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Original Article

Carbon Contained Ammonium Diuranate Gel Particles Preparation in Mid-process of High-temperature Gas-cooled Reactor Fuel Fabrication

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This study investigates the dispersibility of carbon in carbon contained ammonium diuranate (C-ADU) gel particles and the characteristics of C-ADU gel liquid droplets produced by the vibrating nozzle and integrated aging–washing–drying equipment. It was noted that the excellent stability of carbon dispersion was only observed in the C-ADU gel particle that contained carbon black named CB 10. ADU gel liquid droplets containing carbon particles with the excellent sphericity of approximately 1,950 μm were then obtained using an 80–100-Hz vibrating nozzle system. Dried C-ADU gel particles obtained by the aging–washing–drying equipment were thermal decomposed until 500°C at a rate of 1°C/min in an air or in 4% H_2 gas atmosphere. The thermally decomposed C-ADU gel particles showed 24% weight loss and a more complicated profile than that of ADU gel particles.

1. Introduction

Nuclear fuel used in a high temperature gas-cooled reactor is tristructural isotropic (TRISO)-coated particle fuel. Spherical fissile material (UO_2 or UCO) is coated by trilayers such as inner-pyrolytic carbon, SiC, and outer-pyrolytic carbon [1,2] to prevent the release of fission products during the operation of the reactor. Depending on the type of reactor, hundreds of TRISO particles are contained in a pebble or prismatic shaped graphite element loading in the core of a reactor.

The initial form of the spherical fissile material is called ammonium diuranate (ADU) gel particle fabricated using the gel-supported precipitation method modified from the sol–gel processes [3,4]. This method involved the following sequence. First, organic alcohol is added to a uranyl nitrate (UN) solution to produce a broth solution. Second, the broth solution passes

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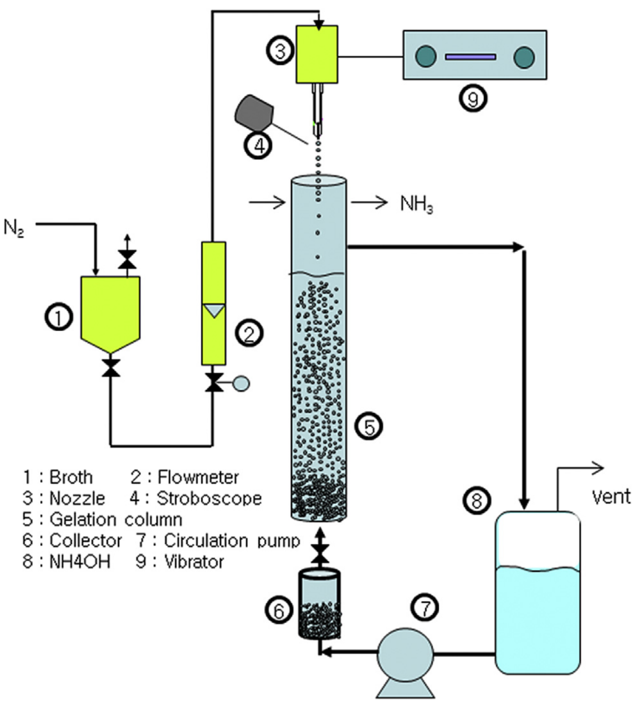

Fig. 1 – Material flow diagram for C-ADU gel particles fabrication.

through the vibrating nozzle system forming spherical ADU gel liquid droplets. Third, uranyl ions existing in the droplets chemically react with ammonium ions in the gelation solution at room temperature. Last, intermediate ADU gel particles after the reaction are formed into spherical-shaped particles and go through aging, washing, drying, heat treatment, reduction, and sintering processes. The particles are then turned into high-density UO_2 microsphere particles.

It is known that CO or CO_2 gas is created by the chemical reaction between excessive oxygen in spherical UO_2 (actually, UO_{2+x}) particles and pyrolytic carbon during the coating process. The formed gaseous phase increases the core pressure of TRISO particles leading to an unstable factor of nuclear fuel [5,6]. The production of the gaseous phase during the coating process can be suppressed by the addition of carbon particles previously in the raw material solution when the spherical UO_2 particle is produced [7]. Excessive oxygen is eliminated in the carbon contained UO_2 called UCO (uranium oxycarbide; $UO_2 + UC_2$) particle.

The external gelation process is developed to replace the internal gelation process for the spherical carbon contained ADU (C-ADU) gel particles. The fabrication method for the spherical UCO particles in the United States is the internal gelation process [8]. Whereas the internal gelation process uses carbon dispersed acid-deficient uranyl nitrate solution, the UN solution contained carbon particles with tetrahydrofurfuryl alcohol (THFA), and polvinyl alcohol (PVA) as broth solution preparation and ammonia solution as gelation medium are utilized in the external gelation process [9]. To obtain this solution, it is important to select the appropriate carbon substance with excellent dispersibility in advance. The current study points to the capability of the external gelation process to yield C-ADU gel particles [10,11] and the selection of a suitable carbon substance to disperse carbon in the UN solution.

2. Materials and methods

2.1. *Selection of carbon substance by simulating solution*

Several simulating solution tests were conducted to select the appropriate carbon substance in advance of producing spherical C-ADU gel particles. A raw material solution with a concentration of 1.97 mol Ce/L was created by dissolving $Ce(NO_3)_3 \cdot 6H_2O$ (99.99%; Kanto Chemical, Tokyo, Japan) powder in distilled water at room temperature to replace the uranium solution utilized in the general ADU gel particle fabrication process. Appropriate amounts of THFA and PVA solutions are then added in the simulating solution. The viscosity of the solution is controlled by adding distilled water. A total of 10 different carbon substances—six substances from Cabot Co. (Cabot Co., Louisiana, USA) and four substances from Colombian Chemicals Co. (Colombian Chemicals Co. Adityabirla, India)—were examined in the current study through the following sequence. First, the carbon substance is added to the simulating solution. Second, carbon particles

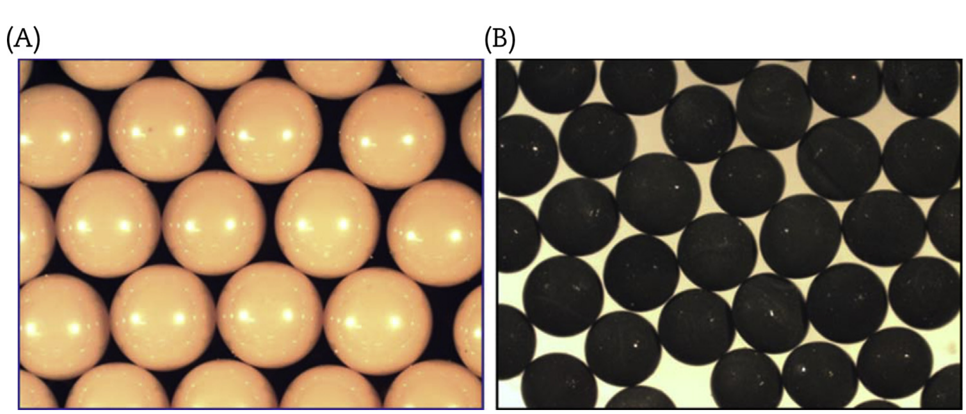

Fig. 2 – ADU gel particles. (A) Without carbon; (B) with carbon.

Table 1 – Physical properties of various carbon black particles.

		BET (cm^2/g)	External surface area (cm^2/g)	Surface area (micropore) (cm^2/g)	Cumulative pore volume (cm^3/g)	Micropore volume (cm^3/g)	Elements (%)		Volatile Content
							O	N	
Colombian Chemicals Co.	CB1	141	114	27	0.10	0.02	N/A	N/A	4.8
	CB2	106	106	0	0.13	0	3.1	0.1	4.1
	CB3	97	95	0	0.07	0	N/A	N/A	3.8
	CB4	81	79	0	0.06	0.01	2.4	0.2	2.3
Cabot Co.	CB5	104	104	0	0.08	0	N/A	N/A	N/A
	CB6	123	123	0	0.09	0	N/A	N/A	N/A
	CB7	N/A	N/A	N/A	N/A	N/A	5.8	0.4	N/A
	CB8	80	80	0	0.06	0	5.8	0.9	N/A
	CB9	85	84	1	0.06	0	5.5	0.2	5.9
	CB10	N/A	350	N/A	0.06	N/A	N/A	N/A	5.69

BET, surface area; N, nitrogen; N/A, not available; O, oxygen.

from the substance are dispersed using the ultrasonic dispersion method. Third, THFA and PVA are mixed with the carbon dispersed simulating solution to produce the broth solution using a high-speed rotating mixer. Fourth, the viscosity of broth solution is adjusted by adding distilled water. Last, the dispersibility and stability of carbon particles in the broth solution is investigated using a dispersion stability analyzer.

2.2. *C-ADU gel particle production*

Fig. 1 shows the schematic layout of C-ADU gel particle fabrication. The broth solution containing dispersed carbon particles was transferred to a gelation column attached with a vibrating nozzle system. ADU liquid droplets were produced by the nozzle system with the proper frequency, amplitude, and flow rate. The produced droplet passes through air, ammonia gas, and ammonia solution, respectively. Due to the recovering of surface tension in air atmosphere, the spherical shape of liquid ADU droplets was obtained. The surface of those spherical droplets was pre-hardened passing through ammonia gas layer. Those pre-hardened droplets reacted and aged in ammonia water yielding ADU gels.

Uranyl and ammonia ions in the spherical ADU liquid droplet and ammonia solution, respectively, were gelled together by chemical reaction yielding C-ADU gel particles. These particles were aged via a maturing process in which the remaining uranyl ions were reacted with ammonia. Dried C-ADU gel particles were then obtained by washing in distilled water and IPA (iso-propyl alcohol) solution and drying in room temperature.

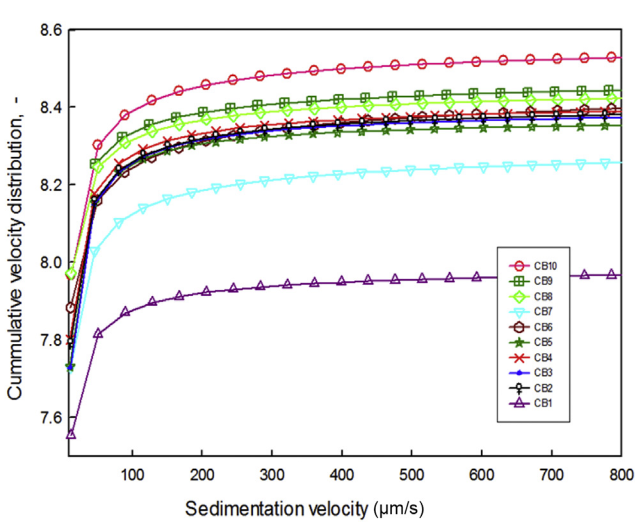

Fig. 3 – Dispersion stabilities of carbon particles in simulated solution.

2.3. *Analyses*

An ultrasonic dispersion device (Sonics CV334; Sonics & Materials Inc., USA) and dispersion stability analyzer (LUMiSizer 610, LUM GmbH, Berlin, Germany) were utilized to measure the intensity of ultrasonic force and the dispersion stability of carbon particles in the broth solution, respectively. The surfaces of the C-ADU gel particles were observed using stereoscopy, microscopy (SMZ 1500; Nikon, Japan), and scanning electron microscopy (Tescan Vega II, Bruo, Czech Republic). The thermal decomposition behavior of C-ADU particles was investigated using the TG/DTA system (SETSYS-1750; SETSYS-Evolution 16/18; Setaram, Caluire, France). In addition, a high-speed camera was used to observe the shape of discrete droplets at the end of the vibrating nozzle.

3. Results

Fig. 2 shows the spherical C-ADU gel, an intermediate phase of the UCO microsphere particle. C-ADU gel particles are smaller and much darker compared with the general ADU gels as shown in the left-hand side of Fig. 2. As noted in the Methods section, C-ADU gel particles were produced from the broth solution containing carbon substances. Various carbon substances utilized in this study have different functional groups at their surfaces and agglomeration characteristics.

An ultrasonic device was used to determine a suitable carbon substance with good dispersibility of carbon particles. The target property of simulating broth solution is a THFA, PVA, and metallic salt mixed solution with well-dispersed

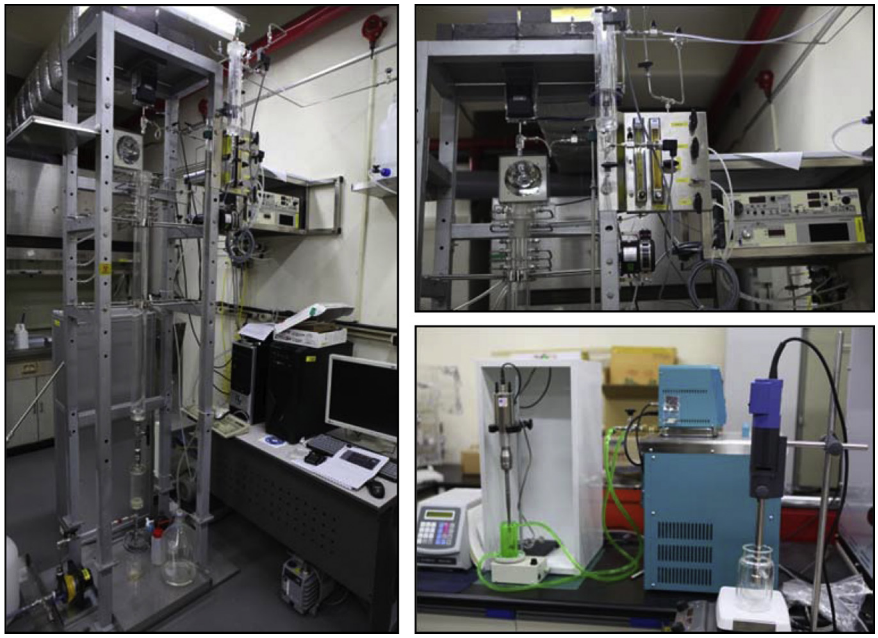

Fig. 4 – Experimental apparatus for C-ADU gel particle fabrication.

nano-sized carbon particles composed of metallic ions, nitrate ions, and organic additives. The measured viscosity of the solution is approximately 80–100 cP.

An experiment to select a suitable carbon substance among the 10 different substances was conducted. Table 1 shows the type and properties of the carbon substances used. A method to produce the simulating broth solution was already reported [12]. An ultrasonic device was used to disperse carbon particles. THFA and PVA solutions were mixed using a mechanical mixer. THFA is an organic alcohol with some viscosity supporting material to prevent the change in properties of a metallic salt solution. In the process of mixing THFA and PVA, the desirable temperature was maintained using a double jacket cooling beaker. Fig. 3 shows the dispersion stability curves of carbon particles in 10 different simulating broth solutions. The dispersion stability is presented by the accumulated velocity distribution curve according to the sedimentation velocity. The horizontal axis shows the sedimentation velocity of carbon particles settling in the broth solution containing carbon, whereas the vertical axis shows the distribution level of sedimentation velocity of carbon particles. It was noted that CB10 showed the highest distribution level and dispersion stability to select for the carbon substance applied in this study.

Fig. 4 shows the experimental apparatus of spherical C-ADU gel droplet production. This apparatus is composed of a broth solution storage vessel, a 1-mm dropping nozzle diameter, an acryl gelation column, a circulating pump of the gelation solution, and a system for providing ammonia gas to preharden the surface of droplets.

Fig. 5 shows the image of liquid droplets formed at the end of the nozzle captured by the high-speed camera. The feed rate of the broth solution was 25–28 mL/min with 80–100 Hz vibration frequency and 4–5*g* vibration amplitude. The values depend on the viscosity of broth solutions and the operating temperature in the droplets-producing system. It is known that if the feed rate and vibration frequency are not properly adjusted, as shown in Fig. 6, undesirable phenomena such as

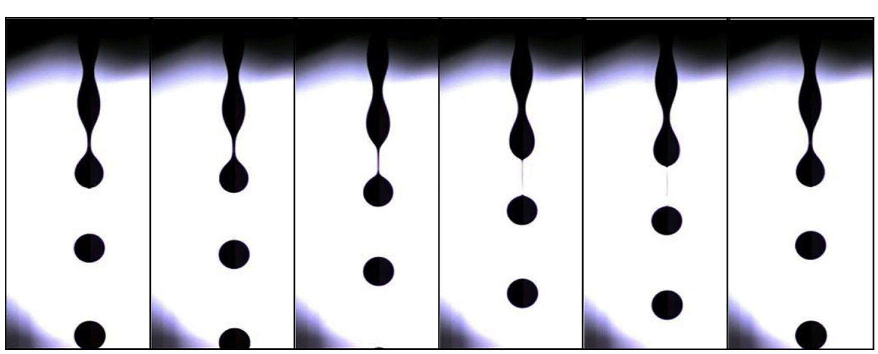

Fig. 5 – Discrete C-ADU liquid droplets formation by well matched feed rate and vibration frequency.

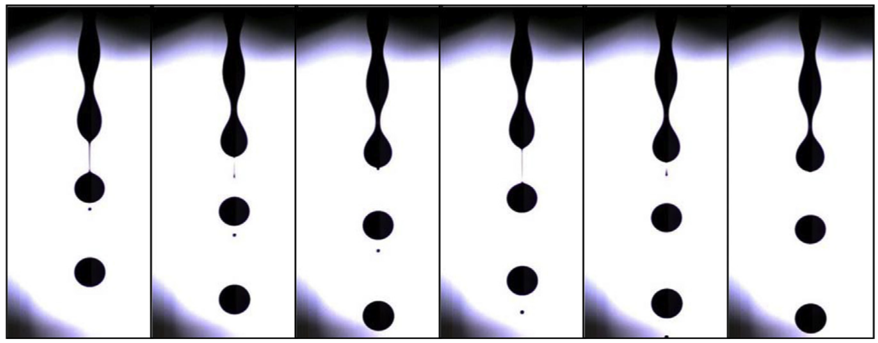

Fig. 6 – Fine satellite formation by mismatch of feed rate and vibration frequency.

microsatellites formed between spherical droplets and irregular-shaped or twinned droplets take place [13]. Therefore, it is essential to select the vibration frequency, amplitude, and feed rate of nozzle within a proper range.

Fig. 7 shows the surface of C-ADU gel and general ADU gel particles. Both particles have good sphericity. The deposited microcarbon particles on the surface of C-ADU gel particle is shown in the upper-right quadrant. Fourier transform-infrared analysis on ADU and C-ADU gel particles was performed to investigate the presence of carbon on the surface of C-ADU particles [14] as shown in Fig. 8. Similar profiles of both particles were expected because those particles have the same compositions except carbon. However, the C-ADU gel particle shows a strong absorption peak at 2,350/cm and rather complicated peaks at 800–1,800/cm. Whereas ADU produced from the direct reaction of the UN solution and ammonia gas is a relatively simple reaction [14], various constituents are involved in the more complicated reaction of C-ADU gel particles.

C-ADU gel particles were calcined in a reducing atmosphere converting to $UO_2 + UC_2$ from C-UO_3. A sintering process was also performed at a high temperature of nearly 2,000°C in identical atmosphere successively to densify C-ADU gel particles. Generally, gaseous constituents of ADU gel

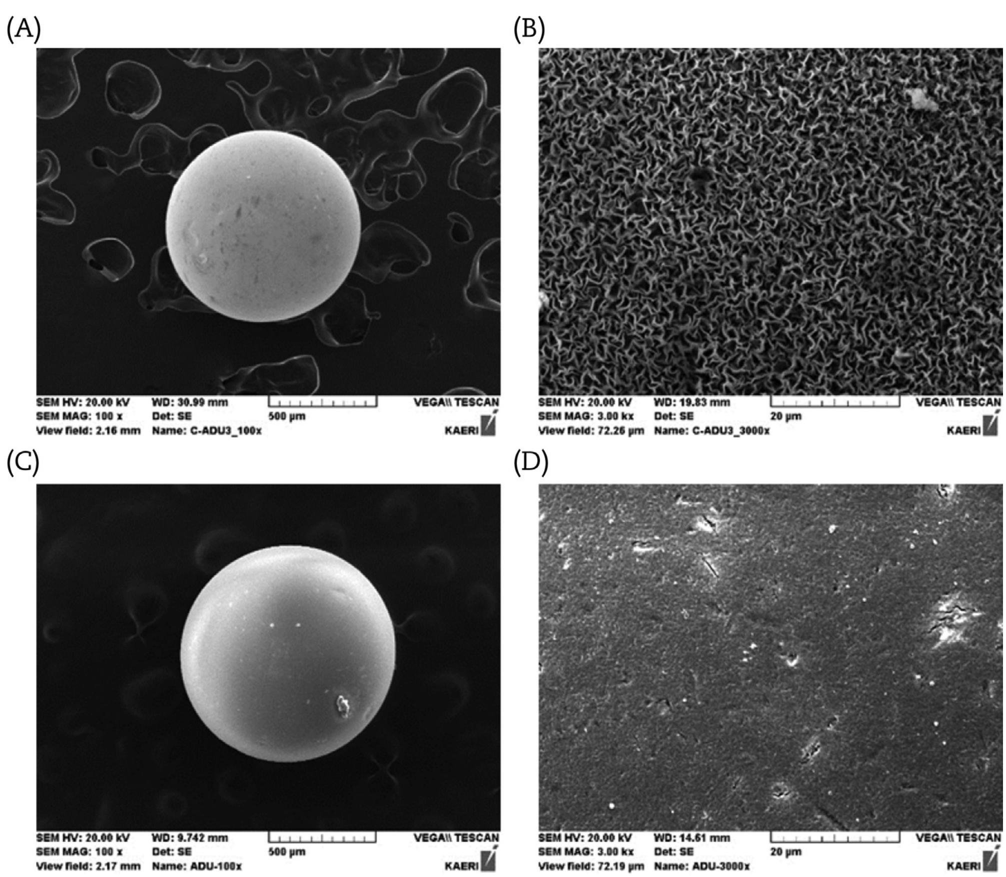

Fig. 7 – Shapes and surfaces of ADU gel particles. (A,B) With carbon; (C,D) without carbon.

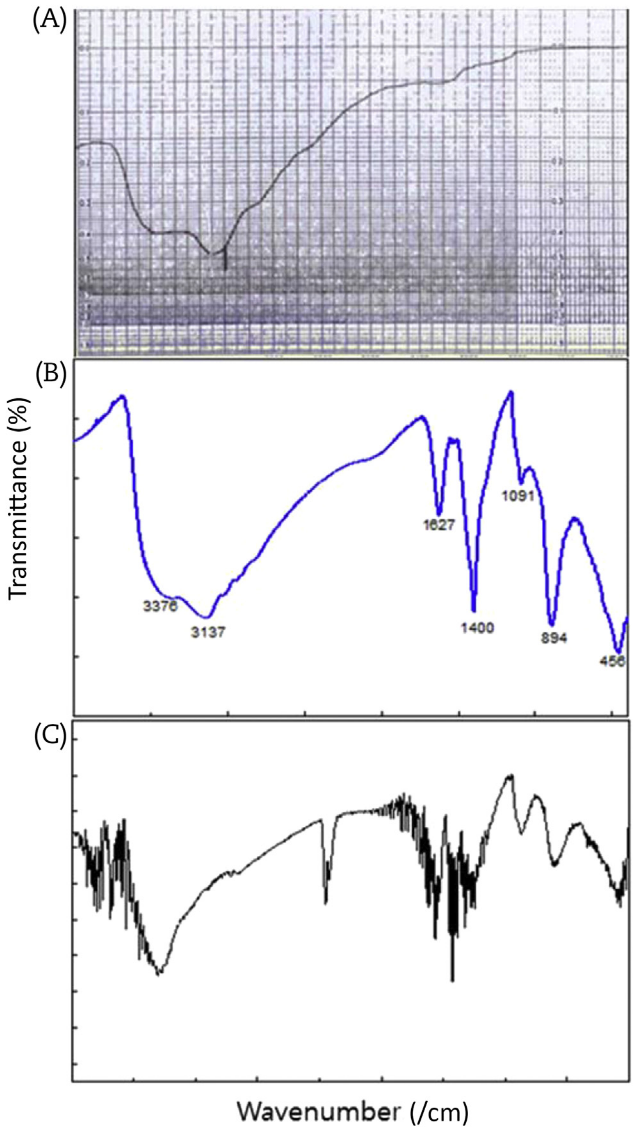

Fig. 8 – FT-IR curves. (A) ADU precipitates; (B) ADU gel (without carbon); (C) ADU gel (with carbon).

particles were thermally decomposed during the calcination process in an air atmosphere. The weight loss by thermal decomposition of ADU gel particles was about 15–16% in this study.

Fig. 9 shows the weight loss curve of ADU and C-ADU gel particles during thermal decomposition in an air atmosphere. The weight loss percentage of both particles decreases with increasing temperature up to 320°C. However, only C-ADU gel particle showed a second weight loss from 370°C to 420°C. The total weight loss of C-ADU gel particles is approximately 24.5%, about 9% higher than that of ADU gel particle. A more complicated thermal decomposition is expected to lead to greater weight loss. More studies on this subject will be conducted in the future.

Fig. 10 shows the weight loss curves obtained by the thermal decomposition of C-ADU gel particles in an air atmosphere and in a 4% H_2 gas atmosphere. The final weight loss is

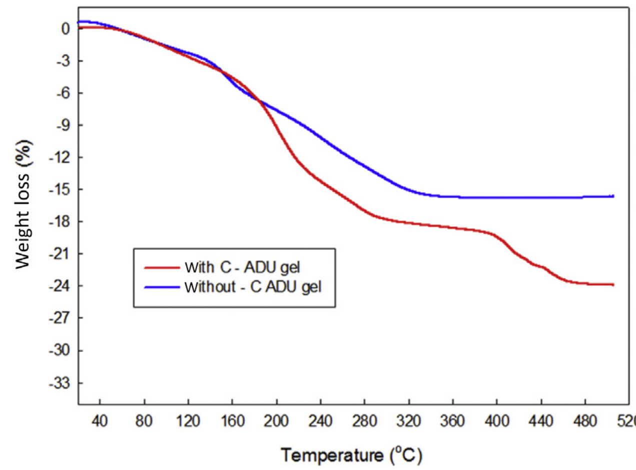

Fig. 9 – Weight loss curves in ADU gel calcination process.

approximately 21% and approximately 24.5%, respectively, in the two different atmospheres. A greater weight loss was obtained in an air atmosphere, because gas phases such as CO_2 or CO were probably formed by the reaction between carbon from broth formation and oxygen in the air atmosphere. Interestingly, the weight loss curve of C-ADU gel particle in a reducing gas atmosphere (4% H_2) shows a similar trend to that of ADU particle in an air atmosphere (Fig. 9). To investigate the further influence of the included carbon on thermal decomposition, C-ADU gel particles containing different amounts of carbon will be prepared in the future.

In conclusion, a basic experiment was conducted to ascertain the suitable carbon substance for an ideal C-ADU gel particle production. Various broth solutions containing different carbon substances were prepared. The appropriate carbon substance was selected by dispersing aggregated nano-sized carbon particles in broth solutions uniformly. The thermal decomposition characteristics of ADU and C-ADU gel particles were also investigated and compared. Supplementary studies will be conducted on the thermal decomposition process in detail.

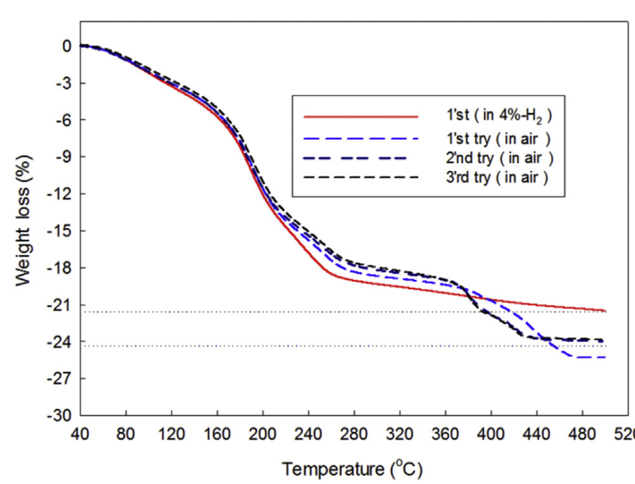

Fig. 10 – Weight loss curves of ADU gels according to calcination atmospheres.

4. Discussion

The following results were obtained from basic studies on the broth solution containing carbon substances, the formation method of spherical C-ADU gel liquid droplets, treatment to dried ADU gel particles, and the thermal decomposition characteristics of C-ADU gel particles.

- A test for selecting the appropriate carbon substance using the simulating broth solution showed that the carbon substance G sample from Cabot Co. had excellent dispersion stability, and thus was used to produce the broth solution using a uranium solution.
- In the process of preparing the broth solution, it was shown that it is possible to produce the broth solution with carbon having dispersion stability and uniform distribution by putting carbon particles into an initial UN solution, dispersing aggregated nano-sized carbon particles using ultrasonic force, and mixing THFA and PVA using a high-performance mechanical mixer.
- This study developed a process to produce C-ADU gel liquid droplets attached to a vibration nozzle system forming spherical C-ADU gel liquid droplets with a good sphericity by properly adjusting the vibration frequency and proper flow rate with the aid of high-speed camera observation.
- The thermogravimetric (TG) analysis of C-ADU gel particle in an air atmosphere showed that it had 9% more weight loss than that of ADU gel particle. Moreover, only C-ADU gel particle showed a two-step weight loss curve. Supplementary studies will be required on the thermal decomposition characteristics.

Conflicts of interest

All contributing authors declare no conflicts of interest.

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