Carbothermic Reduction Behavior of ZrO_2-C Kernels Prepared via Internal Gelation

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1. Introduction

Uranium oxycarbide (UCO) is a key fuel kernel material utilized in TRISO (Tri-structural isotropic fuel) coated particle fuels. UCO consists of a ternary mixture of UO_2, UC, and UC_2. The fabrication of UCO fuel kernels involves the high-temperature heat treatment of spherical intermediate compounds. UCO was developed to combine the advantageous properties of UO_2 and UC, enabling improved performance under high-temperature and high-power operating conditions.

UCO fuel kernels are fabricated by calcining and sintering microspheres of uranium hydroxide gel and carbon mixture produced through internal or external gelation processes. The carbothermic reduction process is utilized for carbide production. Since carbothermal reduction is a solid-state reaction, it is essential to disperse carbon particles with fine size and high surface area within the UO_2 matrix to achieve a densified, crack-free and highly carbide-converted UCO kernel. For this reason, internal gelation is conventionally preferred to homogeneously incorporate carbon black particles into uranium hydroxide gel microspheres. Since the reaction between UO_2 and carbon also has a complex thermochemical process, it is necessary to carefully optimize the reaction temperature and atmosphere.

To establish engineering-scale production of UCO kernels, KAERI (Korea Atomic Energy Institue) is developing a UCO fuel kernel fabrication technology, with particular focus on the heat treatment of gel-derived intermediate compounds. In this study, ZrO_2–C kernel surrogates produced via the internal gelation method [1] are used to investigate optimal heat treatment parameters. This paper reports preliminary results on the carbothermic reduction behavior and kernel characteristics after heat treatment under varying temperatures and gas atmospheres.

2. Experimentals

ZrO_2–C kernels are prepared through internal gelation. Internal gelation is a process that fabricates gel microspheres by drop-casting broth solution into hot silicon oil. To successfully incorporate carbon black into gel microspheres, it must be homogeneously dispersed in the broth solution prior to drop-casting. The size of gel microspheres can be controlled by adjusting the diameter of the needles, the flow rate of the broth solution, and the frequency of the vibrator. After aging, the gel microspheres are washed to remove impurities that cause microcracks during heat treatment.

Three types of gel-derived microspheres were fabricated by the internal gelation process. The kernel samples used in the experiments are summarized in Table 1. The L4 sample is not included in the table and it refers to a spherical compound fabricated by internal gelation, representing the as-fabricated and pre-heat treated sample. The C/Zr ratio was 1.1. Heat treatments were performed under different temperatures and gas atmospheres.

The carbothermic reduction behavior was examined using simultaneous thermal analysis (STA) and thermogravimetry–differential scanning calorimetry (TG-DSC) to monitor weight changes during heat treatment. Post-treatment, structural changes of the kernels were characterized by X-ray diffraction (XRD). For samples in which the carbothermic reduction was incomplete, thermogravimetric oxidation tests were additionally conducted to estimate the residual carbon content.

Table 1. ZrO_2-C kernel samples

Sample	L1	L2	L3-1	L3-2
C/Zr	1.1	1.1	1.1	1.1
Furnace	Electric	Electric	STA TG-DSC	STA TG-DSC
Temperature	1600 ℃	1600 ℃	1467 ℃ 1600 ℃	1467 ℃ 1600 ℃
Atmosphere	Ar-50%CO	Ar-50%CO	Ar	Ar
Time	3h	3h	4h	4h

3. Results

Fig.1 presents the XRD patterns of the as-fabricated L4 sample, and the L1 and L2 samples after heat treatment and subsequent oxidation in air. The as-fabricated L4 shows a broad diffraction peak, indicative of cubic ZrO_2. Heat treatment induces a transformation to monoclinic ZrO_2, with additional diffraction peaks corresponding to carbon. In L1, no ZrC phase is detected, whereas L2 exhibits a minor ZrC peak. After oxidation, the carbon phase disappears, and monoclinic ZrO_2 transforms into the tetragonal phase.

Fig. 2 shows the TGA weight-loss curves of L1 and L2 during oxidation in air. Consistent with the XRD results, the residual carbon in the heat-treated kernels was oxidized, leading to weight loss. Given the negligible ZrC content observed in XRD patterns, the weight loss is attributed entirely to carbon oxidation.

If the L1 and L2 were a mixture of ZrO_2 and ZrC, oxidation of ZrC to ZrO_2 in air would be expected to increase the weight. Since the ZrC phase in L1 and L2 is either absent or only barely detectable, little to no weight change should occur upon oxidation. However, the both samples heat-treated in 50% CO atmosphere, exhibited a marked weight loss. This indicates that L1 and L2 samples remain a mixture of ZrO2 and C, with insufficient progress of the carbothermic reduction. The residual C/Zr ratios in L1 and L2 after heat treatment were estimated as 0.6 and 0.75, respectively.

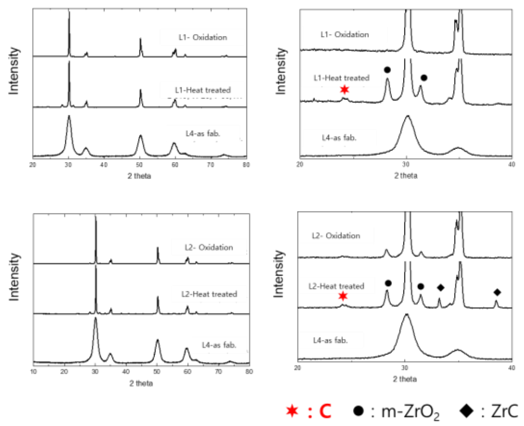

Fig. 1. XRD patterns of kernel samples

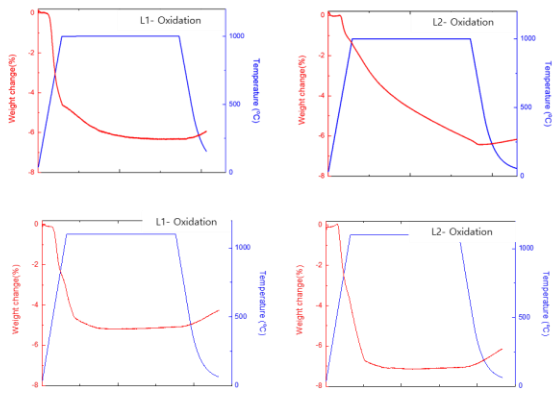

Fig. 2. Weight loss of L1 and L2 kernels during the oxidation in air

Fig. 3 shows the weight-change behavior of L3-1 and L3-2 during heat treatment at 1467 °C and 1600 °C in Ar. A sharp weight loss occurs up to ~900 °C, corresponding to calcination of the gel to ZrO_2. A second weight loss, beginning above 1300°C, is attributed to carbothermic reduction. The reduction proceeds more rapidly at 1600 °C, indicating temperature-accelerated kinetics. Assuming that the calcined kernel is a mixture of ZrO_2-C, the weight change observed above 1300 °C can be attributed to carbothermic reduction. By converting the weight change, the C/Zr ratio in the calcined kernel can be estimated. From the weight change and assuming complete reduction reaction, the C/Zr ratios of the calcined L3-1 and L3-2 samples were estimated to be 0.74 and 0.55, respectively.

In the carbothermic reduction reaction, CO gas is generated, and its equilibrium partial pressure is determined under thermodynamic equilibrium conditions. If the CO partial pressure in the heat-treatment atmosphere exceeds this equilibrium value, the reaction is suppressed [2]. A comparison of the L1 and L2 samples with L3-1 and L3-2 shows that, in the CO-rich atmosphere of L1 and L2, ZrC formation was highly limited. In contrast, L3-1 and L3-2 heat-treated in an Ar atmosphere exhibited a distinct weight loss, indicating that sufficient carbothermic reduction had occurred. The suppression of ZrC formation at higher CO partial pressure has also been reported. The study found that specimens heat-treated at 1550 °C formed ZrC when the CO fraction in the Ar-CO mixture was below 20 %, but not when it exceeded 40 % [3]. Therefore, it is necessary to control the CO ratio in the heat-treatment atmosphere with respect to the equilibrium CO partial pressure at the given temperature. For the L1 and L2 samples, it is likely that the CO partial pressure during surrogate particle heat treatment exceeded the equilibrium value, thereby suppressing the carbothermic reduction reaction.

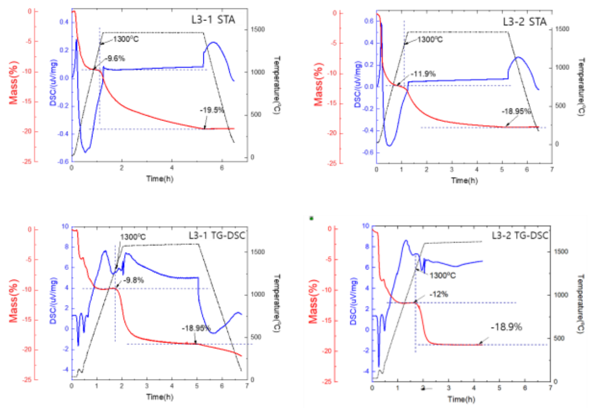

Fig. 3. Weight changes of L3-1 and L3-2 kernels during the heat treatment

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