Preliminary Study of UCO kernel Fabrication Process

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1. Introduction

High-temperature gas reactors (HTGR), which operate with an outlet temperature of over 900 °C, are considered next-generation reactors capable of producing hydrogen in an environmentally friendly manner. HTGRs utilize TRISO fuel, which features spherical UO_2 or UCO kernels coated with carbon and silicon carbide (SiC) to prevent the diffusion of radionuclides. Initially, UO_2 fuel kernels were used, but the high temperature and high thermal gradient environments caused kernel migration (amoeba effect), leading to the failure of the SiC coating layer. The kernel migration phenomenon is mainly driven by the diffusion of gaseous carbon compounds, CO. Therefore, UCO kernels, a mixture of UO_2 and UC_x, is more commonly preferred due to the reduction of CO generation.

UO_2 fuel kernels are fabricated by calcining and sintering uranium hydroxide gel microspheres produced through internal or external gelation processes. For the fabrication of UCO kernels, the carbothermic reduction process of UO_2 is utilized. 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 UC_2-converted (~20 mol%) UCO kernel. For this reason, internal gelation is conventionally preferred to homogeneously incorporate carbon black particles (10-100 nm) into uranium hydroxide gel microspheres. Here, the carbon black dispersion techniques are a major issue for UCO kernel fabrication. Additionally, 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. In this paper, as a preliminary study for engineering-scale production, we reviewed the detailed UCO kernel fabrication process and present the results of the simulated ZrCO kernels.

2. UCO fabrication process

2.1. Internal gelation

Internal gelation is a process that fabricates uranium gel microspheres by drop-casting a uranyl ion (UO_2^{2+})-containing broth solution into hot silicon oil. The broth solution also contains nitric acid, urea, and hexamethylenetetramine (HMTA), which promote the gelation of uranyl ions via reactions (1)-(4) as shown below.

(1) *Complexation/decomplexation:*
$$UO_2^{2+} + CO(NH_2)_2 \leftrightarrow UO_2[CO(NH_2)_2]^{2+}$$

(2) *Hydrolysis:*
$$UO_2^{2+} + 2H_2O \leftrightarrow UO_2(OH)_2 + 2H^+$$

(3) *HMTA protonation:*
$$(CH_2)_6N_4 + H^+ \leftrightarrow (CH_2)_6N_4{\cdot}H^+$$

(4) *HMTA decomposition:*
$$(CH_2)_6N_4{\cdot}H^+ + 3H^+ + 6H_2O + 4NO_3^- \leftrightarrow 4NH_4^+ + 4NO_3^- + 6CH_2O$$

Uranyl ions are prepared as acid deficient uranyl nitrate (ADUN) solution with low pH. Then, the broth solutions are prepared mixing ADUN solution with HMTA and Urea (HMUR) solutions. During internal gelation process, protonated HMTA by nitric acids (3) are thermally decomposed (4) in hot silicon oil. These reactions consume H^+ and rapidly inducing the hydrolysis of uranyl ions (2). Since these processes are sensitive to temperature, it is essential to chill the broth solution near 0 °C before drop-casting to inhibit the pre-hydrolysis. Additionally, the decomposition of HMTA requires sufficient protonation, which needs an adequate amount of nitric acid. However, an excess amount of nitric acid can inhibit the gelation of uranyl ions. Therefore, the [HMTA]/[NO_3^-] ratio should be carefully optimized. Urea stabilizes and prevents the pre-precipitation of uranyl ions by forming complexes (1) at low temperatures. As the temperature increases, urea decomplexes from uranyl ions and catalytically promotes the decomposition of HMTA. Furthermore, urea forms a urea resin through a condensation reaction with aldehyde from the HMTA decomposition, resulting in rigid gel microspheres.

2.2. Carbon black dispersion

To successfully incorporate carbon black into gel microspheres, it must be homogeneously dispersed in the broth solution prior to drop-casting. Due to its fine particle size and hydrophobic surface, carbon black particles tend to aggregate in aqueous medium. Dispersing agents possess hydrophobic chains that

adsorb onto the surface of carbon black, while their hydrophilic chains inhibit carbon black particles agglomeration by generating electrostatic or steric repulsive forces. Many studies have explored the optimal combinations of carbon black and dispersing agents, such as Raven 3500 and Tamol SN, for the fabrication of UCO kernels with desired properties. In relatively recent studies, water-dispersible carbon black, surface-modified with hydrophilic groups (-SO_3Na), has been preferred without the use of dispersing agents, leading to more densified UCO kernels with higher UC_2 conversion.

2.3. Drop-casting

To fabricate gel microspheres, the prepared broth solution is drop-cast into a hot silicon bath. The injected droplets maintain sphericity due to the high interfacial tension with the oil and form a gel within 10 seconds. 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 for 30-60 minutes, the gel microspheres are washed with TCE, NH_4OH, and DI water to remove impurities that cause microcracks during heat treatment.

2.4. Heat treatment

After washing and drying, the gel microspheres are heat-treated under 500 °C in an Ar and H_2 atmosphere to remove residual water, organics, NH_3, or nitrates, and to convert the microspheres to UO_2. Then, the heating temperature is increased above 1600°C to convert UO_2 into UC_x through carbothermal reduction. Further heat treatment at higher temperatures sinters the UO_2 matrix and densifies UCO kernels. During the carbothermal reduction and sintering processes, CO gas can be released through reactions between UO_2 and carbon or UO_2 and UC_x, potentially forming voids in the UCO kernel. For this reason, UCO kernels should be heat-treated under flowing Ar gas with CO to avoid further CO generation.

3. Methods and Results

The UCO kernel fabrication process was demonstrated using ZrCO simulated kernels. Instead of AUDN, zirconium oxynitrate ($ZrO(NO_3)_2$) was dissolved in water with nitric acid. A HMUR solution was prepared by dissolving HMTA and urea. Carbon black and dispersing agents were dispersed in the HMUR solution using ultrasonication. The zirconium nitrate solution and the carbon black-dispersed HMUR were mixed in a chilled bath and drop-cast into a hot silicon oil bath using a syringe needle. After aging, washing, and drying, the gel microspheres were heat-treated at 1500°C in an Ar atmosphere without CO gas.

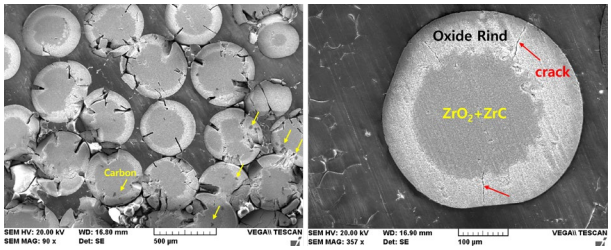

Fig. 1. Scanning electron microscopy images of ZrCO kernels

The cross-section of the fabricated ZrCO kernels reveals distinct regions, including carbon agglomerates, ZrC-ZrO_2 mixed regions, and oxide rind layers. The formation of carbon agglomerates indicates insufficient conversion of ZrO_2 to ZrC. To reduce carbon agglomerates, carbon black should be sufficiently dispersed in the broth solution. The oxide rinds (ZrO_x) form near the surface of the kernels due to a reaction between ZrC and ZrO_2, which releases CO gas. This reaction induces cracks near the surface, as shown in Fig. 1, so CO gas should flow with Ar during heat treatment to inhibit the reaction between ZrC and ZrO_2.

4. Conclusion

UCO kernels are produced via internal gelation and carbothermal reduction. To achieve high densification and UC_2 conversion, it's essential to optimize process, particularly the dispersion of carbon black in the broth solution and the control of heat treatment conditions. In future work, we will explore combinations of carbon black and dispersing agents that can achieve uniform dispersion, as well as optimize the heat treatment process to enhance kernel densification.

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