$_3$-UO$_2$. A) Grain size distribution of Cr$_2$O$_3$-UO$_2$ sintered at 1450°C with 20min hold time. B) Grain size distribution of Cr$_2$O$_3$-UO$_2$ sintered at 1600°C with 0.5min hold time.
Figure 6-8. Grain size distribution of 1500ppm ZrB$_2$-UO$_2$ pellet of 6 mm thickness. The schematic of examined cross section is shown on the right top position. The white dash line represents the OM position from pellet surface to bottom.
Figure 6-9. Grain size distribution of 10 mm ZrB2-UO2 pellet. The schematics of the examined cross section are shown on the right top positions. The white dash line represents the OM positions. A) Radial direction. B) Longitudinal direction.
Figure 6-10. Fracture SEM image of 10 mm ZrB2-UO2 pellet. A) Position 0.1 in Figure 6-9 (A). B) Position 0.5 in Figure 6-9 (A). C) Position 0.9 in Figure 6-9 (A). D) Position 0.1 in Figure 6-9 (B). E) Position 0.5 in Figure 6-9 (B). F) Position 0.9 in Figure 6-9 (B).
Figure 6-11. Current flow during sintering UO$_2$ in SPS. A) Schematic of current flow in UO$_2$ loaded die in SPS. B) OM image of pure UO$_2$ indicating the affected and unaffected areas for the exaggerated grain growth. C) Schematic of affected (red shadowed) and unaffected area (non-shadowed) of a pellet cross section for the exaggerated grain growth.
Figure 6-12. Fracture image of ZrB$_2$-UO$_2$ pellet. A) Image of the fracture cross section. B) The fracture SEM image of pellet surface pointed out with white dash rectangular in (A) indicating the surface grain size distribution. C) The fracture SEM image on the pellet corner circled with red dash triangle in (A) indicating the grain size on the corner of the pellet.
Figure 6-13. Summary of grain size distribution of pure UO₂, Cr₂O₃-UO₂ and ZrB₂-UO₂ pellets.
CHAPTER 7
CONCLUSION AND FUTURE WORK

Conclusion

The investigation of processing parameters during spark plasma sintering of UO$_2$ powder revealed that high-density pellets (up to 97% of the TD) can be fabricated either at moderate sintering temperature with short hold time (1050°C, 0.5 min) or at low sintering temperature with relatively long hold time (750°C, 20 min). Most densification occurred in the temperatures between 720°C and 1000°C. Application of the controlled uniaxial pressure promoted the densification as well as the densification rate. The increase in hold time increased the grain size and reduced porosity. The mechanisms of densification and grain growth were similar with those found in the traditional oxidative sintering process. The O/U ratio of the resulting pellets was found to decrease under SPS, which was possibly due to a chemical reaction between graphite punch and the UO$_2$ powder.

The resulting UO$_2$ pellets had an average Vickers hardness of 6.4±0.4 GPa and Young’s modulus of 204±18 GPa, which were in excellent agreement with values reported in literature for UO$_2$ processed by other methods. The Vickers hardness was increased with density and Hall-Petch relationship is revealed for the high-density pellets. Measurement of Young’s modulus indicated that no internal crack formation was detected for all UO$_2$ pellets. The thermal conductivity of UO$_2$ pellets increased with density but the grain size in the investigated range had no significant influence. The measured thermal conductivity up to 900°C were consistent with the reported literature for conventionally sintered UO$_2$ pellets. This research revealed that the mechanical and thermal properties of UO$_2$ are comparable with the literature and SPS is a feasible tool to process UO$_2$ fuel pellets with reliable mechanical and thermal properties.
Grain growth development was also investigated in pure UO$_2$. It was found that an exaggerated grain growth region with large grains (>50 μm) appeared on the surface of the pellet sintered at 1600°C. By extending the hold time from 0.5 min to 20 min, this exaggerated grain growth region expanded from the surface to the entire pellet interior.

Large-grain-size pellet was partially achieved in Cr$_2$O$_3$-UO$_2$ pellets. In the case of 2000 ppm Cr$_2$O$_3$-UO$_2$ pellet, the grain size distribution was similar with pure UO$_2$ pellet when sintered either at 1600°C for 0.5 min or 1450°C for 20 min. In 1000 ppm and 1500 ppm Cr$_2$O$_3$-UO$_2$, the grain size was increased in a way that grain size decreased with a lower rate than pure UO$_2$ from surface (40 μm) to the interior (15 μm) of the pellet.

Large-grain-size pellet with average grain size of 30 μm was achieved in ZrB$_2$-UO$_2$ pellets. There was no exaggerated grain growth region on the surface of the ZrB$_2$-UO$_2$ pellets. Radially, the grain size was increased from edge to the center of the pellet. Longitudinally, 6 mm and 10 mm pellets exhibited similar grain size distribution where a double-hump grain size distribution was revealed in both pellets.

Thus, processing of UO$_2$ using spark plasma sintering (SPS) offers numerous advantages: significantly reduced processing time, lower sintering temperature, good control of porosity, and stoichiometry, as well as good mechanical and thermal conductivity similar to those of conventionally sintered pellets. Besides, by doping Cr$_2$O$_3$ and ZrB$_2$, full size (10 mm) pellets with large grain size (30-40 μm) is achievable. The benefits of using SPS extend into all three stages of processing: pre-sintering, sintering and post-sintering. In the pre-sintering stage, there is no need for hyperstoichiometric mixture of the starting powders and preparation of green compact. In the sintering step, the heating rate is faster (up to 200°C/min compared to 5-10°C/min in conventional sintering), hold time is shorter (minutes versus hours), and grain growth is better
controlled. Recent literature also revealed that SPS is capable of fabricating difficult-to-sinter 
UO$_2$ composites such as UO$_2$-SiC [105, 106], UO$_2$-Diamond and UO$_2$-CNT [107]. Finally, in the 
post-sintering, SPS pellets do not need additional step of reduction to obtain desired 
stoichiometry (UO$_{2.00}$). Also, due to the fact that the SPS pellet is made in a die cavity, every 
pellet comes out with the same dimension and hence dimensional accuracy is well controlled 
from pellet to pellet. By designing special sintering punches, near-net-shape pellets can be also 
fabricated in SPS, see Figure 7-1 [105]. The efficiency of rapid processing the investigated 
nuclear fuels in our work are compared with other processing techniques in Figure 7-2. By 
comparing with different sintering techniques, the required hold time and total processing time in 
SPS is dramatically decreased by several magnitudes. These advantages of SPS over 
conventional sintering are further summarized in Table 7-1. The features are expected to yield 
significant economic benefit if large scale manufacturing using SPS can be implemented. Such 
efforts are currently underway [21]. Nevertheless, further investigations on better understanding 
of processing-microstructure-property relationship are needed for continued progress in this 
field.

**Future Work**

**Macro-porous UO$_2$ Pellet**

The demand of fission gas capture has arisen the need for development of macro-porous 
UO$_2$ fuel pellet. By engineering the macro-pores inside the pellet, there would be less fission gas 
swelling and leakage and thus the operation safety of nuclear reactor could be enhanced. Macro-
porous UO$_2$ pellet has been successfully produced by using conventional sintering technique, see 
Figure 7-3[108]. However, in those techniques, complicated steps of processing prevents it 
scaling up the productivity into mass production. SPS is proven to be successfully process
nuclear materials. The objective of processing macro-porous UO$_2$ pellet in SPS is to shorten the processing time while engineering the pore size in SPS.

The macro-porous UO$_2$ pellet can be achieved by incorporating burnable pore former with low evaporating temperature, e.g. Poly Methyl Methacrylate (PMMA), see Figure 7-4, supplied by Bangs Laboratories, IN, USA. PMMA is incorporated with UO$_2$ matrix by dispersing it through dry mixing for 1 h. The result of mixing can be seen in Figure 7-5. It is seen that before mixing, PMMA is addicted to the surface of large UO$_2$ particles (Figure 7-5(a)) while after mixing, due to the smaller grain size of UO$_2$, PMMA is wrapped by small UO$_2$ grains which can be clearly seen in the high magnification window in Figure 7-5(b). The mixed powder is then sintered in SPS following the regular procedure at 1600$^\circ$C for 0.5min with 20 MPa uniaxial pressure. The resulting pellet has the density of 93 %TD with the grain size less than 1 $\mu$m. The microstructure, see Figure 7-6, reveals that PMMA delayed the densification as well as grain growth of UO$_2$.

The future work of this study is to investigate the optimal the processing condition for the survival of macro pores. It is seen in Figure 7-6 that macro-pores was not able to form. Instead, only intra-granular pores with regular shape appears. Thus, the effect of maximum sintering temperature, hold time, heating rate and uniaxial pressure in SPS on the formation and elimination of pores is to be examined to better understand the mechanism of processing macro-porous UO$_2$ pellet in SPS.

**ThO$_2$-cored UO$_2$ Pellet**

The idea of ThO$_2$-cored UO$_2$ fuel pellet originated from the high center-line temperature in current UO$_2$ fuel. ThO$_2$ has higher thermal conductivity than UO$_2$. By incorporating ThO$_2$ into the core of UO$_2$, lower center-line temperature is expected to be achieved. The use of ThO$_2$ as a nuclear fuel can be achieved by mixing it with certain amount of enriched UO$_2$ until it produces
enough $^{233}$U to sustain itself [109]. SPS is proved to be a feasible technique to process nuclear materials with faster sintering rate and shorter processing time. Due to the complicated manufacturing steps that may occur during the fabrication of ThO$_2$-cored UO$_2$ pellet in conventional sintering methods, the objective of processing ThO$_2$-cored UO$_2$ pellet in SPS is to shorten the processing time while keeping the integrity of the composite pellet.

Making ThO$_2$-cored UO$_2$ green pellet in SPS die can be achieved by simultaneously loading the ThO$_2$ powder in the center and UO$_2$ powder in the peripheral areas into a die. All the other procedures can be the similar with the regular SPS procedures. Additionally, due to the thermal coefficients mismatch, preliminary study would be focused on tailoring the processing condition as well as the ratio between ThO$_2$ and UO$_2$ to achieve the intact pellet without the crack generation. The demonstrated ThO$_2$-cored UO$_2$ pellet is seen in Figure 7-7. The maximum sintering temperature is 1150$^\circ$C with 5 min hold time. As seen in the figure, cracks surrounding the interface between ThO$_2$ and UO$_2$ indicate the thermal stress induced by thermal coefficient mismatch.
Table 7-1. Comparison of SPS and conventional sintering techniques

<table>
<thead>
<tr>
<th>Sintering stage</th>
<th>Feature</th>
<th>SPS</th>
<th>Conventional</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-sintering</td>
<td>Modification to starting powder</td>
<td>Not required</td>
<td>Required</td>
</tr>
<tr>
<td></td>
<td>Cold compaction of green body</td>
<td>Not required</td>
<td>Required</td>
</tr>
<tr>
<td></td>
<td>Temperature ramp rate</td>
<td>50-200°C/min</td>
<td>2-10°C/min</td>
</tr>
<tr>
<td></td>
<td>Maximum sintering temperature</td>
<td>750-1450°C</td>
<td>1600-1700°C(H₂)</td>
</tr>
<tr>
<td></td>
<td>Hold time</td>
<td>0.5-20 min</td>
<td>1-10 hrs</td>
</tr>
<tr>
<td></td>
<td>Total sintering run time</td>
<td>&lt;1 hr</td>
<td>~15 hrs.</td>
</tr>
<tr>
<td></td>
<td>Pressure</td>
<td>20-80 MPa</td>
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</tr>
<tr>
<td></td>
<td>Sintering environment</td>
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<td>Gaseous environment</td>
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<td>Sintering</td>
<td>Dimensional control</td>
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<tr>
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<td>Pellet stoichiometry during sintering</td>
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<td>Unchanged</td>
</tr>
<tr>
<td></td>
<td>Control of Grain growth</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td></td>
<td>Ability to produce near net shape pellets</td>
<td>Yes</td>
<td>Limited</td>
</tr>
<tr>
<td></td>
<td>Ability to sinter difficult-to-sinter materials</td>
<td>Yes</td>
<td>Limited</td>
</tr>
<tr>
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<td>Requires reduction of sintered pellet to desired stoichiometry</td>
<td>No (if initial powder is at the right stoichiometry)</td>
<td>Yes</td>
</tr>
<tr>
<td>Post-sintering</td>
<td>Pellet requires additional machining to obtain desired final dimensions</td>
<td>May not be required</td>
<td>Yes</td>
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Figure 7-1. Near-net-shape UO$_2$ fuel pellet made by SPS.
Figure 7-2. Comparison of processing efficiency between SPS and other sintering methods to sinter high-density UO₂ related nuclear fuel pellets. A) Comparison of total processing time. B) Comparison of hold time at maximum sintering temperature.
Figure 7-3. Macro-pores of a sintered body by using PMMA fore former[108].
Figure 7-4. PMMA beads with mean diameter of 3.6μm.
Figure 7-5. The morphology of PMMA UO$_2$ mixture. A) Before mixing. B) After mixing. The window on the right side indicates the high magnification picture of PMMA beads.
Figure 7-6. The microstructure of sintered PMMA-UO₂ pellet.
Figure 7-7. ThO$_2$ cored UO$_2$ pellet sintered at 1150°C for 5 min. Note that the white is ThO$_2$ and black is UO$_2$. 
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BIOGRAPHICAL SKETCH

Lihao Ge was born in Nantong City, Jiangsu Province, People’s Republic of China in 1988. His parents are Cao Ge and Fengchun Xu. Lihao graduated with a Bachelor of Science in material science and engineering from Nanjing University of Science and Technology in July 2010. After that, he enrolled in the master’s program of materials science and engineering at University of Florida in August of 2010. In May of 2011, he transferred to the Department of Mechanical and Aerospace Engineering as a PhD student at University of Florida. During his PhD studies, he published three peer-reviewed journal papers, had several conference publications and was a co-inventor of a patent. He received a non-thesis Master of Science degree in December 2013 and received his Doctor of Philosophy degree from the University of Florida in the spring of 2014.