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Intermediate Compound Preparation Using Modified External Gelation Method and Thermal Treatment Equipment Development for UCO Kernel

Jeong Kyung Chai[+], Eom Sung Ho, Kim Yeon Ku, Yeo Seoung Hwan, Kim Young Min, and Cho Moon Sung

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

1. Introduction

VHTR (Very High Temperature Gas Reactor) fuel technology is being actively developed in the US, China, Japan, and Korea for a Next Generation Nuclear Plant (NGNP). The concept of fuel of a VHTR is based on a sphere kernel of UO_2 or UCO, with multiple coating layers to create a gas-tight particle [1]. The fuel particle of a VHTR in the US is based on microspheres containing a UCO, mixture compound of UO_2 and UC_2, coated particles with multi carbon layers and a SiC layer.

This was first prepared through an internal gelation method at ORNL in the late 1970s. The diameter of the UCO spherical kernel ranges between about 200 and 500 ㎛.

A number of techniques have been used to fabricate fuel kernels for coated particles, including sphere melt, powder agglomeration, and gel formation; however, all modern kernel making processes are based upon gel formation where spherical kernels are formed from spherical droplets of aqueous metal solution [2].

The fabrication process of this spherical kernel in internal gelation method of US was based on the sol-gel reaction between ADUN(Acid Deficient Uranyl Nitrate) solution and additives such as HMTA and urea solutions[3].

The UCO kernel preparation procedures from this process are as follow:

- ADUN raw material preparation by dissolution of uranium oxide powder in strong nitric acid
- broth solution preparation containing carbon source
- spherical C-ADU(carbon contained ADU) liquid droplets formation
- C-ADU gelation by chemical reaction of uranyl ion(UO_2^{++}) in ADUN solution and ammonium ion(NH_4^+) in HMTA as ammonium ion source
- ageing , washing, and drying of C-ADU gel particle in integrated AWD apparatus
- thermal treatment (1st step and 2nd step, calcination and reduction)
- carbonization
- sintering

The C-ADU gel particle formation in internal gelation process is based on the following chemical reaction :

$$[2UO_2(NO_3)_2+HMTA+Urea+C]_{drops}+\text{ hot Silicone oil} \rightarrow \text{C-ADU } (C\text{-}(NH_4)_2U_2O_7) + 2NH_4NO_3 + H_2O$$

Carbon black powder as a carbon source in the final UCO kernel is added during the initial broth solution preparation, in the processing of UCO kernel fabrication [4]. The preparation of a good quality UCO kernel is very difficult owing to the homogeneous distribution of carbon source in a final UCO kernel. The key technology used to obtain a good quality sphere (sphericity, density, C/U and O/U ratios) is a uniform distribution of carbon particles into the C-ADU gel particles, i.e., during the gelation step of liquid droplets formation before the C-ADU gelation reaction is progressed.

In this study, we are first developed the intermediate compound, C-ADU gel particle, formation technology using the modified external gelation method, which is already developed successfully during the UO_2 kernel preparation for HTGR fuel. Also, the thermal treatment equipment for prepared C-ADU gel particles conversion into oxy-carbide particles was developed which is a unit integrated apparatus for calcination, reduction, carbothermic reduction, and sintering processes.

The C-ADU gel particles preparation by modified external gelation method in our laboratory is based on the following chemical reaction using depleted UN solution :

$$[2UO_2(NO_3)_2 + C + THFA + PVA]_{drops} + 3NH_4OH \rightarrow \text{C-ADU } (C\text{-}(UO_2NO_3)_{1.5}(OH)_{0.5}) + 2NH_4NO_3 + H_2O$$

The UN solution is mixed with carbon source (with carbon black powder) using a well dispersing method, and a THFA (TetraHydroFurfuryl Alcohol) solution was added and well mixed. Last, PVA (Polyvinyl Alcohol) is added this mixture solution again, and then vigorously mixing with mechanical mixer for carbon dispersion and conditioning the solution property.

The overall material flow and thermal treatment procedure till the final UCO kernel preparation in our modified-external gelation process is simply shown in Fig. 1. The broth solution was transferred to a gelation column attached with a vibrating nozzle system, nozzle diameter is 0.1mm, and spherical ADU liquid droplets were produced from a proper matching of vibration frequency and amplitude in vibration nozzle system, and feed rate control of broth solution.

2. Experiments

We first prepared the C-ADU gel particles using depleted UN solution as a raw material. The concentration of this depleted UN solution is 1.97 moles.

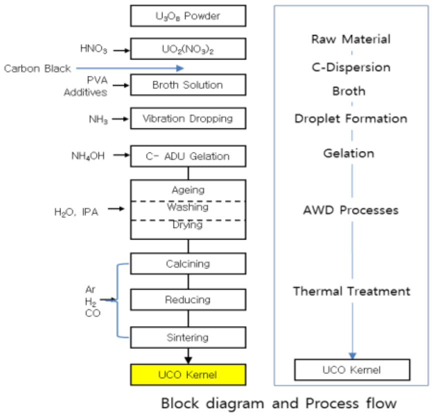

Fig.1. Overall material and process flow diagram for UCO kernel fabrication.

Carbon black powder were selected a Cabot 1800 through the preliminary selection test. Nano-sized carbon black powder is more difficult to disperse. We used the ultrasonic disperser to well dispersing and break-up of the agglomerated or aggregated fine size carbon particles.

This carbon contained UN solution is added with THFA and PVA solution to prepare broth solution. After making a broth solution containing uranyl ion and carbon particles, the spherical liquid C-ADU droplets are prepared by using a vibrating nozzle system.

The C-ADU gel particles obtained from the above procedures in gelation column are transported to the AWD (Aging-Washing-Drying) tank for the ageing, washing, and drying, for washing by an ammonia solution, distilled water, and isopropyl alcohol, and for drying by air atmosphere, respectively. Then the dried C-ADU gel particles are converted into C-UO_3 and mixture compound of UO_2 + UC_2 particles (labeled UCO particle) by the integrated high temperature thermal treatment rotating furnace.

Broth solution preparation condition is following table 1 and experimental apparatus is showed in Fig. 2.

Table 1. Broth solution, C-ADU gel particles formation, and thermal treatment conditions.

Process	Materials	Conditions
Broth solution	UN concentration	1.97 mole
	Carbon black particle	Cabot 1800
	Mixing method	Ultrasonic force
	Additive THFA	99.9% original solution
	Additive PVA	20% solution
Liquid droplets formation	Frequency	90-110 Hz
	Amplitude	3-6G
AWD treating	Ageing	Ammonia water
	Washing	Distilled water and IPA solution
	Drying	Slightly vacuum
Thermal treatment	Calcining step	Ar+H_2
	Carbothermic reduction	Ar+H_2, H_2+CO
	Sintering step	H_2+CO
	Cooling	Ar

Fig. 2. Experimental apparatus (gelation column and carbon black powder dispersion equipment).

3. Results and discussions

Fig. 3 show the images of the shapes of liquid droplets formed at the end of the nozzle captured with a high-speed camera. The feed rate of the broth solution is about 25-28ml/min with about 90-110Hz vibration frequency and 3-6G vibration amplitude. Actually, these values are different according to the viscosity of the broth solution and operating temperature in the droplets-producing system.

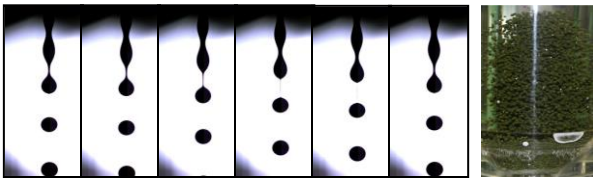

Fig. 3. Discrete spherical liquid droplets and C-ADU gel particle formation.

Otherwise, Fig. 4 shows the SEM photographs of C-ADU gel particles obtained from depleted UN solution using modified external gelation method. In initial stage of spherical C-ADU gel particle preparation, the surface of the prepared C-ADU gel particles occur the cracking phenomena by mismatching between the gelation process parameters such as viscosity of broth, feeding rate, position of ammonia gas contacting point, etc. But nowadays this phenomenon was settled already.

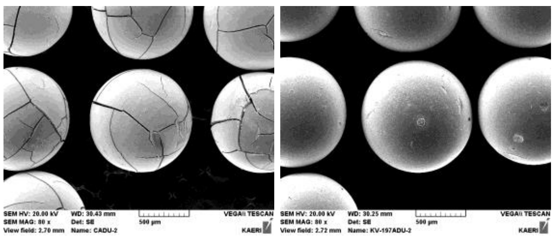

Fig.4. Spherical C-ADU gel particles shapes (left ; cracked surface, right ; normal surface, These particles were obtained after drying process).

Fig. 5 shows the high temperature rotating furnace designed and fabricated in our laboratory. Maximum operation temperature is about 2000℃ and made by graphite heating system. The reactor was composed of Mo cylinder tube with Mo Φ 0.3mm gas supply hole and a screw cap made by graphite for easily treating the sample inlet or outlet. The temperature indicators were C type thermocouples and a IR indicator, and the furnace can be rotated with max. 5 rpm, also tilting operation can be possible.

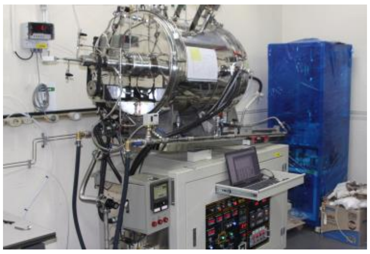

Fig. 5. High temperature kiln type rotating furnace.

Otherwise, FT-IR absorption spectra were obtained in the range of between 400 and 4000cm^{-1} of C-ADU gel particles and converted into UCO compound. Fig. 6 shows the FT-IR curves of C-ADU gel particles and UCO compound from our laboratory, prepared by modified external gelation method and converted by high temperature rotating kiln furnace. FT-IR curves have strong absorption peaks at about 2300-2400 cm^{-1}, perhaps, this peak will be related the U-C-O system.

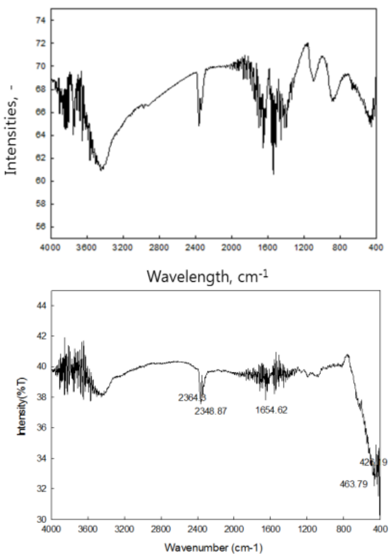

Fig.6. FT-IR curves of C-ADU gel(upper) and UCO kernel (lower).

When comparing compounds without carbon, they show rather complicated peaks at 800-1800 cm^{-1} for C-ADU gel and 350-400 cm^{-1} for UCO kernel because the composition of C-ADU gel or UCO particles are composed of more complicated species than that of ADU gel or UO_2 kernel. More detail analyses on C-ADU gel, converted-UCO kernel characteristics, and its internal structure will be progressed.

4. Conclusions

This study presents;

(1) C-ADU gel particles were prepared using a modified sol-gel process. The particles fabricated with a KAERI-established gelation and AWD processes showed good sphericity and no cracks were found on the surfaces.

(2) High temperature rotating furnace was designed and fabricated in our laboratory, and the maximum operation temperature was about 2000℃. The furnace was equipped with Mo crucible and graphite heating system, and now it is being operated.

(3) Well-prepared C-ADU gel particles were converted into UCO compounds using high temperature rotating furnace, and the physical properties of the UCO kernels will be analyzed.

REFERENCES

[1] K. Sawa, Comprehensive Nuclear Material, Chapter 3.06 "TRISO Fuel Production", Elsevier Ltd, pp.143 - 149 (2012).

[2] L.Sandell, "A Review of Radionuclide Release from HTGR Cores during Normal Operation", EPRI technical report, 1009382, pp.1-12, February (2004).

[3] C.M.Barnes, D.Husser, W.C.Richardson, and M.Ebner, "Fabrication Process and Product Quality Improvements in Advanced Gas Reactor UCO Kernel", HTR-2008, 4th International Topical Meeting on High Temperature Reactor Technology, Sep. 28, Washington DC, USA (2008).

[4] C.I.Contescu, F.S.Baker, R.D.Hunt, J.L.Collins, and T.D.Burchell, "Selection of Water-dispersible Carbon Black for Fabrication of Uranium Oxicarbide Microspheres", *J. Nucl. Mater.,* 375, pp.38-51(2008).