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Spherical UO_2 Particle Preparation for a HTGR Nuclear Fuel

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1. Introduction

In the approaching decades, the entire world will need more energy and an upgraded energy infrastructure to meet the growing demands for electric power and transportation fuels. Nowadays, HTGR (High Temperature Gas Reactor) energy technology development has been spot-lighted for a clean hydrogen gas and electricity production for the countermeasures of supplying a massive energy production in the next decades because other energies such as solar heat, wind power, and tidal energy, can only produce a small scale amount of electricity or they are not as effective[1].

Generally, the production of spherical UO_2 kernels for a HTGR nuclear fuel can be carried out by wet chemical processes, a sol-gel process, based on a solidification of liquid droplets. Sol-gel process has advantages in a high purity atmosphere and at a low processing temperature[2]. However, there are only a few reports on the preparation of a spherical UO_2 kernel by a sol-gel method.

In this study, spherical ADU gel and UO_3 particles *via* an UN(uranyl nitrate, $UO_2(NO_3)_2$) solution as a raw material were prepared with the sol-gel process. And the characteristics of these droplets and the ADU gel and UO_3 particles were analyzed by a Streoscope, FT-IR, TG/DTA, and X-ray.

2. Theory and Method

The UO_2 kernel preparation starts with dissolving uranium oxide powder in nitric acid. U_3O_8 powder was selected as a raw material because it is available as a well defined chemical compound of uranium[3].

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

As shown in the above chemical reaction equation, the UN solution is rather acidic, therefore a pre-neutralization of this solution with an ammonia solution before a ADU gel precipitation has a positive influence on a solidification during a gelation process. To adjust the viscosity of the broth solution and to stabilize the spherical shape of the droplets, PVA is added to the pre-neutralized UN solution. The broth solution is prepared by mixing the following components: UN, THFA, PVA, and pure water. Here THFA as an additive is needed to avoid any damage by a shrinkage of the ADU gel particles during a gelation in the ammonia solution, an ageing and the washing steps[4].

The whole process to produce the UO_2 kernel uses the precipitation of UO_2^{2+} in a $UO_2(NO_3)_2$ solution with NH_3 to produce ADU gel particles which form gelled microspheres.

$$2\ UO_2(NO_3)_{1.5}(OH)_{0.5} + 2\ NH_4OH \rightarrow$$
$$UO_3 \cdot xNH_3 \cdot yH_2O_{(s)} + NH_4NO_3 + H_2O$$

Final, the liquid-ADU gel particle obtained from the above reaction is transferred to the ageing, washing, and drying steps. First, after an ageing with an ammonia solution with a concentration of 7 mole-NH_4OH/ℓ , aged ADU gel particles are washed first with a diluted ammonia solution, and then with pure water and IPA. Ammonium nitrate in the ADU gel particle produced by the reaction of uranyl nitrate solution and ammonia gas (or aqueous ammonia) is finally removed during these washing steps.

3. Results

3.1 Droplet Formation

Figure 1 shows the result of the droplets photographs obtained from the same size droplets formation by our vibrating system. In this step, if the relation between the flow(feeding) rate of the broth solution and frequency/amplitude of the vibrator is not discordant, small satellite drops are formed as shown in the left photograph of Figure 1[5]. Because a modulation between the amplitude and the frequency forming the natural laminar jet flow at a nozzle tip it can affect the droplet sizes so as to create a monodisperse droplet train.

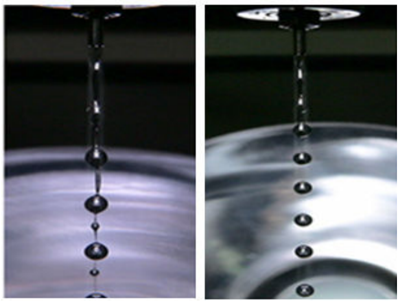

Fig.1. Satellites formation in broth dropping.

This phenomenon of a different size of the droplets is because the feeding rate of the broth solution is so high that the natural laminar jet flow of a steady state was broken at the nozzle tip.

3.2 ADU gel and Its Characteristics

From technical reviews on a HTGR fuel preparation, a basic flow diagram for a UO_2 kernel production is accomplished as shown in Figure 2. The preparation steps were as follows ; UN solution preparation, pre-neutralization of the UN solution, and then making the broth solution by a mixing of above the UN solution and additives such as PVA, THFA, and pure water.

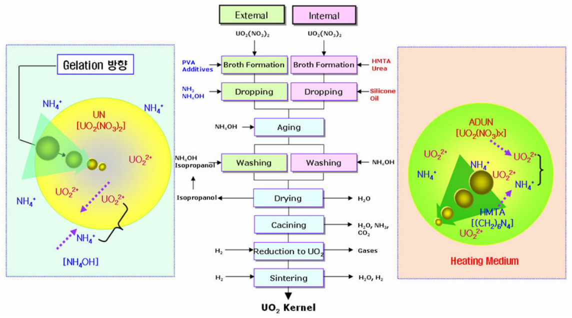

Fig. 2. Gel formation mechanism and block diagram.

Figure 3 shows the droplets, ADU gel, and UO_3 particles obtained from our experiment. The size of a droplet was obtained at about 2000~2100 μ m, at nearly the same size, but not an exact sphere. The reason was the mis-matched of the flow rate of the broth solution and the frequency/amplitude in the vibrating nozzle system.

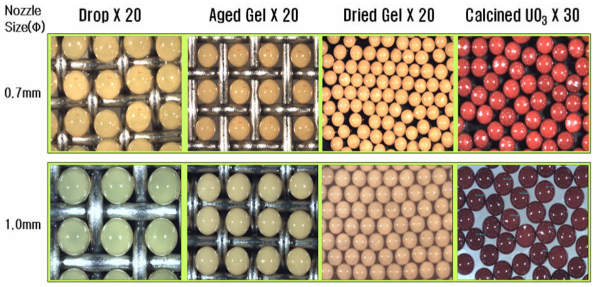

Fig. 3. ADU drops, dried-ADU gel, and UO_3 particles.

This droplets size is about four times bigger than that of the final UO_2 particle, and this value is suitable according to other discussion. Figure 4, the FT-IR spectrum of the ADU gel, exhibited absorption bands associated with a stretching and bending vibration of the O-H molecule in the hydrate water at 3100~3350cm^{-1} , N-H in NH_4^+(sharp) and U-O (sharp), one sharp peak and another sharp peak at 1400 and 889 cm^{-1} respectively. In the ADU Gel of an external gelation process, $NH_3 \rightarrow$group entrapped in the ADU gel solid is apparent. It is likely that the ammonia ion diffused into the broth droplet's surface, that contained a uranyl ion, from the ammonia water in the gelation medium.

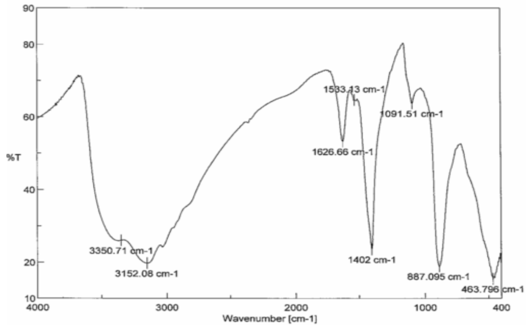

Fig. 4 . FT-IR spectrum of the dried-ADU gel.

3.3 Thermal Treatment of ADU gel

The thermal behavior of the dried ADU gel prepared from a gel supported precipitation process was studied by TG/DTA analysis. Figure 5 is the TG/DTA curves of the dried-ADU gel which was heated at a rate of 1°C/min. in an air atmosphere and cooled down to room temperature. The exothermic peaks showed at around 200 °C and 400 °C. These peaks are due to the thermal decomposition of the PVA contained in the dried-ADU gel particle.

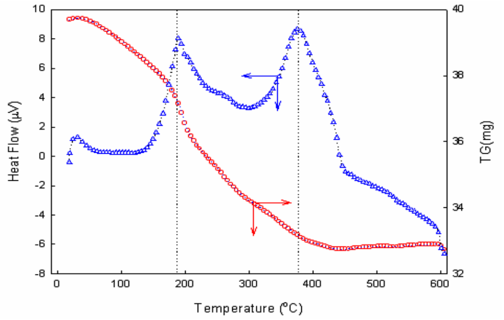

Fig. 5. TG/DTA curves during the thermal treatment.

The PVA decomposition temperature is a very important factor in a thermal treatment process which converts ADU gel to UO_3 particle. If the dried-ADU gel particle receives a thermal shock by a rapid heat during the thermal treatment process, the dried-ADU gel particle burst. Therefore the thermal treatment steps must be progressed very carefully.

4. Conclusion

In this study, the most important factors are the composition ratio of the broth solution, and the harmony of the flow (feeding) rate of the broth solution and the frequency/amplitude of the vibrator. From various analyses, the ADU gel particle was judged to be a $UO_3 \cdot xNH_3 \cdot yH_2O_{(s)}$ form, and the dried ADU gel needs to avoid a rapid heating rate in the range of 150~400 °C during the thermal treatment.

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