

Densification of Spark Plasma Sintered UO_2 -SiC Composites with Varying SiC Volume Fractions

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1. Introduction

The primary ceramic nuclear fuel, Uranium Dioxide (UO_2), has a low thermal conductivity (6.8 W/mK at 373K [1]) which results in extreme centerline temperature and thermal gradient of a nuclear fuel during an operation of a nuclear reactor. These decrease the energy output of a nuclear reactor and safe margin through harmful phenomena such as thermal cracks, fission gas release and swelling.

Due to the benefit of high thermal conductivity of SiC (273.6 W/mK at 373K [2]), it has been shown that the thermal conductivity of UO_2 can be enhanced by including SiC particles or whiskers into UO_2 matrix [3]. When compared to the literature UO_2 value [1], ~14, 26, 43, and 50% increased thermal conductivity were obtained by adding 5, 10, 15, and 20vol% SiC, respectively [4]. These experimentally obtained values were in good agreement with theoretically calculated effective thermal conductivities of UO_2 -SiC composites [5].

In contrast to the conventional sintering method, Spark Plasma Sintering (SPS) technique can sinter UO_2 -SiC composites with enhanced thermal conductivity [3]. SPS is an advanced method to consolidate poorly sinterable materials through high electric current inducing spark discharge, local heating and melting, and particle surface activation which give rise to neck formation between particles. Several researchers have successfully sintered strongly covalent bonded ceramics such as borides (ZrB_2 , TiB_2), oxides (AlO_2), and carbides (WC) at a low temperature in a short time [6-9]. The use of this advanced technique has expanded to the fabrication of nuclear fuels. UO_2 and UO_2 -SiC fuel pellets with high density (>95%TD) were successfully sintered by SPS at as low as 1050°C only for 30sec and 1500°C for 5mins, respectively [10].

Although UO_2 -SiC composite pellets have been successfully sintered in SPS, literature on their SPS processing is limited. In this work, the fundamental densification of UO_2 and UO_2 -SiC composites sintered by SPS was studied to investigate the influence of SiC addition on the densification of UO_2 .

2. Experiments

2.1 Sample Preparation

The uranium dioxide ($\text{UO}_{2.11}$) powder was obtained from AREVA NP, Richland, WA and 1 μm SiC powder was obtained from Superior Graphite, Inc., Chicago, IL,

USA. UO_2 -1 μm SiC composites with 5, 10, 15, and 20vol% were fabricated using SPS. For the comparison study, a UO_2 pellet was also fabricated by SPS. Hold time, up/down ramp rate, maximum hold temperature, and pressure were maintained at 5mins, 100°C/min, 1450°C, and 36MPa for all composite fabrications, respectively.

UO_2 and SiC powders were mixed in a SPEX 8000 blender for 3 hours with the aid of 2,3-Dihydroperfluoropentane. After blending, the mixture was stayed in a hood for 5 hours to dry up 2,3-Dihydroperfluoropentane. Mixed powder was then added into a graphite die with 12.3mm diameter. For SPS sintering, thin graphite foil was placed between mixed powder and graphite die to prevent reaction between powder and graphite wall and ease the extraction of sintered pellet. The filled graphite die then placed into a chamber of Dr. Sinter® SPS-1030 system for sintering.

Fig. 1 shows typical SPS processing parameters during the sintering of UO_2 -SiC composites. Both actual and programmed temperatures are plotted above 600°C because this is the minimum measureable temperature by a pyrometer. The programmed temperature was maintained at 600°C for 7mins and then increased until 1400°C with 100°C/min ramp-up rate. The programmed ramp-up rate was decreased to 50°C/min to provide enough time for pressure control while the temperature is increasing to 1450°C. The programmed temperature was held at 1450°C for 5mins and decreased to 600°C with symmetrical ramp-rates. The actual temperature was calibrated to follow up the programmed temperature during first 7 mins and then increases along with the programmed temperature. The actual hold time is little larger than programmed hold time, 5mins, because the actual temperature was accelerated and retarded to the programmed temperature increase and decrease, respectively. During the ramp rate of 50°C/min, right before the maximum temperature, the pressure was controlled to increase to 36MPa and maintained for 5mins. When the maximum temperature completed the controlled pressure was released. After the entire 29mins sintering process, the graphite die stayed in SPS chamber for 45mins to cool down. The sintered pellet was then extracted from the graphite die and its surface was grounded using 400 grit SiC abrasive paper to eliminate the attached graphite foil.

While the diameter of sintered pellet is same as that of graphite die (12.5mm in this work), the thickness is

determined by the mass of $\text{UO}_2\text{-SiC}$ mixture. Fig. 2 shows the typical shape of $\text{UO}_2\text{-SiC}$ composite. The diameter of sintered composite pellet is similar to that of graphite die, 12.3-12.5mm, and the thickness is about 6.5mm for 8g mixture. 12.5mm graphite die and 8g mixture were used for the fabrication of all $\text{UO}_2\text{-SiC}$ composites.

2.2 Characterization methods

The fabricated composites and UO_2 pellet specimens were mechanically polished with successively smaller grit SiC abrasive paper, diamond particles, and finally $0.06\mu\text{m}$ colloidal silica. Thermal etching at 1350°C for 4hours in Ar ($>99.999\%$ purity) atmosphere was performed using a furnace (Lindberg 1700°C tube furnace) to reveal grain boundaries of composites. The microstructure of composites was observed using Scanning Electron Microscopy (SEM, JEOL JSM-6335F) with $10\mu\text{A}$ electron beam current and 15 kV accelerating voltage. The UO_2 grain size was measured three times at different locations for each composite specimen using the line intercept method [11].

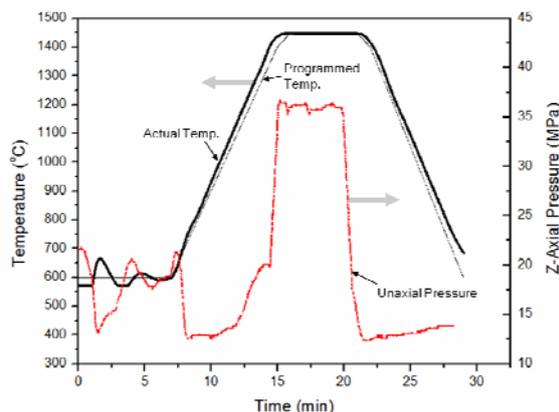


Fig. 1. SPS parameter profiles for $\text{UO}_2\text{-SiC}$ composites containing various volume fractions of $1\mu\text{m}$ SiC particles. The gray arrows indicate the direction of axes labels.

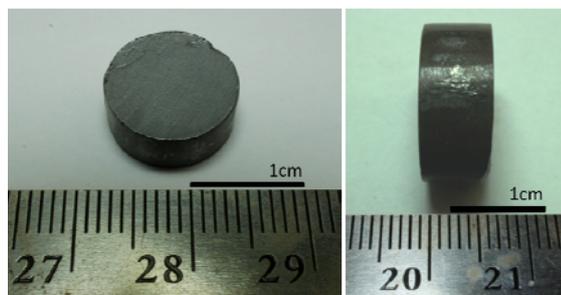


Fig. 2. A SPS sintered $\text{UO}_2\text{-10vol}\%\text{SiC}$ composite with 12.5mm in diameter and 6.5mm in thickness.

3. Results and Discussion

Fig 3 shows the densification behavior (displacement of lower graphite punch) of UO_2 and $\text{UO}_2\text{-SiC}$ composite powders containing various SiC particle volume fractions with increasing SPS sintering time. The change of sintering temperature with time is also plotted. The initial compact of each composite powder is different so that the displacement is set at 0 after SPS adjusts the initial temperature (600°C). When the sintering temperature increases from 600°C each powder start to compact. UO_2 powder is the most sensitive to the initial temperature increase and the compaction is more rapidly proceeded than those of any other composites. The densification of UO_2 is almost completed near 1100°C and further densification is barely appeared. This phenomena is in good agreement with reported primary UO_2 densification range (720°C - 1000°C) in SPS process [10]. The displacement of $\text{UO}_2\text{-SiC}$ composites begins between 680°C and 750°C . Generally, the densification rate decreases with increasing SiC volume fraction due to the hindrance of UO_2 densification. These rates further decrease when the ramp/up rate is decreased to $50^\circ\text{C}/\text{min}$ at 1400°C . When the mechanical pressure (36MPa) is applied just before the maximum temperature (1450°C), the displacement of composites increases. The increase of densification due to the pressure is more pronounced with increasing SiC volume fraction. While the densification rate of the composite containing 5vol% SiC then becomes slow, three composites containing 10, 15, and 20vol% SiC are compacting with steady densification rate during the hold time at maximum temperature with compression. Once the maximum temperature decreases and applied pressure is released, the densification of the composite containing 5vol% SiC is completed is not observed and the composites containing 10, 15, and 20vol% SiC become slow reaching to final displacement. This plot shows the densification hindrance of SiC addition to UO_2 powder; densification is more difficult with increasing SiC volume fraction. Moreover, it is clearly seen that the mechanical pressure is essential for the compaction of $\text{UO}_2\text{-SiC}$ composites in this SPS profile.

To reveal and compare the densification rate of UO_2 and $\text{UO}_2\text{-SiC}$ composite pellets in detail, the densification rate is calculated and plotted in Fig. 4 as a function of sintering temperature. In the densification rate, $d(\Delta L/L_0)/dt$, ΔL is the displacement of graphite and L_0 is the green body thickness just before the temperature increase. While UO_2 desify rapidly and the primary densification range is relatively narrow, 600°C - 1000°C , the densification of $\text{UO}_2\text{-SiC}$ composites slowly occur and cover wider range of temperature. With increasing SiC volume fraction, this phenomenon is well defined. The primary densification range of $\text{UO}_2\text{-5vol}\%\text{SiC}$ and $\text{UO}_2\text{-10vol}\%\text{SiC}$ composites are 750°C - 1400°C , and $\text{UO}_2\text{-15vol}\%\text{SiC}$ and $\text{UO}_2\text{-20vol}\%\text{SiC}$ composites cover almost all sintering processes. Similarly, in general, the densification rate at

the maximum temperature (1450°C) with the applied mechanical pressure (36MPa) is higher with increasing SiC volume fraction. The rate of composites containing 0, 5, 10, 15, and 20vol% SiC are 0.02, 0.04, 0.03, 0.07, and 0.08 mm⁻¹. Except the densification rate at the maximum temperature, the maximum densification rate of UO₂ and UO₂-SiC composites are all located between 800°C and 1000°C. The maximum densification rate decreases with increasing SiC volume fraction. For example, the rate of composites containing 0, 5, 10, 15, and 20vol% SiC are 0.21, 0.12, 0.09, 0.07, and 0.06 min⁻¹, respectively.

Fig. 5 shows the density of UO₂ and UO₂-SiC composites as a function of maximum sintering temperature. The density values of UO₂ pellets in this plot are referenced from Lihao et al. [10]. Utilized SPS conditions for the fabrication of UO₂ and UO₂-SiC composites are identical except mechanical pressure and cooling rate. While 40MPa and natural cooling rate are utilized to fabricate UO₂ pellets in this reference, UO₂-SiC composites are fabricated at 36MPa and controlled cooling rate in this study. Because the inconsistency is relatively small, it is assumed that the influence of these discrepancies on the density is negligible for comparison study. It is clearly seen that the composite containing higher volume fraction of SiC obtains lower density. While the relative density of UO₂ is near 97% at 1050°C, the composites containing 5 and 10vol% SiC only have 83% and 70.5% relative densities, respectively. Higher sintering temperature range, 1350°C-1450°C, is necessary to fabricate higher than 95% relative density UO₂-5vol%SiC and UO₂-10vol%SiC composite pellets. Even higher than 1450°C sintering temperature is probably required to fabricate higher density UO₂-20vol%SiC composite pellets than 95% relative density.

The grain size of UO₂ in UO₂-SiC composites containing various volume fractions of 1µm SiC particles is measured to evaluate the influence of SiC addition on the grain size of UO₂. Fig. 6 shows that the UO₂ grain size is significantly reduced with SiC addition. The initial SPSed UO₂ grain size, 6µm, is reduced to 1.5µm with only 5vol% SiC addition. With increasing SiC volume fraction, however, from 5vol% to 10, 15, and 20vol%, the grain size of UO₂ matrix is maintained at similar level near 1.3-1.6µm. This reduction in the grain size is due to the pinning effect of SiC particles. The influence of pinning effect is not changed by the further addition of SiC volume fraction.

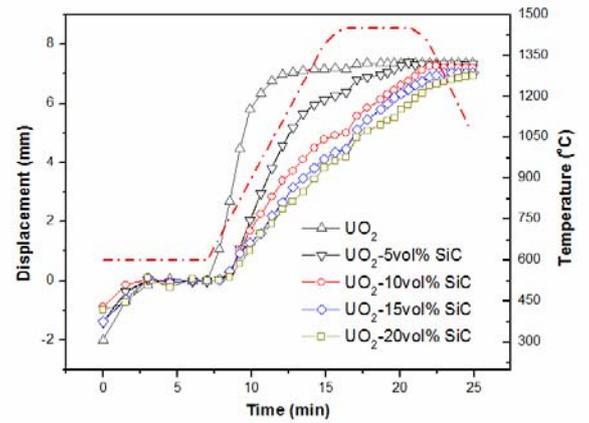


Fig. 3. Sintering behavior of UO₂ and UO₂-SiC composite containing various volume fractions of SiC during SPS process.

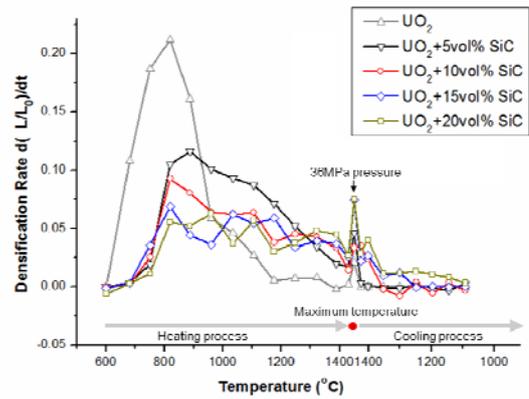


Fig. 4. Densification rate of UO₂ and UO₂-SiC composites containing different volume fractions of SiC as a function of temperature.

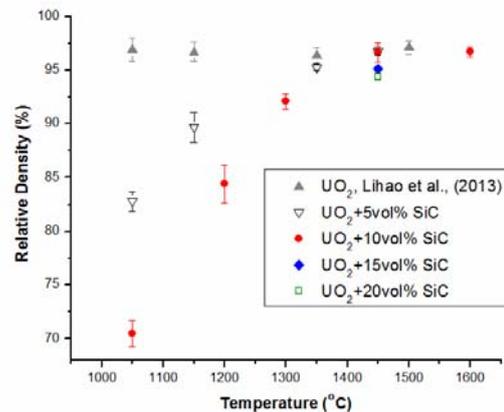


Fig. 5. Densification rate of UO₂ and UO₂-SiC composites containing different volume fractions of SiC as a function of temperature.

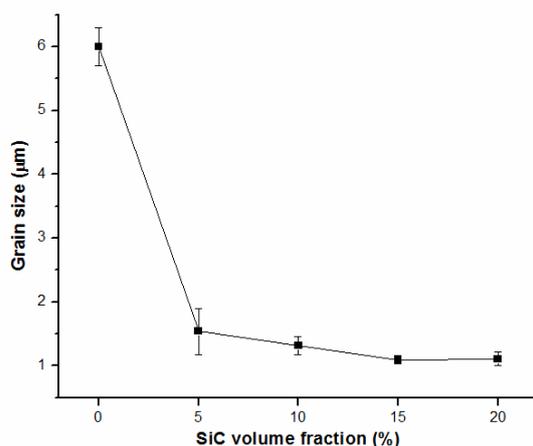


Fig. 6. Grain size of UO_2 -SiC composites containing different volume fractions of SiC addition.

4. Conclusions

The influence of SiC addition of UO_2 -SiC composite fuels on the densification of UO_2 was studied. The mechanical pressure during SPS sintering was essential for the densification of UO_2 -SiC composites. UO_2 -SiC composites are more difficult to sinter with increasing SiC volume fraction. The densification rate of composites containing 0, 5, 10, 15, and 20vol% SiC were 0.21, 0.12, 0.09, 0.07, and 0.06 min^{-1} , respectively. While the high density UO_2 pellet near 97% is obtained at 1050°C, higher sintering temperature range, 1350°C-1450°C, is necessary to fabricate high density UO_2 -5vol%SiC and UO_2 -10vol%SiC composite pellets. Moreover, even higher temperature probably is required to sinter the composites containing 15 and 20vol% SiC. The grain size measurement revealed that the initial grain size reduction by adding 5vol% SiC was significant. However, the further addition of SiC didn't have much influence on the grain size.

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