Thermal Decomposition Characteristics of ADU Gel Spheres

Jeong Kyung Chai+, Eom Sung Ho, Kim Yeon Ku, Kim Young Min, Kim Woong Ki,
Kim Bong Ku, Lee Young Woo, and Cho Moon Seoung
HTGR Fuel Technology Development Division, Kaeri, Daejeon 305-353, Korea
**Corresponding author:kcjeong@kaeri.re.kr*

1. Introduction

The VHTR (Very High Temperature Gas Reactor) is one of the reactor concepts in the Gen IV International Collaboration[1]. Unlike light water reactor currently in use in Korea, a HTGR actually functions as a gas-cooled reactor where the high temperature heat generated from nuclear fission in a reactor is cooled by He gas, with uranium dioxide (UO_2 is globally used) used as fuel for the nuclear fission.

Generally, nuclear fuel used in a HTGR is fabricated into a TRISO (TRi-ISOtropic) structure that can prevent the leakage of nuclear fission products at high temperatures. HTGR nuclear fuel uses a modified sol-gel GSP (Gel Supported Precipitation) method, which is a wet method used in most countries. ADU(Ammonium DiUranate) gel particles fabricated in this way pass through thermal treatments and become final UO_2 microspheres.

The washing characteristics such as washing volume, duration, and times during AWD(ageing, washing and drying) process after the spherical ADU gel particles preparation by the GSP method was studied.

2. Experiments

2.1 ADU gel particle fabrication

An UN (Uranyl Nitrate, $UO_2(NO_3)_2{\cdot}xH_2O$) solution, which is a uranium stock solution, is mixed with organic additives such as PVA and THFA before it is pretreated to make a precursor solution, which is fed into a vibrating oscillation system to make spherical liquid ADU gel droplets. These droplets are aged in an ammonia solution and made into ADU gel particles through chemical reactions between the uranyl ions (UO_2^{2+}) in the precursor solution and the ammonium ions (NH_4^+ ion) in the ammonia solution as follows[2]:

$$[UO_2(NO_3)_2{\cdot}xH_2O)+THFA+PVA+H_2O\ ] + NH_4OH \rightarrow UO_3{\cdot}xNH_3{\cdot}yH_2O(\text{ADU gel}) + NH_4NO_3 + H_2O$$

2.2 ADU gel particle calcining

The following residues along with the ADU gel uranium compound fabricated in 2.1 remain in the ADU gel particles: a small portion of water that was not completely removed during the drying process; organic alcohol and PVA, which are organic additives added to make spherical particles; and NH_4NO_3, a byproduct, as shown in the reaction equation. Namely, in dried ADU gel particles, the ADU compound exists as a gel diffused in a PVA medium[3]. Thererfore, the conversion of ADU gel particles into UO_3 means the removal of PVA in ADU gel particles by pyrolysis, and the calcination of gel particles to induce a phase change from ADU gel into UO_3. Fig.1 shows the material block diagram of the fabrication processes for UO_2 kernel.

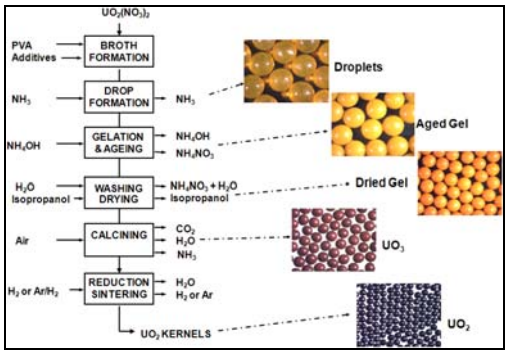

Fig.1. Material flow diagram for UO_2 kernel.

In this study, to investigate the impact of heating rate change on the final UO_2 particles in the ADU gel→UO_3 calcining process, the 5 specimens were collected from the dried ADU gel particles, upon which pyrolysis to UO_3 was conducted using the TG/DTA thermal analyzer.

3. Results and discussions

First, five specimens fabricated under the same conditions were heated up to 200°C with elevation conditions of 0.5°C /min, 1.0°C/min, 2.0°C/min, 3.0°C /min, and 5.0°C/min, and then heated constantly at 1.95°C/min up to 200-450°C. After 1 hour of cooling, ADU gel particles are converted into UO_3 while the heating rate changes from 0.5 to 5.0°C/min. (Fig.2).

The TG/DTA analysis results from the previous experiment showed that in all specimens, the final weight of UO_3 particles obtained according to the heating rate change decreased to approximately 13.0-14.0% of the initial weight of ADU gel particles and there was a relatively constant amount of residues. This indicates that the same calcining process was undergone in a similar calcining temperature range of this study.

Fig. 3 shows the exothermic characteristics measured from the DTA curve plotted according to the

change in heating rate during the conversion of ADU gel particles into UO_3. In Fig. 3, the horizontal axis represents the pyrolysis temperature, and the vertical axis represents the DTA curve plotted according to the level of generated heat, indicating that the conversion of ADU gel particles into UO_3 conducted under an air atmosphere in this study goes through an exothermic process.

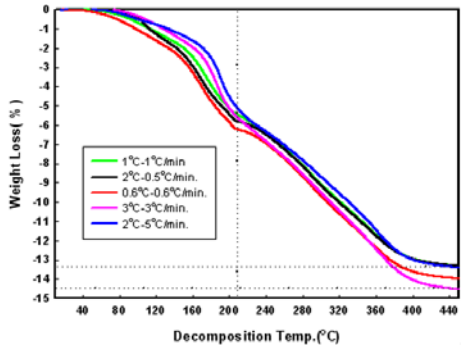

Fig. 2. TG curves during ADU gel decomposition.

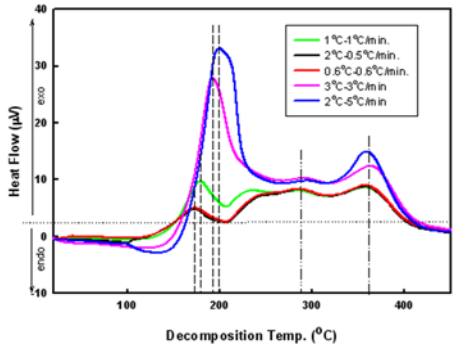

Fig. 3. DTA curves during ADU gel→UO_3 calcination.

As shown in the figure above, during the calcining process of ADU gel particles, as the initial pyrolysis rate increases, the exothermic amount increases; thus, its temperature curve is shifted to the right. The reason for this can be explained as follows: as the external heating rate increases for ADU gel particles, the exothermic amount released from ADU gel particles increases. Also, this exothermic amount is not released according to the heating rate, but has some time delay, resulting in the temperature peak shifting to the right and an increase in the exothermal amount.

UO_3 particles obtained after pyrolysis according to the heating rate change are shapeless, the internal structure of UO_3 particles was observed through the SEM after crushing the center of a microsphere with a micro-gauge, which is shown in Fig. 4. In Fig. 4, (A) represents the cross section of crushed UO_3 particles, and (B) represents an enlarged center of the cross section. If carefully observed, shells that are not densified in the center can be found, and the enlarged images of these shells show crystalline structures with different shapes, as shown in (C) and (D). This is because the gelation is not completed in the center of ADU gel particles when the particle size shrinks in the sequential ageing and washing processes after the fabrication of initial liquid spherical ADU gel particles.

If these incomplete ADU gel particles are converted into UO_3 particles and then fabricated into the final sintered UO_2, the final particles obtained will have voids in their centers, as shown in Fig. 4 (E), which is undesirable for nuclear fuel particles. Therefore, an appropriated process control is necessary during the calcination of ADU gel particles into UO_3.

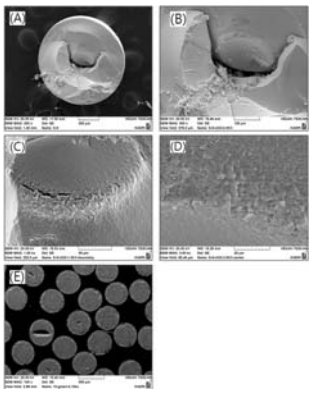

Fig.4. SEM photographs of UO_3 and UO_2 particle: (A)UO_3 cross section , (B) UO_3 magnification (X500), (C) UO_3 shell part, (D) magnification of C (X3500), and(E) UO_2 cross section.

4. Summary

The heating rate is changed from room temperature to 200°C during the calcining process of dried ADU gel particles to UO_3 to examine the pyrolysis characteristics, UO_3 particles with heating rates kept below 5°C/min were not crushed or cracked during the reduction and sintering to final UO_2 particles. Also, when the washing process for aged ADU gel particles was optimized and the thermal treatment conditions with an elevating heating rate were used during the initial calcining process, a relatively excellent internal structure of sintered UO_2 particles could be obtained.

REFERENCES

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