Spherical UO_2 kernel Particle Preparation for HTGR fuel in Korea

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1. Introduction

A VHTR(Very High Temperature Reactor) is an important reactor concept for a near-term deployment under the nuclear R&D program of the Ministry of Education and Science Technology in Korea. The proposed nuclear fuel for the preliminary reactor concept is a TRISO(Tri-Isotropic or multi-layered structure) coated particle prepared by pyro-carbon and silicone coatings on a spherical UO_2 kernel surface as a fissile material.

Generally, the HTGR nuclear fuel production processes have been classified as five categories of research and development[1] ;

- Spherical UO_2 kernel preparation
- Pyro-carbon(PyC) and silicon carbide(SiC) coatings
- Pebble or Prismatic block preparation by using graphite matrix powder
- Fuel performance including a fission products release
- Advanced and improved fuel development

Several proven fuel production processes are currently available for a spherical UO_2 kernel production. The typical processes are an internal gelation process and an external gelation process. The well-known GSP(gel supported precipitation) process is one of the modified process for an external gelation method NUKEM of Germany[2]. As developed above mentioned, both processes are based on the reaction of UN(Uranyl Nitrate, $UO_2(NO_3)_2$)) and ammonia.

The fundamental difference between the internal and external processes is in method of an ammonia supply to a liquid medium. The ammonia is supplied from an ammonium hydroxide solution within a gelation column in the external gelation process, whereas, in the internal gelation process, the ammonia is supplied from a thermal decomposition of an ammonia precursor solution which is included the HMTA(Hexa-Methylene Tetra Amine, $C_6H_{12}N_4$) chemical. Here, the HMTA chemical contains the ammonia functional group at a low temperature condition.

A schematic flow diagram for a UO_2 kernel preparation is shown in Figure 1. In this study, spherical ADU gel and UO_3 particles *via* an UN solution as a raw material were prepared with the GSP process. And the spherical UO_2 particles were obtained by a conversion of UO_3 in a sintering furnace. The characteristics of the ADU gel, UO_3, and UO_2 particles were analyzed by a Streoscope, FT-IR, TG/DTA, and X-ray.

2. UO_2 kernel preparation

As shown in Figure 1, a spherical UO_2 particle was prepared using a modified external gelation process. First, U_3O_8 powder was dissolved in conc.-HNO_3 to form the UN solution by the following chemical reaction:

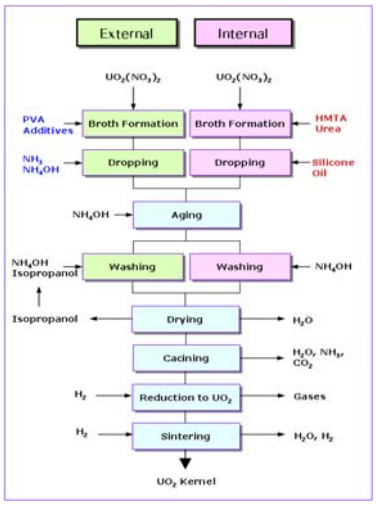

Fig.1. A schematic flow diagram for UO_2 kernel preparation.

$$3U_3O_8 + 20HNO_3 \rightarrow 9UO_2(NO_3)_2 + 10H_2O + 2NO$$

Secondly, the casting solution was prepared by mixing organic additives, such as PVA and THFA, and the UN solution. This process is a simple mechanical mixing process of all the components.

Here, the viscosity and surface tension of the droplets were controlled by these additives. And then, the casting operation was carried out in a gelation column filled with ammonia water. ADU gel particle was formed by the following chemical reaction:

$$2UO_2(NO_3)_{1.5}(OH)_{0.5} + 2NH_4OH \rightarrow (NH_4)_2U_2O_7 + NH_4NO_3 + H_2O$$

The wet ADU gel particles were transferred to an AWD(Ageing-Washing-Drying) apparatus, where the ageing, washing, and drying processes were carried out. Following the drying process, ADU gel particles were calcined in an air atmosphere at about 450°C. From about 300°C, the ADU was converted to UO_3 by the following chemical reaction:

$$(NH_4)_2U_2O_7 + H_2 \rightarrow 2UO_3 + 2H_2O + NO$$

After the calcining step follows the reduction and sintering steps from UO_3 to UO_2 at a high temperature in a sintering furnace. The process was carried out

under 100%-H_2 atmosphere(or 4% H_2 + Ar mixed gas) at a high temperature(about 1700 ^oC), and the final reaction was the by following:

$$UO_3 + H_2 \rightarrow UO_2 + H_2O$$

The experimental apparatus for the spherical liquid droplets preparation mainly consisted of a broth solution storage tank, a flow-meter, a nozzle and vibrating system, a gas supply system, and a gelation column, as shown in Figure 2.

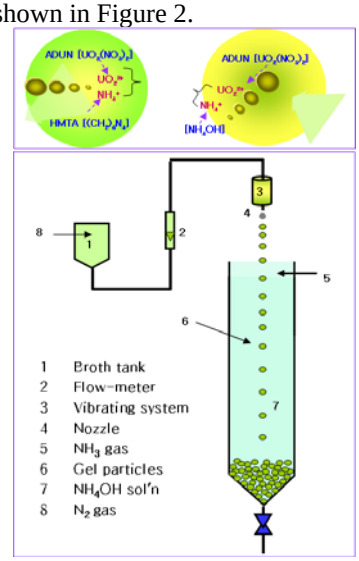

Fig.2. Experimental apparatus.

3. Results

Experimental parameters for a broth solution making such as the polymer type, uranium concentration of the broth solution, PVA/THFA mole ratio, and the viscosity and feeding rate of the broth have been studied extensively.

In the initial liquid spherical droplet preparation process, the most important factors influencing the spherical shape are the broth feed rate and the vibrating frequency when using a droplet forming nozzle size of a 1 mm diameter. If these two factors are not accorded with liquid droplets are not formed as a sphere shape and a small satellite occurs. The spherical ADU gel, UO_3, and UO_2 particles prepared in our laboratory are shown in Figure 3.

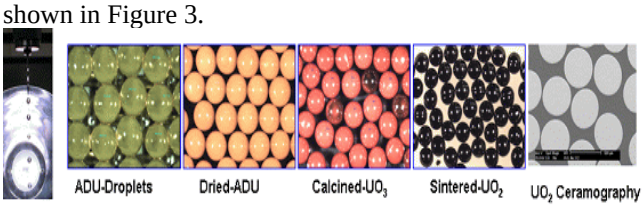

Fig.3. The shapes of spherical droplet, ADU gel, UO_3, and UO_2 particles.

In the washing step of the ADU gel, a well-developed washing method and procedure are very important for no cracked of the final UO_2 particles. If these processes are not sufficient, the final UO_2 particles are almost always broken during the calcining or sintering steps. The sphericity and surface quality of the final UO_2 particle and its ceramography with a diameter of 460 to 500 μm are shown in Figure 4. The shape of all the UO_2 particles were observed with sphere form and the sphericity was within 1.0+0.15 from the ceramography observation.

The relationship between the shrinkage factor and the uranium concentration in the final broth solution is shown by the following equation[3];

Shrinkage factor =

$$([U] \text{ in kernel}/[U] \text{ in initial droplet})^{0.333}$$

Generally, the droplet diameter could be guessed approximately as 2000 μm to the final UO_2 kernel with 500 μm, in the case of using a 1mm nozzle. Otherwise, at a constant heating rate of 3^{o}C/min. in the calcining process, the dried ADU microspheres in the TG/DTA began to slowly lose their free water and hydrated water, and the decomposition of the reaction product NH_4NO_3, and the organic additives were completely decomposed by 300 and 380^{o}C, respectively.

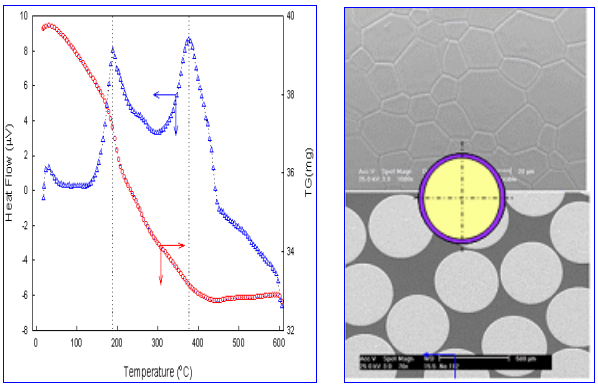

Fig.4. TG/DTA curves and ceramography of UO_2.

3. Conclusion

In this study, to obtain a spherical UO_2 kernel, the most important factors for the droplets preparation are the composition ratio and viscosity of the broth solution, and the frequency/amplitude of the vibrator. Uranium concentration is 0.5~0.8mol/l, viscosity is 50~80 centi-Poise, vibration frequency is about 100Hz. Also the heating rate in the calcination process must be kept below 3^{o}C/min., and the optimum conditions of the sintering were in a 4%H_2-Ar mixture gas atmosphere and a 3 steps heating mode till 1650 ^{o}C.

REFERENCES

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