TiO₂ doped UO₂ Fuels Sintered by Spark Plasma Sintering

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Abstract:

UO₂ fuels doped with oxide additives Cr₂O₃ and TiO₂ display larger grain size, improving fission product retention capability and thus accident tolerance. Spark plasma sintering (SPS) was applied to consolidate TiO₂-doped UO₂ 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 UO₂ fuel pellets to improve fuel performance.

Keywords: UO₂; TiO₂ Doped fuel; Spark Plasma Sintering; Accident Tolerant Fuels

1. Introduction

The accident at the Fukushima Daiichi nuclear plant have led to urgent research demand for the development of accident-tolerant fuels (ATF) which can better tolerate a loss of active coolant while maintaining or improving fuel performance during normal operation as compared to the currently-widely used UO_2 -zircaloy system [1-3]. Key properties of ATF fuels include: high thermal conductivity, oxidation resistance, and suitable high temperature mechanical performance, which culminate to result in improved accident tolerance. Previously-proposed ATF concepts include SiC-UO_2 composite fuels, microencapsulated ceramic fuels, and nitride-based fuels [4]. The synthesis, characterization and performance evaluation of different fuel forms are currently under extensive investigation. An important consideration for development of accident tolerant fuels is the fission product retention capability. It has been envisioned that the fuels with larger grain size possess elongated pathways for fission product diffusion from within grains to the grain boundaries and thus can greatly improve the fission product retention capability and in turn the safety margin of the reactor performance, particularly under the extreme conditions associated with a loss of coolant accident.

To manipulate microstructure and obtain larger grain-sized UO_2 fuel pellets, oxide dopants were used as sintering additives [5-10] including TiO_2 [11, 12], Cr_2O_3 [13], Al_2O_3 [14], and MgO [15] were studied with the focus on their effects on fission gas retention and fuel swelling in-pile performance. Unique features of oxide-doped fuels include greatly-enlarged grain size, as large as $100\text{ }\mu\text{m}$, significantly larger than that of standard fuel ($10\text{-}15\text{ }\mu\text{m}$). Large fission gas bubbles with the average size of $\sim 0.2\text{ }\mu\text{m}$ are found to be trapped within enlarged UO_2 grains doped with MgO [16] at a burn up of $28,500\text{ MWd/t(U)}$, indicating the inability of diffusion of fission gases to the grain boundary. Increased grain size significantly reduces both

fission gas release and dimensional change of fuel pellet during irradiation [17]. However, similar to the pure UO_2 fuel pellets, the conventional fabrication of the oxide-doped fuels with grain size $\sim 100 \mu\text{m}$ requires sintering at high temperature and a long duration (*e.g.*, 1750°C for 4 hours) in a hydrogen reducing environment.

Advanced sintering methods, involving fast volumetric heating based on fast field-assisted technologies (FAST) such as spark plasma sintering (SPS) or microwave sintering, have attracted extensive attentions during past decades due to significantly-reduced sintering time and/or lower temperature. During SPS sintering, a concurrently-applied hydraulic pressure facilitates the densification, resulting in a dense microstructure with limited grain growth, and the grain growth can be obtained at elongated sintering time after densification. Very recently, Ge *et al.* [18] applied SPS to sinter pure UO_2 pellet, and indicated that the pellet sintered in simple vacuum conditions ($\sim 10 \text{ Pa}$), instead of controlled hydrogen atmosphere, was reduced to stoichiometric $\text{UO}_{2.00}$ during sintering process from the starting hyper-stoichiometric $\text{UO}_{2.16}$ due to the reducing environment of graphite dies of SPS system. The entirety of SPS sintering lasts less than one hour, greatly reducing the sintering time required as compared to traditional fuel fabrication approaches. These features underline the advantages of SPS as compared to conventional sintering methods for UO_2 fuel fabrication. Furthermore, the elongated sintering required for a grain growth process in order to obtain microstructure with large grain size can be reduced by the addition of oxides as sintering additive, and it is possible to achieve dense UO_2 fuel pellets with greatly enhanced grain-size by SPS at relatively short sintering duration and/or lower temperature.

In this work, we report the fabrication and characterization of dense UO_2 fuel pellets with enlarged grain size by doping with TiO_2 and subsequently sintering by SPS. Their thermal and mechanical properties are also investigated. UO_2 powder was firstly doped by 0.5 wt. % anatase

TiO₂ through high energy ball milling (HEBM), and subsequently consolidated into dense pellets (> 95 % TD) using SPS at various temperatures (1500 °C, 1600 °C, and 1700 °C) with an applied pressure of 40 MPa. Microstructural evolution, phase and chemical compositions, and fuel stoichiometry of the sintered fuels are characterized by scanning electron microscopy (SEM), x-ray diffraction (XRD), Raman spectroscopy and Energy-Dispersive X-ray spectroscopy (EDX) measurements, respectively. The secondary phase formation was studied in order to elucidate the mechanism of TiO₂ additive in promoting UO₂ sintering and grain growth. Micro-hardness testing and a laser flash analysis were applied in investigating the hardness, crack propagation, thermal diffusivity and conductivity, respectively. The effects of TiO₂ doping on UO₂ grain growth, fuel chemistry, and thermal-mechanical properties are discussed correlating with the microstructure evolution and stoichiometry of the SPS densified doped fuels.

2. Experiment

2.1 Powder fabrication

Pure UO₂ (hereafter unless specified, this formula does not necessarily mean an O/U ratio of 2) powders (Fig. 1a) were purchased from International Bio-analytical Industries Inc. (Boca Raton, Florida, USA). 0.05 g anatase TiO₂ (anatase, 45 nm, MTI corp.) was mixed with 10 g UO₂ powder in a 80 ml Tungsten carbide bowl and mechanically milled by 10 mm WC milling balls. HEBM (Fritsch, Pulverisette 7, Idar-Oberstein, Germany) was conducted at 500 rpm for 30 mins by a nonstop milling without liquid milling media. After milling, composite powders were stored in glove box for subsequent sintering.

2.2 Spark plasma sintering

SPS sintering was conducted on a Dr. Sinter ® SPS-211 Lx system for both control and doped powders. For each pellet, around 2 g powders were loaded into a graphite die with 15 mm inner diameter wrapped by a graphite felt to prevent radiative heat loss during sintering and mitigate thermal gradient to the cold chamber. A 0.20 mm thick graphite paper was placed between powder and punch & inner surfaces of the graphite die to facilitate post-sintering pellet dismounting. The assembled die was located between two graphite spacers connecting with stainless steel electrode on each side. Temperature was monitored by a pyrometer focusing on the graphite die, 2 mm away from powder samples. It firstly increased to 600 °C from 465 °C (lowest temperature that can be detected by a pyrometer) in 4 mins. After holding at 600 °C for 2 mins, temperature increased to 1200 °C at a rate of 100 °C/min. Later on, the temperature increase rate was lowered to 50 °C/min. Sintering was carried on at different target temperatures (1500 °C, 1600 °C, and 1700 °C) for various holding time (hereafter those samples are refereed as 1500-doped, 1600-doped, and 1700-doped samples). After sintering, slow cooling and holding at 1300 °C for 5 mins were applied to prevent formation of thermal-induced cracking so that a whole pellet with a well maintained structural integrity can be obtained. A uniaxial pressure of 40 MPa was applied at the beginning of sintering and released to minimum loading (around 1.7 MPa) during cooling to 1300 °C. Power was shut down after this holding step. A control pellet was also sintered directly from the starting UO_2 powder at 1500 °C by similar sintering parameter (hereafter referred as 1500-undoped).

2.3 Microstructure characterization

After sintering, all pellets were mechanically polished using a 600 grit SiC sand paper to remove residual graphite paper. The density of sintered pellets was measured based on Archimedes method using an Adam ® analytical scale with an accuracy of a millionth gram and

a hanging system (Danbury, NY, USA). Distilled water was used as the immersing medium. Crystallization information was obtained by a Panalytical X' Pert (Westborough, MA, USA) x-ray diffractometer with a copper target as x-ray source ($\text{Cu } K_{\alpha} = 0.15406 \text{ nm}$) and the scanning step is 0.0131° . Raman spectra of sintered pellets were obtained using a Renishaw Raman spectrometer (Renishaw PLC., UK) with argon laser (514 nm) focused on sample surface with a spot size of $\sim 1 \text{ }\mu\text{m}$. A Carl Zeiss Supra (Jena, Germany) field emission SEM was used to character microstructural features of sintered pellets focusing on grain size, pores and secondary phase formation. Before SEM characterization, a layer of platinum was deposited on sample surfaces in an argon atmosphere using a Denton Sputter (Denton Vacuum, LLC, NJ, USA).

2.4 Mechanical and thermal properties measurement

Micro-hardness testing was performed with the load of 1 Kg on the sintered fuel pellets in order to obtain hardness and crack propagation behavior upon indentation on TiO_2 -doped fuels. Laser flash apparatus (LFA-457, NETZCH, Germany) was used to measure thermal diffusivity of sintered pellets. An 8 mm square sample was cut from sintered pellets with thickness direction parallel to applied force during SPS for thermal diffusivity measurement, and consequently polished down to around 0.5 mm thick. Both upper and lower surfaces of the sample were coated with graphite spray that can withstand temperature up to 1100°C . Measurements were conducted in an argon inert atmosphere at a flow rate of 150 ml/ min. Half time for signal receiving was restricted to be less than 200 ms. Cape-Lehman and pulse corrections were applied to fit the signal – time curve so as to determine the thermal diffusivity. Thermal conductivity was calculated based on $K = \alpha\rho C_p$, where α and ρ is measured thermal diffusivity and density of pellets, respectively; C_p denotes specific heat of the sample. In this study, C_p values of UO_2 from literature [19] was used for sintered pellets as the loading ratio of TiO_2 is only 0.5 wt. %.

Bulk density measured at room temperature was used throughout the temperature span without considering thermal expansion.

3. Results and discussion

3.1 *HEBM process to dope TiO₂-into UO₂ powders*

The starting UO₂ powder sample are agglomerates of ~0.5 μm crystalline (Fig. 1a). After TiO₂ doping by HEBM, the agglomerates are crumbled with no appreciable size change of UO₂ crystalline. Notable are the excessive TiO₂ nano particles uniformly decorates on UO₂ crystalline (Fig. 1b), indicating a homogenous doping achieved by HEBM. TiO₂ has a limited solubility (between 0.07-0.13 wt.% at 1650 °C [20]) in UO₂ matrix, well below the doping concentration of 0.5 wt.% and as a result, it is reasonable to observe those excessive nano-size TiO₂ on UO₂ crystalline surface. On the other hand, upon mechanical attrition by HEBM the mixture of TiO₂ and UO₂, excess TiO₂ may be dissolved into UO₂ crystal lattice beyond the solubility predicted by thermodynamics.

XRD spectrum (Fig. 1c) reveals the crystal structure modification after TiO₂ doping. For starting UO₂ powder, (111) diffraction peak (Insert in Fig. 1c) was located at a 2θ degree higher than the value reported for stoichiometric UO₂ (28.23°, marked as dash line in Fig.1c insert) [18, 21], 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 [22], 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 TiO_2 can be observed in the XRD patterns (Fig. 1c) for the doped powders upon HEBM, most likely due to the low concentration of TiO_2 (~0.5 wt.%) and as well as the incorporation of partial TiO_2 into UO_2 lattices forming a solid solution. However, all XRD peaks of TiO_2 doped UO_2 shifts to lower 2θ angles than that of the starting UO_2 . Such a shift indicates an increase of UO_2 lattice parameter by HEBM doping. The shift of XRD peaks and lattice parameter change for UO_2 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 Ti^{4+} (0.074 nm for 8 coordination) than that of eight-coordinated U^{4+} (0.1 nm) and U^{6+} (0.086 nm) [22], 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 [23], large enough to allow readily accommodation of Ti^{4+} . Consequently, UO_2 lattice would be expanded by the incorporation of interstitial Ti^{4+} ions and lead to the shift of the (111) peak of UO_2 lattice toward a lower 2θ . This claim is also in line with previous experimental results [24]. The incorporation of the interstitial Ti^{4+} ions and a slight lattice expansion of the oxygen-enriched UO_2 crystal structure may promote the sintering and grain growth due to the potentially enhanced atom diffusion at the absent of liquid phase formation.

3.2 Density and microstructure of the SPS densified UO_2 doped with TiO_2

After SPS processing, pellets sintered from un-doped and doped powders with different density and microstructure (Table.1) were obtained. 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. 2a-2d) and ceramography (Fig. 2e-2g) of the polished surface of the densified doped and undoped UO₂ pellets with different sintering conditions. Inter-granular fractures dominate the fracture surface of the 1500-undoped sample with pores distributed on the grain boundaries (Fig. 2a). Grain size is estimated to be $13 \pm 5 \mu\text{m}$ for the pure UO₂ pellet. However, fracture surface of the 1500-doped pellet (Fig. 2b) shows a mixture of inter- and trans-granular patterns with the estimated grain size of $17 \pm 5 \mu\text{m}$. Increasing the sintering temperature further to 1600 °C (Fig. 2c) enlarges the average grain size to $28 \pm 4 \mu\text{m}$. Further increase in the sintering temperature to 1700 °C (Fig. 2d) results in significant grain growth as revealed by the grain size up to $81 \pm 10 \mu\text{m}$ (Fig. 2g). Inter-granular fracture dominates fracture behavior of the 1700-doped sample. The enhanced grain sizes for the TiO₂-doped pellets at higher sintering temperatures are also evidenced by the ceramography (Figs. 2e-2g).

High magnification SEM images of the fracture surfaces (Fig. 3) of the fuel pellets doped with TiO₂ show distinct microstructural features including secondary phase formation and pore distribution. For the 1500-doped pellet, bar-shaped TiO₂ crystallites with length of several μm can be found across the UO₂ grain boundaries and also within inner grains. Intra-granular pores are also identified within UO₂ grains. The lower density of TiO₂ and microstructural cavities may be responsible for the relatively-lower density for the 1500-doped pellet as compared with the pure UO₂ pellet. The bar-shaped TiO₂ secondary phase for the 1500-doped pellet evolved into a more spherical shape (Fig. 3b) for the pellet sintered at 1600 °C, and the TiO₂ spheres were located at the grain boundaries of the UO₂ 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 °C, a distinct interfacial phase can be identified across grain boundaries and triple junctions showing highly porous features (Figs. 3c and 3d). A slight decrease in density was observed for the pellet sintered at 1700 °C as compared to the 1600-doped pellet. The porous phase (Fig. 3d) 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 °C, higher than the reported eutectic temperature of 1645 °C.

UO_2 has a high melting point, ~ 2800 °C, and sintering UO_2 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 [25] in which the uranium diffusion significantly affects the densification and sintering of dense UO_2 fuel pellets. To achieve a higher densification rate at a relatively low temperature, hyper-stoichiometric $\text{UO}_{2.25}$ [26] 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 UO_2 that can accelerate the sintering process [27].

Doping UO_2 with transitional metal oxides, such as Nb_2O_5 [28-31], Cr_2O_3 [5, 13, 15, 32-34], and TiO_2 [8, 12, 20, 30, 33, 35, 36] 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 [28]. For example, for Nb_2O_5 , Nb^{5+} ions can directly substitute U^{4+} 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 [37]. In contrast, the direct substitution of Cr^{3+} and Ti^{4+} on U^{4+} 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 TiO_2 -doped UO_2 (*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 Ti^{4+} 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 [34], and the enhanced uranium diffusion rate promotes sintering process. The incorporation of Ti^{4+} into interstitial sites of the uranium lattice can be inferred by the shift of XRD peaks of UO_2 induced by HEBM milling. As a result of enhanced uranium diffusion in an expanded structure, a noticeable grain growth was also found in 1500-doped pellet ($17 \pm 5 \mu\text{m}$) as compared with 1500-undoped ($13 \pm 5 \mu\text{m}$) using same sintering parameters.

EDX elementary mapping (Fig. 4) and linear composition scanning (Fig. 5) were performed on the doped pellets sintered at different temperatures in order to investigate composition evolution of both UO_2 fuel and secondary phase either within or at UO_2 grain boundary. Consistent with fracture surfaces shown in Fig. 3, 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 (Fig. 4a, 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 UO_2 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. 3d). EDX mappings (Figs. 4d and e) show that those phases are titanium enriched and oxygen depleted as compared with the surrounding UO₂ matrix. Small amount of uranium also diffused into the secondary phases, which is further confirmed by linear scanning results (Fig. 5).

The composition difference between UO₂ grain and secondary phases were quantitatively analyzed by EDX line scanning (Fig. 5). With increasing of sintering temperature, oxygen content profile (Fig. 5e) across the secondary phase on UO₂ grain boundary changed from convex (1500 °C) to flatten (1600 °C), and further to concave (1700 °C) as compared to the surrounding UO₂ matrix, indicating a gradually depletion of Oxygen with increasing of sintering temperature. However, titanium becomes enriched with increased sintering temperature, indicating that the segregation of the Ti from inner UO₂ grains to the secondary phases. Uranium can hardly be detected when sintering temperature is lower than 1600 °C. The diffusion of uranium into secondary phase for the pellet sintered at 1700 °C is evidenced in Fig. 5f by the gradually change of concentration across the secondary phases. This result indicates the formation of a new phase by the reaction between TiO₂ additive and UO₂ at the sintering temperature of 1700 °C, which is above the proposed eutectic point (1645 °C) based on the TiO₂-UO₂ phase diagram [36]. A stable compound with a nominal chemical composition of UTi₂O₆ can form with a brannerite structure [38-40]. However, the new phase was not detected by XRD for the pellet sintered at 1700 °C, potentially due to the limited amount new phase and very low initial TiO₂ doping content. Previous literature also reported the eutectic phase in the binary system of UO₂-TiO₂ enriched with titanium [8, 12, 20, 30, 33, 35, 36], confirmed by EDX linear scanning in this work. A similar liquid phase from Nb₂O₃-doped UO₂ fuel pellets was

identified as UNb_2O_6 by electron micro-probe analysis (EMPA) [29]. Those factors suggest that a liquid eutectic brannerite phase enriched with titanium may form and solidify in the TiO_2 -doped UO_2 fuel pellet upon the SPS sintering at 1700 °C.

3.3 Fuel Chemistry and Stoichiometry by XRD and Raman analysis

XRD and Raman spectra were analyzed to determine the stoichiometry, vibration properties and crystal structure of the SPS-densified TiO_2 doped UO_2 fuel pellets. Both XRD and Raman spectrum analysis are widely used to reveal crystal structure information of UO_2 . XRD analysis can characterize structural information of the uranium sub-lattices due to a much larger scattering of uranium than oxygen. Raman spectra are sensitive to the distortion of both uranium and oxygen sublattice and thus can reveal the structural characteristics with a low symmetry resulting from developed discrete oxygen clusters within UO_2 host lattice, critical to understand the variation of the oxidation state of the uranium and the phase transition between UO_2 and U_4O_9 [41].

As briefly mentioned earlier, a close correlation exists between the stoichiometry of UO_2 and the (111) diffraction peak position. For example, the lattice constant derived from XRD obtained from UO_2 pellets sintered by SPS [18] is estimated to be perfect UO_2 with the (111) peak located at 28.22°. The 2 θ of the (111) diffraction peak for U_4O_9 locates at 28.42° [42]. As a result, the peak position of the (111) diffraction allows the determination of the stoichiometry of the SPS-densified TiO_2 -doped pellets. Fig. 6 shows a close up of the (111) peaks for sintered pellets without removing K_{a2} shoulder peaks. For pure UO_2 pellets sintered at 1500 °C, the (111) diffraction peak is located at 2 theta of 28.22°, suggesting that the pellet sintered by SPS maintains a nearly perfect stoichiometry with O/U close to 2. In contrast, the (111) diffraction peaks for the starting UO_2 powder is located at ~28.5° (Fig. 1c), suggesting a

hyper-stoichiometric feature with oxygen enrichment. For hyper-stoichiometry UO_{2+x} in which the dominant defects are oxygen interstitials, U^{5+} and U^{6+} are required to maintain the charge neutrality, and the smaller-sized U^{6+} as compared to tetravalent U^{4+} leads to a structural contraction and thus XRD peak shifts towards increasing 2θ . The significant shift of the (111) diffraction peak towards stoichiometric UO_2 from the oxygen-enriched composition indicates that SPS process enables the control of sintered pellets' stoichiometry from the highly reducing graphite environment. The stoichiometric control of fuel pellets sintered by SPS without pre- or post-treatments was also reported in recent literature [18] in which the hyper-stoichiometric $\text{UO}_{2.16}$ was reduced to stoichiometric UO_2 upon brief low temperature SPS.

For the doped UO_2 pellets sintered by SPS at different temperatures, a continuous shift of the (111) peak toward increasing 2θ was observed from the pure pellet to the doped pellets at 1500 °C and 1600 °C (28.26°), indicating a continuously-increased hyper-stoichiometry with a greater O/U ratio. This result suggests that the doping of the TiO_2 retards the reduction of the hyper-stoichiometry to perfect UO_2 induced by SPS. In reality, TiO_2 was applied to induce hyper-stoichiometry in UO_2 , resulting a coexistence of hyperstoichiometric UO_2 and substoichiometric TiO_2 [11]. Further increases in the sintering temperature up to 1700 °C, the (111) peak shifts back aligned with that of the 1500-doped pellets, indicating a similar stoichiometry for both samples. Its reason may lie on the consumption of Oxygen ions supplied by UO_2 grains to form the liquid phase during sintering, successfully lowering the oxygen content within in UO_2 and decreasing its hyperstoichiometry.

Fig. 7 shows the Raman spectra of the sintered UO_2 pellets. Due to the low concentration of anatase TiO_2 in doped powders, only Raman peaks of UO_2 are observed. For $Fm3m\text{-UO}_2$, the T_{2g} U-O stretch model at 445 cm^{-1} , perfectly predicted by classical group theory [43, 44], can be

assigned to the symmetric stretch of oxygen vibrations around U^{4+} of the fluorite structure, and thus this peak is considered an indicator for the integrity of UO_2 crystal. The T_{2g} U-O stretch model at 445 cm^{-1} experiences a loss of intensity and shifts to a higher angle with excess oxygen into the host UO_2 crystal structure [41]. The Raman peak at $\sim 918\text{ cm}^{-1}$ can be assigned tentatively to 2 TO_R model [45]. The peak at $\sim 1150\text{ cm}^{-1}$, originally claimed to be associated with electronic origin [46] can be assigned to be an overtone (2LO) of the LO phonon mode at $\sim 575\text{ cm}^{-1}$ [45]. This peak behaves as a characteristic “finger print” [47] of the hyper-stoichiometric of uranium dioxide UO_{2+x} with the x value less than 0.09, and the peak intensity gradually decreases and eventually disappears with the change of stoichiometry from UO_2 to $UO_{2.09}$. On the other hand, the T_{2g} model shifts to a higher angle and its intensity is weakened by excess oxygen being incorporated into UO_2 structure, resulting in a transition from fluorite to tetragonal phases.

Using the 2LO mode at $\sim 1150\text{ cm}^{-1}$ as an indicator of hyper-stoichiometry, the peak intensity decreased accordingly from 1500-undoped, 1500-doped and 1600-doped samples, suggesting an increasing hyper-stoichiometry for the fuel pellets sintered at higher temperatures. This is consistent with the continuous shift of the (111) diffraction peak toward a higher 2 theta observed in the XRD patterns (Fig. 6). The Raman spectrum of the 1500-undoped sample shows the highest intensity at $\sim 1150\text{ cm}^{-1}$. 1500-doped and 1700 doped pellets displayed similar 2LO mode peak intensity at this shift, suggesting a similar stoichiometry between these two samples, again similar to the observation of the exact (111) diffraction peak shifting as observed in the XRD pattern. The 1600-doped pellet displayed the lowest intensity for the 2 LO mode, indicating the highest hyper-stoichiometry among all of the samples.

For doped UO_2 fuels, another feature of the Raman spectra is the peaks between 500 and 700 cm^{-1} . The intensity of the peaks in this region appeared to increase with accumulation of structure defects introduced to UO_2 crystal lattice by oxide doping [48]. Another study underlined the appearance of peaks at this range for U_4O_9 ; whereas no peaks were found in this region for UO_2 [49]. In our study, the intensity of peaks (Figs. 7b-7e) at this range, mainly the peak at $\sim 570 \text{ cm}^{-1}$, increased consistently from pure UO_2 to 1600-doped pellets and decreased for the doped pellet sintered at 1700 °C. This trend is also consistent with the variation of the stoichiometry as revealed from XRD diffraction patterns in which the pure sample was nearly perfect UO_2 and 1600-doped pellets shows the most hyper-stoichiometry.

Another peak, located at $\sim 630 \text{ cm}^{-1}$, displayed noticeable intensity changes which can attributed to cuboctahedra constituting U_4O_9 phase [47, 49]. However, this assignment has been questioned recently since this peak can also be observed at stoichiometric SIMFUEL UO_2 (simulated high burn-up fuel) [48]. Similarly, this peak appears on the spectrum obtained from stoichiometric 1500-undoped UO_2 pellet. However, the intensity for this peak is remarkably high for the 1600-doped pellet as compared to the 1500-doped and 1700-doped pellets. This result suggests that the intensity of this peak may be partially correlated with excessive interstitial oxygen within UO_2 crystal structure.

Based on systematic XRD, Raman, EDX and SEM investigations, a correlation can be established among the phase and fuel stoichiometry, microstructural and morphological evolutions, as well as the chemical doping of the TiO_2 -doped UO_2 upon SPS sintering at varying sintering temperatures (see schematic view of the Fig. 8). TiO_2 dopant undergoes morphology evolution from bar shaped to sphere with increase of sintering temperature from 1500 °C to 1600 °C. Comes along with this evolution is the oxygen inter diffusion between TiO_2 and UO_2 .

Further increase sintering temperature to 1700 °C, high porous secondary phase covers the triple junction area of grain boundary (highlighted by the blue phase in Fig. 8c). This phase is believed to be liquid at the sintering temperature based on $\text{TiO}_2\text{-UO}_2$ phase diagram as discussed before and thus promotes the U ion diffusion at the solid-liquid interface and the UO_2 grain growth during sintering.

In general, doped UO_2 fuel pellets can be densified at temperature above 1500 °C. The increase of sintering temperature from 1500 °C to 1600 °C enlarges the grain size from ~17 to ~27 μm . Extensive mechanical attrition induced by ball milling may introduce significant amount of TiO_2 into the UO_2 matrix beyond its solubility, and the incorporation of the Ti^{4+} into the uranium interstitial site can lead to a lattice expansion, promoting sintering and densification processes.

SPS processing can greatly reduce the stoichiometry of the initial hyper-stoichiometric UO_2 powders during sintering to obtain a nearly perfect stoichiometric UO_2 fuel pellet. However, TiO_2 doping will impede the reduction of the stoichiometry induced by SPS, leading to higher hyperstoichiometry as compared with undoped samples. In addition, extra TiO_2 introduced into the UO_2 crystal above its solubility induced by non-equilibrium HEBM may be segregated out upon high temperature sintering and precipitate into μm -sized bar-shape secondary phases, in which the nano-sized TiO_2 decorated onto the UO_2 surface may behave as the heterogeneous sites for precipitation and growth. Upon sintering at 1600 °C and thus greater atomic mobility, the secondary TiO_2 phase undergoes a morphological evolution from bar to spherical shapes, which is primarily distributed at grain boundary. By comparison, 1600-doped pellets show increased solubility of TiO_2 and are in turn more hyper-stoichiometric than the 1500-doped pellets. Further increasing sintering temperature to 1700 °C above the eutectic point of $\text{UO}_2\text{-TiO}_2$,

a new liquid eutectic phase forms upon the reaction between TiO_2 and UO_2 and distribute at the triple junction of the UO_2 grains, significantly improving the sintering kinetics and a drastic size increase up to 80 μm . The significantly-reduced Ti incorporated into the UO_2 grain (as shown in Fig. 4d) and SPS process at higher temperature drive the fuel pellets to be more stoichiometric as compared to the 1500-doped pellets.

3.4 Mechanical and Thermal Properties of the SPS sintered TiO_2 -doped UO_2 pellets

Vickers micron hardness tests were performed on the sintered fuel pellets to study the hardness (Fig. 9) and probe crack propagation behavior (Fig. 10). A load of 0.49 N was applied to generate dents of $\sim 10 \mu\text{m}$ in diagonal length. As the size of dents is comparable with that of grains within 1500-undoped, 1500-doped, and 1600-doped pellets, grain boundary spalling is observed and in line with previous study [33, 50]. Therefore, the Vickers hardness values are affected by both the interiors of grains and the grain boundary properties. The Vickers hardness value for 1500-undoped sample was $6.3 \pm 0.5 \text{ GPa}$, displaying an excellent agreement with reported micron hardness values for UO_2 [51, 52]. This value remains nearly unchanged for 1500-doped pellet with a value of $6.4 \pm 0.6 \text{ GPa}$. However, appreciable increase of micro hardness can be found in 1600-doped sample as compared to the 1500-doped sample. This is consistent with the previous literature in which hyper-stoichiometric UO_2 displayed a higher hardness than stoichiometric UO_2 [11, 53]. Further increase in sintering temperature to 1700 $^\circ\text{C}$, as revealed by Fig. 3d, resulted in grains as large as 80 μm with porous secondary phases located at triple junction area of grain boundaries, which may be responsible for the lower Vickers hardness observed.

Upon indentation, radial cracks dominate fracture patterns as observed in 1500-undoped, 1500-doped, and 1600-doped pellets. With increases in sintering temperature and grain size, a

perceptible transition from inter-granular fracture in 1500-undoped and 1500-doped pellets to mixture of trans- and inter-granular fracture in 1600-doped pellet was also observed Fig. 10. After liquid phase formation at triple conjunction grain boundaries, radial cracks almost disappear and a quasi-lateral crack pattern is observed in doped-1700 pellet. The number of cracks was reduced due to the larger grain size although the propagated length for each crack remains comparable. Indentation-induced crack propagates trans-granularly for the pellet sintered at 1700 °C due to the significantly-enlarged grain size.

Temperature dependent thermal diffusivity of the doped pellets was measured by a Laser flash method from 300 K to 1300 K, and the thermal conductivity was determined by the measured thermal diffusivity and heat capacity in literatures. A typical behavior of nonconductive ceramic materials was observed for the doped fuel pellets with reduced thermal diffusivities at elevated temperatures (Fig. 11). The thermal conductivity of UO_2 is primarily the sum of three contributions: phonon transport or lattice vibrations, an ambipolar contribution which arises as a result of small polaron production, and a radiation contribution. The phonon transport dominates the thermal conductivity of UO_2 at low temperature, and as a result, the enhanced phonon scattering rates with increased temperature significantly reduces the thermal conductivity of UO_2 pellets. Since doping is typically expected to reduce the phonon contribution to the thermal conductivity due to phonon scattering, the comparable thermal conductivity of the doped UO_2 pellets with respect to the standard UO_2 pellets at higher temperature may be attributed to the increased contribution from small-polaron production. These results underlines the immense potential of SPS in fabricating of TiO_2 doped large grain size UO_2 nuclear fuel with unimpaired thermal performance.

Conclusions

Dense UO_2 fuels with significantly enlarged grain size can be synthesized by SPS at temperatures from 1500 to 1700 °C within short sintering time. The incorporation of sintering additive TiO_2 significantly enhances grain growth sintering and powder sinterability, TiO_2 -doped fuel pellets with grain as large as 80 μm can be obtained by sintering at 1700 °C for 20 mins. XRD and Raman analysis that SPS can reduce the hyper-stoichiometry UO_2 powder to nearly perfect stoichiometric UO_2 , and the addition of TiO_2 increases the hyper-stoichiometry of the doped fuel. A secondary TiO_2 was identified within grains and also grain boundaries for the pellets sintered below eutectic points. At higher temperature, an eutectic phase forms, greatly enhancing the sinterability of the powders and promoting grain growth. The doped fuel pellets show comparable thermal conductivity with the standard UO_2 pellets. These results suggest that SPS, as a unique field assisted sintering technology, holds great potentials for fabricating large grain sized fuels within very short times, and the doping of TiO_2 may be beneficial to the fuel performance based on significantly enlarged grain size and exceptional thermal transport behavior.

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Figure Captions

Fig. 1. SEM images of starting UO_2 powder (a) and TiO_2 -doped UO_2 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°

Fig. 2. 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)

Fig. 3. High magnification SEM images showing the secondary phase formation in 1500-doped (a), 1600-doped (b), 1700-doped (c), and an enlarged view of the eutectic phase acquired from the yellow box highlighted in (c)

Fig. 4. 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.

Fig. 5. EDX elementary line scanning across the secondary phase showing the chemical variation from the UO_2 grains to the secondary phases: (a) 1500-doped, (b) 1600-doped, (c) 1700-doped fuel pellets. Correspondingly elemental profiles (d: Ti; e: O and f: U) are also presented

Fig. 6. XRD of sintered pellets showing the shift of the UO_2 (111) diffractions with sintering temperature and variation of the fuel stoichiometry

Fig. 7. (a) Raman spectra of the fuel pellets sintered at different temperatures; and peak deconvolution within the range of 400 cm^{-1} to 700^{-1} for 1500-undoped (b), 1500-doped (c), 1600-doped (d), and 1700-doped fuel pellets (e)

Fig. 8. Schematic of secondary phase formation and morphology evolution for TiO_2 doped UO_2 pellet sintered at 1500 °C (a), 1600 °C (b), and 1700 °C (c) (not down to scale).

Fig. 9. Micro-hardness of the TiO_2 -doped UO_2 fuel pellets

Fig. 10. SEM images of dent from micro-hardness test on 1500-undoped (a), 1500-doped (b), 1600-doped (c), and 1700-doped (d) by a load of 1 kg weight force

Fig. 11. Thermal diffusivity (a) and thermal conductivity (b) of the sintered doped pellets with literature value of thermal conductivity for comparison

Fig. 1. Yao *et al.*

Fig. 2. Yao *et al.*

Fig. 3. Yao *et al.*

Fig. 4. Yao *et al.*

Fig. 5. Yao *et al.*

Fig. 6. Yao *et al.*

(a)

(b)

(c)

(d)

(e)

Fig. 7. Yao *et al.*

Fig. 8. Yao *et al.*

Fig. 9. Yao *et al.*

Fig. 10. Yao *et al.*

Fig. 11. Yao *et al.*

Table 1. Sintering parameter and physical density of the TiO₂-doped UO₂ pellets sintered by SPS.

Powder	Sintering parameters	Density (% TD)
Starting UO ₂	1500-5	98.35
TiO ₂ doped UO ₂	1500-5	97.17
TiO ₂ doped UO ₂	1600-20	98.40
TiO ₂ doped UO ₂	1700-20	98.27