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High temperature thermal physical performance of BeO/UO_2 composites prepared by spark plasma sintering (SPS)

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ABSTRACT

In this paper, 10 vol% BeO/UO_2 composites were fabricated by SPS technique. The thermal physical performance above the sintering temperature was reported for the first time. The thermal conductivity of BeO/UO_2 was significantly enhanced compared to pure UO_2, especially in the high temperature range close to an accident condition. The coefficient of thermal expansion (CTE) presented rapid falling trend above the sintering temperature, owing to the stress release and further sintering. Such results were of considerable importance for the design of nuclear fuel system.

UO_2 is utilized as nuclear fuel for commercial light-water reactors due to its high melting point, high radiation resistance, good compatibility with claddings and excellent corrosion resistance to water steam. Nevertheless, the low thermal conductivity of UO_2 may induce sharp temperature gradient inside UO_2 pellets and further leads to pellet failure or even melting during a serious loss of coolant accident (LOCA). McCoy and Mays [1] pointed out that even modest (5–10%) thermal conductivity increment would significantly reduce center temperature, internal pressures and fission gas release. It is an effective approach to improve the fuel safety by promoting thermal conductivity. Consequently, high thermal conductivity phases, such as SiC [2,3,4,5], diamond [6,7], BeO [8,9,10,11] and carbon nanotubes [12], are introduced into UO_2 pellets to improve the thermal conductivity.

Among these additives, BeO exhibits high thermal conductivity (230–330 $W \cdot m^{-1} \cdot K^{-1}$) [13], low capture cross section, good neutron moderation, high resistance to water steam and excellent compatibility with UO_2 below 2160 °C. Therefore, it has been considered as a promising additive for increasing thermal conductivity. The thermal conductivity of BeO/UO_2 is mainly affected by the fraction and the distribution of BeO. Usually, a larger BeO addition amount corresponds to a higher thermal conductivity. However, considering on the uranium inventory, BeO addition needs to be limited to a moderate value. 10 vol% BeO has been confirmed as an optimized addition as it can reduce the fuel pellet center temperature by 320 °C with only slight uranium inventory decrease during LOCA [14]. On the other hand, a continuous BeO structure is more effective than a dispersed structure in promoting UO_2 thermal conductivity according to the investigation of Ishimoto S. [8] and Solomon et al. [9,10,11]. Heat tends to transfer through the continuous BeO structure due to its low resistance. 10 vol% BeO addition with a continuous structure could gain 80–100% enhancement in thermal conductivity below 250 °C [15]. Therefore, it is an excellent choice to add 10 vol% BeO with continuous structure on considering both thermal conductivity and uranium inventory.

To obtain continuous structure, it usually needs creating large UO_2 granules and coating them with fine BeO powders. During the subsequent compression molding and sintering, BeO powders link to each other and form continuous structure. In conventional methods, BeO/UO_2 composites are usually pressureless sintered at 1700 °C or even higher temperature for several hours. The whole sintering process takes >20 h to obtain densified pellets. Therefore, the anisotropic grain growth of BeO is inevitable, which increases the risk of pellet cracking during irradiation.

SPS technique, as a field assisted sintering method, can realize fast sintering at relatively low temperature [16]. It is in expectation that BeO grain growth can be inhibited by utilizing SPS. Furthermore, the fabrication process can be greatly shortened and simplified. Recently, SPS technique has been applied to fabricated UO_2 [3,17], SiC/UO_2 [2,3,4] and $diamond/UO_2$ pellets [6,7]. It has been proved that SPS is an effective route to maximize the effect of second phases on improving thermal conductivity. Firstly, O/U ratio can be automatically reduced to 2.00 due to the reaction between UO_2 powders and graphite

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environment [18]. Moreover, the harmful interface reaction can be restrained due to fast sintering. However, little reference reports the performance of BeO/UO_2 composites prepared by SPS.

Currently, the property characterization of BeO/UO_2 emphasizes on thermal conductivity. The pellet temperature can exceed the sintering of BeO/UO_2 during a serious LOCA. It is necessary to investigate BeO/UO_2 performance at such high temperature. However, the thermal physical properties of BeO/UO_2 above the sintering temperature are seldom reported.

In this paper, BeO/UO_2 composites with continuous BeO structure were prepared by SPS. The thermal physical properties above the sintering temperature were studied for the first time. The results provided necessary supporting information to the design of BeO/UO_2 nuclear fuel system.

A pre-sintering process was adopted for the granulation of UO_2. The starting UO_2 powders were 3–5 μm in particle size and >99.9% in purity. UO_2 sintering compacts were prepared by SPS at 700 °C for 5 min with argon protection. A pressure of 25 MPa was applied during the whole SPS process. The received compacts were ~65% TD. Such compacts were ground, sieved to −30 mesh screen size, and then self-milled for 2 h in a Nylon jar to obtain UO_2 granules. The UO_2 granules together with 10 vol% BeO powders (1–3 μm, purity > 99.9%) were mixed in a ZrO_2 jar for 24 h.

The mixtures of UO_2 granules and BeO powders were placed in a graphite die for SPS. The graphite die was rapidly heated to 1300 °C with argon protection. Then a slower heating rate of 50 °C/min was employed to reach the sintering temperature of 1400 °C. The immersing time was 10 min. A pressure of 25 MPa was applied on the graphite punches during the whole SPS process. For comparison, UO_2 samples with a close density were sintered at 1200 °C for 5 min.

The sample density was measured by Archimedes method. Three samples were utilized for checking repeatability.

The thermal conductivity of BeO/UO_2 was tested by a laser flash apparatus (LFA 427, Netzsch, Germany). The sample dimension was about Φ 12.7 × 3 mm. The testing temperature range was 25–1600 °C, with an interval of 200 °C.

CTE was tested by DIL 402 E high temperature dilatometer (Netzsch, Germany). The testing sample was about 8 mm in diameter and 15 mm in length. The testing temperature ranged from 25 °C to 2000 °C, with a heating rate of 5 °C/min. The reference temperature for CTE calculation was 25 °C in this paper.

The microstructure was analyzed by laser scanning confocal microscope (LSCM, LEXT OLS4000, Olympus) and scanning electron microscope (SEM, Helios NanoLab 600i, FEI).

The SPS behavior of BeO/UO_2 can be firstly learned from its temperature and displacement curves, as shown in Fig. 1. These curves of UO_2 are also presented for comparison. Due to the fast heating speed in the beginning, a small hump occurs around 600 °C on both temperature curves. On the displacement curve of BeO/UO_2, a platform is detected between 1.4 and 1.8 min, which corresponds to the temperature range of 610–650 °C. The displacement increases sharply before the platform, while the increasing speed slows down after the platform. This indicates the compact starts to sinter below 600 °C and "pauses" sintering during 610–650 °C. A similar platform can be observed on the displacement curve of UO_2. Therefore, the sintering behavior below 600 °C is mainly caused by UO_2. In the following SPS process, the displacement of BeO/UO_2 reaches its maximum value at 1050–1150 °C and then slowly drops. The descending segment manifests the expanding speed gets faster than the sintering speed.

The UO_2 and BeO/UO_2 pellets are prepared by the SPS process shown in Fig. 1. The densities of UO_2 and BeO/UO_2 are 96.1 ± 0.3% and 95.3 ± 0.4% TD, respectively. The microstructure is investigated to further study the high temperature thermal physical performance. Fig. 2 shows the LSCM and SEM images of UO_2 and BeO/UO_2. It can be seen from Fig. 2a that the average UO_2 grain size is around 5 μm. Little grain growth can be observed due to the relatively low sintering temperature and short immersing time. In addition, small pores can be observed inside UO_2 grains, which are probably caused by the fasting sintering speed [17]. Gas products are inevitable during SPS process as UO_2 reacts with the carbon environment. The fast-formed necks trap these gases, resulting in the intra-grain pores. As shown in Fig. 2b, BeO particles distribute along the boundary of UO_2 granules and form a continuous net structure. It can be expected that such microstructure will bring considerable enhancement in thermal conductivity. Further SEM image in Fig. 2c shows that some small pores distribute inside the UO_2 granules. The pores may be harmful to mechanical properties. But a moderate pore mount will increase the inclusivity of fission gases and promotes the pellet performance in reactors. For commercial UO_2 pellets, the porosity is often controlled at 5 ± 1%. The BeO/UO_2 pellets in this paper have a close porosity and thus can be expected to exhibit good inclusivity of fission gases. The morphology of BeO continuous structure is presented in Fig. 2d. It can be seen BeO particle size is around 2 μm. Little particle growth can be observed owing to the fast sintering speed. Such small BeO particles can reduce the crack risk induced by anisotropic irradiation growth [9]. Some fine UO_2 particles can be also detected in the BeO net structure. These particles may be introduced through the grinding and self-milling process of UO_2. Such UO_2 particles may slightly lower the thermal conductivity. However, they can also inhibit the grain growth of BeO and enhance the pellet safety in reactors.

Thermal conductivity and CTE are two crucial parameters for the nuclear fuel pellets. This work will focus on both parameters. Fig. 3a shows the CTE of BeO/UO_2 composites. The CTE slowly grows from 9.06 × 10^{-6}/K to 10.95 × 10^{-6}/K with temperature increasing from 100 °C to 1500 °C. Nevertheless, it then rapidly drops to 1.35 × 10^{-6}/K with temperature further rising to 2000 °C. The thermal expansion curve in

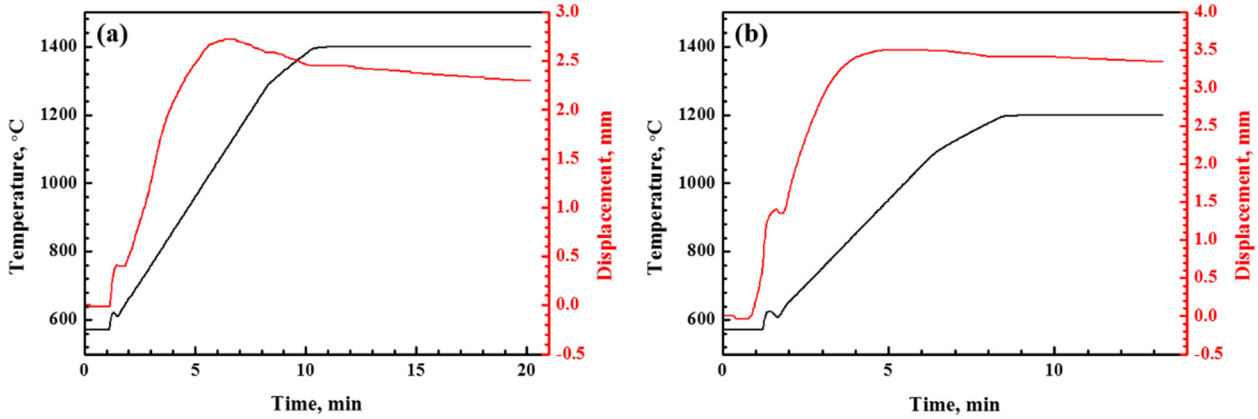

Fig. 1. The actual temperature and displacement curves of BeO/UO_2 composites (a) and UO_2 (b) during SPS process.