Preliminary Study on the Preparation of UCO Kernel with C-ADU Gels for VHTR Fuel

Advanced Fuel Development Division, Korea Atomic Energy Research Institute
1045 Daedeck-daero, Yuseong, Daejeon 305-353, Republic of Korea

Kyung-chai Jeong*, Sung-whan Yeo, Yeon-ku Kim, Sung-Ho Eom, Moon-sung Cho, and Eung-sun Kim

HTGR Fuel Technology Development Division, Kaeri, Daejeon 305-353, Korea
**Corresponding author:kcjeong@kaeri.re.kr*

1. Introduction

UCO(Uranium oxy-carbide, UO_2 + UC_2) kernels have been developed in the United States to overcome some of the disadvantages of UO_2 kernels that have been developed and generalized in many countries[1,2]. Based on the sol-gel method, which has been studied extensively in the chemical field, carbon black particles and organic additives are homogeneously mixed in a raw UN solution, and dropped with vibrating nozzle system and brought into contact with gelation medium to obtain C-contained ADU gel particles [3]. The fuel particle manufacturing process can be divided into an internal gelation process and an external gelation process. The merits and disadvantages of each process are already known [4,5].

In this study, UCO particles were fabricated by converting C-contained ADU gel particles prepared by KAERI external gelation process which was developed in the previous study [6] for UO_2 kernel manufacturing (Fig.1). A high-temperature rotating reactor was used for heat treatment.

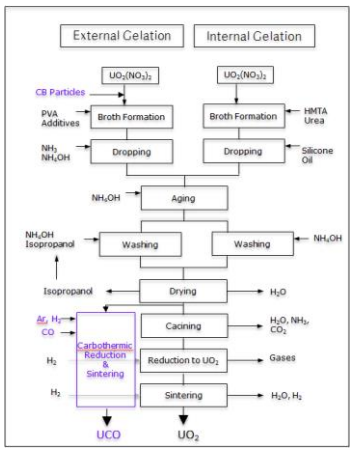

Fig.1. Material flow of UCO kernel preparation.

The manufacturing step is;

- Dispersing carbon black particles in UN solution, adding various organic additives and preparing a broth solution,
- Preparation of broth solution, spherical droplets, and gelation in gelation column
- Aging, washing and drying the formed gel particles
- Conversion of C-contained ADU gel particles into UCO compounds through heat treatment.

The preliminary experiments were carried out for a series of processes.

2. Experiments

2.1 Broth solution preparation process improvement

The carbon black particles used initially for the preparation of the broth solution, which is a pretreatment step for C-contained ADU gel particles, were the Cabot Emperor 1200 imported from Cabot Co. However, in the course of the research, Cabot Emperor 1800 powder, which is known to have improved surface properties, was used. Carbon black particles were added to the UN solution, and de-aggregation and uniform dispersion were performed using an ultrasonic force.

In the first study, the THFA solution was mixed by a single mixing method, ultrasonic force, but the method was changed into a mechanical mixing in order to prevent the heat from being generated during the mixing of the THFA. This heat can change the viscosity during the broth solution preparation when PVA is added in the next step. Fig. 2 below shows the shape of the carbon black particles used in this study.

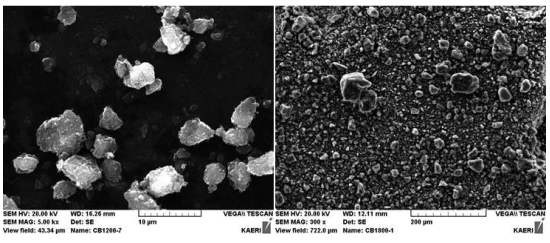

Fig.2. SEM photographs of carbon black particles (left:initial stage, right: after improvement).

Table 1 below briefly summarizes the dispersion method of carbon black particles and the mixing method of organic additives when preparing the broth solution.

Table 1. Broth solution preparation method.

Mixed material	Mixing method	
	Before change	After change
Used raw material	UN solution	
CB dispersion	Ultrasonic force	Ultrasonic force
Pre-neutralization	Magnetic stirrer	
THFAmixing	Ultrasonic force	Mechanical mixer
PVA solution mixing	Mechanical Mixer (type I)	Mechanical mixer (type II)
Viscosity control	Magnetic stirrer	

2.2 C-contained ADU gel particles formation

Broth solution was made into spherical liquid droplets through vibration nozzle system which controls flow rate and vibration frequency and amplitude, and it was repeatedly performed gelation in the gelation column. The C-contained ADU gel particles prepared at the beginning of the study were not spherical, but the sphericity of the gel particles was much improved by controlling the operating parameters and using a nozzle with an appropriate size. Fig. 3 shows the shape of the C-contained ADU gel particles prepared to the initial fabrication conditions.

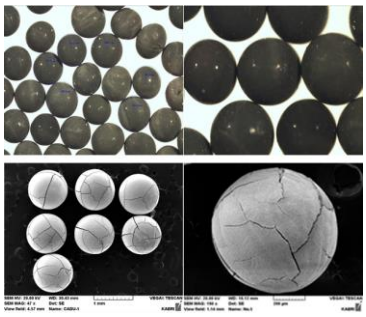

Fig.3. C-contained ADU gel particles obtained before process improvement.

With the modified conditions, C-contained ADU gel particles with improved sphericity were prepared, but cracks were found all over their surfaces. It was the same with the final UCO fuel. The same phenomenon was experienced in the process of manufacturing the UO_2 kernel, which was carried out in the previous study.

It is necessary to precisely control the washing and drying processes after the preparation of spherical C-contained ADU gel particles, and it means that the normal C-contained ADU gel particles can be obtained without defects in gelation and AWD procedures.

Fig. 4 shows the spherical shapes of C-contained ADU gel particles without cracks obtained by appropriately controlling the process parameters during the manufacturing of the C-contained ADU gel particles. The amount of carbon black particles in the broth solution was through repeated experiments within the range of 50~100% of the theoretical amount. And the process variable was also improved. The amount of organic additive was optimized in the subsequent process. As results, even in the process of forming spherical liquid droplets, individual droplets were separated clearly and their sphericities were sufficiently maintained.

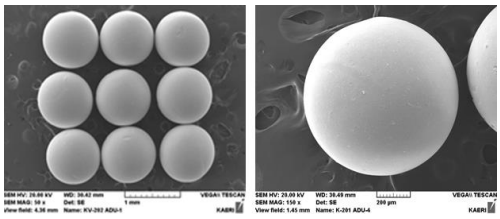

Fig.4. C-contained ADU gel particles obtained after process improvement.

The spherical droplets that were formed ~~enter~~ falls into the gelation column and gelation proceeds through a chemical reaction with the ammonia solution. The aging and the washing processes also utilize various process parameters obtained in the previous study to remove reaction byproducts and impurities from the gel particles~~.~~ As shown in the figure, the surface of the C-contained ADU gel particles obtained after the drying process is smooth and the sphericity is maintained in good state and no crack is found at all.

2.3 UCO kernel conversion

C-contained ADU gel particles are manually loaded into the Mo reactor, and the reactor is mounted inside the high temperature rotating system shown in Fig.5. In the process of manufacturing UO_2 kernel, it is known that spherical ADU gel particles are damaged due to rapid exothermic reaction in the process of pyrolysis of organics (PVA, reaction products) constituting ADU gel particles in their initial pyrolysis process (calcination process). In this initial heating process, the rotating of ADU gel particles has to be suppressed.

Fig.5. High temperature rotating furnace and reactor.

In order to prevent the above-mentioned phenomenon in the manufacturing process of the UCO fuel particles, the rotation of the reactor was stopped to prevent the moving of particles in the heating period up to 550℃. This work was extended to 800℃, which is the temperature at which the pyrolysis process is completely terminated. The fluidizing of calcined particles started at 800℃ and continued to the temperature at which the sintering was completed.

At this time, the rpm of rotating system can be changed. The number of revolutions of the reactor was

fixed to 1 rpm to conduct a blank test for heating from 800 to 1940 ℃. In this study, the heating profile is set as shown in Fig. 6.

The following is a summary of the actual operating conditions of the high temperature rotating reactor in this study. The amount of carrier and reaction gases supplied at each temperature interval needs to be adjusted-depending on the scale of the reactor size.

- room temperature to 100℃ : 100% Ar, moisture removal and drying
- 100℃ to 515℃ : 6%H_2-94%Ar, calcination
- 515℃ keeping : 6%H_2-94%Ar
- 515℃ to 1675℃ : 60%CO-40%H_2, reduction and carbothermic conversion
- 1675℃ keeping : 60%CO-40%H_2
- 1675℃ to 1940℃ : 60%CO-40%H_2, sintering
- 1940℃ keeping : 60%CO-40%H_2
- 1940℃ to room temperature : 100%Ar, cooling

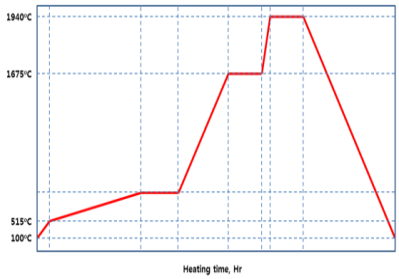

Fig. 6. Heating profile for UCO conversion.

3. Results and discussions

Fig. 7 shows the shape of the UCO compound obtained by performing the heat treatment (water removal, calcination, carbothermic reduction, sintering) under the above gas supply and heating conditions. The shape of the UCO kernel is spherical, but the sphericity is decreased. The size of the UCO fuel particle is about 500μm, but the size distribution is relatively different from that of the conventional UO_2 kernel. The obtained UCO kernel is believed to have broadened particle size distribution due to the existence of twin or crushed particles.

The surface of the particles also showed a sphericity lower than that of the particles obtained from the conventional UO_2 kernel production, and some wrinkles were observed on the particle surface. This can be seen by looking closely at the microscope image of Fig. 7.

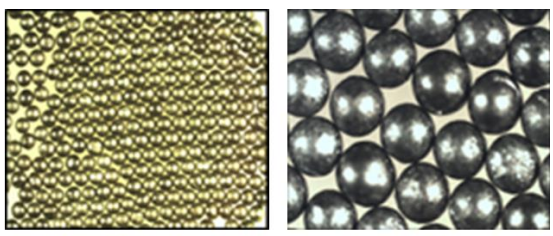

Fig.7. Microscope image of spherical UCO kernel.

On the other hand, it is important that the internal structure of the particles has the characteristics suitable for a kernel even if the sphericity is acceptable. The UCO kernel obtained in this study were processed for ceramography. Fig. 8 shows the SEM photograph of the inside of the UCO kernel prepared at the initial experiments. It was observed that many voids were formed inside the kernel. This is because there are factors that can cause the voids during the manufacture of spherical droplets and thermal treatment.

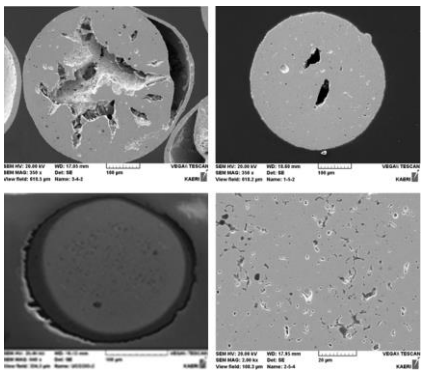

Fig.8. Internal structure of UCO kernel obtained from initial our experiment.

In this study, additional experiments were conducted to convert UCO kernel by changing the heating profile and CO gas feed rate. The temperature range of the heating program used in Fig. 6 was changed, and the amount of CO gas used in the carbothermic reduction process was also changed. To confirm the external shape and internal structure of the UCO kernel, the starting temperature of the carbothermic reduction process was lowered, and also, experiments to increase the feed rate of CO gas were performed.

Fig. 9 shows the outline of the UCO kernel prepared by changing the heating program and changing the amount of CO gas supplied in the carbothermic reduction and sintering steps. The surface is relatively smooth and the sphericity is improved as compared with the outer shape in Fig. 7.

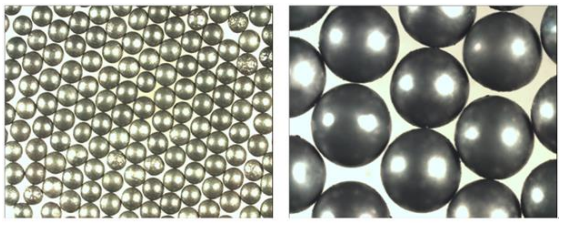

Fig.9. The shape of UCO kernel obtained from process improvement.

Fig. 10 shows the microscope and internal structure of the thermally converted UCO kernel after controlling the heating profile and increasing the amount of supplied CO gas. In addition to the improvement of the outer shape, the internal pores also disappeared but the density of UCO kernel was lowered. This is presumably because the final sintering temperature was relatively lowered during the heat treatment. If the sintering temperature is raised and the sintering duration is maintained for a longer time in suitable CO atmosphere, the density is expected to increase without changing the internal structure.

From the results of these experiments, the chemical composition of UO_2 and UC_2 has not yet been analyzed and the quantitative analysis results of UCO compounds are not known. However, it is shown in the following figure as a result of actual experiments according to the change of heating profile and supply amount of CO gas, therefore, if more detailed control of the process parameters is performed in the future, it is predicted that the UCO kernels with better quality can be manufactured.

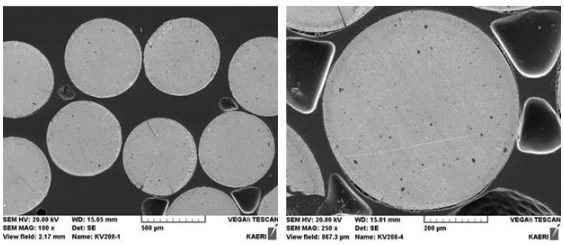

Fig.10. The SEM phtographs on internal shapes of UCO kernel from process improvement.

Fig. 11 shows the results of the EDS analysis. The quantitative analysis of uranium matrix materials by performing elemental analysis for C and O is not performed, but it can be seen that C and O are relatively uniformly distributed in the internal section from this qualitative analysis. This is because the carbon particles entering the carbon-containing ADU gel particle process are first calcined while being subjected to the heat treatment process, after reduction process, and then, in the reducing atmosphere of the CO gas supplied to the reaction gas in the carbothermic reduction process, it was predicted that the UC_2 (or UC) phase and UO_2 phase were converted, and then sintered by increasing temperature.

Quantitative analysis to proper interpretation in this field should be continued in the future. In order to confirm the physical properties of the UCO kernel obtained in this study, a sample was subjected to XRD analysis. It is shown in Fig. 12 briefly.

The UO_2 peak of the uranium compounds in the UCO (UO_2 + UC_2) was analyzed to be clear and sharp. UC_2 peak was observed in relatively small form. This is because the amount of carbon added to the broth solution is relatively small and the partial pressure of CO gas in the carbothermic reduction process was not precisely controlled. It was interpreted that the reaction between carbon and uranium was not a stoichiometric reaction.

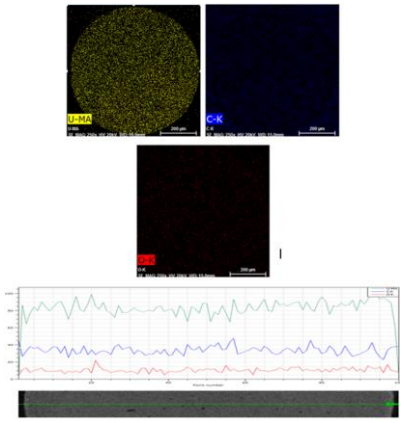

Fig. 11. EDS analysis results on the map and line profiles of UCO kernel from process improvement.

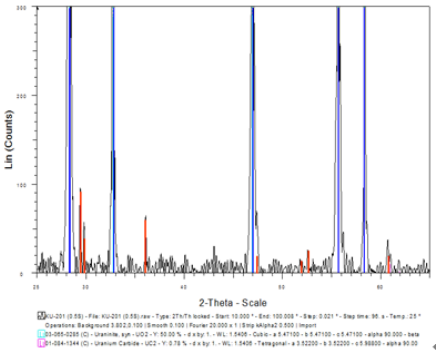

Fig.12. XRD phase analysis peaks of UCO kernel.

As a result, to confirm the feasibility of using the UCO kernel prepared in this study, it will be necessary to increase the uranium concentration and increase the amount of carbon black added to the broth solution for the C-contained ADU gel particles. Also, the improvement of the process of optimizing the carbothermic reduction process by precisely controlling the amount of CO gas used during the heat treatment will be needed, and the quantitative analysis of the particles obtained at each step to improve the quality of kernel will be needed. And study should be continued for these improvements.

4. Conclusions

C-contained ADU gel particles were prepared by external gelation process and then converted into UCO compound in a high temperature rotating reactor, in this study.

As results, first, an ultrasonic force was used to disperse the carbon black particles in the UN solution, and a mechanical mixing method was used for homogeneous mixing of organic material such as THFA and PVA. Spherical C-contained ADU liquid droplets were formed by using the broth solution and spherical droplets which were initially prepared with uneven quality were uniformly fabricated by the process improvement.

Secondly, the sphericity of the C-contained ADU gel particles was found to be improved and the spherical C-contained dried ADU gel particles without cracks were also produced by the process improvement.

Third, a high temperature rotating reactor capable of operating up to about 2000 ℃ was designed and manufactured. The C-contained dried-ADU gel particles prepared were heat-treated to a heating profile and converted into UCO compound. As a result of analysis of the physical properties of the converted UCO kernel, the sphericity was found to be lower than that of the conventional UO_2 kernel, but it was improved than that of initial products. The internal structure was confirmed to have voids inside the kernel, and the sintering density was revealed to be low. Although qualitative analysis using XRD showed that the UO_2 and UC_2 phases were mixed, additional studies should be continued to obtain the UCO kernel composition suitable for the fuel specification.

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