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ARTICLE

External Gelation Conditions in Fabrication of Nitride Fuel for Transmutation of Minor Actinides

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Toward the establishment of fabrication technology of nitride fuel for the transmutation of minor actinides, optimal external gelation condition was investigated by using dysprosium nitrate as surrogate for trivalent minor actinides nitrate. The external gelation tests were performed under the various viscosity and pressure conditions of solution as parameters to obtain the spherical gel particle less than 600 µm in diameter. Smaller gel particles with higher sphericity were achieved at pressure above 300 kPa under 36 mPa·s condition and above 490 kPa under 54 mPa·s condition. The results indicates that higher viscosity required higher optimal pressure, and the range of optimal viscosity and pressure conditions was experimentally determined. For the carbothermic nitridation, carbon was added into the gel particles at the optimal condition, and it was observed that excessive carbon addition led to the formation of cracks on the particle surface and adhesion of fine powders including carbon. From these results, it was confirmed that gel particles with required specifications could be prepared by adding approximately 1.0 wt% polyvinyl alcohol to the drop solution, adjusting the viscosity of about 30 to 35 mPa·s, and maintaining a carbon to dysprosium atomic ratio to approximately 1.75, and a droplet formation pressure of 300 kPa.

KEYWORDS: transmutation, minor actinides, accelerator driven system, external gelation, nitride fuel

I. Introduction

Nitride fuel has been selected as the most promising candidate fuel for transmutation of long-lived minor actinides (MAs) using accelerator-driven system (ADS) under the double-strata fuel cycle concept in Japan.[1] Nitride fuel has advantages such as high thermal conductivity and high mutual solubility among MA elements. There are two concepts for nitride fuels for MAs transmutation: one is a solid-solution type, where Pu and MA nitrides are dissolved in a zirconium nitride (ZrN) matrix, and the other is a particle-dispersed type, where Pu and MA nitride particles are dispersed in a titanium nitride (TiN) matrix.[2] The solid-solution type fuels with ZrN can relatively enhance the chemical stability against moisture during handling.[3] and existing fabrication technologies can be applied. In contrast, although challenges remain in fabrication of fuel pellets with high density, the particle-dispersed fuel has been proposed as a high-performance fuel concept to achieve efficient MA transmutation.[4] The TiN based fuel pellet with dispersed MA nitride particles has several advantages; (a) more flexible and wider range of the Pu and MA composition is achievable, (b) the density of MA nitride particles and TiN matrix can be controlled independently, and (c) irradiation damage by fission fragments and solid fission product accumulation may be localized within and near the MA nitride particles.

The external gelation technology allows the direct use of nitride sphere particles for the fabrication of particle-dispersed fuel. This technology has additional advantages from an engineering perspective such as reducing radioactive dust compared to conventional methods by eliminating the powder fabrication process. So far, particle synthesis technology using external gelation methods has been explored previously.[5,6] However, there has been almost no studies specifically targeting MA nitride particles. Therefore, we have started the development of fabrication technology for TiN based fuel pellet with dispersed MA nitride particles using external gelation methods.

Figure 1 shows a schematic fabrication flow of TiN based fuel pellet with dispersed MA nitride particles. MAs separated from high-level liquid waste are converted into gel particles through the external gelation method from nitrate solution, and then nitrided to synthesize nitride particles through calcination and carbothermic reduction. By mixing the nitride particles with TiN powder, pressing and sintering, TiN based fuel pellets with dispersed MA nitride particles are fabricated. Previous study shows that the smaller size of nitride particle is preferable and should be smaller than 250 µm to prevent degradation of thermophysical and mechanical properties of the nitride fuel.[4] Since particle size shrinks to nearly one-third of its original size by calcination and nitridation,[7] it is preferable for the gel particles to initially have a size of less than 750 µm. In addition, to minimize stress concentration and thermal anisotropy in the sintering of particle-dispersed pellets, it is crucial that the particle maintain a spherical shape with minimal distortion.

Therefore, as part of the development of fabrication technology of TiN based fuel pellets with dispersed MA

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nitride particles, optimal external gelation condition for synthesis of nitride particles was investigated by using dysprosium (Dy) nitrate as surrogate for MA nitrates. Since the viscosity and pressure of the dropping solution were the most critical parameters, external gelation tests were performed with these parameters to synthesize spherical gel particle smaller than 600 μm aiming for the nitride particle size of approximately 200 μm. And then, the optimal condition of carbon addition for the nitridation process was investigated.

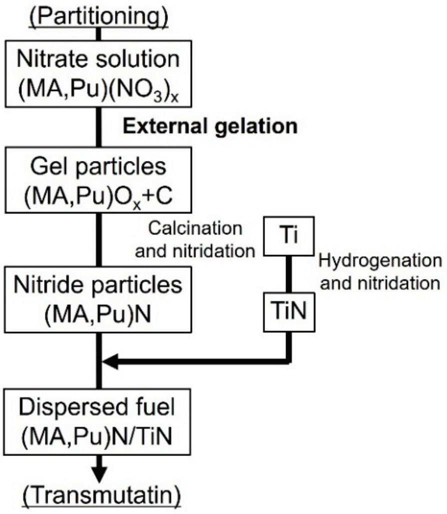

Fig. 1 Schematic fabrication flow of TiN based fuel pellet with dispersed MA nitride particles

II. Experimental

1. Dropping Solution

Table 1 shows the composition of dropping solution. The dropping solution consisted of dysprosium nitrate, polyvinyl alcohol (PVA) as the thickener (mean degree of polymerization: 3,100 - 3,900, degree of saponification: 86 - 90 mol%), tetra hydro furfuryl alcohol (THFA) as the polymeric stabilizing agent and water. Gelation was induced by the reaction of this solution with 28% ammonia solution, as shown in Eq. (1).

Viscosity of the solution was controlled by concentration of PVA. The droplet system has no temperature control system for solution, leading to viscosity fluctuation due to changes in the ambient room temperature. Since variation of 5℃ could cause an approximately 6% change in viscosity,[8)] the PVA concentration was adjusted to keep the viscosity of the target values according to the temperature as per Table 1.

In optimizing viscosity and pressure parameters for external gelation, the carbon dispersions required for the nitridation reaction was excluded, and optimal conditions for preparing gel particles were investigated under this simplified condition (see Table 1 (A)). After confirming the conditions for the synthesis of gel particles, external gelation tests were performed using the dropping solution with carbon dispersions (see Table 1 (B)). The amount of carbon was determined based on the required amount for the nitridation reaction shown in Eq. (2). The atomic ratio of the carbon (C) to dysprosium (Dy) in the dropping solution, expressed as C/Dy should be at least 1.50,[9)] but the target amount was set to higher value to reduce residual oxygen during the nitridation process.

$$\boldsymbol{Dy(NO_3)_3 + 3NH_4OH = Dy(OH)_3 + 3NH_4NO_3} \quad (1)$$

$$\boldsymbol{DyO_{1.5} + \tfrac{3}{2}C + N_2 = \tfrac{1}{2}DyN + \tfrac{3}{2}CO} \quad (2)$$

Table 1 Composition of dropping solution

Solution	$Dy(NO_3)_3$ [wt%]	C [wt%]	PVA [wt%]	THFA [wt%]	H_2O [wt%]
(A)	20-23	0	1-2	25-30	50-60
(B)	20-23	1-2	1-2	25-30	50-60

2. Gelation System and Condition

Figure 2 shows a schematic view of the external gelation system. The dropping system mainly consists of a stock tank, a dispenser, and a syringe with a vibration exciter. Small droplets were formed by the vibration of 150 Hz and dropped from the syringe nozzle, which had an inner diameter of 250 μm, into ammonia solution. Droplet formation was observed by a camera using a stroboscope synchronized with the vibration frequency.

Regarding the frequency for droplet formation, although higher frequencies could fabricate finer droplets, frequencies above 150 Hz caused excessive vibrations in the exciter and perfluoroalkoxy alkane tube, leading to bubble formation that interfered with droplet formation. Therefore, the upper frequency limit was set at 150 Hz. Regarding the size of the syringe nozzle, it was necessary to use a nozzle with a smaller inner diameter to reduce the size of the gel particles. However, the maximum supply pressure available in the system (500 kPa) limited the inner diameter of nozzle, and it was fixed at 250 μm.

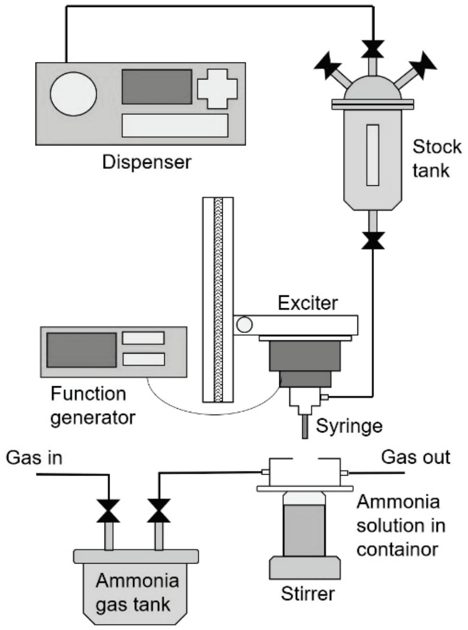

Fig. 2 External gelation system

The syringe and ammonia solution container were enclosed in a polyethylene cell, where ammonia gas was sprayed to harden the surface of the droplets. To ensure efficient gelation and to disperse the gel particles throughout the solution, a magnetic stirrer was placed at the bottom of the solution container. Under the condition using the stirrer, approximately 500 ml of ammonia solution was required to produce 3 to 5 g of gel particles per batch.

3. Gelation Condition

The viscosity conditions were set to less than 60 mPa·s to ensure smooth processing in the gelation system based on previous studies on uranium oxide.[10,11] The feed pressure was kept below 500 kPa due to the working pressure limitations of dispenser. The gel particles dropped into the ammonia solution were heated at 60°C for approximately 1 hour to complete gelation throughout the particles. This aging process also facilitated the removal of residual ammonia and ammonium compounds from the particles during subsequent washing.

After washing, the gel particles were extracted, dried, and subjected to observation of appearance using a stereoscopic microscope. Particle size was measured through image analysis, and sphericity, defined as the ratio of the major radius to the minor radius, was calculated.

III. Result and Discussion

1. Determination of Gelation Condition

Figure 3 shows the particle size distribution and sphericity of gel particles under the viscosity condition of 35 (±6%) mPa·s and pressures ranging from 300 to 400 kPa. It is desirable for the plots shown in Fig. 3 to concentrate near smaller diameter and a sphericity of 1.00. However, due to instantaneous pressure changes at the beginning and end of the droplet formation, there was some variation in the particle size and sphericity of the droplet in this study. Under the conditions of 36 mPa·s as shown in Fig. 3, particles smaller than 600 μm were obtained above 300 kPa. The number of particles with sphericity above 1.20 increased at 300 kPa, which indicates that the pressures of 350 kPa and 400 kPa are better to obtain better spherical particles. **Figure 4** shows the appearance of the dried gel particles under the 36 mPa·s and 350 kPa condition. No crack or other defects were observed on the surface, confirming that spherical gel particles were successfully obtained**.**

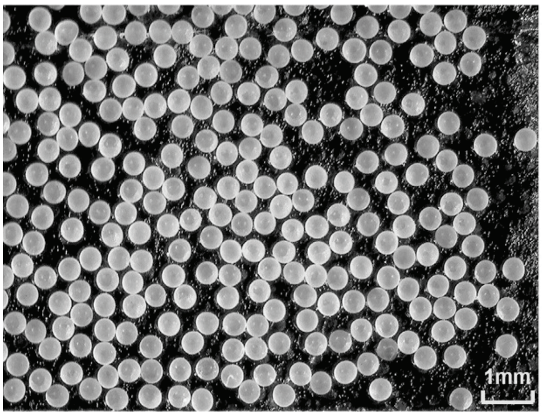

Fig. 4 Photomicrograph of dried gel particles under 36 mPa·s and 350 kPa condition

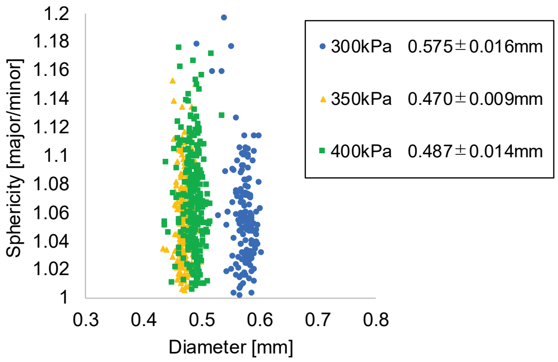

Fig. 3 Correlation between diameter and sphericity at each pressure in 36 mPa s condition

Figure 5 shows the particle size distribution and sphericity of gel particles under the viscosity condition of 55 (±6%) mPa·s and pressure ranging from 450 to 490 kPa. Smaller particles than 600 μm with better sphericity were obtained at 490 kPa, which were higher than those for the 36 mPa·s condition.

The gelation reaction proceeds through the hydrolysis and polycondensation of the precursor molecules, and it has been reported that higher viscosities of the initial solution (with denser reactive molecules) tend to result in larger particles.[12] In this study, although the pressure conditions are not identical, a comparison between the data at 400 kPa with 36 mPa·s and at 450 kPa with 54 mPa·s indicates that higher viscosity leads to large particle sizes, as with previous study. The result suggests that higher pressure is required to fabricate small particles for higher viscosity condition.

The results in this study indicate that smaller particle with better sphericity can be obtained at higher pressure condition in the case of the same viscosity. However, although most particles were spherical ones, fragmentation of particles caused by interaction between mass flow of solution and vibration of exciter was observed. On the other hand, the spherical particles could not be obtained due to distortion of droplet shapes in the case of lower pressure.

Figure 6 shows optimal conditions of viscosity and pressure in external gelation for spherical gel particles smaller than 600 μm in this study. The optimal pressure is higher with

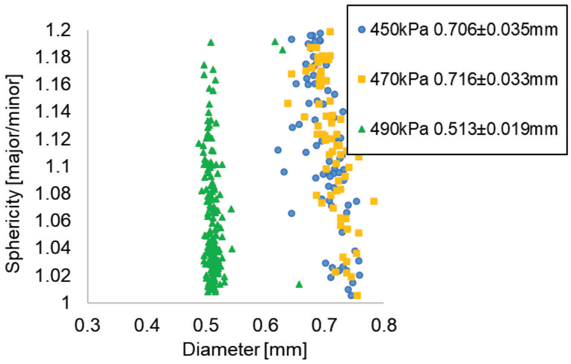

Fig. 5. Correlation between diameter and sphericity at each pressure under 54 mPa s condition

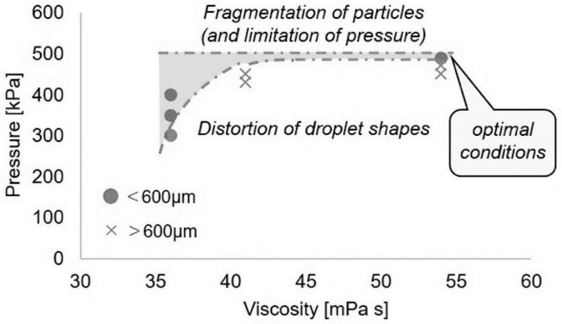

Fig. 6. Optimal conditions of viscosity and pressure for synthesis of spherical gel particles

higher viscosity, and the range of optimal viscosity and pressure were experimentally determined.

2. Addition of Carbon into Gel Particle

Based on the optimal conditions for viscosity and pressure determined above, gel particles were synthesized using a drop solution containing carbon dispersions (Table 1(B)). **Figure 7** shows the particle size distribution and sphericity of gel particles under varying C/Dy ratios at the viscosity of 32 (±6%) mPa·s and the pressure of 300 kPa.

The change in viscosity due to the addition of the carbon dispersion solution was adjusted to the target viscosity of 35 (±6%) mPa· s by adjusting the amount of PVA. Since the viscosity resulted in lower than 36 mPa· s in the test, the droplet formation pressure was accordingly set to a lower value of 300 kPa. As shown in Fig. 7, it was confirmed that gel particles with carbon addition could be successfully synthesized under the droplet conditions established in III.1, demonstrating that the range of conditions determined in the simplified system without carbon addition was indeed appropriate. In addition, it was found that both the particle diameter and sphericity were independent on the C/Dy ratio. **Figure 8** shows an appearance of the gel spheres synthesized from the drop solution with carbon dispersions with C/Dy ratio of 1.76. Spherical particles with uniform shapes were obtained, and it was confirmed that there was no deterioration with surface condition**.**

On the other hand, as mentioned in II.1, the target C/Dy ratio was set to approximately 1.80, and it was found that cracks occurred in the particle synthesized when the C/Dy ratios were higher than 1.80. **Table 2** presents the state of the particles in C/Dy ratio from 1.76 to 1.96. **Figure 9** shows an appearance of carbon-added particles with the C/Dy ratio of 1.96. Under the conditions with the C/Dy ratios over 1.80, the fraction of particles with cracks increased, and above 1.89, the particles were fragmented as shown in Fig. 9. In addition, it was observed that unbound carbon leached into the ammonia solution, hindering the stable formation of gel spheres by adhesion of fine powders including carbon. The dispersed carbon did not chemically bind with the structure of the gel spheres but is physically incorporated into the oxide structure. Therefore, it is assumed that the carbon could not be incorporated into the particles due to the presence of other substance such as Dy oxide, PVA, the gelling agent, which led to leaching into the solution. In this study, it was suggested that the maximum carbon addition limit was between 1.75 to

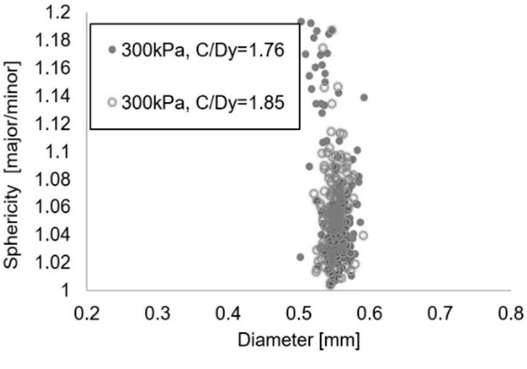

Fig. 7 Correlation between diameter and sphericity at each C/Dy condition under the 32mPa·s condition

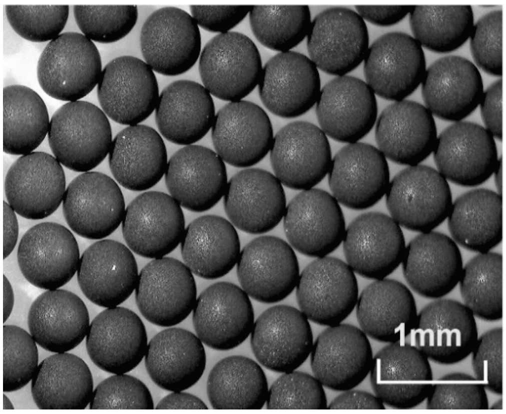

Fig. 8 Photomicrograph of added carbon dried gel particles under the C/Dy=1.76 condition

Table 2 The state of the particles in C/Dy ratio from 1.76 to 1.96 (PVA:1wt%)

C/Dy	State	Notes
1.76	○	No cracks
1.80	△	Few cracks
1.85	×	Many cracks
1.89	×	Fragmented and many cracks
1.96	×	Fragmented and many cracks

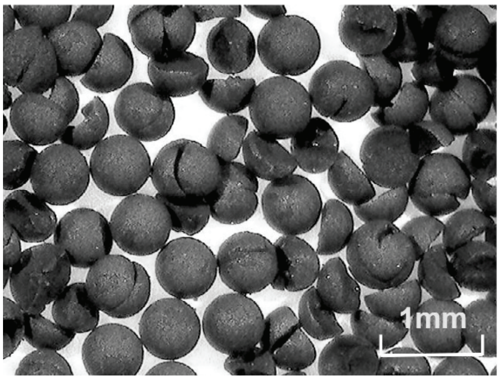

Fig. 9. Photomicrograph of carbon-added dried gel particles with the C/Dy ratio of 1.96 condition

1.80 of C/Dy ratios for a drop solution with 20 wt% Dy and 1 wt% of PVA. From the results of this study, it can be said that the amount of carbon should be adjusted considering the total amount of component in gel particle.

In the case where the preparation of nitrides from the actual MA nitrate solution using this technology, it is assumed that spherical small particles can be fabricated under similar conditions by maintaining the composition ratio of the dropping solution because the lattice constants of nitride and oxide for MA are not different significantly from those of Dy. [13,14] Additionally, considering the potential for temperature changes due to decay-heat of actual MA, it would be necessary to maintain a lower temperature throughout the process to achieve precise viscosity control. On the other hand, approximately 500 ml of waste liquid was produced from just 30 ml of solution per batch to obtain 5 g of gel particles in this study, including washing liquid. Therefore, the amount of secondary waste is expected to be enormous in large-scale engineering process, necessitating the development of waste treatment technologies.

IV. Conclusion

The optimal external gelation condition was investigated for the fabrication of MA nitride particles toward development of fabrication technology of high-performance nitride fuel for MAs transmutation. The external gelation tests were performed in the various viscosity and pressure conditions of dropping solution as key parameters to obtain the spherical gel particles less than 600 μm in diameter.

The results show that the smaller particles with excellent sphericity was obtained at the higher pressures of 350 to 500 kPa at each viscosity of 30 to 50 mPa·s with positive correlation. Carbon dispersion solution was added within the specified viscosity and pressure ranges for nitride particle preparation. Under the conditions where the C/Dy ratios exceeded 1.80, unbound carbon components leached into the ammonia reaction solution, and by inhibiting particle bonding, deteriorated the surface condition of the particles. Therefore, although these conditions need to be further optimized considering subsequent fabrication process of nitride particle such as calcination and nitridation through carbothermic reduction, it was concluded that following optimal conditions for the spherical small gel particle were achieved: adding approximately 1.0 wt% PVA to the drop solution, adjusting the viscosity to about 30 to 35 mPa·s, maintaining a C/Dy ratio approximately at 1.75, and droplet formation pressure of 300 kPa.

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