Thermal Transport and Fracture Behavior of Sintered Fuel Pellets: Experimental Validation of NEAMS Tool MARMOT

NEAMS-1 (Nuclear Energy Advanced Modeling and Simulation)

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Thermal Transport and Fracture Behavior of Sintered Fuel Pellets: Experimental Validation of NEAMS Tool MARMOT

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Executive Summary

The project targets at experimental validation of NEAMS tool MARMOT for predicting thermal transport and fuel fracture. The key components of the project include: (1) sintering UO$_2$ samples with well-controlled microstructures (grain size, pore, fission bubble, porosity and pore distribution either in intra- or inter-granular pores); (2) thermal conductivity measurements of these well-characterized polycrystalline samples; (3) indentation testing of sintered UO$_2$ with various grain size, porosity and stoichiometry to obtain fracture and crack propagation mechanisms (inter or intra-granular fracture); and (4) validation and uncertainty quantification of the MARMOT thermal transport and fracture models. The high quality experimental data will be used to validate the predictions of MARMOT for thermal transport and fracture, using average data and local microstructure information.

In this work, UO$_2$ fuels with controlled microstructure (grain size, pore size/structure and fuel chemistry) were successfully prepared by high energy ball milling of the hyper-stoichiometric UO$_{2+x}$ powders purchased commercially, and consolidated by spark plasma sintering. Dense nano-sized UO2 fuel pellets with controlled stoichiometry were sintered by SPS. The effects of different SPS sintering parameters on the pore size and distribution were investigated, and the correlation among the SPS parameter – microstructure control – stoichiometry/defect structure was established. To further control the pore structure and fuel chemistry, systematic thermal annealing of the sintered fuels with the controlled pore structure was performed in a reduced. The controlled microstructure and fuel chemistry enable the investigation of the separate effects of pore structure and fuel chemistry on thermal transport behavior.

The mechanical properties of the sintered UO$_2$ fuels were tested by nanoindentation and microindentation testing at different temperatures. The fracture behavior of the sintered fuels as functions of grain structure and temperature was investigated. Nanocrystalline UO$_2$ display higher hardness than microcrystalline counterpart, consistent with the Hall-Petch strengthening mechanism. Greater Young’s modulus and fracture toughness are also identified for the nanocrystalline UO$_2$, and hardness and Young’s modulus decrease with temperature, suggesting better ductility of oxide fuels at greater temperature at small length scale. Hyper-stoichiometric UO$_2$ specimen displays higher hardness and fracture toughness than stoichiometric UO$_2$, due to the impediment of the crack propagation by the oxygen interstitial atoms. These results are useful in understanding the mechanical properties of the high burn-up structure (HBS) formed in nuclear fuels during reactor operation, and also provide critical experimental data as the input for the development and validation of the MARMOT fracture model of nuclear fuels.

The thermal properties of the sintered UO$_2$ fuel pellets with controlled grain structure, fuel chemistry and pore structures are measured by laser flash and the impact of the microstructure characteristics on the thermal transport properties is elucidated. Through a close collaboration with the MARMOT team at Idaho National Laboratory, the thermal properties of the sintered oxide fuel pellets with controlled microstructures are measured experimentally, and modeled using the developed MARMOT thermal transport models for a joint effort of demonstrating high spatial resolution measurements at the microstructural level on as-fabricated nuclear fuels and materials and obtain critical experimental data for model validation and properties predictions. In this work, we also conducted sensitivity analysis and uncertainty quantification (UQ) on a mesoscale simulation.
that has been applied to understand the effective thermal conductivity of UO$_2$ reactor fuel using the MARMOT tool. We also conducted UQ on mechanistic macroscale models that have been developed to predict the effective thermal conductivity. The most sensitive parameter is the thermal conductivity of bulk UO2 for the thermal conductivity models. In the future, the predicted simulation distributions need to be compared to experimental data for validation of the models.
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Chapter 1. Background and Motivation

The US Nuclear Energy Advanced Modeling and Simulation (NEAMS) program is developing science-based next generation fuel performance modeling as part of its Fuel Product Line in order to facilitate the predictive capability of nuclear fuel performance tools and assist the design and analysis of reactor systems. The NEAMS Toolkit is based on the MOOSE-BISON-MARMOT (MBM) suite of codes, where MOOSE is the finite element framework and BISON is a macroscale fuel performance tool. MARMOT is a mesoscale fuel performance tool that is being used to develop materials models based on microstructure rather than burnup. MARMOT predicts the coevolution of microstructure and properties in reactor fuel and cladding. Current MARMOT efforts are focused on investigating fuel behavior in four key areas: (1) grain boundary (GB) migration and grain growth, (2) fission gas migration, (3) thermal conductivity and (4) fracture. In each of these areas, atomistic simulations along with MARMOT simulations are being used to elucidate the basic mechanisms and inform the development of materials models for BISON. A critical aspect of this model development must include validation of the MARMOT tool. However, validation efforts have been limited due to the lack of detailed data at the level of microstructure on reactor fuel and cladding. MARMOT must be validated by comparing to the measured evolution of average descriptions of the microstructure, such as the average grain size, but it must also be compared to data characterizing local changes in the microstructure.

The Marmot grain growth model has been verified against a well-established analytical GB migration model, but it has not been fully validated. A current NEUP project in the NEAMS area is using state-of-the-art characterization techniques to collect data on grain growth in UO₂ that will be used to validate the model. However, additional critical experimental data are needed to validate other MARMOT models, particularly models used to determine the effective thermal conductivity and fracture of irradiated UO₂ fuel.

1.1 Current Status of MARMOT, Critical Data Needed, and Relevance of the Proposed Work

Fundamental understanding of thermal transport of the nuclear fuel elements is essential to predicting critical aspects of fuel performance, such as radial temperature profile, heat flux, fission gas release and species migration. The thermal transport of fuel pellets evolve dynamically in space during the lifetime of a fuel element, and strongly depend on its microstructure and radiation damage. Microstructure evolution, such as thermal and irradiation-driven grain growth, precipitation, defect accumulation, fission gas migration, bubble nucleation and coalescence, and fuel chemistry variation, significantly impact thermal transport. Fracture of UO₂ fuel pellets induced by high thermal stress during service due to high temperature gradients also profoundly impacts fuels performance, dimensional stability, thermal conductivity and fission gas release of nuclear fuel pellets. The successful prediction of thermal transport and fracture of fuel elements is critical for the efficient and safe utilization of nuclear energy.

Current existing fuel performance codes (e.g., FRAPCON, FALCON) are based on empirical models and phenomenological equations and thus are generally valid for only limited conditions. These codes are serial with inefficient solvers and high programming complexity and only model LWR fuel in 1.5 or 2-dimensions (2D). The empirical models cannot accurately extrapolate out of their test regions, and are not applicable to accident conditions or new reactor fuel concepts. These
empirical models are typically correlated to burnup, which is not a unique measure of the fuel history and its microstructure.

**Current Status of MARMOT modeling.** MARMOT is a mesoscale multiphysics simulation tool that is being used to develop mechanistic macroscale materials models based on microstructure rather than burnup [1]. The MARMOT tool predicts evolution of microstructure and physical properties due to applied load, temperature and radiation damage using the phase field method coupled with solid mechanics and heat conduction solved with implicit finite elements using INL’s MOOSE framework. Key features of the MARMOT tool include the capability for 1D, 2D and 3D modeling and massively parallel computing. It can also be coupled to other simulation tools, such as the BISON macroscale fuel performance tool, for multiscale modeling. MARMOT has demonstrated great success in developing mechanistic understanding of a wide range of fuel behaviors including grain growth, fracture, and bubble nucleation and growth.

Extensive progress has been made recently by the MARMOT team and the national laboratory partner in developing physical models of thermal transport and fracture for BISON informed by MARMOT simulation results. Thermal transport in UO$_2$ is primarily mediated by phonon transport at typical reactor LWR temperatures. However, irradiation damage causes defects that scatter phonons, lowering the thermal conductivity. In addition, additional phases such as solid fission products and pores filled with gaseous fission products impact the effective thermal conductivity. To determine the impact of irradiation induced microstructure evolution on the thermal conductivity, work under the NEAMS program has used atomistic and mesoscale modeling and simulation to quantify the impact of defect scattering on thermal conductivity as well the impact of GBs and pores. For example, molecular dynamics simulations have been used to quantify the impact of dispersed xenon atoms within the fuel matrix on the fuel thermal conductivity. A mesoscale model was developed to investigate the influence of intergranular gas bubbles on effective thermal conductivity in a polycrystalline fuel matrix. They were found to have significantly higher resistance to heat transport than randomly-distributed pore structures. These GB bubbles effectively increase the GB thermal (or Kapitza) resistance as a function of the percentage of the GB covered by fission gas, or the GB coverage. The lower length scale simulations results have been used to inform the development of an analytical model that couples the thermal conductivity model in BISON with the existing fission gas release model. Initial results compare well with experiments without requiring any fitting to experimental data, as shown in Figure 1. However, the effective thermal conductivity predictions in MARMOT used to develop this model have never been validated against experimental data.

![Figure 1.1: Fuel center line temperature predicted in the RISO AN3 test using the BISON tool. Results are shown for an empirical and a mechanistic thermal conductivity model, with the mechanistic model showing somewhat better performance without requiring fitting.](image)
The fracture model currently in BISON is a semi-empirical smeared cracking model using a fracture stress to determine the onset of cracking. While fracture in LWR fuel primarily occurs along GBs, the current model does not consider the impact the GB fission gas bubbles have on the fracture stress. In order to identify the impact of GB bubbles on fracture in UO₂, an atomistically-informed mesoscale fracture model was developed. Atomistic MD simulations [6] were performed to calculate traction-separation laws for transgranular and intergranular fractures, and the surface and GB energies were calculated to determine the critical energy release for GB fracture. Mesoscale simulations, using the information from the atomistic simulations, predict crack propagation through polycrystals of various grain sizes and various levels of porosity (as shown in Figure 2) to develop a macroscale fracture model for BISON, including the effects of temperature, grain size and GB bubble density on crack initiation and propagation behavior. The physical-based GB separation model [7], as a mechanism for fission release in complementary to gas bubble interlinkage, was also developed considering the impact of gas bubble pressure and hydrostatic stress. Depending on the bubble geometry and fractional coverage, both stable and unstable crack propagations can occur. A critical GB bubble coverage of 0.5 exists, above which unstable crack growth and GB separation occur, and a relationship between the stress intensity factor at crack initiation and fraction coverage was derived. However, these fracture predictions also require validation before confidence can be placed in the results.

1.2. Critical Data Needed on Thermal Transport and Fracture Model Validation. While the MARMOT thermal transport and fracture models developed under the NEAMS program are verified against analytical models and other codes, critical experimental data are still needed in order to validate them. This validation is absolutely required if the simulation predictions are to be used to inform the development of high quality models for BISON. The critical data needed for MARMOT model validation of the thermal transport model include GB thermal resistance and effective thermal conductivity of UO₂ fuels across a wide range of microstructural features with varied porosity/distribution, grain/pore/bubble size, GB coverage and defects/stoichiometry. For the fracture model, the fracture behavior of UO₂ fuels must be understood as a function of temperature, grain size, porosity and stoichiometry. The transition from brittle to ductile fracture and the crack initiation/propagation/interaction behavior are also needed.

Some data already exist for the effective thermal conductivity of unirradiated and irradiated UO₂, as does some fracture data for UO₂. However, these data, are not suitable for validation of the MARMOT models as their microstructures were not well characterized. Data suitable for validating the microstructure-dependent models in MARMOT require average information about the microstructure and properties but also require detailed characterization of the local microstructure information. This required level of detail in the characterization makes the validation of the microstructure-informed models very challenging. Dealing with irradiated materials makes the

![Figure 1.2: Example of a phase field fracture model conducted using MARMOT in which the fracture behavior of predicted for various amounts of intergranular bubbles. Similar simulations were conducted using various grain sizes.](image)
characterization even more difficult, so one approach to avoid this issue is to fabricate unirradiated samples with microstructures similar to those in irradiated UO₂ fuel and conduct separate effects tests.

1.2. Goal and Motivation

The project aims at experimental validation of NEAMS tool MARMOT for predicting thermal transport and fuel fracture. The key components of the project include: (1) sintering UO₂ samples with well-controlled microstructures (grain size, pore, fission bubble, porosity and pore distribution either in intra- or inter-granular pores); (2) thermal conductivity measurements of these well-characterized polycrystalline samples; (3) indentation testing of sintered UO₂ with various grain size, porosity and stoichiometry to obtain fracture and crack propagation mechanisms (inter or intra-granular fracture); and (4) validation and uncertainty quantification of the thermal transport and fracture MARMOT models. The high quality experimental data will be used to validate the predictions of MARMOT for thermal transport and fracture, using average data and local microstructure information. Note that the knowledge and approach developed in designing target experiments with well controlled microstructure to obtain critical data needed for NEAMS validation can also be extended to multiple fuel systems other than conventional LWR oxide fuels.

The progress under the support of this NEUP project is summarized as follows: Chapter 2 – SPS sintering of UO₂ fuels and Microstructure Design; Chapter 3 - Correlation between thermal transport behavior and microstructure; Chapter 4 – Mechanical Properties of the Sintered UO₂ with controlled microstructure; Chapter 5 – Validation of MARMOT Thermal Transport Model; and Chapter 6 – Uncertainty Quantification.
Chapter 2. SPS Sintering of UO$_2$ fuels and Microstructure Design

In this chapter, we report the progress and deliverable on sintering UO$_2$ samples with controlled microstructures (grain size, pore, porosity and pore distribution either in intra- or inter-granular pores, and defects) and explore the correlation among SPS parameters (temperature, duration and pressure), microstructure control, stoichiometry and physical properties. The thermal transport behavior was characterized as functions of microstructures. Particularly, nanocrystalline UO$_{2+x}$ powders were prepared by high-energy ball milling and consolidated into dense fuel pellets (> 95 %) under high pressure (750 MPa) by spark plasma sintering at low sintering temperatures (600-700 ºC). The grain size achieved in the dense nano ceramic pellets is between 60 ~ 110 nm as controlled by sintering temperature and duration. Fuel chemistry characterized by X-ray diffraction indicates that the sintered fuel pellets are single phase UO$_{2+x}$. Micro-Raman measurements suggest the prevailing defect form in UO$_{2.03}$ and UO$_{2.11}$ is random oxygen interstitial and Willis cluster, respectively. The correlation among the SPS parameter – microstructure control – stoichiometry/defect structure was established. The key results are summarized below

- Hyperstoichiometric UO$_{2+x}$ powders purchased commercially were pre-processed in a highly reduced environment to obtain pure stoichiometric UO$_2$ powders for pellet sintering
- Dense UO$_2$ fuel pellets with large grain size up to 80 microns were sintered by SPS and the effects of temperatures on physical density and phase composition were analyzed.
- Controlled samples of UO$_2$ with nearly perfect stoichiometry and porosity with different grain size varying from 125 nm to 7.5 microns were prepared.
- Materials sintering by SPS with the goal of controlling pore size and pore structures. The effects of different SPS sintering parameters on the pore size and distribution were investigated, and the grain boundary coverage was also estimated based upon microstructure characterization through SEM images.
- To further control the pore structure and fuel chemistry, systematic thermal annealing of the sintered fuels with the controlled pore structure was performed in a reduced environment of Ar-4%H$_2$ and structure characterization was conducted with the focus on the pore structure evolution and fuel chemistry. The fuel chemistry was reduced from hyper-stoichiometry toward more stoichiometry and no significant variation in microstructure occurred for the thermally-treated sintered fuels. The controlled microstructure and fuel chemistry enable the investigation of the separate effects of pore structure and fuel chemistry on thermal transport behavior.
- Microstructure evolution of the nano-sized UO$_2$ by SPS upon isothermal annealing in an inert environment (Ar gas) and grain growth kinetics were also studied with focus on grain growth, pore coarsening, and their interaction. Both hyper-stoichiometric UO$_{2.11}$ and more stoichiometric UO$_{2.03}$ experience thermally-induced grain coarsening and pore coalescence. Larger grain sizes were observed in nano-sized UO$_{2.11}$ as compared UO$_{2.03}$ with different grain growth kinetics. Derived grain growth components indicate that nano-sized UO$_{2+x}$ generally follows the classical grain coarsening mechanism upon isothermal annealing, and the activation energy of grain coarsening is significantly lower than that of the bulk counterpart. Grain boundary diffusion may dominate the grain growth kinetics of the nano-sized UO$_{2+x}$, depending on the grain size and stoichiometry of the fuel matrix.

2.1 UO$_2$ fabrication by Spark plasma sintering and high energy ball milling
Using SPS process combining with high energy ball milling, we have demonstrated the possibility of synthesizing oxide fuels with well controlled length scale from nano to micron-sized. Due to the unique approach of SPS for rapid consolidation with short time and lower temperature, the nano-sized features in the milled powders by HEBM is well preserved, leading to the fabrication of nano-sized UO$_2$ (600 °C under high pressure environments).

To further increase the grain size, an oxide additive was added to increase the sintering kinetics, greatly promoting the grain size of the sintered UO$_2$ by SPS (up to 80 microns under 1700 °C for 20 mins) (see Figure 2.1). Large sized UO$_2$ is important for enhanced fuel properties to improve the fission production retention capability and thus accident tolerance. Different oxides additives such as Cr$_2$O$_3$ and TiO$_2$ were applied to increase grain size of the sintered fuel pellets. In this study, SPS was applied to consolidate TiO$_2$-doped UO$_2$ fuel pellets with 0.5 wt% dopant concentration, above its solubility, in order to induce eutectic phase formation and promote sintering kinetics. The largest grain achieved is up to 80 μm by sintering at 1700 °C for 20 mins, and liquid U-Ti-O eutectic phase occurs at the triple junction of grain boundaries and significantly improves grain growth during sintering. The oxide additive also impedes the reduction of the initial hyperstoichiometric fuel powders to more stoichiometric pellets upon SPS. Thermal-mechanical properties of the sintered doped pellets including thermal conductivity and hardness are measured and compared with undoped pellets. The enlarged grain size (80 μm) and densification within short sintering duration highlight the immense possibility of SPS in fabricating large grain UO$_2$ fuel pellets to improve fuel performance.

### 2.1.1 HEBM process to dope TiO$_2$-into UO$_2$ powders

The starting UO$_2$ powder sample are agglomerates of ~0.5 μm crystalline (Fig. 2.2a). After TiO$_2$ doping by HEBM, the agglomerates are crumbled with no appreciable size change of UO$_2$ crystalline. Notable are the excessive TiO$_2$ nano particles uniformly decorates on UO$_2$ crystalline (Fig. 2.2b), indicating a homogenous doping achieved by HEBM. TiO$_2$ has a limited solubility (between 0.07-0.13 wt.% at 1650 °C) in UO$_2$ matrix, well below the doping concentration of 0.5 wt.% and as a result, it is reasonable to observe those excessive nano-size TiO$_2$ on UO$_2$ crystalline surface. On the other hand, upon mechanical attrition by HEBM the mixture of TiO$_2$ and UO$_2$, excess TiO$_2$ may be dissolved into UO$_2$ crystal lattice beyond the solubility predicted by thermodynamics.

XRD spectrum (Fig. 2.2c) reveals the crystal structure modification after TiO$_2$ doping. For starting UO$_2$ powder, (111) diffraction peak (Insert in Fig. 2.2c) was located at a 20 degree higher than the value reported for stoichiometric UO$_2$ (28.23°, marked as dash line in Fig. 2.2c insert),
indicating that the starting UO₂ powder has a higher oxygen content than stoichiometric UO₂. Because of the excess oxygen, U ions with higher covalent values, i.e. U⁵⁺ and/or U⁶⁺ coexist with U⁴⁺ to maintain charge neutrality. These ions have smaller ionic radii than tetravalent uranium, resulting in the reduction of the lattice parameter as compared with stoichiometric UO₂, and in turn a higher two theta angle for the (111) diffraction peak.

No diffraction peaks from anatase TiO₂ can be observed in the XRD patterns (Fig. 2.2c) for the doped powders upon HEBM, most likely due to the low concentration of TiO₂ (~0.5 wt.%) and as well as the incorporation of partial TiO₂ into UO₂ lattices forming a solid solution. However, all XRD peaks of TiO₂ doped UO₂ shifts to lower 2θ angles than that of the starting UO₂. Such a shift indicates an increase of UO₂ lattice parameter by HEBM doping. The shift of XRD peaks and lattice parameter change for UO₂ can be attributed to the formation of the solid solution of two starting oxides. During HEBM, Ti ions could either substitute host U ions or occupy interstitial crystal cavity sites. Partial substitution of uranium ions by titanium ions would reduce sub-lattice parameters of urania due to the smaller ionic radius of Ti⁴⁺ (0.074 nm for 8 coordination) than that of eight coordinated U⁴⁺ (0.1 nm) and U⁶⁺ (0.086 nm), and XRD peaks should shift to higher angles. However, this trend is contradict to obtain XRD spectrums. On the other hand, instead of substitution, Ti ions can also occupy the interstitially-vacant sites as the tetrahedral cavity of U sublattice is 0.1 nm, large enough to allow readily accommodation of Ti⁴⁺. Consequently, UO₂ lattice would be expanded by the incorporation of interstitial Ti⁴⁺ ions and lead to the shift of the (111) peak of UO₂ lattice toward a lower 2θ. This claim is also in line with previous experimental results. The incorporation of the interstitial Ti⁴⁺ ions and a slight lattice expansion of the oxygen-enriched UO₂ crystal structure may promote the sintering and grain growth due to the potentially enhanced atom diffusion at the absent of liquid phase formation.

2.1.2. Microstructure of the SPS densified UO₂ doped with TiO₂

![Fig. 2.2. SEM images of starting UO₂ powder (a) and TiO₂-doped UO₂ powder (b); XRD patterns (c) of those two powder samples and inserted is a close-up view of the (111) diffraction peak ranges from 27° to 30°](image-url)
The densities of pellets sintered from TiO$_2$-doped powder are lower than that of pellets sintered from starting UO$_2$ powders. The density of the doped pellets increased with temperature up to 1600 °C, and slightly decreased when sintered at 1700 °C. SEM images show the microstructure and morphology of the fracture surface (Fig. 2.3a-3d) and ceramography (Fig. 2.3e-3g) of the polished surface of the densified doped and undoped UO$_2$ pellets with different sintering conditions. Intergranular fractures dominate the fracture surface of the 1500-undoped sample with pores distributes on the grain boundaries (Fig. 2.3a). Grain size is estimated to be 13 ± 5 μm for the pure UO$_2$ pellet. However, fracture surface of the 1500-doped pellet (Fig. 2.3b) shows a mixture of inter- and trans-granular patterns with the estimated grain size of 17 ± 5 μm. Increasing the sintering temperature further to 1600 °C (Fig. 2.3c) enlarges the average grain size to 28 ± 4 μm. Further increase in the sintering temperature to 1700 °C (Fig. 2.3d) results in significant grain growth as revealed by the grain size up to 81 ± 10 μm (Fig. 2.3g). Inter-granular fracture dominates fracture behavior of the 1700-doped sample.

High magnification SEM images of the fracture surfaces (Fig. 4) of the fuel pellets doped with TiO$_2$ show distinct microstructural features including

![Fig. 2.3. SEM images showing fracture behaviors and microstructures of the 1500-undoped (a), 1500-doped (b), 1600-doped (c), and 1700-doped (d); Ceramography of polished surfaces for 1500-undoped (e), 1600-doped (f), and 1700-doped (g).](image)

![Fig. 2.4. High magnification SEM images showing the secondary phase formation in 1500-doped (a), 1600-doped (b), 1700-doped (c), and an enlarged view (d) of the eutectic phase acquired from the yellow box highlighted in (c).](image)
secondary phase formation and pore distribution. For the 1500-doped pellet, bar-shaped TiO$_2$ crystallites with length of several $\mu$m can be found across the UO$_2$ grain boundaries and also within inner grains. Intra-granular pores are also identified within UO$_2$ grains. The lower density of TiO$_2$ and microstructural cavities may be responsible for the relatively-lower density for the 1500-doped pellet as compared with the pure UO$_2$ pellet. The bar-shaped TiO$_2$ secondary phase for the 1500-doped pellet evolved into a more spherical shape (Fig. 2.4b) for the pellet sintered at 1600 $^\circ$C, and the TiO$_2$ spheres were located at the grain boundaries of the UO$_2$ and also triple junctions. No obvious cavities were observed between the UO$_2$ and TiO$_2$ phases, consistent with the increased physical density for the samples sintered at higher temperature.

For the doped pellet sintered at 1700 $^\circ$C, a distinct interfacial phase can be identified across grain boundaries and triple junctions showing highly porous features (Figs. 2.4c and 4d). A slight decrease in density was observed for the pellet sintered at 1700 $^\circ$C as compared to the 1600-doped pellet. The porous phase (Fig. 2.4d) in the triple junction can be attributed to the solidified liquid phase resulting from an eutectic reaction between UO$_2$ and TiO$_2$ at sintering temperature of 1700 $^\circ$C, higher than the reported eutectic temperature of 1645 $^\circ$C.

![Fig. 2.5. EDX elementary mappings showing morphology evolution and composition variation of the secondary phases for 1500-doped (a), 1600-doped (b) and (c), 1700-doped (d) and (e) pellets](image)
UO₂ has a high melting point, ~2800 °C, and sintering UO₂ fuel pellets with larger grain sizes, e.g., above 20 µm, require high temperatures (1750 °C) for an extended time (e.g., 8 hrs) in a reducing hydrogen atmosphere in which the uranium diffusion significantly affects the densification and sintering of dense UO₂ fuel pellets. To achieve a higher densification rate at a relatively low temperature, hyper-stoichiometric UO₂₀.₂₅ may be used as starting powder, and the enhanced uranium cation diffusion as a result of excessive interstitial oxygen and thus more U vacancies as compared with the stoichiometric UO₂ that can accelerate the sintering process.

Doping UO₂ with transition metal oxides, such as Nb₂O₅, Cr₂O₃, and TiO₂ with various covalent states, can generate excessive interstitial oxygen, increase cation vacancy and uranium ion diffusion rate, and ultimately promote grain growth processes. However, due to different covalent states of the transition metals, different mechanisms have been proposed for the enhanced grain growth. For example, for Nb₂O₅, Nb⁵⁺ ions can directly substitute U⁴⁺ ions in the cation sublattice, and the positively-charged uranium sublattice requires excessive interstitial oxygen to maintain charge neutrality. Consequently, more U vacancies are generated following the Schottky defect equilibrium principle. In contrast, the direct substitution of Cr³⁺ and Ti⁴⁺ on U⁴⁺ does not positively charge the uranium sublattice, and thus has no influence on cation diffusion/grain coarsening.

The enhanced sintering and grain growth kinetics observed in the TiO₂-doped UO₂ (e.g., the grain size as large as 81 µm upon sintering at 1700 °C for 20 minutes) may be explained by the improved uranium diffusion as a result of the lattice expansion with Ti⁴⁺ ions incorporated into the tetragonal interstitial of uranium sublattice. This is consistent with previous studies in which Ti and Cr ions can occupy the interstitial sites, and the enhanced uranium diffusion rate promotes sintering process. The incorporation of Ti⁴⁺ into interstitial sites of the uranium lattice can be inferred by the shift of XRD peaks of UO₂ induced by HEBM milling. As a result of enhanced uranium diffusion in an expanded structure, a noticeable gain growth was also found in 1500-doped pellet (17 ± 5 µm) as compared with 1500-undoped (13 ± 5 µm) using same sintering parameters.

EDX elementary mapping (Fig. 2.5) and linear composition scanning were performed on the doped pellets sintered at different temperatures in order to investigate composition evolution of both UO₂ fuel and secondary phase either within or at UO₂ grain boundary. A morphological evolution from a bar shape to spherical geometry was clearly observed when sintering temperature increased from 1500 °C to 1600 °C. Elementary mapping (Figs. 2.5a, b, and c) clearly depicts the absence of U ions within those secondary phases, suggesting that these are still Titanium oxide. Oxygen appears to distribute uniformly through the mapped area within pellets. The incorporation of Ti into the UO₂ grains was also clearly evidenced by the EDX mapping. When sintering temperature was increased to 1700 °C, the secondary phases become porous, corresponding to a solidified liquid phase distributing over the triple junction of grains (Fig. 2.5.d). EDX mappings (Figs. 5d and e) show that those phases are titanium enriched and oxygen depleted as compared with the surrounding UO₂ matrix.

### 2.2. Microstructure control – Pore size/structure and Stoichiometry

#### 2.2.1 Pore Size and Pore Structure Control
The control of pore structure and distribution is very challenging as the sintering process involves densification by eliminating pores and grain coarsening. It is the interplay of the diffusion of the atoms through different mechanisms and grain growth eventually determine the pore size and pore structure. By controlling the SPS parameters, we have demonstrated the flexibility in controlling the pore size and grain size simultaneously. For example, as shown in Fig. 2.6, the grain sizes can be controlled from ~2.2 μm up to 3.8 μm, and the pore size also increases from 163 nm to ~300 nm upon consolidation of SPS at greater temperatures.

Further possibilities were demonstrated in controlling the pore distribution (Fig. 2.7), in which all of the pores are distributed on the grain boundaries and triple junctions for SPS-densified pellets UO$_{2.21}$ upon consolidated at 1100 °C for 5 mins. The dominant pore distribution at the grain boundaries can be attributed to the neck formation, and the grain size was determined as ~1.2 μm. No significant growth coarsening was observed as a result of relatively lower SPS temperature. With further increase in the sintering temperature to 1200 °C for 5 mins, the microstructure of the fuel pellets experienced a grain coarsening and the average grain size increased to 2.6 μm. Accompanying with the grain coarsening and grain boundaries migration at high temperature, the pores distributed at the grain boundaries and triple junctions were embedded inside the large-sized grains to form inner-granular pores. In addition to the grain size and pore distribution, fuel chemistry also varied approaching to more stoichiometry from UO$_{2.21}$ to UO$_{2.03}$ with higher sintering temperatures due to the in-situ reduction process resulting from SPS sintering. Different pore geometries occurred including sphere pores within grains, triangle pores at grain boundaries and triple junctions, and elliptical pores at grain boundaries. We have performed systematic analysis on the pore size and distributions for pores with different geometries, and the pore coverage areas were also determined.

![Fig. 2.6. Control of the pore and grain sizes simultaneously by SPS process.](image)

![Fig. 2.7. Control of pore distribution by varying SPS parameters: (a) 1100 °C for 5 mins, UO$_{2.21}$; (b) 1200 °C for 5 mins, UO$_{2.08}$; (c) 1300 °C for 5 mins, UO$_{2.03}$; and (d) pore distributions with sintering temperatures.](image)
2.2.2 Pore Size/Pore Structure and fuel chemistry Control by ex-situ thermal annealing

We demonstrated the possibility of controlling the pore structure by varying the SPS conditions in which almost 100% pores are distributed at the grain boundaries including triple junctions, offering the possibility of investigating how the pore structure and grain boundaries coverage affecting thermal transport properties. On the other hand, the fuel chemistry also varies with a hyper-stoichiometric range from UO$_{2.21}$ to U$_{2.03}$, depending sintering conditions. It is highly desirable to have a similar stoichiometry for the sintered samples but with drastic different pore structures (see Figure 2.7) such that the separate effects of the pore structure/distribution and fuel chemistry can be probed.

In this quarter, a new batch of samples was synthesized to demonstrate the reproducibility of controlling microstructures, and the effects of the starting powders (e.g., with different starting stoichiometry UO$_{2.38}$) with different sinterability on the sintering behavior were probed. Fig. 2.8A shows the pore evolution as a function of sintering temperature. Similarly, almost 100% pores were located at the grain boundaries or triple junctions for the sample sintering at 1000 ℃ for 5 mins. The dominant pore distributions at the grain boundaries can be attributed to the neck formation and subsequent pore elimination. Grain size was determined to be around 0.43 microns. With further increase in the sintering temperature to 1100 ℃ for 5 mins, the microstructure of the fuel pellets experienced a grain coarsening and the average grain size increased to 1.5 microns, and 3.1 micron for the sample sintered at 1300 ℃. Accompanying the grain coarsening and grain boundary migration at higher temperature, the distribution of pores gradually shifts from grain boundaries and triple junctions to grain interior, forming inner-granular pores (see Fig. 8A). This result is consistent with the previous batch samples (as shown in Fig. 2.7) despite that the temperature for pore control and pore evolution are different, mainly due to the different starting stoichiometry affecting sintering behavior. This further confirms the flexibility and reproducibility that different pore structures can be manipulated by SPS process, depending sintering conditions and powder sinterability.

Post-sintering thermal annealing was performed on the second batch samples in a reduced Ar-4%H$_2$ environment in order to further control the fuel stoichiometry. Figs. 8B and 8C show the XRD patterns of the pellets densified by at 1100 and 1300 ℃ for 5 mins at different durations up to 96 hours. A consistent shift of the XRD diffraction peaks was identified for both samples as a result of reduction of the fuel chemistry from hyperstoichiometric UO$_{2+x}$ to more stoichiometry. Figure 8D
shows the fuel chemistry evolution for both samples, and it shows clearly that initial reduction up to 24 hrs leads to significant reduction of the stoichiometry. At longer durations, the reduction of fuel chemistry is level off with much change to \( \sim UO_{2.05} \). Microstructure characterization by SEM was shown in Fig. 2.9 before and after thermal annealing. No significant microstructure evolution was observed. For example, for the 1300-pellet annealed for 96 hours, grain size was changed with the uncertainty from 1.5 (±0.3) \( \mu m \) after sintering to 1.7 (±0.3) \( \mu m \). Pore density (evaluated at numbers of pores/\( \mu m^2 \)) are 54 (±6) to 48 (±5); and the grain boundary coverage percentages by the pores are 7.5 (±1.3) and 6.8 (±1.2) for as-sintered and 96 hr-annealed samples. This comparison suggests that the fuel chemistry can be well tuned without microstructure and pore structure changes by simply post-sintering annealing and thermal reduction at a low annealing temperature of 600 °C.

2.3. Grain growth Kinetics and Pore Coarsening in dense nano-crystalline \( UO_{2+x} \) fuel pellets

Dense nano-sized \( UO_{2+x} \) pellets are synthesized by spark plasma sintering with controlled stoichiometries (\( UO_{2.03} \) and \( UO_{2.11} \)) and grain sizes (~100 nm), and subsequently isothermally annealed to study their effects on grain growth kinetics and microstructure stability. The grain growth kinetics is determined and analyzed focusing on the interaction between grain boundary migration, pore growth and coalescence.
Fig. 2.10. Microstructure features of the UO$_{2.03}$-103 nm (a), UO$_{2.03}$-144 nm (b), UO$_{2.11}$-66 nm (c), and UO$_{2.11}$-165 nm (d) in as sintered condition (first column), after annealing at 700 °C (second column), 800 °C (third column), and 900 °C (fourth column) all for 8 hours.

Fig. 2.10 summarizes the microstructural evolution of the dense nc-UO$_{2+x}$ pellets after 8 hrs annealing at different temperatures. The key observations can be made:

- Grain size increases exponentially with time in a relatively short time less than 2 hrs upon isothermal annealing, and then saturates due to the loss of driving force resulting from curvature driven-growth process;
- Higher annealing temperatures leads to larger grains as a result of enhanced grain boundary mobility;
- A dramatically morphological difference of pore growth behavior was observed in the two hyper-stoichiometric UO$_{2+x}$ samples. Closed intergranular pores are prevalent in UO$_{2.03}$ pellets; while pores in UO$_{2.11}$ pellets grows to a significantly larger size and coalesced upon annealing;
- Few intra-granular pores were observed in all pellets, indicating pore grows and migrates with grain boundaries regardless of grain sizes, stoichiometries, and porosity;
- Starting at similar grain sizes, grain growth in UO$_{2.11}$ pellets is more substantial than UO$_{2.03}$ pellets as evidenced by much bigger grain sizes after thermal annealing.

The isothermal annealing-induced grain coarsening to larger sizes for the nano-sized UO$_{2.11}$ than UO$_{2.03}$ is consistent with the fact that hyper-stoichiometric UO$_{2+x}$ is typically used for fuel sintering and fabrication. Excessive O ions in hyper-stoichiometric UO$_{2+x}$ occupy interstitial positions, leading to surplus U ion vacancies and enhancing the U ion diffusion rate and thus powder densification. The grain growth component (n) of the nc-UO$_{2.11}$ pellets is determined to be ~2.0, suggesting a classical grain growth kinetics as driven by curvature. For more stoichiometric nano-sized UO$_{2.03}$ pellets, the grain growth component is derived as ~2.5 (Fig. 2.11). The activation energies of the grain growth for UO$_{2.03}$ and UO$_{2.11}$ are determined as ~1.0 and 1.3~2.0 eV, respectively.

Hyper-stoichiometric nano-sized UO$_{2.11}$ displays greater activation energies for grain growth as compared to more stoichiometric UO$_{2.03}$, which may be attributed to the interaction between O interstitials and grain boundaries. The excess oxygen interstitials in hyper-stoichiometric UO$_{2+x}$
induce extra U vacancies in the U sublattice and thus promote the U diffusion through the vacancy mechanism, beneficial for the fuel sintering and densification. The excess oxygen interstitials can also pin grain boundaries and impedes grain boundary movement, and thus reduce the activation energy for grain coarsening. As compared with the micron-sized UO$_2$ in which volumetric diffusion dominates the grain coarsening with an activation energy of ~3.0 eV, the enhanced grain growth kinetics in nano-sized UO$_{2+x}$ suggests that grain boundary diffusion controls grain growth. The higher activation energy of more hyper-stoichiometric nano-sized UO$_{2.11}$ may be attributed to the excessive O interstitials pinning grain boundary migration.

2.4 Dense Nanocrystalline UO$_{2+x}$ Fuel Pellets Synthesized by High Pressure Spark Plasma Sintering

Upon HEBM, typically micro-sized agglomerates consisting of nanocrystalline UO$_2$ at ~30 nm in spherical shape are obtained (Fig. 2.12a). XRD (Fig. 2.12b) peaks of the prepared powder shift to higher angles than the starting reduced UO$_{2.006±0.002}$ powder, suggesting there is oxygen pickup during HEBM processing for both batches of nano-sized UO$_{2+x}$ powders milled in air or Ar environment. Based on the empirical correlation between stoichiometry and lattice parameters: \( a = 5.4705 - 0.132x \), the stoichiometry of powders changes from UO$_{2.006±0.002}$ to various hyper-stoichiometry UO$_{2+x}$ depending on the sealing environment. Minimum oxygen pickup for the UO$_{2.03±0.02}$ is found for powder milled in argon; On the contrary, appreciable oxygen pickup is evidenced by a higher stoichiometry of UO$_{2.11±0.03}$.

Besides the peak shifting due to change of oxygen concentration, the peak intensities are also much lower and peak shape broader (Note Fig. 2.12b is rescaled to better show peak shifting) than starting reduced UO$_{2.006±0.002}$ powders. This can be attributed to high concentration of point defects introduced into powders by HEBM. Those point defects could provide additional diffusion enhancement, along with a greatly-enlarged surface area, to facilitate U ion diffusion during sintering.

![Fig. 2.12. Morphology of UO$_{2+x}$ nano crystalline powder prepared by HEBM (a); XRD (b) results suggests there is various amount of oxygen being picked up by UO$_{2+x}$ nano crystalline powder depending on milling environment. Milling in air leads to higher derivation from stoichiometry than in Ar environment. SEM of fracture surface of pellets (inserted in c) densified by various sintering conditions: (c) UO$_{2.03}$ by 700 °C for 5 min, (c) UO$_{2.03}$ by 700 °C for 20 mins, (d) UO$_{2.11}$ by 600 °C for 20 min, (e) UO$_{2.11}$ by 700 °C for 20 mins](image-url)
To densify the nano crystalline $\text{UO}_2+x$ powder into dense pellet form, pulsed high electric current passing through powder compact in graphite dies was adopted during the SPS process and spark discharge was generated with localized high temperature zone up to ten thousands °C. Therefore, necks form on particle surface generally display features of melting state. This factor allows powder densification occur at much lower temperature so as to avoid significant grain growth during densification. It distinguishes SPS from other sintering methods, such as pressureless sintering, hot isothermal pressing, and microwave sintering. Despite these advantages, it is still very challenging to densify HEBMed nc-$\text{UO}_2$ powders by SPS meanwhile maintaining the original nano-sized grain structure of the powdered samples. The lowest temperature for fully dense UO$_2$ pellet (> 95 % TD) was reported as 1000 °C with grain size around 1 µm.

In general, graphite dies typically used for SPS can hold pressure up to ~ 100 MPa. By replacing graphite with silicon carbide or tungsten carbide, it is possible to hold pressures up to several hundred MPa during sintering to enhance sintering kinetics. Additionally, the change of die materials also avoids severe carbon contamination from graphite dies on sintered pellets. Through HPSPS, dense nano alumina, yttria, and zirconia have been obtained and found to be transparent due to high density, i.e. low porosity usually < 0.1 %.

As summarized in Table.1, nanocrystalline UO$_2$ powders are successfully densified (> 95 % TD) at low temperatures of 600-700 °C into dense pellets (inert in Fig. 1c-f) by HPSPS. The sintered grain size generally ranges from 50 to 200 nm, suggesting the nano feature has been well preserved during HPSPS. Instead of trans-granular fracture for the micron-sized $\text{UO}_2+x$ fuel, intergranular pattern dominates the fracture surface of the sintered nano $\text{UO}_2+x$ fuel pellets. Furthermore, compared with the sphere-shaped powder crystallites, grains in sintered pellets as revealed by SEM from the fractured surface are polyhedron shaped, suggesting the occurrence of grain boundary migration and grain growth during sintering.

XRD and Micro-Raman are combined to provide insight into the fuel chemistries of the sintered dense nano $\text{UO}_2+x$ fuel pellets. Both techniques have been widely used to study crystal structure, stoichiometry and defects of $\text{UO}_2+x$. Stoichiometric UO$_2$ has a fluorite structure with $Fm-3m$ asymmetry (No. 225). The crystal can be described as a simple cubic O$^2-$ ion sublattice inside a face centered cubic U$^{4+}$ ion sublattice. One feature of UO$_2$ fluorite structure is its flexibility and capability to incorporate large amount of foreign O ions to form various oxide phases. *Ab initio* DFT calculation indicates the formation of foreign oxygen interstitials in fluorite UO$_2$ structure is negative, suggesting the incorporation of O ions into the UO$_2$ base structure is a spontaneous process.

With increase of hyperstoichoimetry of UO$_2+x$ in the compositional range between UO$_2$ and UO$_3$, as much as 16 distinctive phases have been identified. The incorporation of interstitial oxygens distort the ideal UO$_2$ fluorite structure, and may lead to the transition from ideal fluorite to new crystal structures. For example, between stoichiometric UO$_2$ and U$_4$O$_9$ (UO$_{2.25}$), increased amount of incorporated O ions bridge the neighboring U ions and augment their electronic interactions, resulting in the formation of U$^{6+}$ ions to maintain the charge balance. Those high valence state U ions have smaller ionic radius and would lead to a shrinkage of U ion sublattice. Meanwhile, the crystal structure of UO$_2+x$ remains essentially cubic same as stoichiometric UO$_2$. Instead, the lattice parameter varies with the degree of non-stoichiometry $x$, allowing the determination of the stoichiometry of fuel chemistry based on lattice parameters calculated from XRD results for UO$_{2.25}$. Beyond this stoichiometry range, however, oxide phases begin to evolve into different crystal structures, for
example, tetragonal pseudocubic for \( \text{U}_3\text{O}_7 \) and orthorhombic [30] structure for \( \text{U}_3\text{O}_8 \). The fuel chemistry of the pellets is determined as \( \text{UO}_{2.03} \) and \( \text{UO}_{2.11} \) for the sintered pellets. All XRD peaks show appreciable peak shifting for \( \text{UO}_{2.11} \) pellets to higher angle than \( \text{UO}_{2.03} \), consistent with stoichiometry estimated by peak position.

Table 3.1: Sintering conditions and properties of sintered fuel pellets

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<tr>
<th>Sample ID</th>
<th>Sintering Temp. °C</th>
<th>Sintering time/mins</th>
<th>Pressure MPa</th>
<th>Density % TD</th>
<th>Grain size nm</th>
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<td>750</td>
<td>96.0±1.1</td>
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<td>750</td>
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</tbody>
</table>

XRD diffraction (Fig. 2.13a) patterns of the sintered dense \( \text{UO}_{2+x} \) pellets indicate a single phase \( \text{UO}_{2+x} \) for the pellets densified by SPS. Generally, based on U-O phase diagram, single phase \( \text{UO}_{2+x} \) is metastable and only exists at temperature above 400-1100 °C varying with \( x \) values. Therefore, dual phases of \( \text{UO}_2 \) and \( \text{U}_4\text{O}_9 \) should co-exist at room temperature for the sintered pellets with fuel chemistry \( \text{UO}_{2.03} \) or \( \text{UO}_{2.11} \). The existence of \( \text{UO}_{2+x} \) single phase in the nano-sized densified pellets at room temperature is attributed to highly non-equilibrium conditions of rapid quenching. In our SPS, the cooling rate is kept at 50 °C/min, fast enough to keep the high temperature single \( \text{UO}_{2+x} \) phase.

To validate our hypothesis, post-sintering annealing was conducted at 900 °C for 4 hrs for nano \( \text{UO}_{2.03} \) pellets. The temperature is deliberated chosen to guarantee the phase purity of \( \text{UO}_{2+x} \) based on U-O phase diagram, the phase should be single phase \( \text{UO}_{2+x} \). Upon cooling to room temperature, the resultant phase is highly cooling rate dependent (Fig. 2.13b). For instance, when the annealed sample is cooled down at a speed of ~50 °C, the consequential phase is single phase \( \text{UO}_{2+x} \); however, if a cooling rate of ~20 °C is applied, the resultant phase is a dual phase mixture of \( \text{UO}_{2+x} + \text{U}_4\text{O}_9 \). Such a cooling rate dependence confirms the hypothesis that high cooling rate of SPS is the primary reason for the successful phase preservation of \( \text{UO}_{2+x} \) to room temperature. Similar single

![Fig. 2.13. XRD results of sintered dense nano \( \text{UO}_{2+x} \) pellets indicates sintered pellets are single phase \( \text{UO}_{2+x} \) with shifted peak positions to higher angle for \( \text{UO}_{2.11} \) than \( \text{UO}_{2.03} \) pellets due to larger derivation of stoichiometry.](attachment:image.png)
phase UO$_{2+x}$ pellets at room temperature have also been reported by SPS.

Micro-Raman is utilized to provide information on interaction between U and O ions in the sintered pellets. Based on previous literature interpretation on correlation between Raman peaks profile and stoichiometry of UO$_{2+x}$, the dominant defects within each stoichiometry is predicted. For a $x$ value less than 0.05, O ion interstitials randomly distribute in UO$_2$ base structure without interaction between each other, and U ion sublattice preserves the cubic symmetry. Therefore, XRD spectra, due to the much larger scattering factor of U ions than O ion, remain essentially the same except slight peak shifting. At this stoichiometry range, three typical Raman peaks are observed: 445 cm$^{-1}$ for T$_{2g}$ U-O stretch, 575 cm$^{-1}$ for a F$_{1u}$ IR active longitudinal optical (LO) model, and 1150 cm$^{-1}$ for 2LO model. Although there is a debate in literature about the origin of 2LO @ 1150 cm$^{-1}$, its existence in Raman spectrum for stoichiometric UO$_2$ have been experimental verified. The intensity of this peak fades with increase of degree of hyperstoichiometry and disappears when $x$ is higher than 0.09. Also, the integrated area underneath this peak was used as an index for integrity of UO$_2$ subject to laser beam damage induced oxidation in air.

For UO$_{2.03}$ pellets, three characteristic Raman peaks for stoichiometric UO$_2$ dominates the acquired Raman spectra (Fig. 2.14). Furthermore, the intensity of 2LO model at 1150 cm$^{-1}$ is much stronger than T$_{2g}$ U-O stretch @ 445 cm$^{-1}$. Such a dominance in peak intensity has also been observed for nuclear fuel grade stoichiometric UO$_2$ fuel excited by same laser source, indicating that the sintered dense nano UO$_{2.03}$ pellets are nearly stoichiometric. In the sintered dense nano UO$_{2.03}$ pellets, randomly distributed O interstitials dominates.

With increase of $x$ value to a range from 0.05 to 0.15, Willis defect cluster begins to form due to increased concentration of O ion interstitials incorporated. Willis defect clusters accommodate two O interstitials, two displaced oxygen interstitial atoms and two oxygen vacancies. Such a 2:2:2 configuration of oxygen defect clusters was firstly reported by Willis through neutron scattering, and thereafter named as Willis cluster. Due to distortion on the O sublattice, multiple Raman peaks merge, and the featured Raman active models include 1 A$_{1g}$, 2 B$_{1g}$ and 3 E$_{g}$. Therefore, for the sintered dense nano UO$_{2.11}$ pellets, the featured peaks for low degree of hyperstoichiometry, such as T$_{2g}$, LO, and 2LO peaks are replaced by two main broad peaks. The low shift bands from 200 to 650 cm$^{-1}$ can be perfectly assigned to the abovementioned Raman active models for Willis clusters, indicating it is the dominant defect type in those pellets. Peaks at $\sim$ 800 cm$^{-1}$ can be attributed to the harmonics of A$_{1g}$ and E$_{g}$ U-O stretch modes. As a matter of factor, the estimated stoichiometry UO$_{2.11}$, closely match with Willis’s estimated degree of hyperstoichiometry, UO$_{2.12}$, for Willis cluster to be the dominant defect type.
2.5 Stoichiometry – Defect – Post sintering processing

Isothermal annealing at 600 °C was also performed on the slightly oxygen enriched composition nano-sized UO$_{2+x}$. Hyperstoichiometry UO$_{2.02}$ in a reducing environment in order to achieve nearly perfect stoichiometry UO$_2$. No grain coarsening occurred upon isothermal annealing without grain coarsening as observed in Figs. 3.4A and 4B. Systematic X-ray diffraction shows the shift of the (311) and (420) upon thermal annealing for 24 hrs as a result of reduction and more nearly perfect fluorite lattice without structural distortion. A distinct feature was observed in which the XRD peaks become narrow with increased annealing time, mainly as a result of the microstrain relaxation with isothermal annealing. No peak shift occurred for the samples annealed with shorter duration less than 24 hrs, suggesting a similar chemical composition for these materials.

Uranium oxide also demonstrate a complex defect behavior associated with the degree of non-stoichiometry from isolated oxygen interstitial, di-interstitial, split interstitial to Willis defect clusters. The bond environment and structures of the ideal fluorite structure vary with different defect behavior, specifically at oxygen sublattices. As X-ray diffraction is mainly sensitive to the scattering of uranium lattice, the subtle structure distortion and defect behavior are also characterized using Raman spectroscopy with high sensitivity to oxygen sublattices. Fig. 2.16 shows the Raman spectra of the nano-sized UO$_2$ annealed at different duration and thus different stoichiometry (e.g., UO$_{2.006}$ annealed for 24 hrs; UO$_{2.019}$ annealed for 16 hrs). Characteristics Raman peaks of T$_{2g}$ (vibration mode of the U-O bond) at 445 cm$^{-1}$, longitudinal optical mode at ~575 cm$^{-1}$, and the second order of the longitudinal optical phonon mode (2LO) at 1150 cm$^{-1}$ were clearly identified, suggesting a nearly perfect fluorite structure in the UO$_2$. With increased annealing time, a distinct feature was observed in which the intensity of the 2LO mode increases more rapidly than LO and T$_{2g}$, indicating the possible dissociation of the order oxygen interstitial clusters at oxygen enriched samples to more disordered/isolated oxygen interstitial and thus less structural distortion from the ideal fluorite.
Chapter 3. Thermal Transport of Sintered UO$_2$ fuels

3.1. Microstructure control and thermal transport of the sintered UO$_2$ fuels

In this work, UO$_2$ fuels with controlled microstructure (grain size, pore size/structure and fuel chemistry) were prepared by high energy ball milling of the hyperstoichiometric UO$_{2+x}$ powders purchased commercially, and consolidated by spark plasma sintering. Dense nano-sized UO$_2$ fuel pellets with controlled stoichiometry were sintered by SPS. The effects of different SPS sintering parameters on the pore size and distribution were investigated. To further control the pore structure and fuel chemistry, systematic thermal annealing of the sintered fuels with the controlled pore structure was performed in a reduced environment of Ar-4%H$_2$. The controlled microstructure and fuel chemistry enable the investigation of the separate effects of pore structure and fuel chemistry on thermal transport behavior. Thermal transport behavior of these sintered UO$_2$ fuels are characterized by laser flash measurement and correlated with different microstructure. The detailed microstructure control and thermal transport are elaborated below.

3.1.1. Experimental

UO$_{2.16}$ powders purchased from International Bio-analytical Industries Inc. USA were firstly reduced to UO$_{2.006}$ (±0.002) by thermal annealing in a reduced environment before HEBM. Two batches of nanocrystalline UO$_{2+x}$ powders were prepared by sealing HEBM milling jar in either a glove box environment (<30 ppm O$_2$) or ambient air environment, respectively. The HEBM was performed with 20 hours of milling at a speed of 500 rpm with 15 minutes on and 10 minutes off in ambient environment. The zirconia ball (2 mm diameter) to powder weight ratio was 10:1. HPSPS was conducted in an argon environment using a WC die. The temperature was monitored by a K-type thermocouple buried in the WC punch, which is 2 mm away from the powdered sample. Temperature and pressure increased simultaneously during SPS sintering until a peak pressure of 750 MPa was achieved with the final sintering temperature, and a cooling rate of 50 °C/min was adopted. With WC used as die materials, no significant reduction of the oxides, typically observed from graphite dies during SPS sintering, was expected during sintering for the investigated sintering temperature and durations.

Post-sintering microstructure characterization was conducted using a Carl Zeiss Supra 55 (Jana, Germany) field emission SEM. Grain size was determined using a rectangular intercept method following ASTM E122-88 standard (1992). The average size is given by

$$D = \sqrt{\frac{4A}{\pi \left( N_I + \frac{N_0}{2} \right)}}$$

Where A is the area of an arbitrary draw rectangle, $N_I$ and $N_0$ are the numbers of grains in the rectangle and on the boundary of the rectangle, respectively. At least two hundred grains were analyzed for each pellet. Error bars are standard deviations of the measured grain size for the same pellet from different locations.

X-ray diffractions of the sintered pellets were acquired by a Panalytical X’Pert XRD system (Westborough, MA, US.) using Cu $K\alpha$ ($\lambda = 1.5406$ Å) irradiation. Before each run, the x-ray beam was aligned with a direct beam through a 0.2 Cu beam attenuator, and further calibrated from scanning
on a standard Al₂O₃ sample. Sample height was aligned with the x-ray beam bisected. A scanning step of 0.013° with 2 seconds per step was adapted. The O/U ratio was determined from the following empirical equation: 

\[ a = 5.4705 - 0.132x \]

where \( a \) is the derived lattice parameter and \( x \) is the stoichiometry derivation of UO₂ₓ from stoichiometric UO₂. For the purpose of O/U ratio determination from XRD spectra, peaks collected around a scanning span of 25 to 90 was statistically summarized.

Micro-Raman spectra were collected at room temperature through a Renishaw system Micro-Raman spectrometer equipped with an argon-ion laser (514.5 nm). A typical spectrum was acquired with an exposure time of 10 seconds and 10 accumulations under an operation power of 20 mW. An extended scanning region from 200 to 1500 cm⁻¹ was chosen since it contains the featured peaks for UO₂. For each pellet, multiple locations were checked so that the spectrum is representative. The laser power was fixed at 100% as lower laser power yielded similar spectra but a higher background to signal ratios.

Thermal diffusivity of the sintered pellets was measured by a NETZSCH LFA 457 MicroFlash in a purged Ar environment (industrial level, 300 ppm O₂) from 400 K to 900 K. Both sides of samples were coated with sprayed graphite. Furnace temperature increased at a rate of 5 °C/min and stayed at each measuring temperature for roughly 30 minutes for better temperature stability and data point acquisition. At each temperature, 10 data points were obtained by fitting the signal-time curve using Cape-Lehman model. 3% are added to thermal diffusivity and thermal conductivity due to the used laser flash technique. Thermal conductivity was calculated as the product of thermal diffusivity, density, and specific heat capacity. The effect of thermal expansion on density was considered by using the empirical equation from literature. The specific heat capacity as functions of stoichiometry and temperature was used in the calculation of thermal conductivity.

Both thermal diffusivity and conductivity were normalized to 100% TD using the Loeb equation

\[ \lambda_{measured} = \lambda_{100\% TD}(1 - P \beta) \]

where \( P \) is the measured porosity, and \( \beta = 2.46 - 0.70 \times 10^{-3} T (K) \), a temperature dependent value experimentally fitted for UO₂. Pellet phase compositions before and after LFA were also studied by XRD and micro-Raman measurements.

### 3.2. Thermal transport behavior with microstructure

#### 3.2.1. Defect behavior and stoichiometry effects on Thermal Transport

Uranium oxide demonstrate a complex defect behavior associated with the degree of non-stoichiometry from isolated oxygen interstitial, di-interstitial, split interstitial to Willis defect clusters. The bond environment and structures of the ideal fluorite structure vary with different defect behavior, specifically at oxygen sublattices. As X-ray diffraction is mainly sensitive to the scattering of uranium lattice, the subtle structure distortion and defect behavior are also characterized using Raman spectroscopy with high sensitivity to oxygen sublattices. Fig. 3.1A shows the Raman spectra of the nano-sized UO₂ annealed at different duration and thus different stoichiometry (e.g., UO₂ₐ₀₆ annealed for 24 hrs; UO₂₀₁₉ annealed for 16 hrs). Characteristics Raman peaks of T2g (vibration mode of the U-O bond) at 445 cm⁻¹, longitudinal optical mode at ~575 cm⁻¹, and the second order of the longitudinal optical phonon mode (2LO) at 1150 cm⁻¹ were clearly identified, suggesting a nearly perfect fluorite structure in the UO₂. With increased annealing time, a distinct feature was observed in which the intensity of the 2LO mode increases more rapidly than LO and T2g, indicating
the possible dissociation of the order oxygen interstitial clusters at oxygen enriched samples to more disordered/isolated oxygen interstitial and thus less structural distortion from the ideal fluorite.

The nearly perfect stoichiometric composition (UO$_{2.006}$) shows enhanced thermal conductivity than UO$_{2.02}$ as expected (Fig. 3.1B). For the samples with same stoichiometry UO$_{2.02}$, thermal conductivity varies significantly with the subtle of defect structure changes in the oxygen sublattice, highlighting important effects of the defect structure on thermal transport behavior of the UO$_2$ fuels.

### 3.2.2 Thermal conductivity of SPS densified nano-sized UO$_{2+x}$ pellets

Thermal diffusivity of the densified nano-sized UO$_{2+x}$ pellets (see Fig. 3.2) is measured by micro laser flash, and thermal conductivity is calculated accordingly. Both measured thermal diffusivity and calculated thermal conductivity for the sintered dense nano-sized UO$_{2+x}$ pellets decrease with temperature up to 900 K, showing a typical behavior of ceramic materials due to the deteriorated Umklapp scattering of phonons with increased temperature. The reversed temperature dependence for the two different UO$_{2.03}$ fuel pellets indicates the dominant phonon scattering mechanism is Umklapp scattering at the presence of low concentration of random oxygen interstitial defects. Compared with UO$_{2.03}$ fuel pellets, the thermal conductivity of UO$_{2.11}$ fuel pellets is relative insensitive to temperature, indicating the major scattering for phonons is not from Umklapp scattering, rather atomic level crystal defects, i.e. the Willis clusters. Furthermore, the thermal conductivities of UO$_{2.11}$ fuel pellets are much lower than these of UO$_{2.03}$ throughout the investigated temperature, indicating the Willis clusters have a greater influence than randomly distributed oxygen interstitials on phonon scattering.

![Fig. 3.1. Raman spectroscopy of the UO$_2$ samples annealed at different durations (A) (green: 24 hrs; blue, 16 hrs; red: 8 hrs; and black: as sintered) and thermal conductivity measurement (B) showing important effects of the defects in UO$_2$ structure](image)
**Fig. 3.2** Thermal diffusivity (a), and conductivity (b) of the sintered dense nano-sized UO$_{2+x}$ pellets normalized to 100 % TD, demonstrating a dominant role played by fuel chemistry on thermal properties. Suppression of the thermal conductivity is also observed for the nano-sized UO$_{2.11}$ as a result of the enhanced grain boundary scattering due to the refinement of grain size to 66 nm.

Literature data reported on temperature dependent thermal diffusivity of the micron-sized nominal UO$_{2+x}$ with various x values are also plotted in Fig. 3.2a for comparison. Thermal transporting properties for the sintered dense nano-sized UO$_{2+x}$ pellets reported here show overall a good match with those literature data for micron-sized UO$_{2+x}$. For example, the thermal diffusivity of the nano-sized UO$_{2.03}$ is consistent with the micron-sized counterpart with a similar stoichiometry UO$_{2.02}$ (see Fig. 3.2a). This result suggests that the impact of the increased grain boundaries on the phonon transport above room temperature with the grain size above 100 nm is less noticeable.

On the other hand, with the further refinement of the grain size below 100 nm, a systematic reduction of ~25% in thermal diffusivity in general is identified for the nano-sized UO$_{2.11}$ with a grain size reduction from 165 nm to 66 nm based on statistical analysis of data at different measurement temperatures. The effect of the phase evolution during laser flash measurement on thermal properties at different temperature regime is analyzed in next session. Since the grain size is the only variable and the fuel pellets have the same stoichiometry UO$_{2.11}$, the inferior thermal transport behavior of the 66 nm UO$_{2.11}$ can be attributed to the additional scattering of phonons from increased grain boundary area beside the defect scattering from Willis clusters. As compared with micron-sized UO$_{2+x}$, the thermal diffusivity of the nano-sized UO$_{2.11}$ is close to that of the micron-sized counterpart with a chemical stoichiometry of UO$_{2.2}$ (see Fig. 3.2a for comparison). The reduction of thermal conductivity resulting from the grain boundary scattering of nano-sized grain structure is comparable to the suppression effect of increasing degree of non-stoichiometry from UO$_{2.11}$ to UO$_{2.2}$.

These results underscore the decisive role played by fuel stoichiometry on the thermal properties of oxide fuels. The effects of grain size on thermal transport behavior above room temperatures is subtle, and may be more significant with the length scale below 100 nm and at lower temperatures. Although direct measurement of thermal conductivity of nano-sized UO$_2$ dense pellets is not previously reported in literature, there is a fairly large amount of reports on yttria stabilized ZrO$_2$ (YSZ) being investigated as thermal barrier coating materials. Dense nanocrystalline pure zirconia was reported to show no difference in thermal conductivity with larger grain-sized one in spite of refined grain size of 63 nm. A consistent reduction of thermal conductivity of YSZ with grain size from 98 nm to 10 nm was reported and the value for 10 nm sample is nearly half of that for coarse grained or single crystal YSZ. An implication of these observations is that grain size has a direct impact over the thermal conductivity of ceramic oxides if the grain size below a certain value comparable to the mean free path of the phonons. Further experimental data are needed to fully elucidate the effects of grain size on the suppression of thermal conductivity of oxide fuels with controlled fuel stoichiometry at different temperatures.

### 3.2.3. Formation of U$_4$O$_{9-y}$ in SPS densified nano-sized UO$_{2+x}$ pellets by Laser Flash Measurements

As indicated in the U-O phase diagram, UO$_{2+x}$ coexists with U$_4$O$_{9-y}$ in thermal equilibrium conditions up to a temperature range from 700 to 1500 K depending on oxygen concentration when x is less than 0.21. As a result, the single phase UO$_{2+x}$ in the as-sintered pellets is thermodynamically
metastable and can experience phase decomposition during LFA thermal diffusivity measurements. With slight increase of measuring temperature, the as sintered single phase UO$_{2+x}$ could change to a mixture of UO$_{2+x}$ and U$_4$O$_{9-y}$. Further increase the measuring temperature into single phase UO$_{2+x}$ solid solution regime, the U$_4$O$_{9-y}$ phase may re-dissolve into the matrix and reform the single phase UO$_{2+x}$ matrix. The aforementioned phase change behaviors have been studied previously through neutron irradiations and the precipitation of U$_4$O$_{9-y}$ from single phase UO$_{2+x}$ can be initiated at a low temperature of 350 K during heating$^{44}$. The impact of the formation and dissolution of U$_4$O$_{9-y}$ phase on thermal conductivity of the sintered dense nano-sized UO$_{2.03}$ pellets are summarized in Fig. 3.3 and Fig. 3.4.

**Fig. 3.3.** Phase analysis and impacts on the thermal performance of the UO$_{2.03}$ dense nano-sized pellets based on phase diagram summarized in literature Ref. [43]. The curve is fitted using the data at single phase UO$_{2+x}$ regime above ~770K based on model proposed in literature.

Fig. 3.3 depicts the temperature dependent thermal conductivity as well as phases projected based on U-O phase diagram. The thermal conductivity data for single phase nano-sized UO$_{2+x}$ above ~770K was fitted against an empirical model$^{45}$ with equation of thermal conductivity (TD) = 1/(A+B*T), where A denotes thermal conductivity of UO$_2$ from the contribution of phonon scattering at paramagnetic U ions and atomic crystal defects which is temperature insensitive; and B is a fitting constant that manifest the role played by temperature. Obtained A and B value is 3.6 cm·K/W and 0.0296 cm/W, respectively, matching closely with values reported for polycrystalline UO$_2$ of 3.45 cm·K/W and 0.0229 cm/W. The extrapolated thermal conductivities from the fitting at the two-phase, i.e UO$_{2+x}$ and U$_4$O$_{9-y}$ coexisting regime, i.e. below ~770 K, is lower than measured values. This finding is consistent with results reported in a previous literature$^{40}$. Such an enhancement of thermal conductivity by precipitation of U$_4$O$_{9-y}$ from UO$_{2+x}$ matrix may lie on the removal of O interstitials in the UO$_{2+x}$ lattice during the formation of U$_4$O$_{9-y}$$^{46}$, in which the U$_4$O$_{9-y}$ phase acts as O interstitial sinks for the surrounding microstructure. Hypothetically, as compared with secondary phase U$_4$O$_{9-y}$, the phonon scattering at O interstitials has a greater impact over thermal conductivity of UO$_{2+x}$. Upon the removal of oxygen interstitials to form secondary U4O9-y phase, the dominant UO$_{2+x}$ phase becomes more stoichiometric toward UO$_2$ and thus the two-phase composite display higher thermal
conductivity. This is also consistent with the drop of thermal conductivity from two-phase coexisting regimes into the single phase $\text{UO}_{2+x}$ regime above $\sim 770$ K.

Fig. 3.4. Phase transformation from single phase $\text{UO}_{2+x}$ to a two-phase mixture of $\text{UO}_{2+x}$ and $\text{U}_4\text{O}_9$.\textsubscript{y} before and after LFA measurement are manifested by XRD (a, b) and Raman (c) spectrum. The effects on thermal diffusivity (d) are shown by different values obtained at room temperature before (boxed values) and after (unboxed ones) LFA measurements.

After LFA measurements, the samples are cooled down to room temperature at a cooling rate of 20 K/min. The dominant phase remains unchanged as $\text{UO}_{2+x}$ (Fig. 3.4a); however, because of the slow cooling rate, the as-cooled phase is a mixture of $\text{UO}_{2+x}$ and $\text{U}_4\text{O}_{9-y}$ (as shown in Fig. 3.4b). Raman spectrum measurements also show increasing intensity of the peak at 630 cm\textsuperscript{-1} and shift of the 445 cm\textsuperscript{-1} peak to high wavelengths (Fig. 3.4c). This further corroborates the formation of $\text{U}_4\text{O}_{9-y}$ phase after LFA thermal measurements. It is noted that the room temperature thermal diffusivity of the mixture phases after LFA measurements decreases slightly as compared with that of single phase $\text{U}_{2+x}$ before LFA measurements. The reduction of the thermal diffusivity during cooling cycle than heating cycle at room temperature LFA measurement maybe due to the lower thermal diffusivity for $\text{U}_4\text{O}_{9-x}$ as compared with the single phase $\text{UO}_2$. Structural variations, e.g., intergranular pores or grain boundary cracks due to the density mismatch between $\text{UO}_2$ and $\text{U}_4\text{O}_9$ (Fig. 3.4d) may also occur, impacting thermal transport behavior of dense nano-sized $\text{UO}_{2+x}$ pellets.

3.2.4 Effect of pore structures on thermal conductivity

3.2.4.1. Pore size and structure control
The control of pore structure and distribution is very challenge as the sintering process involves densification by eliminating pores and grain coarsening. It is the interplay of the diffusion of the atoms through different mechanisms and grain growth eventually determine the pore size and pore structure. By controlling the SPS parameters, we have demonstrated the flexibility in controlling the pore size and grain size simultaneously. For example, as shown in Fig. 3.5, the grain sizes can be controlled from ~2.2 μm up to 3.8 μm, and the pore size also increases from 163 nm to ~300 nm upon consolidation of SPS at greater temperatures.

![Fig. 3.5. Control of the pore and grain sizes simultaneously by SPS process.](image)

Further possibilities were demonstrated in controlling the pore distribution (Fig. 3.6), in which all of the pores are distributed on the grain boundaries and triple junctions for SPS-densified pellets UO$_{2.21}$ upon consolidated at 1100 °C for 5 mins. The dominant pore distribution at the grain boundaries can be attributed to the neck formation, and the grain size was determined as ~1.2 μm. No significant growth coarsening was observed as a result of relatively lower SPS temperature. With further increase in the sintering temperature to 1200 °C for 5 mins, the microstructure of the fuel pellets experienced a grain coarsening and the average grain size increased to 2.6 μm. Accompanying with the grain coarsening and grain boundaries migration at high temperature, the pores distributed at the grain boundaries and triple junctions were embedded inside the large-sized grains to form inner-granular pores. In addition to the grain size and pore distribution, fuel chemistry also varied approaching to more stoichiometry from UO$_{2.21}$ to UO$_{2.03}$ with higher sintering temperatures due to the in-situ reduction process resulting from SPS sintering. Different pore geometries occurred including sphere pores within grains, triangle pores at grain boundaries and triple junctions, and elliptical pores at grain boundaries. We have performed systematic analysis on the pore size and distributions for pores with different geometries, and the pore coverage areas were also determined.

![Fig. 3.6. Control of pore distribution by varying SPS parameters: (a) 1100 °C for 5 mins, UO$_{2.21}$; (b) 1200 °C for 5 mins, UO$_{2.08}$; (c) 1300 °C for 5 mins, UO$_{2.08}$; and (d) pore distributions with sintering temperatures.](image)
3.2.4.2 Pore Size/Pore Structure and fuel chemistry Control by ex-situ thermal annealing

We demonstrated the possibility of controlling the pore structure by varying the SPS conditions in which almost 100% pores are distributed at the grain boundaries including triple junctions, offering the possibility of investigating how the pore structure and grain boundaries coverage affecting thermal transport properties. On the other hand, the fuel chemistry also varies with a hyper-stoichiometric range from UO$_{2.21}$ to UO$_{2.03}$, depending sintering conditions. It is highly desirable to have a similar stoichiometry for the sintered samples but with drastic different pore structures (see Figure 3.6) such that the separate effects of the pore structure/distribution and fuel chemistry can be probed.

Further experiments were demonstrated the reproducibility of controlling microstructures, and the effects of the starting powders (e.g., with different starting stoichiometry UO$_{2.38}$) with different sinterability on the sintering behavior were probed. Figure 3.6A shows the pore evolution as a function of sintering temperature. Similarly, almost 100% pores were located at the grain boundaries or triple junctions for the sample sintering at 1000 °C for 5 mins. The dominant pore distributions at the grain boundaries can be attributed to the neck formation and subsequent pore elimination. Grain size was determined to be around 0.43 microns. With further increase in the sintering temperature to 1100 °C for 5 mins, the microstructure of the fuel pellets experienced a grain coarsening and the average grain size increased to 1.5 microns, and 3.1 micron for the sample sintered at 1300 °C. Accompanying the grain coarsening and grain boundary migration at higher temperature, the distribution of pores gradually shifts from grain boundaries and triple junctions to grain interior, forming inner-granular pores (see Fig. 3.6). This result is consistent with the previous batch samples despite that the temperature for pore control and pore evolution are different, mainly due to the different starting stoichiometry affecting sintering behavior. This further confirms the flexibility and reproducibility that different pore structures can be manipulated by SPS process, depending sintering conditions and powder sinterability.
Post-sintering thermal annealing was performed on the second batch samples in a reduced Ar-4%H₂ environment in order to further control the fuel stoichiometry. Figs. 3.7b and c show the XRD patterns of the pellets densified by at 1100 and 1300 °C for 5 mins at different durations up to 96 hours. A consistent shift of the XRD diffraction peaks was identified for both samples as a result of reduction of the fuel chemistry from hyperstoichiometric UO₂₊ₓ to more stoichiometry. Figure 3.7D shows the fuel chemistry evolution for both samples, and it shows clearly that initial reduction up to 24 hrs leads to significant reduction of the stoichiometry. At longer durations, the reduction of fuel chemistry is level off with much change to ~UO₂₀.₅. Microstructure characterization by SEM was shown in Fig. 3.8 before and after thermal annealing. No significant microstructure evolution was observed. For example, for the 1300-pellet annealed for 96 hours, grain size was changed with the uncertainty from 1.5 (±0.3) µm after sintering to 1.7 (±0.3) µm. Pore density (evaluated at numbers of pores/µm²) are 54 (±6) to 48 (±5); and the grain boundary coverage percentages by the pores are 7.5 (±1.3) and 6.8 (±1.2) for as-sintered and 96 hr-annealed samples. This comparison suggests that the fuel chemistry can be well tuned without microstructure and pore structure changes by simply post-sintering annealing and thermal reduction at a low annealing temperature of 600 °C.

### 3.2.4.3 Thermal Transport behavior and the effect of pore distribution

Those three pellets have similar grain sizes but dramatically different on pore size/distribution and temperature dependent thermal conductivity (Fig. 3.9a). The difference of thermal conductivity is most appreciable at low temperature when phonons are the primary carrier of heat. The phonon wave length, proportionally determining thermal conductivity of ceramics, decreases with increase of scattering sources like point defects, pores, and grain boundary surface. At the as-sintered conditions, due to coupled effects from different hyper-stoichiometry (an indicator of concentration of point defects) and pore size/distribution, it is impossible to single out the decisive factor.

Through annealing in Ar-4 vol% H₂ environment at 600 °C, we were be able to reduce the aforementioned hyperstoichiometric UO₂₊ₓ pellets into lower hyper level by controlling the reducing duration without alternation of microstructure due to the low reducing temperature. Stoichiometries are estimated by XRD peak position as shown in Fig. 3.9b. As shown in Fig. 3.9c, full density thermal conductivity at 300 K for different UO₂₊ₓ pellets could have dramatically different thermal conductivity values while stoichiometry is comparable, especially between two pellets sintered at 1100 to 1300 °C. Since the difference caused by various grain size at this micron level is negligible, those results indicates there is profound effect from the pore size/distribution on thermal conductivity of UO₂₊ₓ pellets.
Fig. 3.9. Calculated and normalized to full density thermal conductivity shows greatly difference between the pellets prepared by three sintering conditions. Post sintering annealing was conducted at 600 °C for various duration to achieve designed stoichiometry without change of microstructure features for pellets sintered at 1100 °C for 5 mins (b). The stoichiometry is estimated based on XRD peak positions. The correlations between stoichiometry and thermal conductivity at 300 K (c).
Chapter 4. Mechanical properties and Fracture behavior of the sintered UO\textsubscript{2} fuels

The mechanical properties of the sintered UO\textsubscript{2} fuels were tested by nanoindentation and microindentation testings at different temperatures of 25 °C, 300 °C, and 600 °C. The fracture behavior of the sintered fuels as functions of grain structure and temperature was investigated. Nanocrystalline UO\textsubscript{2} display higher hardness than microcrystalline counterpart, consistent with the Hall-Petch strengthening mechanism. Greater Young’s modulus and fracture toughness are also identified for the nanocrystalline UO\textsubscript{2}, and hardness and Young’s modulus decrease with temperature, suggesting better ductility of oxide fuels at greater temperature at small length scale. Hyper-stoichiometric UO\textsubscript{2} specimen displays higher hardness and fracture toughness than stoichiometric UO\textsubscript{2}, due to the impediment of the crack propagation by the oxygen interstitial atoms. These results are useful in understanding the mechanical properties of the high burn-up structure (HBS) formed in nuclear fuels during reactor operation, and also provide critical experimental data as the input for the development and validation of the MARMOT fracture model of nuclear fuels.

4.1. Introduction

Uranium dioxide (UO\textsubscript{2}) has been widely used as a major nuclear fuel form in boiling water reactor (BWR) and pressurized water reactor (PWR) for decades because of its stability and outstanding corrosion resistance. When the fuel pellet is burned in the reactor, a significant temperature gradient is generated across the fuel pellets. Meanwhile, fission products with kinetics energy of 100 MeV will generate thermal spikes and collision cascade, contributing to the drastic microstructural defects and evolution. A high burn-up structure (HBS) will form at the outer region of the nuclear fuel pellets after the burnup reaching to ~ 75 GWd/tHM. In this region, microcrystalline (referred as mc- hereafter) grains subdivide from 10 ~ 15 μm into nanocrystalline (referred as nc- hereafter) grains with an average grain size of several hundreds of nano-meters. Nc-materials usually exhibit superior mechanical properties than the conventional coarsen-grain materials, such as higher hardness, strength, improved thermal diffusivities and electrical resistivity. However, the mechanism behind the enhanced properties is still under debate. Hall derived the relationship of strength and hardness with grain size based on the pile up of the dislocations close to grain boundaries, which did not work well for very fine grained materials. A new mechanism of volume fraction of triple junctions was later proposed to explain the hardness and strength drop when the grain size became too small. It has been accepted now that the critical point of grain size exists, above which the hardness of the material will increase with finer grains and below which the Hall-Petch effect will start to reverse.

To mimic the HBS morphology and compare its properties with mc-UO\textsubscript{2} at different temperatures, high density nc-UO\textsubscript{2} and mc-UO\textsubscript{2} pellets with controlled microstructure and stoichiometry are desired. Traditionally, the synthesis of bulk UO\textsubscript{2} pellets involves high temperature sintering, e.g., above 1700 °C for hours. Amato et al. has reached over 95% theoretical density (TD) using hot-pressing at 4000-8000 psi and 1100-1400 °C, ranging from 10 to 60 mins. Yang et al. has adopted microwave sintering in H\textsubscript{2} atmosphere at 1600 °C for an hour. The grain size of the pellets these authors synthesized ranges from several to dozens of microns. Recently, rapid consolidation method has been widely used to sinter ceramic materials in a short period and was proven to be effective to sinter bulk pellet with a nano-sized grain structure. Spark plasma sintering (SPS) is an example of rapid consolidation, which utilizes high DC current to enable the consolidation and the synthesis of the material. As a result of rapid consolidation of materials at short duration and lower temperature, the grain structure of the starting materials can be well preserved upon sintering without
significant grain growth, enabling the densification of nanoceramics. Microstructure of the densified materials can also be controlled by adjusting the SPS sintering parameters such as temperature, pressure, and holding time during sintering. Ge et al. has studied the effects of the variation of these parameters to the densification, grain size, and hardness of UO2. SPS has been adopted to many materials, such as nc-ZrO2 (3Y), nc-(UO2, SiC) compound, nc-UO2 and mc-UO2.

Microindentation and nanoindentation are typically used to test mechanical properties of materials such as hardness, elastic modulus, and fracture toughness. Microindentation testing method is commonly used to measure material hardness on a microscopic scale utilizing a precision diamond indenter to penetrate the material surface and produce an impression. Microhardness can be calculated based on the load and the area of the impression. On the other hand, nanoindentation employs a more precise tip to press the material and produce an indentation area of several square micrometers or even less, and hence can be used on thin film and small volumes. During the testing, the load and displacement data are continuously recorded, allowing the calculation of Young’s modulus and many other mechanical properties.

In this chapter, we present a systematic study of materials sintering by SPS and mechanical testing of the sintered UO2 with controlled microstructure and stoichiometry in which the nano-sized UO2 can mimic the HBS with a comparable length scale of hundreds of nano-meters. Microindentation and nanoindentation were performed in order to understand the mechanical properties of the sintered UO2 as functions of grain structures and temperatures. The main results derived from nanoindentation include hardness and Young’s moduli for UO2 with various grain sizes at three temperature levels, i.e., room temperature (referred as RT hereafter), 300 °C, and 600 °C. The results obtained from microindentation include hardness and fracture toughness for the fuels with different stoichiometry and grain size at RT. The experimental data acquired are be compared with literature values in the literature and will also be fed to the NEAMS tool to develop MARMOT fracture models.

4.2 Experimental Procedure

4.2.1. Sintering UO2 with controlled microstructure and stoichiometry

The dense UO2 ceramics with different microstructure and grain size were fabricated by the combination of high energy ball milling (HEBM) and Spark Plasma Sintering (SPS). Specifically, polycrystalline UO2 fuel pellets with different grain sizes (7.2 and 1.5 microns and 125 nm) were sintered by SPS from various batches of powder samples prepared from UO2.16 powders purchased from International Bio-analytical Industries Inc. USA. Ball milling of the as-received powders was conducted to decrease the particle size and enhance sinterability. Chemical reduction of the starting powders with UO2.16 was also performed to reduce the stoichiometry to UO2.03.

Large-sized UO2 pellets with a grain size of 7.2 µm was sintered directly from the as-purchased UO2.16 powder at 1600 °C for 5 mins under a pressure of 40 MPa. The pellets with a grain size of 1.8 µm were sintered from nanocrystalline UO2.03 powders at 1300 °C for 30 mins under a pressure of 40 MPa. Due to the graphite die used in those two sintering routes, the pellets were in-situ reduced to hypo-stoichiometric. The pellets with a grain size of 125 nm were sintered at 700 °C for 5 mins under a pressure of 500 MPa in WC die. The densified nano-sized pellets are
hyperstoichiometric and a post-sintering annealing was conducted in a tube furnace in 4\% H\_2/Ar gas atmosphere. Prior to reducing, the furnace was purged by 4 hrs gas flow at a rate of 200 ml/min. The reducing was conducted at 600 °C for 24 hours at a gas flow rate of 50 ml/min to render the pellets a stoichiometry of UO\(_{2.006}\). The bulk density of the pellets was measured by an immersing method using DI water as the media. Density was calculated based on weight difference in air and water. The relative density was calculated against a theoretical value of 10.97 g/cc for UO\(_2\).

4.2.2. Stoichiometry and microstructure of the sintered pellets

X-ray diffractions (XRD) spectra of the sintered pellets were collected by a Panalytical X'Pert XRD system (Westborough, MA, USA) using Cu \(K_\alpha (\lambda = 1.5406 \text{ Å})\) irradiation at room temperature. The stoichiometry of the sintered pellets was determined from x-ray diffraction collected by The O/U ratio was determined from the following empirical equation: \(a = 5.4705 - 0.132 \cdot x\), where \(a\) is the derived lattice parameter and \(x\) is the stoichiometry derivation of UO\(_{2+x}\) from stoichiometric UO\(_2\).

Microstructure characterization of the sintered UO\(_2\) with controlled microstructure was conducted using a Carl Zeiss Supra 55 (Jena, Germany) field emission SEM. Grain size was determined using a rectangular intercept method following an ASTM E122-88 standard (1992). The average size is given by:

\[
D = \left[ \frac{4A}{\pi (N_i + \frac{N_0}{2})} \right]^{\frac{1}{2}}
\]

where \(A\) is the area of an arbitrary drawn rectangle, \(N_i\) and \(N_0\) are the numbers of grains in the rectangle and on the boundary of the rectangle, respectively. At least two hundred grains were analyzed for each pellet. The grain size uncertainties are standard deviations of the measured grain size for the same pellet from different locations. In the nanoindentation testing, the images and length measurements of the indents were acquired with a FEI Quanta FEG dual beam SEM/FIB system at UC Berkeley in the Biomolecular Nanotechnology Center (BNC). The standard measuring tool was used to perform the measurements of the crack lengths and was calibrated prior to use.

4.2.3. Nanoindentation Testing of the sintered pellets at different temperatures

Nanoindentation testing was performed on the densified UO\(_2\) pellets with controlled microstructure and stoichiometry at 25 ºC (298 K), 300 ºC (573 K), and 600 ºC (873 K) at UC Berkeley with a MicroMaterials platform. The platform was equipped with a nanoindenter that can independently heat the nanoindentation tip and the sample up to 750 ºC. This unique ability allows for isothermal contact between the tip and the sample, critical to minimize the thermal drift and enable the measurements of mechanical property, such as hardness and elastic modulus, at elevated temperatures. During the measurement, the instrument is capable of continuously measuring the load versus displacement. For a typical measurement, the indenter was firstly tested on fused silica for calibration. The sample was mounted on a hot stage using Omega 700 cement and the chamber was then purged with UHP Ar overnight with a flow rate of 10 liters/min in order to reduce the oxygen particle pressure to the magnitude of 10\(^{-4}\). Then, Ar + 5\% H\(_2\) was flowed into the chamber 60 to 90 minutes prior to the testing and maintained thereafter until the end. The tip and the sample were both
heated to the desired temperature with a heating rate of 1.6 °C/min. After the desired temperature was reached, the sample was held for 1 additional hour to allow for thermal stabilization. After the thermal stabilization period the sample would be moved a slight distance (20-30 µm) away, where a test indentation could be performed to evaluate the difference in temperature between the tip surface and the sample surface. This was done by monitoring at the thermal drift of an indent. The temperature of the tip and the sample was deemed satisfactorily the same when the thermal drift of the indent was less than ±0.15 nm/s. The thermal drift was measured by holding at 10% of the max impressing load for 60 seconds and only the last 60% of the data was used to calculate the drift to remove any artifacts from elastic or plastic behavior at the beginning of the holding period.

During the testing, the nanoindentation was performed in load control mode with a loading time around 20 seconds, and an unloading time of around 10 seconds. Approximately the same depth (~ 800 nm) was maintained for each indentation performed at all temperature levels. The load and the displacement were continuously recorded. To ensure the precision of the indentation, all impressions that had high thermal drifts (> 0.2 nm/s) were removed from the dataset. In addition, the dwell time was set as 20 seconds for the RT indentations, 35 seconds for 300 °C, and 45 seconds for 600 °C to ensure that the unloading was completely elastic. At all three temperatures, 5 to 10 indentations were performed on each sample to reduce the experimental error. The reduced modulus was calculated based on formula (2), where \( E_r \) is the reduced modulus, \( \beta \) is a geometrical constant on the order of unity, and \( s \) is the stiffness of the unloading curve, respectively. The reduced modulus was then converted to elastic modulus using formula (3) proposed by Oliver and Pharr [26]. This formula depicts the relationship between reduced modulus \( E_r \) and elastic modulus \( E \), where \( \nu \) is Poisson’s ratio and \( E_i \) is elastic modulus of the indenter. The material of the indenter used is cubic boron nitride; therefore, \( \nu_s = 0.1 \) and \( \nu_i = 0.32 \) are used for the calculation. The Young’s modulus \( E_i \) of the indenter is calculated based on the Wachtman’s equation shown in formula (4), in which \( E_0 \) is a constant representing Young’s modulus at absolute zero, \( A \) is an exponential fitting constant, and \( T_0 \) is the characteristic temperature at which Young’s modulus shows a linear correlation with temperature. As for the material of the indenter, \( E_0 = 681.6 \) GPa, \( A = 0.0442 \), \( T_0 = 526.52 \) K. This approach takes into account the indenter compliance [29] and can be used to evaluate hardness and Young’s modulus without the measurement of contact area.

\[
E_r = \frac{1}{\beta} \frac{\sqrt{\pi}}{2} \frac{s}{\sqrt{A}}
\]

(2)

\[
\frac{1}{E_r} = \frac{1 - \nu^2}{E} + \frac{1 - \nu_i^2}{E_i}
\]

(3)

\[
E_i = E_0 - AT \exp \left( -\frac{T_0}{T} \right)
\]

(4)

### 4.2.4. Microindentation Testing

Microindentation testing was performed at 25 °C in order to determine the hardness and to study the crack propagation behavior of samples with various grain sizes and stoichiometries. The micro indenter is a Leco M-400 Microhardness Tester. The load was kept at 1000 gf (~9.8 N) for 15 seconds for all indentations. Crack lengths for each indentation were measured based on the SEM
images. A schematic of the length measurement is shown in Fig. 4.1. Similar to nanoindentation, 10 microindentations were performed for each sample. Hardness is calculated using formula (5), where $P$ is the load and $a$ is the arithmetic mean of the diagonal lengths of the indentation. Fracture toughness was calculated based on formula (6), where $\delta$ is an indenter geometry related parameter, $E$ is elastic modulus, $H$ is hardness, and $c$ is the arithmetic mean of the four crack lengths.

$$H = 1.854 \frac{P}{a^2}$$  \hfill (5)

$$K_{IC} = \delta \left( \frac{E}{H} \right)^{0.5} \left( \frac{P}{C^{1.5}} \right)$$  \hfill (6)

*Figure 4.1: Schematics of the microindentation*

4.3. **Microstructure control and stoichiometry the sintered UO$_2$ by SPS**

Fig. 4.2 shows microstructural analysis of the densified UO$_2$ pellets as observed by the SEM images acquired from the fractured surface. The chemical stoichiometry of the sintered pellets was determined by X-ray diffraction patterns (data not shown here). Uniform microstructures across the polycrystalline pellets are obtained with different length scales varying from hundreds of nanometers (Fig. 4.2A) to several microns (Figs. 4.2B and 2C), attributing to the fine control of microstructure by SPS process. The stoichiometry is controlled to almost identical (close to nearly stoichiometric UO$_2$) for the densified pellets with different microstructures by the SPS sintering process and also post sintering chemical reduction, and thus the effects of the grain structure on fracture mechanisms and mechanical properties can be determined at similar chemical stoichiometry. Dense nano-sized UO$_{2.11}$ pellets (Fig. 4.2D) with hyperstoichiometry (oxygen-enriched) was fabricated with a comparable grain structure (160 nm) as the dense nano-UO$_2$ pellets (125 nm), and the effects of the oxygen non-stoichiometry on mechanical properties can be explored. The physical properties (grain
size, physical density and porosity) of different UO$_2$ pellets for mechanical testing are summarized in Table I.

![Figure 4.2](image)

**Figure 4.2.** Synthesized dense UO$_2$ fuel pellet with various grain size range: (A) 125 nm stoichiometric UO$_2$; (B) ~2 $\mu$m stoichiometric UO$_2$; (C) 7 $\mu$m, and (D) 165 nm hyper-stoichiometry UO$_{2.11}$.

The microstructure analysis of the densified UO$_2$ pellets with different grain structures also reveal distinct variations in fractured surfaces, suggesting different fracture mechanisms. Specifically, for nc-UO$_2$, the fractured surface shows typical intergranular fracture with cracking propagation along the grain boundaries as a result of the nano-scale grain structure. The intergranular fracture was also observed in hyper-stoichiometric UO$_{2.11}$ (Fig. 4.2D). On the other hand, micron-sized polycrystalline UO$_2$ pellets shows characteristic features of the transgranular fractures, and fractured facets are observed as a result of crack penetration through the grains. The intergranular fracture mechanism suggests better ductility for the nano-sized UO$_2$ as compared with micron-sized counterpart, implying potentially-enhanced fracture toughness for the high burn-up structure formed in oxide fuels upon reactor operation.
Table 4.1: Summary of sample details for nanoindentation and microindentation testing

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Sample type</th>
<th>Porosity</th>
<th>Stoichiometry</th>
<th>Grain Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Nano</td>
<td>3.5%</td>
<td>2.006 ± 0.020</td>
<td>125 ± 7 nm</td>
</tr>
<tr>
<td>2</td>
<td>Micron</td>
<td>4.2%</td>
<td>1.996 ± 0.004</td>
<td>1.8 ± 0.2 μm</td>
</tr>
<tr>
<td>3</td>
<td>Micron</td>
<td>3.7%</td>
<td>1.979 ± 0.004</td>
<td>7.2 ± 1.2 μm</td>
</tr>
<tr>
<td>4</td>
<td>Nano-hyper</td>
<td>1.6%</td>
<td>2.11</td>
<td>165 ± 6 nm</td>
</tr>
</tbody>
</table>

4.4 Hardness and Young’s modulus of UO₂ measured by nanoindentation testing

The mechanical properties (hardness and Young’s modulus) of the densified UO₂ are determined by nanoindentation as functions of grain structures and temperature. Fig. 3 shows the SEM images for the nanoindentation on the UO₂ pellet (sample #3) with the grain size of 7.2 μm, at different temperatures of 25 °C (a), 300 °C (b), and 600 °C (c), respectively. The hardness and Young’s modulus acquired from nanoindentation is summarized below in Table II-IV.

Table 4.II: Results of the nanoindentation testing on nano-sized UO₂ (sample #1, grain size: 125 nm)

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Indentation Depth (nm)</th>
<th>Load (mN)</th>
<th>Hardness (GPa)</th>
<th>Reduced Modulus (GPa)</th>
<th>Young’s Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>677</td>
<td>100</td>
<td>12.50 ± 0.48</td>
<td>194.83 ± 3.38</td>
<td>244.27 ± 6.53</td>
</tr>
<tr>
<td>573</td>
<td>748</td>
<td>100</td>
<td>7.63 ± 0.33</td>
<td>167.61 ± 6.28</td>
<td>199.86 ± 10.89</td>
</tr>
<tr>
<td>873</td>
<td>864</td>
<td>100</td>
<td>5.89 ± 1.32</td>
<td>148.89 ± 15.86</td>
<td>172.24 ± 25.62</td>
</tr>
</tbody>
</table>

Table 4.III: Results of the nanoindentation testing on the micron-sized UO₂ (sample #2, grain size: 2 μm)

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Indentation Depth (nm)</th>
<th>Load (mN)</th>
<th>Hardness (GPa)</th>
<th>Reduced Modulus (GPa)</th>
<th>Young’s Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>1086</td>
<td>200</td>
<td>9.30 ± 0.35</td>
<td>178.26 ± 3.43</td>
<td>215.77 ± 6.20</td>
</tr>
<tr>
<td>573</td>
<td>790</td>
<td>65</td>
<td>4.30 ± 0.21</td>
<td>164.57 ± 7.97</td>
<td>195.76 ± 13.65</td>
</tr>
<tr>
<td>873</td>
<td>850</td>
<td>35</td>
<td>1.98 ± 0.08</td>
<td>149.17 ± 16.25</td>
<td>172.24 ± 26.27</td>
</tr>
</tbody>
</table>
Table 4.IV: Results of the nanoindentation testing on the micron-sized UO$_2$ (sample #3, grain size: 7 μm)

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Indentation Depth (nm)</th>
<th>Load (mN)</th>
<th>Hardness (GPa)</th>
<th>Reduced Modulus (GPa)</th>
<th>Young’s Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>812</td>
<td>100</td>
<td>8.54 ± 0.72</td>
<td>184.92 ± 12.35</td>
<td>227.39 ± 22.92</td>
</tr>
<tr>
<td>573</td>
<td>876</td>
<td>65</td>
<td>4.22 ± 0.43</td>
<td>174.44 ± 15.33</td>
<td>210.13 ± 27.30</td>
</tr>
<tr>
<td>873</td>
<td>888</td>
<td>30</td>
<td>1.77 ± 0.15</td>
<td>153.97 ± 6.39</td>
<td>179.75 ± 10.52</td>
</tr>
</tbody>
</table>

Figure 4.3: SEM images showing nanoindentations on the sample No. 3 with 7-micron grain size at (A) 25 °C, (B) 300 °C, (C) 600 °C
Figure 4.4: (A) The temperature dependence of hardness obtained from nanoindentation testing, along with microindentation testing data for comparison, (B) Linear fitting of ln $H$ and temperature for UO$_2$ specimens with various grain sizes, (C) Variation of hardness with grain size at different temperature, (D) Variation of Young’s modulus of UO$_2$ with temperature for different grain sizes. Hardness decreases with temperature and nc-UO$_2$ displays a higher hardness than microcrystalline UO$_2$, while two microcrystalline specimens with different grain size have very close hardness. Young’s modulus decreases with temperature and there is not a strong relationship between Young’s modulus and grain size.

The temperature dependence of hardness for sample No. 1 to 3 is shown in Fig. 4.4A. Two data points (shown as black dots) measured from microindentation testing are also included for comparison. Several observations can be made from this plot. Firstly, hardness decreases exponentially with the increase of temperature, which matches well with the relationship depicted by Kutty, Sengupta, and Basak. The relationship of hardness and temperature is given as formula (7), where $H$ is hardness, $T$ is temperature in the unit of K, and $A$ and $B$ are intrinsic hardness and thermal softening coefficients respectively. The negative correlation might be explained by the mechanism of slip at low temperature and increased dislocation activity at high temperature.

$$H = A \exp(-BT)$$  \hspace{1cm} (7)
Fig. 4.4B shows the correlation between $\ln H$ and temperature for UO$_2$ specimens with different grain structures. The linear relationship confirms that hardness is exponentially related with temperature. The values of $A$ and $B$ are extrapolated and listed in Table V. The intrinsic hardness $A$ is the hardness of material at $T = 0$, and the thermal softening coefficient $B$ describes the hardness decreasing rate when temperature increases. The two mc-UO$_2$ specimens have very close intrinsic hardness, which is much higher than the reported value. The reason might be due to less porosities for the samples densified by SPS and different measuring techniques. It was found that nc-UO$_2$ has slightly lower intrinsic hardness and small negative thermal softening coefficient than the other two mc-specimens.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$A$ (GPa)</th>
<th>$B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nano</td>
<td>17.58</td>
<td>0.001302</td>
</tr>
<tr>
<td>2 μm</td>
<td>20.49</td>
<td>0.002689</td>
</tr>
<tr>
<td>7 μm</td>
<td>19.65</td>
<td>0.002739</td>
</tr>
</tbody>
</table>

Secondly, the hardness of nc-UO$_2$ is higher than the other two mc-UO$_2$ samples. The phenomenon can be well explained by the Hall–Petch effect, which demonstrates that the strength and the hardness of the material can be improved by the grain refinement. Nc-UO$_2$ introduces more grain boundaries. Various grain orientations at different sides of the grain boundaries will impede the dislocation movement, thus requiring more energy for the deformation and demonstrating higher yield strength of the material. Generally, hardness shows a positive correlation with strength, thus refinement of grains will lead to the enhancement of hardness, as long as grain size is larger than the critical grain size.

Fig. 4.4C shows the variation of hardness with temperature and grain size. It confirms that when grain size increases from nc-scale to mc-scale, hardness decreases drastically due to Hall-Petch effect. Within the mc range, hardness at room temperature has a sharper decreasing rate than at elevated temperature, which matches with Sengupta’s findings. The two mc-specimens have very close hardness at elevated temperature, which can be explained by lower boundary strength and easy release of dislocation piled up stress.

Lastly, hardness measured in microindentation testing is lower than the value measured by nanoindentation testing, which can be attributed to the variation of load in the nanoindentation and microindentation tests. In the hardness evaluation of UO$_2$, (U$_{0.9}$,Ce$_{0.1}$)O$_2$, and (U$_{0.8}$,Ce$_{0.2}$)O$_2$, the authors also noticed that nanohardness is higher than microhardness and they found a negative relationship between hardness and load, i.e., greater hardness with lower load.

Fig. 4.4D shows the variation of Young’s modulus with temperature and grain size. The measured Young’s modulus of UO$_2$ at room temperature is very closed to the reported value. It can also be noticed that Young’s modulus is highly related with temperature and shows a negative correlation. This might be explained by elastic anisotropy and grain boundary slip. The relationship can be depicted by formula (4), in which $T_0$ is taken as 135 K. $E_0$ and $A$ are fitted and shown in Table VI.
where $E_0$ is Young’s modulus at absolute zero and $A$ is a fitting constant. The fitted $E_0$ for two mc-specimens are very closed to the reported value and nc-specimen has a slightly higher $E_0$ than mc-specimens. Young’s modulus of the two mc-specimens do not show a strong relationship with grain size, as indicated in the literature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>A</th>
<th>$E_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nano</td>
<td>0.128</td>
<td>264</td>
</tr>
<tr>
<td>2 μm</td>
<td>0.079</td>
<td>231</td>
</tr>
<tr>
<td>7 μm</td>
<td>0.085</td>
<td>245</td>
</tr>
</tbody>
</table>

**4.5. Hardness and fracture toughness of $\text{UO}_2$ measured from micro-indentation testing**

Fig. 4.5 shows the SEM images of microindentations on three specimens, along with images showing crack propagations. The fracture mode is highly dependent on grain size. Materials with finer grains is very likely to have a fracture mode of intergranular fracture, while transgranular fracture for coarse-grained materials. According to the formula proposed by Petch shown in formula (8), where $\sigma_f$ is fracture strength, $\sigma_0$ is the stress moving dislocations, $K$ is related with fracture initiation energy, and GS is the average grain size, fracture strength has a negative correlation with grain size, thus the nc-specimen will have more ability to resist fracture. In the current case, the fractography of the mc-specimen displays transgranular fracture with smooth fracture and no sharp edges while the fractography of the nc-specimen displays intergranular facture characteristics with jaggy paths.

$$\sigma_f = \sigma_0 + K (\text{GS})^{-1/2}$$

**Figure 4.5:** SEM images for three $\text{UO}_{2+x}$ specimens with various stoichiometry and grain size. (A) stoichiometric 7-μm $\text{UO}_2$ (sample No. 3), (B) stoichiometric nc-$\text{UO}_2$ (sample No. 1), (C) hyper-
Microhardness and fracture toughness measurements were also performed on sintered UO$_2$ with different stoichiometry and grain size and evaluated with formula (4) and (5). Microhardness for each specimen is summarized in Table VII and is also plotted in Fig. 6 for better comparison. From the figures, there are two observations can be made. Firstly, it is found that nc-specimens have higher hardness and slightly higher fracture toughness than mc-specimen. The higher hardness measured for nc-specimens is consistent with nano-indentation measurement as shown in Fig. 4.4A. Secondly, nc-hyper-stoichiometric specimen displays higher hardness and fracture toughness than nc-stoichiometric specimen. The enhanced fracture toughness can be explained by the fact that nc-specimen has more grains per volume. Thus, more grain boundaries lead to a more complexity of the dislocation structures among grains and will hamper the movement of the dislocations and the propagation of the cracks. When a crack is moving across the grain boundary, it is more difficult for the crack to pass through those grain boundaries with more complex dislocation structures and will therefore require more energies. For the second observation, it was reported that there is a strong relationship between U/O ratio and hardness. Hardness will rapidly increase when O/U ratio initially increases from 2.00. Surface energy $\gamma$ can be expressed as a function of fracture toughness $K_{IC}$ as shown in formula (9), where $\nu$ is Poisson’s ratio and $E$ is Young’s modulus. The excess oxygen will lead to the increase of $\gamma$ in UO$_{2+x}$, such that hyper-stoichiometric specimen will possess a higher value of fracture toughness than stoichiometric specimen.

$$2\gamma = \frac{1 - \nu^2}{E} K_{IC}$$  \hspace{1cm} (9)

Table 4.VII: Hardness and fracture toughness of three specimens with various grain size and stoichiometry.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Load (gf)</th>
<th>Microhardness (GPa)</th>
<th>Fracture Toughness (MPa/m$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7 $\mu$m</td>
<td>1000</td>
<td>6.86 ± 0.38</td>
<td>1.01 ± 0.11</td>
</tr>
<tr>
<td>Nano</td>
<td>1000</td>
<td>10.90 ± 0.66</td>
<td>1.08 ± 0.15</td>
</tr>
<tr>
<td>Nano-hyper</td>
<td>1000</td>
<td>12.86 ± 0.14</td>
<td>1.32 ± 0.08</td>
</tr>
</tbody>
</table>
Figure 4.6: (A) Microhardness and (B) Fracture toughness of three specimens with various stoichiometry and grain size measured from micro-indentation testing. Nc-UO$_2$ has a higher value than microcrystalline UO$_2$, and hyper-stoichiometric UO$_2$ has a higher value than stoichiometric UO$_2$.

In summary, nanoindentation and microindentation testing were conducted on SPS-sintered UO$_2$ with controlled stoichiometry and grain size. Hardness and Young’s modulus at three different temperature levels were evaluated during nanoindentation testing, while hardness and fracture toughness at RT was derived from microindentation. Hardness of nc-UO$_2$ is higher than mc-UO$_2$, while mc-UO$_2$ specimens with different grain sizes have similar hardness. Both hardness and Young’s modulus decrease with temperatures. Results from microindentation testing confirm that nc-UO$_2$ has a higher hardness and fracture toughness than mc-UO$_2$ and it can be explained by the theory of grain boundary strengthening. Hyper-stoichiometric UO$_2$ exhibits higher hardness and fracture toughness than stoichiometric UO$_2$ and is explained by the impediment of crack propagation induced by excess oxygen atoms and the enhanced fracture surface energy. As the study of mechanical properties on UO$_2$ with controlled microstructure, stoichiometry, and temperature is scarce in the literature, this systematic investigation of hardness, elastic modulus, and fracture toughness using nano- and micro-indentation testing may provide a profound understanding of the relationship between grain size, stoichiometry, temperature and the mechanical properties of UO$_2$. This work also provides experimental data of mechanical properties and fracture mechanisms to the NEAMS tool MARMOT framework, which enables the advanced fuel modeling and fuel performance prediction.
Chapter 5. Validation of MARMOT Thermal Transport and Fracture Models

In this chapter, we report the results on the validation of the MARMOT thermal transport model. This work is in a close collaboration with the MARMOT team of Idaho National Laboratory as part of efforts demonstrating high spatial resolution measurements at the microstructural level on as-fabricated nuclear fuels and materials. The results reported in this milestone report on validation of the MARMOT model were reported in the technical report (FY2016 PEMP 1.1A Summary Report - Demonstrate high spatial resolution measurements at the micro- structural level on as- fabricated nuclear fuels and materials). Here, we reported: (1) sintering UO$_2$ with controlled microstructure and stoichiometry; and (2) MARMOT Calculations of UO$_2$ Conductivity at Various Grain Sizes and model validation.

5.1 Sintering UO$_2$ with controlled microstructure and stoichiometry

The dense UO$_2$ ceramics with different microstructure and grain size were fabricated by the combination of high energy ball milling (HEBM) and Spark Plasma Sintering (SPS). Specifically, polycrystalline UO$_2$ fuel pellets with different grain sizes (7.2 and 1.5 microns and 125 nm) were sintered by SPS from various batches of powder samples prepared from UO$_2$)$_{1.6}$ powders purchased from International Bio-analytical Industries Inc. USA. Ball milling of the as-received powders was conducted to decrease the particle size and enhance sinterability. Chemical reduction of the starting powders with UO$_2$ projection was also performed to reduce the stoichiometry to UO$_2$$_{0.3}$.

Large-sized UO$_2$ pellets with a grain size of 7.2 $\mu$m was sintered directly from the as-purchased UO$_2$$_{1.6}$ powder at 1600 $^\circ$C for 5 mins under a pressure of 40 MPa. The pellets with a grain size of 1.8 $\mu$m were sintered from nanocrystalline UO$_2$$_{0.3}$ powders at 1300 $^\circ$C for 30 mins under a pressure of 40 MPa. Due to the graphite die used in those two sintering routes, the pellets were in-situ reduced to hypo-stoichiometric. The pellets with a grain size of 125 nm were sintered at 700 $^\circ$C for 5 mins under a pressure of 500 MPa in WC die. The densified nano-sized pellets are hyperstoichiometric and a post-sintering annealing was conducted in a tube furnace in 4% H$_2$/Ar gas atmosphere. Prior to reducing, the furnace was purged by 4 hrs gas flow at a rate of 200 ml/min. The reducing was conducted at 600 $^\circ$C for 24 hours at a gas flow rate of 50 ml/min to render the pellets a stoichiometry of UO$_2$. The bulk density of the pellets was measured by an immersing method using DI water as the media. Density was calculated based on weight difference in air and water. The relative density was calculated against a theoretical value of 10.97 g/cc for UO$_2$.

5.1.1 Stoichiometry and microstructure of the sintered pellets

X-ray diffractions (XRD) spectra of the sintered pellets were collected by a Panalytical X'Pert XRD system (Westborough, MA, USA) using Cu $K_\alpha$ ($\lambda = 1.5406$ Å) irradiation at room temperature. The stoichiometry of the sintered pellets was determined from x-ray diffraction collected by The O/U ratio was determined from the following empirical equation: $a = 5.4705 - 0.132 \cdot x$, where $a$ is the derived lattice parameter and $x$ is the stoichiometry derivation of UO$_2$$_{2+x}$ from stoichiometric UO$_2$. Microstructure characterization of the sintered UO$_2$ with controlled microstructure was conducted using a Carl Zeiss Supra 55 (Jana, Germany) field emission SEM. Grain size was determined using a rectangular intercept method following an ASTM E122-88 standard (1992). The average size is given by:
\[ D = \left( \frac{4A}{\pi \left( N_i + \frac{N_0}{2} \right)^2} \right)^{1/2} \]  

where \( A \) is the area of an arbitrary drawn rectangle, \( N_i \) and \( N_0 \) are the numbers of grains in the rectangle and on the boundary of the rectangle, respectively. At least two hundred grains were analyzed for each pellet. The grain size uncertainties are standard deviations of the measured grain size for the same pellet from different locations.

Micro-Raman spectra were collected at room temperature using a Renishaw Micro-Raman spectrometer excited by a green argon laser (514 nm). A typical spectrum was acquired with an exposure time of 10 seconds and 3 accumulations with a laser power of 20 mW. An extended scanning region from 200 to 1500 cm\(^{-1}\) was chosen since it contains the featured peaks for UO\(_2\). For each pellet, multiple locations were checked so that the spectrum is representative.

5.1.2 Microstructure of the sintered UO\(_2\) fuel pellets

Fig. 5.1 shows the morphology of the sintered UO\(_2\) pellets and bar with controlled microstructure and stoichiometry at RPI and sent to INL for thermal measurements. Fig. 5.2a-c shows the dense microstructure with various grain size as the major difference. As summaries in Table. 1. All pellets are fully densified with measured density higher than 95 \% TD. Fig. 1d shows the whole XRD spectrum shows the sintered pellet are single phase UO\(_{2+x}\). Detailed spectrum at high angle area (Fig. 5.2e) shows well-separated K\(\alpha_1\) and K\(\alpha_2\) for the peaks for the (331) and (420) plans. The line added sits on the exact two-theta angles for 0.125 \(\mu\)m samples. The peaks for 1.8 \(\mu\)m shifted slightly to lower angles, while the ones for 7.2 \(\mu\)m have a much larger degree of peak shifting, indicating a different level of change of lattice parameter at various stoichiometries. However, the superimposing feature of Raman spectrums (Fig. 2f) shows the chemical bonding in those three-different grain sized samples are very similar, indicating comparable localized defect interaction with the crystal structure of UO\(_2\).

![Fig. 5.1. Sintered UO\(_2\) pellets and bars prepared for thermal measurements](image)
5.2. MARMOT Calculations of UO₂ Conductivity at Various Grain Sizes

Thermal conductivity of UO₂ is affected by stoichiometry (O/M ratio) and many microstructure features including grain size, porosity and lattice defects. To connect the microstructure characterization and thermal measurements with modeling, mesoscale simulations using the MARMOT code were carried out for better understanding of the contribution from each microstructure feature and from chemistry (Fig. 5.3).

Here, MARMOT simulations were performed to investigate the effect of grain size in the temperature range of 300 K to 1500 K. Three grain sizes, 7.2 µm, 1.8 µm and 0.125 µm, were considered, in accordance to the RPI samples. All simulations were performed using a 2-D square domain (Fig. 4). The size of the domain varied by the grain size used. The cells for 7.2 µm and 1.8 µm grain sizes contained 32 grains, and the one for 0.125 µm contained 64 grains. To improve computation efficiency, mesh adaptivity capability in MOOSE was activated to give a good resolution at grain boundary regions (Fig. 5.3). After being set up, the simulation cells were relaxed at 1500 K to quickly reach the equilibrium grain boundary width. After the microstructures were relaxed, the thermal conductivity was calculated using the Fourier’s law at desired temperatures by setting up a temperature gradient as shown in Fig. 5.3. In MARMOT calculations for overall thermal conductivity,
each microstructural feature is assigned with a different conductivity. The thermal conductivity of UO$_2$ matrix, $K_0$, is described using the Fink model. The grain boundary conductivity was set to be proportional to $K_0$ with a coefficient of 0.578 which gives a grain boundary thermal conductivity of 5.0 W/mK at 300 K.

![Figure 5.3. Comparison of sample grain structure with MARMOT generated finite element meshes.](image)

![Figure 5.4. Schematic of a 2D simulation cell for polycrystalline UO$_2$. The grain boundaries are decorated by refined meshes. A temperature gradient is set up from left (hot) to right (cold).](image)
Figure 5.5. Comparison of thermal conductivity measurements and MARMOT simulations evolved with grain structure and temperature.
The MARMOT simulations were carried out with fully dense UO$_2$. As shown by the results in Fig. 5, thermal conductivity of polycrystalline UO$_2$ decreases with decreasing grain size. This is because grain boundaries have a lower conductivity than that of bulk UO$_2$, and the volumetric density of boundaries increases as grain sizes decreases. However, such a trend was not followed in the experimental measurements, due to the fact that the experimental samples were porous and non-stoichiometric, i.e., with O/M ratios other than 2.0. From the laser flash measurements, above room temperature the 1.8 μm sample has a higher conductivity than the 7.2 μm one.

To better understand the experimental results, the modeling results were adjusted to account for the effects of porosity and off stoichiometry. Because the RPI samples were with similar densities, the corrections for porosity did not change the trend established by grain size. In contrast, the three RPI samples vary a lot in terms of O/M ratio. Following Hobson et al., the MARMOT results were fitted with respect to temperature T using $K=1/(A+CT)+BT^3$, with A, B, C being fitting parameters. Both A and C are O/M ratio dependent, with extra contribution from off-stoichiometry. For UO$_{2-x}$, extra resistance can be estimated using $A=A_0+2.85x$, and $C=C_0-7.15E-4x$, following Popov et al. While making these corrections, O/M ratios were taken from Table 2. The measurements were done before the samples were shipped from RPI to INL. After the corrections (Fig. 5.6), the 7.2 μm sample was of lower conductivity than the 1.8 μm due to its lower O/M ratio, i.e., larger x. Therefore the trend observed in MARMOT simulations agreed with that from experiments.

The MARMOT results matched those from the PPMS measurements well except for the 7.2 μm sample. However, some discrepancies between modeling and experiments, or between different experimental measurements, were still noticed regarding the absolute values. Possible reasons include uncertainties in different measuring methods, and the change in fuel microstructure and chemistry during experimental processing. It was suspected that the samples might have been further oxidized during delivery, i.e., the O/M ratio could be higher than those measured in RPI. The results shown here demonstrated the capabilities developed for microstructure level characterization, and the importance of doing that for predicting fuel properties and thus fuel qualification. A close tie between modeling and experiments has also been established considering effects of microstructure features such as grain size. The comparison between modeling and experiments also calls for the need of full characterization of the evolving fuel microstructure and chemistry in order to accurately estimate fuel properties such as thermal conductivity.

In summary, a set of samples of UO$_2$ having grain sizes ranging from 100 nm to several μm were fabricated at RPI. The samples were characterized for grain size, morphology, stoichiometry, and thermal properties. A model was established in the MARMOT fuel material property code to simulate the behavior of UO$_x$ thermal conductivity with grain size and temperature. The purpose of this combined experimental and modeling simulation effort was to demonstrate the capability of predicting the thermal property evolution with grain structure. A close connection between modeling and experiments has been established and demonstrated using oxide and silicide fuels. The minor discrepancies between modeling and experiments and between different measurement techniques indicate the importance of capturing the evolving microstructure and chemistry.

**Figure 5.6.** Thermal conductivities of UO$_2$ samples with different grain sizes as function of temperature. The dash lines are MARMOT results without corrections for stoichiometry and the solids lines are after corrections.
5.3. Validation of a UO$_2$ phase field fracture model in MARMOT

5.3.1. Simulating nanoindentation

The experiments conducted at RPI used a Berkovich indenter for the nanoindentation and a Vickers indenter for the microindentation. The geometries of these two indenter types are shown in Fig. 1. It is convenient to analyze the indentation process with respect to an axis-symmetric indenter than the asymmetric pyramidal geometry of the Berkovich and Vickers indenters. It has been shown that the area to indentation depth ratio of a conical indenter with a cone angle of $70.3^\circ$ is the same as both indenter geometries. The selected mesh geometry is shown in Fig. 5.7.

![Figure 5.7: 2D nanoindentation mesh](image)

It is noteworthy that the nanoindentation process in the RPI experiments did not result in any radial cracking of the UO$_2$ at any temperature. However, in the microindentation experiments, radial cracking was observed in all three samples at all three temperatures. To simulate radial cracking, 3D simulations are needed. However, due to the computational cost of running 3D contact simulations, we chose to perform 2D simulations initially.

For simulation of nanoindentation, the Berkovich indenter was approximated as the equivalent cone, and a vertical plane cross-section of the indentation was used for a 2D simulation of the nanoindentation. The experimental results showed that the UO$_2$ is brittle, but also deforms inelastically under indentation conditions. Typically, we do not expect inelastic deformation from
brittle materials. However, under the high shear conditions of indentation, even brittle materials like UO$_2$ display permanent deformation. In order to be able to simulate this behavior, we modeled the UO$_2$ as a brittle material with an elastic-plastic transition. Under tension, the UO$_2$ will fracture well before it can enter the plastic region, but shear stress will cause plastic deformation in the UO$_2$. In order for a plastically deforming material to fracture in a brittle manner, it must display strain hardening. We assumed the UO$_2$ displays power law hardening in accordance with the equation:

$$\sigma = \sigma_y + K\epsilon^n$$

where $\sigma_y$ is the yield strength, $K$ is the strength coefficient, and $n$ is the strain hardening exponent. There are no good values for these constants in the literature, so the values were estimated from other experimentally measured values. More details about this are provided in the next section of the report. The Young’s modulus, Poisson’s ratio, and Griffith energy release rate of the UO$_2$ were obtained from the literature [1,2,3]. (E =200 GPa, $v$ = 0.32, $G_C$ = 2e-3 GPa-µm)

The SiC indenter tip was modeled as a brittle material with a very high Griffith energy release rate since we assume the tip will not fracture during indentation. The Young’s modulus and Poisson’s ratio values of silicon carbide were obtained from the literature. (E =1050 GPa, $v$ = 0.2, $G_C$ = 100 GPa-µm)

Constrain based contact was used to implement the contact force application of indentation, where the indenter was created with a coarse mesh and was the master surface for the contact. The UO$_2$ surface was the slave surface, and the UO$_2$ block had a finer mesh. The force applied on the indenter along the y-axis and the indentation depth was tracked for each timestep of the indentation simulation. Fig. 5.8 shows an example nanoindentation simulation result when the indentation depth was set to 0.8 µm. This depth is the same as the RPI nanoindentation experiments. The nanoindentation led to the formation of a clear median crack, which can be seen as the red line along the indenter axis.
**Figure 5.8:** Median crack formation in UO$_2$ after nanoindentation

The load-displacement curve of the simulation was then plotted using the postprocessor CSV output file data generated by MOOSE. This graph is shown in Fig. 5.9. Using the peak applied load and the slope of the unloading curve, the hardness of the simulated material can then be calculated. The value of the simulation came out to be 15.87 GPa. The sample in RPI nanoindentation experiment from which the Yield strength and strain hardening exponent of this simulation were estimated had a hardness of 12 GPa. There is some mismatch between the simulation results and the experimental data, and there are a few possible reasons for this mismatch. Firstly, the simulation is 2D, and the 3D extension of the triangular indenter in the simulation would be a wedge, not a cone. Secondly, the Yield Strength $\sigma_y$ and strain hardening exponent $n$ for this simulation were estimated using an empirical relation, so their values may not be accurate.

![Load-displacement curve for nanoindentation](image)

**Figure 5.9:** Load-displacement curve for nanoindentation experiment with maximum indentation depth 800 nm

### 5.3.2: Estimating Yield strength and strain hardening exponent of UO$_2$

Three approaches were tested for calculating the Yield stress of UO$_2$. The first approach was calculating the yield stress as a function of the hardness $H$ of the material. Cahoon et. Al (1971) proposed the following formula for calculating yield strength of materials:

$$\sigma_y = \left(\frac{H}{3}\right) (0.1)^{m-2}$$

where $m$ is the Meyer coefficient. For UO$_2$ no Meyer indentation data is available in the literature. The strain hardening exponent $n$ is related to the Meyer coefficient by

$$n = m - 2$$
However, we also do not know the strain hardening exponent for UO₂, as no room temperature stress-strain curves for UO₂ are available in the literature. In future experiments, we recommend Meyer indentations of UO₂, as these will provide valuable information about the hardening properties of UO₂.

The second approach that was looked at was the inverse modeling algorithm published by M. Dao et. al [6]. This approach uses analytical relations between material mechanical properties and indentation data to allow for calculation of material properties if the indentation data is provided. A Python script that implements the algorithm was written and fed the load-displacement data from the RPI nanoindentation experiment for Sample #1 at 298 K. The algorithm calculated a yield strength of 0.613 GPa and n = -0.577. In addition, analysis of the loading curve showed that the load P = C*h⁰.₃, where h is the indentation depth. The power of h is expected to be 1 for flat punch, 1.5 for spherical indenters and 2.0 for sharp conical indenters. This suggests that the indenter tip used for the nanoindentation might have been broken. Unfortunately, load-displacement curves were not available for other nanoindentation samples and temperatures, and no microindentation load-displacement curve could be obtained. Thus, these results cannot be checked for temperature, stoichiometry and applied load dependence.

The third approach that was looked at was fitting high-temperature yield strength measurements for UO₂ to an exponential temperature dependence equation using a least-squares approach. The experimental data for the yield strength was obtained from the master’s thesis of McDonald R. [7]. The yield strength in the experiments was calculated using the plastic pileup zone radius of the indentation experiments. The fit was then used to extrapolate the value of the yield strength at 298 K. The regression fit is shown in Fig. 4. The extrapolation gave a yield strength of 3.32 GPa, and n = 0.1303. This method predicts a value of yield strength that is nearly 6 times the calculations made on the RPI data.

The inverse modeling and extrapolation approach both predict a negative strain hardening exponent for UO₂. This does not make sense if UO₂ follows the power hardening rule. However, UO₂ only follows the power hardening rule at higher temperatures. At lower temperatures, it has a 2 Yield strength behavior. This behavior is shown in Fig. 4, where the transition to power law hardening takes place at around 1400°C. The yield strength of UO₂ is also highly stoichiometry dependent. In the future, a mechanistic model for plasticity will be added to the indentation simulation to account for this behavior.

In summary, the phase field fracture model in MARMOT can be successfully used to model the nanoindentation of UO₂. The load-displacement curve of the simulation can be used to calculate the mechanical properties of the sintered UO₂. As mentioned previously in the report, the values of the yield strength and strain hardening exponent of UO₂ are not known. In addition, estimations of these parameters made from indentation experiments have a wide variation in values. Thus, when performing validation using indentation experiments, there is uncertainty about whether the model is accurate, but also uncertainty in the input parameters. This makes it very difficult to validate the model, as validation requires very low uncertainty about the model input parameters.

Nanoindentation of the UO₂ samples did not produce any radial cracking. The simulations show the formation of median cracking during nanoindentation. However, it is very difficult to measure median crack length experimentally. As a result, the only way to compare the
nanoindentation experiments to the simulations is by the load-displacement curves, which seem to depend only on the plasticity properties of UO₂, and not on the fracture properties. Thus, it is recommended that future fracture studies of UO₂ should not use nanoindentation, but focus more on microindentation studies. It has also been shown that fracture toughness measurements using indentation have limited accuracy due to slow crack growth affecting measured crack length [9].

Thus, more work is required in the future to validate the phase field model in MARMOT. There are two recommendations for future fracture model validation studies. Firstly, if indentation is to be used to validate the fracture model in MARMOT, Meyer indentation tests should be performed on the UO₂ to allow calculation of the plasticity properties. Secondly, a better approach than indentation is to use strength testing methods such as 3-point or 4-point bending loads for studying fracture properties of UO₂. The tensile loads applied by these methods better resemble the loading conditions present in reactor conditions, for which the phase field fracture model in MARMOT is designed. Under tensile loads, UO₂ is expected to display purely elastic behavior at low temperatures. At higher temperatures, the stress-strain curves from the loading experiments can provide information about the yield strength and hardening behavior of UO₂, data on which is lacking in the literature.

![Figure 5.10: Typical compressive stress-strain curves for UO₂. Tachibana T. et. al (1976)](image)

Figure 5.10: Typical compressive stress-strain curves for UO₂. Tachibana T. et. al (1976)
Chapter 6. Uncertainty Quantifications

The US Department of Energy Nuclear Energy Advanced Modeling and Simulation program is using lower length-scale simulations to assist in the development of improved materials models for fuel performance codes that are based on microstructure rather than burnup. However, it is important to quantify the uncertainty in the lower length-scale simulations. In this work, we conducted sensitivity analysis and uncertainty quantification (UQ) on a mesoscale simulation that has been applied to understand the effective thermal conductivity of UO₂ reactor fuel using the MARMOT tool. We also conducted UQ on mechanistic macroscale models that have been developed to predict the effective thermal conductivity. The most sensitive parameter is the thermal conductivity of bulk UO₂ for the thermal conductivity models. In the future, the predicted simulation distributions need to be compared to experimental data for validation of the models.

6.1. Introduction

Nuclear reactor fuel performance codes predict the thermomechanical behavior of reactor fuel and cladding during reactor operation. Modeling fuel performance is complicated by the various microstructure evolution that occurs within the fuel and cladding during operation. Historically, this evolution has been accounted for using empirical or semi-empirical materials models that are fit to data. However, these models are limited because they only apply to the range of conditions used to obtain the experimental data they are fit to. In addition, these empirical fits are typically correlated to temperature and burn-up (a measure of how much fissioning has occurred within the fuel). However, there is not a unique relationship between burn-up and fuel microstructure.

To overcome these issues with the existing empirical materials models, the US Nuclear Energy Advanced Modeling and Simulation (NEAMS) program has taken a new approach to fuel performance models, summarized by Tonks et al. In this approach, the material property values are based on the current state of the microstructure rather than the burn-up. Mechanistic structure/property relationships are used to define the values of the material properties as functions of the temperature and the microstructure variables. The major disadvantage of this approach is that it is a difficult and time-consuming process to develop all of the necessary microstructure evolution models and structure/property relationships.

In the approach being taken by the NEAMS program, the development of the necessary evolution models and structure property relationships is accelerated by using lower length-scale modeling and simulation to investigate the fundamental mechanisms that are driving the fuel behavior. Mesoscale simulations are used to investigate microstructure evolution and the impact of microstructure on various material properties. The MARMOT tool has been developed by the NEAMS program for such mesoscale simulations. The results from these lower length-scale simulations are used with experimental data to inform the development of the models and relationships needed for a fuel performance code. This multiscale approach to develop mechanistic materials models for fuel performance codes was initially focused on traditional LWR fuel (UO₂) and cladding (zircaloy), but has since been expanded to accident tolerant fuel and cladding concepts and advanced reactor fuel. While the development of these new models is far from complete, preliminary results are promising.

The most critical consideration with regards to both reactor efficiency and safety is how well the fuel can conduct the heat that is generated within it out to the cladding. Unfortunately, the thermal conductivity of UO₂ is very low and gets lower due to microstructure changes that occur during reactor operation. A
mechanistic model is needed that calculates the thermal conductivity as a function of temperature and the values of the microstructure variables. Because the multiscale approach of developing mechanistic models relies heavily on lower length-scale simulations, it is essential that its accuracy be well understood. This requires both uncertainty quantification (UQ) and rigorous validation against experimental data. Methods for UQ and validation at the lower length-scale is still in its early stages, but it is critical to provide sufficient confidence in the new fuel performance materials models.

In this report, we summarize our efforts to conduct UQ on the heat conduction mesoscale modeling focused on porous UO₂. The mesoscale heat conduction simulation is used to determine the relationship between the thermal conductivity and the fuel microstructure. We begin with an introduction of the UQ methods used in this work, followed by a summary of the heat conduction model. We then report how the UQ is conducted on the heat conduction model and the results. We end with some conclusions.

6.2. Applying UQ at the Mesoscale

The purpose of UQ is to quantify the impact of uncertainty on the predictions of a simulation, including uncertainty in the values of input parameters, uncertainty in the form of the model, and numerical error. In essence, UQ considers the fact that, due to uncertainty, simulation predictions are not deterministic but rather are stochastic and can be characterized by a distribution rather than a single deterministic value. The goal of UQ is to accurately propagate all sources of uncertainty through the simulation and to quantify the distribution of the resultant prediction. In this work we will apply UQ to the mesoscale MARMOT simulations of UO₂ heat conduction behavior and to the macroscale mechanistic microstructure evolution model that has been informed by the mesoscale simulations. Three separate analyzes were carried out for the simulation and model: sensitivity estimation for each uncertain parameter, calculation of the mean and standard deviation using a linear approximation with the sensitivities, and a full Monte Carlo (MC) UQ analysis.

The sensitivity of a given parameter is the partial derivative of the value of interest resulting from the model or simulation (represented by the function \( f \)) with respect to one of the input parameters \( c_i \),

\[
S_{c_i}^f = \frac{\partial f}{\partial c_i}.
\] (1)

The sensitivity is typically calculated using the mean value of all the input parameters. The sensitivities can be calculated exactly for an analytical model, but for a simulation the sensitivities must be estimated and there are various methods available for such estimation. In this work, we use the Dakota toolkit to estimate the sensitivities of the MARMOT simulations. It is often useful to compare sensitivities, to determine which parameters have the largest impact on a given result. Each sensitivity has different units and cannot be directly compared, however they can be normalized for comparison. In this work, normalized sensitivities are calculated according to

\[
\tilde{S}_{c_i}^f = \frac{\tilde{c}_i}{\tilde{f}} \frac{\partial f}{\partial c_i},
\]  (2)

64
where $\bar{\chi}$ denotes the mean values of $\chi$.

The uncertainty in the calculated value $f^*$ can be estimated using the mean $\bar{f}$ and the standard deviation $S_f$. The mean is determined by evaluating the model or simulation using the mean value for all input parameter values. $S_f$ can be estimated using the sensitivity values according

$$S_f = \sqrt{\sum_i S_{\chi_i}^2 \sigma_{\chi_i}^2}.$$  

However, this equation assumes that the model is a linear function of each input parameter and that there is no significant covariance between the various parameters. These assumptions are rarely correct, so this approach can be inaccurate. A more accurate, but much more computationally expensive, approach to UQ is the MC approach. When using MC for UQ, the function is evaluated many times, with input parameter values sampled from their corresponding distribution. The Dakota toolkit was used in this work to carry out the MC UQ analysis of the MARMOT simulations.

6.3. Model summaries

The mesoscale simulations of heat conduction have primarily focused on determining how fission gas bubbles impact the thermal conductivity of the fuel. The fission gas is present in the fuel in three general forms: individual atoms distributed in the UO$_2$ crystal lattice, intragranular bubbles that are typically small except at high burnup, and intergranular bubbles that can grow to much larger sizes. The intergranular bubbles grow and interconnect, and eventually provide pathways for the fission gas to escape the fuel pellets. These bubbles are filled with Xe, Kr, and other fission product gases that do not conduct heat efficiently. Thus, the fuel thermal conductivity goes down with time, but each form of fission gas impacts the thermal conductivity in a different way. Mesoscale simulations have focused on determining the impact of the intergranular gas bubbles on the thermal conductivity. All of this information has been put together to create a mechanistic thermal conductivity model that accounts for the three forms of fission gas.

The effective thermal conductivity of a UO$_2$ microstructure is determined using a homogenization approach based on solutions of the steady state heat conduction equation. In MARMOT, the effective thermal conductivity for a give microstructure is determined using asymptotic expansion homogenization. The microstructure of the material is spatially represented in 2D or 3D, and different local thermal conductivities are assigned inside of each feature. The microstructure is randomly generated using a Voronoi tessellation for the grains with spherical bubbles randomly distributed along the GBs. The effective thermal conductivity depends on the values of the local conductivities, the fraction of the overall material taken up by each feature, and the configuration of the features within the material. An example simulation domain is shown in Fig.1. These types of simulations can be carried out in 2D or 3D, where 3D simulations are more accurate but also much more computationally expensive. In this work we carry out 2D simulations, and 3D simulations will be carried out in the future.
Figure 6.1: Example mesoscale domain used to estimate the effective thermal conductivity, where the red regions are bulk UO$_2$, the green regions are the GBs, and the blue regions are the bubbles.

The mesoscale simulation model describes three types of features: bulk UO$_2$, GBs, and fission gas bubbles. The thermal conductivity of bulk UO$_2$ $k_{UO_2}$ is determined from semi-empirical functions of the temperature $T$ and stoichiometry $x$

$$K_{bulk} = \frac{1}{0.0257 + 3.336x + (2.206 - 6.85x)10^{-4}T} + \frac{6400}{(T/1000)^{5/2}} \exp\left(\frac{-16350}{T}\right).$$

(4)

The thermal conductivity of the GB is a function of the thermal resistance of the GB $R_{GB}$ (Kapitza resistance), the bulk UO$_2$ conductivity, and the width of the GB used in the mesoscale representation of the microstructure $w_{GB}$ according to the expression

$$k_{GB} = \frac{k_{UO_2} w_{GB}}{R_{GB} k_{UO_2} + w_{GB}},$$

(5)

where values for the GB thermal resistance in UO$_2$ have been determined using molecular dynamics simulations, shown in Table 2. The thermal conductivity within the bubbles $k_{gas}$ is the thermal conductivity of Xe gas as a function of temperature

$$k_{gas} = \sum_{i=0}^{n} a_i T^{i-1},$$

(6)

where the values for the coefficients $a_i$ are given in Ref. [23].
The mechanistic macroscale model presented by Tonks et al. accounts for the dispersed gas atoms, intragranular bubbles, and intergranular bubbles. Each is included using a different portion of the model. The microstructure is defined in terms of the average grain size $\bar{D}$, the fractional coverage of the GBs by bubbles $f_c$, and the average bubble radius $r_b$. Other parameters used in this macroscale model are $k_{UO_2}$, $k_{gas}$, $x$, $R_{GB}$, and the concentration of Xe gas atoms in the bulk $c_{gas}$.

In this work, results from the macroscale model were compared with those from the mesoscale simulation in both the sensitivity analysis and UQ. Therefore, the parameters must be consistent between the two for them to be comparable. Thus, the same values will be used for $k_{UO_2}$, $k_{gas}$, $x$, $R_{GB}$, and $c_{gas}$. The values used in the macroscale model for the variables defining the microstructure, $\bar{D}$, $f_c$, and $r_b$, were determined from the mesoscale microstructures to ensure a good comparison. The average grain size in the 2D microstructure was calculated according to

$$\bar{D} = 2 \sqrt{\frac{A}{\alpha N}}$$  \hspace{1cm} (7)

where $A$ is the area of the simulation domain, $N$ is the number of grains in the domain, and $\alpha$ is the shape parameter. For the 2D domains used here, $\alpha = 0.6983$. The GB fractional coverage $f_c$ is calculated using

$$f_c = \frac{N_B \pi r_B^2}{A_{GB}}$$  \hspace{1cm} (8)

where $N_B$ is the number of bubbles in the mesoscale simulation, and $A_{GB}$ is the GB area present in the simulation domain.

For all the simulations in this work, we neglect gas atoms within the UO$_2$ matrix, such that $c_{gas} = 0$. The impact of dispersed gas atoms will be investigated in future work.

### 6.4. Sensitivity Analysis

Sensitivity analysis of the effective thermal conductivity $k$ is conducted for both the macroscale model (referred to as “model”) and the mesoscale simulation (referred to as “simulation”). The sensitivities of the model are represented by the partial derivative of the UO$_2$ effective thermal conductivity $k$ with respect to each parameter as
Using Eq. (2) to normalize the sensitivity. DAKOTA is used to sample a few points very close to the mean value of the parameters in the simulation, and calculate the corresponding effective thermal conductivity. The slope of the values of $k$ versus each parameter value are used to estimate the sensitivity. Normalized sensitivities of UO$_2$ at 300K, 800K, and 1500K are shown in Fig. 6.2 and also summarized in Table 1. The sensitivities of the parameters compare very well between the model and simulation, with $k_{bulk}$ having the largest impact. $r_b$ has a lower sensitivity. The sensitivities of $k_g$ and $R_{GB}$ are negligible comparing with the other two.

\[
\begin{align*}
\tilde{S}_{k_{bulk}}^k &= \frac{\partial k}{\partial k_{bulk}} \\
\tilde{S}_{k_{gas}}^k &= \frac{\partial k}{\partial k_{gas}} \\
\tilde{S}_{R_{GB}}^k &= \frac{\partial k}{\partial R_{GB}} \\
\tilde{S}_{r_B}^k &= \frac{\partial k}{\partial r_B}
\end{align*}
\]

Figure 6.2: Normalized sensitivities of the effective thermal conductivity $k$ with respect to the parameters from the model and simulation, where the values for 300 K are shown on the top left, for 800 K on the top right, and for 1200 K on the bottom.
Table 6.1 Normalized sensitivities of the model and simulation at different temperatures

<table>
<thead>
<tr>
<th></th>
<th>300K model</th>
<th>sim.</th>
<th>800K model</th>
<th>sim.</th>
<th>1500K model</th>
<th>sim.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tilde{S}^k_{\text{bulk}}$ ($\times 10^{-3}$)</td>
<td>0.89</td>
<td>1.00</td>
<td>0.95</td>
<td>1.00</td>
<td>0.97</td>
<td>0.99</td>
</tr>
<tr>
<td>$\tilde{S}^k_{\text{gas}}$ ($\times 10^{-3}$)</td>
<td>0.79</td>
<td>0.65</td>
<td>0.82</td>
<td>2.54</td>
<td>0.76</td>
<td>6.25</td>
</tr>
<tr>
<td>$\tilde{S}^k_{\text{R}_{\text{GB}}}$ ($\times 10^{-3}$)</td>
<td>-2.66</td>
<td>-4.77</td>
<td>-0.83</td>
<td>-1.44</td>
<td>-0.33</td>
<td>-0.56</td>
</tr>
<tr>
<td>$\tilde{S}^r_B$</td>
<td>-0.49</td>
<td>-0.23</td>
<td>-0.23</td>
<td>-0.23</td>
<td>-0.13</td>
<td>-0.21</td>
</tr>
</tbody>
</table>

Table 6.2 $R_k$ and $\sigma_{GB}$ at different temperatures

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$R_k$ ($\times 10^{-9}$) (W/mK)</th>
<th>$\sigma_{R_{GB}}$ ($\times 10^{-9}$) (W/mK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>1.48</td>
<td>0.13</td>
</tr>
<tr>
<td>800</td>
<td>0.97</td>
<td>0.057</td>
</tr>
<tr>
<td>1500</td>
<td>0.66</td>
<td>0.087</td>
</tr>
</tbody>
</table>

6.5. Uncertainty quantification

The uncertainty of the effective thermal conductivity $k$ can be approximated using the linear approximation using Eq. 3 or using MC simulation. Here we carried out both approaches and compare the results.

For the linear approximation of the standard deviation of $k$, using Eq. 3, the values for the sensitivities are taken from Table 1. The standard deviation of the input parameters are the same for the model and simulation, with $\sigma_{kb_{ul}k} = 0.06\tilde{k}_{b_{ul}k}$, $\sigma_{kg_{as}} = 0.02\tilde{k}_{g_{as}}$, and $\sigma_{r_b} = 0.3\tilde{r}_b$. The values for $\sigma_{kb_{ul}k}$ and $\sigma_{kg_{as}}$ were determined from experimental data. $\sigma_{r_b}$ was assumed to be one third of the mean value. The value of $\sigma_k_{GB}$ changes with temperature, where the values are shown in Table 2.

The mean value of the effective thermal conductivity is estimated by evaluating the value using the mean parameter values for the model and simulation. The mean and standard deviation obtained from the linear approximation for both the model and simulation at different temperatures are shown in Table 3. The relative contribution of each parameter to the overall variance $\sigma^2$ for the model and simulation are shown in Fig. 6.3.

MC UQ of the analytical model and the MARMOT simulations were conducted with Latin Hypercube Sampling (LHS). 300 samples were used with both the analytical model and the MARMOT simulations. The UQ comparison of the model and simulation at different temperatures are shown in Fig. 6.4. The mean and standard deviation values of the model are shown in Table 3.
Figure 6.3: The relative contributions of each parameter to $\sigma^2$ for the model (left) and simulation (right). In both figures, the contribution of $k_{\text{bulk}}$ is shown in blue and that of $r_B$ is shown in yellow. In the model, $k_{\text{bulk}}$ makes up of 41% in the total uncertainty, and $r_B$ is 59%. In the simulation, $k_{\text{bulk}}$ is 43%, and $r_B$ is around 57%. The other parameters have very small contributions. The relative contributions do not vary significantly with temperature.

Figure 6.4: The distribution of the calculated effective thermal conductivity using the model and simulation at different temperatures, where 300 K are shown on the top left, 800 K on the top right, and 1500 K on the bottom. The solid lines are the mean value of the effective thermal conductivity, and the dashed lines are the mean +/- standard deviation.

Both the macroscale model and mesoscale simulation predict effective thermal conductivity distributions obtained by the MC analysis that are fairly symmetric and could be treated as normal. The $\bar{k}$ and $\sigma_k$ values vary between the model and the simulation. The mean values vary by 3% at 300 K, 9% at 800 K, and 11% at 1500 K; the standard deviation values vary by 45% at 300 K, 36% at 800 K, and 32% at 1500 K,
indicating that the straight-forward mechanistic model is captures the mean and the shape of the thermal conductivity distribution fairly accurately but that the standard deviation is predicted much less accurately. This can be accounted for by the fact that the model uses a series of resistors to approximate the effective bubble-laden GB thermal resistance. It is a simplified system compared with the mesoscale heat conduction solution used in the simulation.

Table 6.3: Linear approximation and MC simulation of the mean and uncertainty of thermal conductivity at different temperatures

<table>
<thead>
<tr>
<th></th>
<th>300K model</th>
<th>800K model</th>
<th>1500K model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear</td>
<td>300K model</td>
<td>800K model</td>
<td>1500K model</td>
</tr>
<tr>
<td>Approximation</td>
<td>sim.</td>
<td>sim.</td>
<td>sim.</td>
</tr>
<tr>
<td>$\bar{k}$ (W/mK)</td>
<td>9.16</td>
<td>4.44</td>
<td>2.62</td>
</tr>
<tr>
<td>$\sigma_k$ (W/mK)</td>
<td>1.43</td>
<td>0.40</td>
<td>0.18</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>300K model</th>
<th>800K model</th>
<th>1500K model</th>
</tr>
</thead>
<tbody>
<tr>
<td>MC Simulation</td>
<td>300K model</td>
<td>800K model</td>
<td>1500K model</td>
</tr>
<tr>
<td>sim.</td>
<td>sim.</td>
<td>sim.</td>
<td>sim.</td>
</tr>
<tr>
<td>$\bar{k}$ (W/mK)</td>
<td>9.15</td>
<td>4.43</td>
<td>2.62</td>
</tr>
<tr>
<td>$\sigma_k$ (W/mK)</td>
<td>0.49</td>
<td>0.25</td>
<td>0.15</td>
</tr>
</tbody>
</table>

In table 3, the simulations by linear approximation and MC simulaitons are very close, indicating that a full MC analysis may not be needed in the future. As shown in Fig.3, the linear approximation predicts that rB has the largest impact on the variance of the thermal conductivity. This is in different that what was shown by the sensitivity analysis (Fig. 6.2). This is because even if kbulk has a higher sensitivity value than rB does, the standard deviation of rB is 30% of the mean value, much higher than the standard deviation of kbulk which is 6% of the mean value. The uncertainty in the predicted thermal conductivity depends on the sensitivities and the standard deviations of the parameters.

Since the simulation only has bubbles on the GB, future work needs to be done to add bubbles inside the grains in the MARMOT simulation and to include the intragranular bubble effect multiplier in the model. To further compare the model and simulation with experiment, point defects effects such as oxygen interstitial and cluster also need to be incorporated into the $K_{bulk}$ equation.

6.6. Conclusions

In this chapter, we have applied preliminary sensitivity analysis and UQ to the effective thermal conductivity model of porous UO$_2$. Both mesoscale simulations using the MARMOT tool and macroscale mechanistic models are employed. The sensitivity analysis identified the bulk thermal conductivity of UO$_2$ to be the most critical parameter for the effective thermal conductivity measurement. Both the mesoscale simulation and the macroscale model had similar parameter sensitivities, indicating that the macroscale models represent the physics in a similar way to the mesoscale models.
UQ was carried out using both a linear approximation based on the sensitivities and using the MC method. The standard deviation predicted by the linear approximation was close to the MC calculated value. The linear approximation was also used to estimate the relative impact of the various parameters on the final variance, giving a different result from the sensitivity analysis regarding which parameter contributed the most to the uncertainty of the final predictions due to the standard deviation dependency of the uncertainty. The mechanistic model resulted in similar uncertainty to the MARMOT simulations, again indicating that the models are a good representation of the physics.

The UQ analysis carried out in this work is an important step to understanding the uncertainty in the model predictions being used as part of the NEAMS-funded effort to improve our fuel performance codes. However, much work is still needed. In particular, the predicted model distributions need to be compared to experimental data to validate the models and provide a confidence level on their predictions.
A List of Publications and Technical Reports Published under the Support of This Project.

(1) Journal publications: 9 journal articles published


- Yinbin Miao; Tiankai Yao; Jie Lian; Jeffrey Fortner; Laura Jamison; Ruqing Xu; Abdellatif Yacout, Correlation between Crystallographic Orientation and Surface Faceting in UO₂, *Journal of Nuclear Materials*, 478 (2016) 176-184.


(2) Journal papers under preparation and submission:


2. K. Shrestha, Tiankai Yao, J. Lian, D. Antonio, Michael Tonks, and K. Gofryk, The grain boundary effect on thermal conductivity of uranium dioxide, to be submitted.
(3) Books or other non-periodical, one-time publications:


- Yinbin Miao, Kun Mo, Laura M. Jamison, Jie Lian and Tiankai Yao, and Sumit Bhattacharya, Experimental studies of Micro- and Nano-grained UO$_2$: Grain Growth Behavior, Surface Morphology, and Fracture Toughness, ANL/NE-16/12.

- Jon Carmack, Lori Braase, Cynthia Papesch, David Hurley, Yongfeng Zhang, Krzysztof Gofryk, Jason Harp, Xianming Bai, Brandon Miller, Assel Aitkaliyeva, James King, Rita Hoggan, Adrian Wagner, Kate Richardson, Scott Middlemas, and Jie Lian, FY2016 PEMP 1.1A – Summary Report - Demonstrate high spatial resolution measurements at the micro-structural level on as-fabricated nuclear fuels and materials.
Acknowledgments

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**OVERVIEW**

**Purpose:** To obtain critical experimental data of how different microstructure features of sintered UO₂ fuels affecting thermal transport and fracture behavior, and validate NEAMS tool MARMOT for predicting thermal transport and fuel fracture.

**Objectives:**
- Sintering UO₂ samples with controlled microstructures (grain size, pore, fission bubble, porosity and pore distribution either in intra- or inter-granular pores);
- Thermal conductivity measurements of these well-characterized polycrystalline samples;
- Indentation testing of sintered UO₂ with various grain size, porosity and stoichiometry to obtain fracture and crack propagation mechanisms (inter or intra-granular fracture);
- Validation and uncertainty quantification of the MARMOT thermal transport and fracture models. The high quality experimental data will be used to validate the predictions of MARMOT for thermal transport and fracture, using average data and local microstructure information.

**IMPACT**

**Logical Path:**

Design and synthesis of UO₂ with well-controlled Microstructure $\iff$ Experimental Data of Thermal-mechanical Properties $\iff$ MARMOT modeling and validation

**Outcomes:**
1. Synthesis of UO₂ fuel pellets with well-controlled and quantified microstructures;
2. High quality quantitative data on thermal transport and fracture in well-characterized microstructures;
3. Validation and uncertainty quantification of the MARMOT thermal transport and fracture models;
4. Fracture models; Scientific articles in peer-reviewed journals and conferences and presentations

**RESULTS**

1. Sintering and fabrication of the UO₂ with controlled microstructure and fuel chemistry as model systems for MARMOT validation.
2. Obtaining critical experimental data on thermal transport and mechanical properties of the sintered UO₂.
3. Validation of the MARMOT thermal transport and fracture models.
4. Uncertainty Quantification and sensitivity analysis of the MARMOT thermal transport and fracture models.

**Accomplishments:**
- 9 journal articles published in total and two papers in submission/preparation.
- 4 Technical reports to DOE NE;
- 3 conference papers published in ANS 2016 Transaction;
- 11 invited talks on MST, TMS, MRS, AFC, PARIM, ANS, and CARAT annual meetings

**DETAILS**

**Principal Investigator:** Jie Lian  
**Institution:** Rensselaer Polytechnic Institute

**Collaborators:** Michael Tonks (Univ. Florida); Wen Jiang and Krzysztof Gofryk (INL)

**Duration:** 3 years  
**Total Funding Level:** $800,000

**TPOC:** C. Brooks Weingartner

**National Technical Director:**  
David Pointer

**Federal Manager:** Dan Funk

**Workscope:** NEAMS-1  
PICSNE Workpackage #:  
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