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A new internal gelation process for fuel microsphere preparation without cooling initial solutions

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Abstract

A new method for preparing the broth for internal gelation without cooling was developed, and it was applied to UO_2 microsphere preparation. The broth was prepared by mixing two components just before drop formation: one was an uranyl nitrate solution and the other a hexamethylenetetramine solution. In addition, the technique for preparing a small volume broth by the above method was developed. Moreover, for easily drying the 'UO_3'-gel microspheres obtained from the broth with microwave heating, the aging in an NH_4NO_3 solution was tried. The gel microspheres produced by using the new techniques were easily converted into UO_2 microspheres with high density around 98% TD. © 1998 Elsevier Science B.V.

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1. Introduction

Internal gelation method [1–10] has been applied to the fabrication of ceramic microspheres of nuclear fuel, such as UO_2 and UN. The method is characterized by that hexamethylenetetramine (HMTA) dissolved previously in the broth — including fuel nitrate (e.g., uranyl nitrate) and urea — causes internal gelation of the broth drops when they are heated. Since the broth is gelled with HMTA even at room temperature, hitherto, it has to be prepared under cooling by mixing a fuel nitrate solution and a mixed solution of HMTA and urea. Moreover, the formation of the broth drops has to be conducted under cooling. Thus cooled drops are heated and gelled; the heat for the gelation is either provided *externally* from hot oil [1–5,8–11] or generated *internally* with a microwave heating device [6,7,12].

For the cooling, a considerably large device is needed and some troubles tend to occur. Therefore, if possible, the cooling steps should be excluded from the internal gelation process. In the preliminary work [13,14], it was tried *without cooling* to prepare the broth by mixing an acid-deficient uranyl nitrate (ADUN) solution and a HMTA-urea mixed solution just before drop formation. Thus obtained drops with U concentration of 0.68 mol/l were successfully gelled by *internally heating* with the microwave heating device. However, the shape and homogeneity of gelled microspheres were slightly poor for higher U concentrations around 1 mol/l and further improvement was needed.

The second improvement was done for the aging condition; the aging process was necessary for the gel microspheres to be easily dried without degradation of their shape. Generally, the *internally heating* for the internal gelation was conducted during a very short time of ~ 0.1 s, while the *externally heating* was carried out during 10 s or longer in hot oil before the contact of gel microspheres with an aqueous media for washing. Even after heating and gelling, the pH of the broth for the internal gelation process was usually acidic ($pH < 7$) [15]. The solid particles in the gel were very fine at first and then were grown during aging, depending on the chemical composition of the broth; in more acidic media, the size of the particles became larger [16]. The microspheres heated and gelled in air with the microwave device were usually collected in an aqueous ammonia solution [6,7,12–14], for avoiding the use of organic solvent whose waste should be decreased. As a result, just after gelation, the pH of the gel microspheres was increased by the ammonia solution. Therefore,

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the obtained gel microspheres were less aged than those gelled by externally heating in hot oil. The less aged gel microspheres were difficult to be dried without cracking or deformation.

In the present study, the apparatus and conditions for broth preparation, gelation and gel microsphere collection were improved to obtain satisfactory gel microspheres with higher U concentrations around 1 mol/l. Additionally, a technique for small batch preparation was developed. Moreover, a weak acid solution of 0.1 mol/l NH_4NO_3 was used for the aging to grow easily crystallizes in the gel microspheres without dissolving them. These improvements enabled us to prepare homogeneously gelled microspheres from the broth with higher U concentrations around 1 mol/l and to convert them into high density (98% TD) UO_2 microspheres without loss due to their degradation during drying and sintering.

2. Experimental

2.1. Preparation and feed of the broth solution

The broth solution for internal gelation was prepared without cooling by mixing statically an ADUN solution and a mixed HMTA-urea (HMUR) solution just before drop formation. These solutions were indirectly pumped by using the apparatus shown in Fig. 1 [17] as follows.

(1) The path in both valves A and B was set to loading mode.

(2) Either the ADUN or the HMUR solution was filled in path c and most of loading tube 7, leaving a little air near connector 2. (The air acts as a separator between the solution and water, in later step (4).)

(3) Water was filled in the part of 9–1–a–6–10–11 for both valves by the respective pump 8.

(4) The path in both valves was changed to mixing-feed mode, and both pumps were operated.

Both solutions in each loading tube (PFA Teflon®, 2 mm ID × 1500 mm) were supplied by help of the remaining air which was pressurized by water sent with each pump (Nihon Seimitsu Kagaku, NP-FX-3U type) and mixed in the mixing portion 10 to prepare the broth fed to the nozzle 11. By this procedure, even a few ml broth was prepared and fed for drop formation.

The mixing portion was a commercial T-typed tube-joint improved to minimize its inner volume. The nozzle used was a stainless steel tube which was 0.5 and 0.7 mm in inner and outer diameters, respectively. The tube connecting between the nozzle and the mixing portion provided

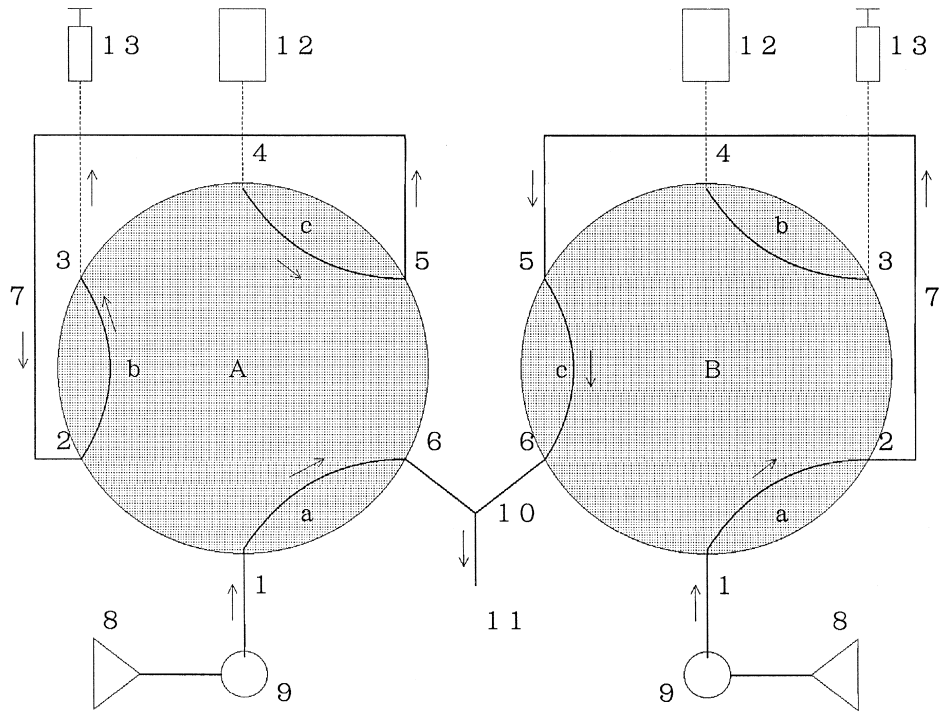

Fig. 1. Apparatus for preparation and feed of the broth for internal gelation. (A, B) 6-way valve, (a–c) path in 6-way valve (in valve A: loading mode, in valve B: mixing-feed mode), (1–6) tube connectors of 6-way valve, (7) loading tube for either ADUN or HMUR solution, (8) pump, (9) pressure gauge, (10) mixing portion, (11) nozzle for drop formation, (12) tank for either ADUN or HMUR solution, (13) injection syringe.

the narrowest path in the nozzle set consisting of the three parts, i.e., the nozzle, the tube and the mixing portion. In the experiments two nozzle sets were used: the connecting tube was 0.1 mm ID × 50 mm or 0.25 mm ID × 105 mm, and the inner volume of the nozzle set was 3.35 or 6.61 μl, respectively. The total feed rate of the broth was fixed to 3 ml/min, and the time for the broth passing through each nozzle set was 67 or 145 ms, respectively.

The ADUN solution used was prepared to be 1.55 in nitrate/U molar ratio by the controlled denitration of uranyl nitrate [18], and U concentrations in the solution were 1.36 to 3.0 mol/l. The mixed HMTA-urea (HMUR) solution was an equimolar mixture of 2.5 to 3.0 mol/l. The broth was prepared by mixing ADUN and HMUR solutions in two manners: (1) ADUN = 1.5 ml/min and HMUR = 1.5 ml/min (1/1 mixing), and (2) ADUN = 1.2 ml/min and HMUR = 1.8 ml/min (2/3 mixing). By selecting the mixing manner and the concentrations of ADUN and HMUR solutions, broth solutions with a wide-ranged composition of HMUR/U molar ratio and U concentration can be prepared.

2.2. Microwave heating and collection of microspheres

The broth drops were internally heated and gelled while falling in a quartz tube positioned at the center of the cavity resonator (221 mm height) of the microwave heating device [12]. The nozzle was placed at 70 mm above the upper end of the cavity; in the space between the nozzle and the cavity, a dish-typed shutter was inserted for rejecting inhomogeneous broth formed at the beginning and end of feed.

The gelled microspheres falling out of the cavity resonator were collected into the hot NH_4OH solution of 0.5 mol/l, which was heated at 60 or 80°C by hot water circulating in the jacket of a collecting receptacle; a collecting device including the receptacle is illustrated in Fig. 2. For keeping the collecting solution temperature constant, it was flowed slowly from the bottom of the receptacle, and overflowed to a side tube. The level of the solution surface was controlled to be 60 mm below the lower end of the cavity. (This distance was needed to avoid electric discharge; this would occur with abrupt evaporation of a small droplet of the collecting solution which was formed by impact of the gelled microsphere on the collecting solution surface and then reached the quartz tube surface within the cavity resonator.)

The air in the quartz tube was continuously exhausted through the side tube by an air pump; this prevented the electric discharge which would occur with accumulation of water vapor and gaseous ammonia generating from the collecting solution and/or the falling gel microspheres.

2.3. Aging

After gelation, the microspheres collected in the receptacle were continuously heated at the same temperature for 10 min in the NH_4OH solution flow, and then cooled. Thereafter, the flowing solution was changed to 0.1 mol/l NH_4NO_3 solution for the aging, and then the temperature was raised again up to a temperature of 60–80°C, and kept for 0.5 or 1 h.

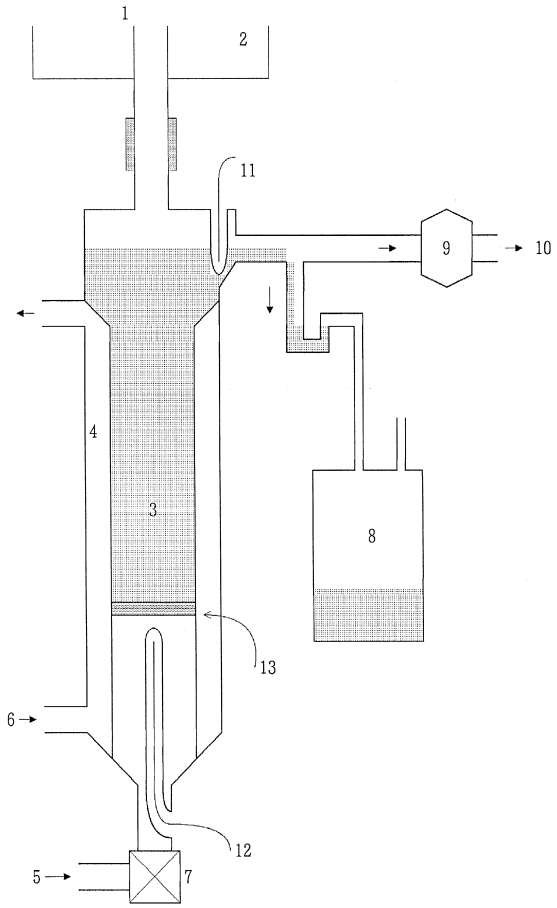

Fig. 2. Collecting device for gelled microspheres. (1) quartz tube, (2) cavity resonator, (3) receptacle for gelled microspheres, (4) jacket, (5) collecting or aging solution, (6) hot water, (7) valve, (8) waste tank, (9) air pump, (10) to duct, (11, 12) thermocouple, (13) glass filter.

2.4. Washing, drying and sintering

After aging and cooling, the gel microspheres were washed by flowing 0.5 mol/l NH_4OH solution, while electric conductivity of the effluent was monitored. The washed microspheres were transferred to form a monolayer on a sieve in the similar solution. After the sieve was removed from the solution, the surface of the microspheres

was dried at room temperature either statically or by flowing air until the solution remaining among the sieve and microspheres were evaporated. Thereafter, the sieve was covered with top and bottom caps, and heated at 130°C for 2 h in a dryer. The dried microspheres were sintered at 1300°C for 3 h in a flow of Ar–4%H_2.

3. Results and discussion

3.1. Broth preparation and its gelation behavior

3.1.1. Gelation behavior depending on broth composition

Preparation of stock solutions of ADUN and HMUR with higher concentration than 3 mol/l was difficult; this is the reason why the highest concentration of both solutions was 3 mol/l. The composition of producible broths, therefore, was limited; HMUR/U molar ratio for a U concentration is limited in the range below the dotted curves drawn for 3.0 mol/l HMUR in Fig. 3. Therein, the boundary curves for the gelation behaviors (areas A to D) reported by Vaidya et al. [8] are also drawn with the solid curves. Their results suggest that, in the present method, the broth with the composition in the area D is gelled either within or on the nozzle and fails in formation of spherical gel microspheres; on the other hand the broth in the area A is not converted into completely gelled microspheres which are not deformed when they fall into the collecting solution. The composition in the areas B and C is estimated to result in good gelation.

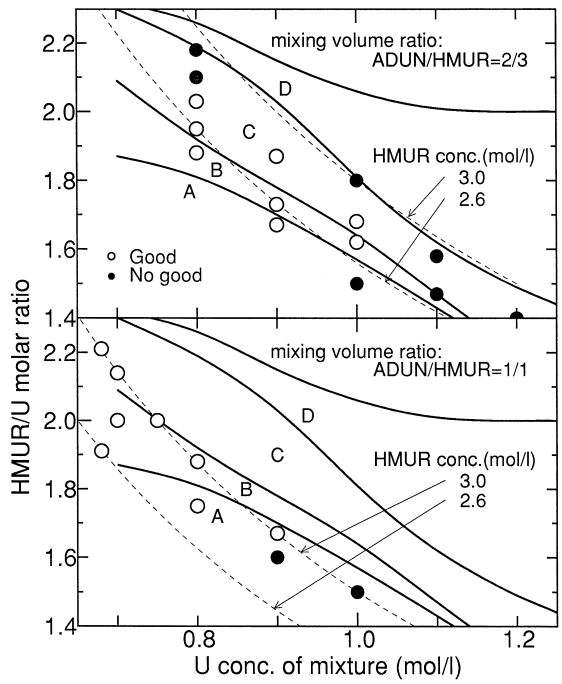

Fig. 3. Gelation behavior depending on the broth composition. The solid lines dividing A, B, C and D areas have been reported in Ref. [8] to distinguish the gelation behaviors: (A) incomplete gelation, (B) single phase gel at 50–70°C, (C) single phase gel at 25–50°C, (D) single phase at 20–25°C.

In the present method of mixing statically ADUN and HMUR solutions, the most homogeneous broth must be prepared by feeding the two solutions at the same rate of 1.5 ml/min (1/1 mixing). It is seen in Fig. 3, however, that the broth with U concentration higher than 0.85 mol/l cannot be prepared with the 1/1 mixing, except for the composition in the area A (incomplete gelation). As mentioned above, therefore, the mixing of ADUN and HMUR solutions at respective feeding rates of 1.2 and 1.8 ml/min (2/3 mixing) was also examined for the broth with higher U concentration, although the mixing was undesirable.

The observed gelation behavior of the broth prepared by using the nozzle set with the 0.1 mm ID tube is shown with open and solid marks in Fig. 3. The general trend of the gelation behavior was compatible with that of Ref. [8], although there was difference in the methods for distinguishing between good and no good behaviors.

In the area C near D, the viscosity of the broth may increase during the mixing at high room temperatures and, as a result, the shape of gel microspheres may become poor. Even in the area B, the broths with high U concentrations of 1.1 and 1.2 mol/l, prepared with the 2/3 mixing, were not satisfactorily gelled into microspheres; this may be caused by inhomogeneous mixing due to high viscosity of highly concentrated (2.75 or 3.0 mol/l) ADUN solution in addition to the undesirable 2/3 mixing.

As mentioned above, the broth with composition in the area A is assumed from Ref. [8] to be gelled incompletely before contact with the collecting NH_4OH solution. However, the good gelation in the area A near B was observed in some cases; this may be caused by the additional gelation in the collecting NH_4OH solution.

In the case of U = 1 mol/l and HMUR/U = 1.5, the 1/1 mixing brought microspheres with only slight inhomogeneity (although it was classified as no good in Fig. 3), while the 2/3 mixing completely deformed ones. This difference indicates that the 1/1 mixing obtains more homogeneous broth than the 2/3 mixing, as presumed.

3.1.2. Broth composition adequate to each purpose

The broth with high U concentration is desired for the later heat treatment of the resultant 'UO_3' gel microspheres, because of less shrinkage rate. (In the aqueous media, the solid formed by the reaction of a uranyl salt and ammonia is $UO_2(OH)_{2-x}(ONH_4)_x$ [19], which is called 'UO_3' hereafter.) On the other hand, in the case of applying the present internal gelation method to prepare ('UO_3' + C) gel microspheres for conversion to UN, carbon black is needed to be added to either ADUN or

HMUR solution. From the viewpoints of high concentration of the applicable HMUR solutions and of the necessity for carbon to be homogeneously mixed with U, it is considered that the carbon should not be mixed with HMUR solution but with ADUN solution, which is applicable even at low U concentration. Because of easiness of carbon dispersion, the broth with low U concentration is desired.

3.1.3. Broth homogeneity depending on its composition or mixing ratio

For the above two purposes, the two broths were selected for the later study: (1) U = 0.7 mol/l and HMUR/U = 2.0 (1/1 mixing), and (2) U = 1.0 mol/l and HMUR/U = 1.68 (2/3 mixing). From the former broth, satisfactory gel microspheres were obtained by using the nozzle set with 0.25 mm ID tube as well as with 0.1 mm ID tube. This means that both nozzle sets make similarly homogeneous broth with the 1/1 mixing. This will be of great advantage in the future study for the preparation of carbon dispersed broth which has the possibility of containing aggregated carbon particles of 30 μm or larger [11].

On the other hand, from the latter broth, only the nozzle set with 0.1 mm ID tube brought good gel microspheres; this means that the nozzle set with 0.25 mm ID tube cannot make homogeneous broth with the undesirable 2/3 mixing of relatively highly concentrated 2.5 mol/l ADUN and 2.8 mol/l HMUR solutions. It is clear that the broth homogeneity depends on its composition or mixing ratio in addition to the mixing efficiency of the nozzle set.

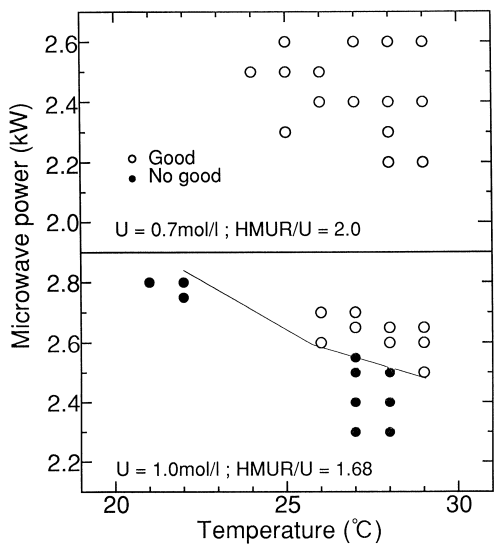

Fig. 4. Gelation behavior depending on microwave power and temperature.

3.1.4. Microwave power necessary for good gelation

Fig. 4 shows the dependencies of the gelation behavior on microwave power and on room temperature. In general, higher microwave power is necessary at lower room temperature to heat a broth drop up to a temperature. Therefore, the border line dividing good and no good gelation should have a negative slope in Fig. 4. In the case of U = 0.7 mol/l, no good gelation was not observed in the range examined; the border line would exist in the area lower than that examined. In the case of U = 1.0 mol/l, the border line was observed in higher range than that estimated for the case of U = 0.7 mol/l. This may mean that, in the case of the higher concentration of U = 1.0 mol/l, higher temperature is necessary for sufficient gelation, and/or that the temperature of the internally heated drops of higher concentration is lowered, as observed previously in Ref. [12] that larger power was necessary for more concentrated simulated-broth to be heated up by a constant degree with microwave heating.

3.2. Aging

The gel microspheres collected and washed (or aged) at 60°C in 0.5 mol/l NH_4OH solution were difficult to be dried without cracking or deformation. In a preliminary work they were dried in an incubator under various sets of temperature and humidity. Most of microspheres were cracked at low humidities, or deformed with partial peptization at high humidities. For drying without any trouble, they had to be treated around room temperature under a medium humidity for a long time; even so slight deformation was not avoided.

To improve the drying behavior of the gel microspheres, the new aging technique described in Section 2.3 was developed; the aging was conducted in the NH_4NO_3 solution of 0.1 mol/l. This solute, NH_4NO_3, was selected since it was a weak acid and the same to one of gel components. The measured pH of 0.1 mol/l NH_4NO_3 solution was 5.3 at 25°C and 4.6 at 77°C: it was higher at lower temperature. As mentioned above, the crystallite growth in the gel proceeds faster at lower pH [16]. It is considered, therefore, that the higher temperature aging grows the crystallites more effectively due to the effect of pH in addition to temperature, but that the lower temperature substitution of the NH_4NO_3 solution for the NH_4OH solution is favorable since the rapid change of circumstance for the gel microspheres tends to result in cracking. It was confirmed by the present experiment that the gel microsphere damage was not observed after the substitution of NH_4NO_3 solution at room temperature, while at high temperature a little, and that the change of color and transparency of the gel was faster at 80°C than at 60°C.

The pH of the solution contacting with the gel, however, was around 7 even after rinsed by flowing the aging solution at 80°C for 0.5 h or at 60°C for 1 h. This slow decrease of the pH may be caused by the slow release of

ammonia from $UO_2(OH)_{2-x}(ONH_4)_x$ in the gel due to the high NH_4^+ concentration in the aging solution. Even so, the present aging method brought about the desired effect on drying the gel microspheres easily.

3.3. Density of sintered UO_2 microspheres

The aged gel microspheres were easily dried and sintered by the method described in Section 2.4. In Fig. 5, the

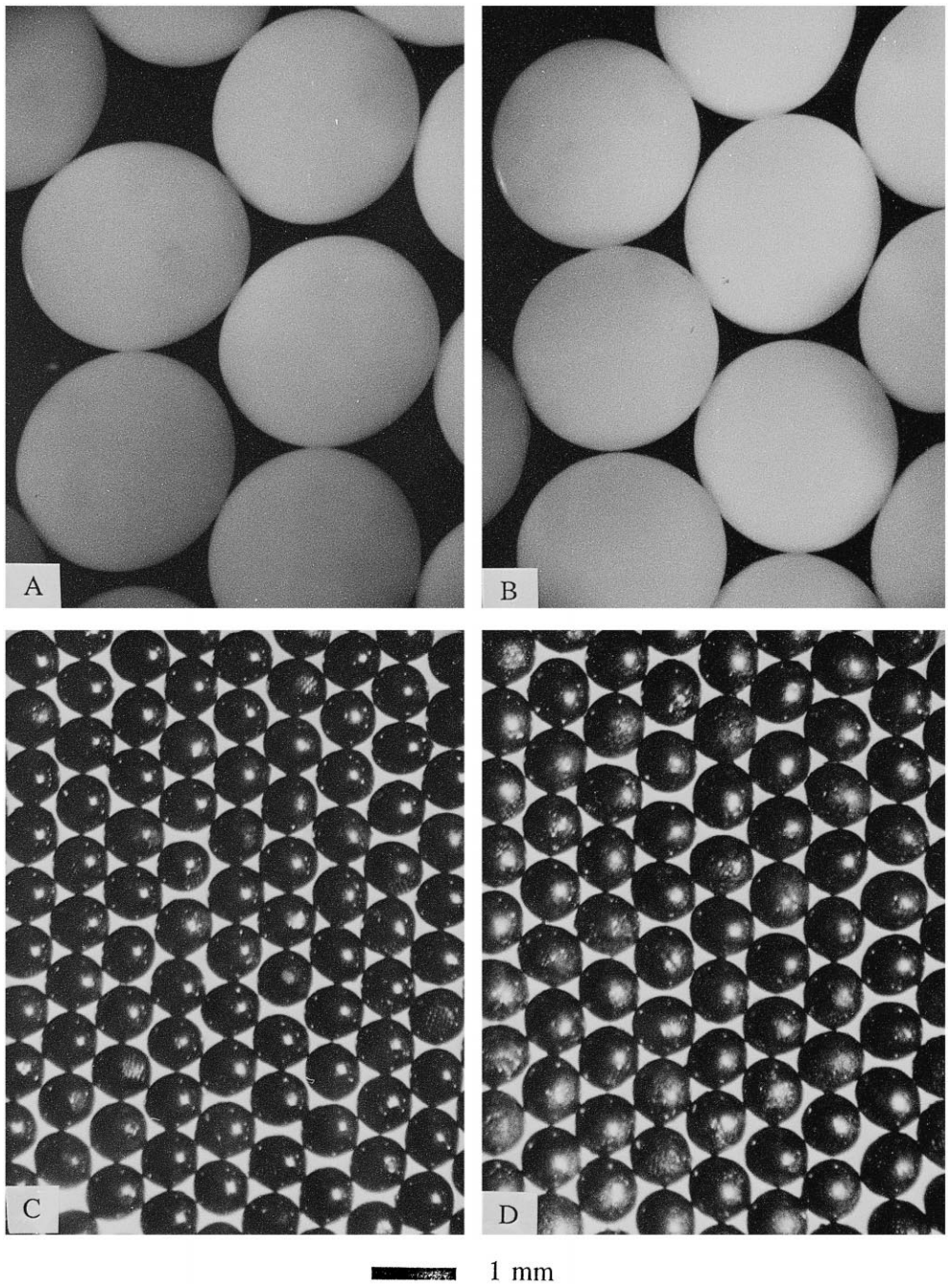

Fig. 5. Photographs of microspheres of 'UO_3' gel (A, B) and sintered UO_2 (C, D). Photographs (A) and (B) were respectively obtained from the broths of U = 0.7 mol/l (HMUR/U = 2.0) and U = 1.0 mol/l (HMUR/U = 1.68). Photographs (C) and (D) were derived from the gel A and B, respectively, and the density of both samples was 98 %TD.

Table 1
Density of sintered UO_2 microspheres

Gel. No.	Broth composition		Collecting solution temp. (°C)	Aging		Density (%TD)
	U conc. (mol/l)	HMUR/U		temp. (°C)	time (h)	
322	0.7	2.00	80	80	0.5	98.2
318	0.7	2.00	80	80	1	97.6
271	0.8	1.88	60	90	1	97.7
314	0.9	1.67	80	80	1	97.2
321	1.0	1.68	80	80	0.5	98.2
331	1.0	1.68	60	80	1	97.9
325	1.0	1.68	80	80	0.5	68.7[a] 78.1[b] 98.1

[a] Preheated in air at 1000°C for 3 h before the normal sintering.
[b] Preheated in air at 1300°C for 3 h before the normal sintering.

photographs of the sintered UO_2 microspheres are shown together with their precursor gel microspheres; they were collected in 0.5 mol/l NH_4OH solution at 80°C, cooled and aged in a flow of 0.1 mol/l NH_4NO_3 solution at 80°C for 0.5 h. Their density was 98.2% TD; in this study the density was measured within the error below 0.4% TD by the high accuracy method [20]. Densities of other examples sintered normally under sufficient feed of hydrogen reached around 98% TD, as listed in Table 1. However, when hydrogen was not sufficiently supplied, the density was decreased; the minimum observed was about 60% TD. As shown in Table 1, the density of sample, which was preheated in air at 1000 or 1300°C for 3 h before the normal sintering, was 69 or 78% TD, respectively. This may be due to the same reason that the densification of sol–gel (Th, U)O_2 microspheres was affected by sintering atmosphere [21].

4. Conclusions

A new internal gelation process without cooling the broth was developed, and it was applied to the preparation of UO_2 microspheres. At room temperature, an ADUN solution and a HMUR solution, which were components of the broth, were fed by separate pumps and mixed statically just before drop formation. In addition, another new technique was developed for preparing and feeding a small volume broth by the above method. By this, a little broth below 10 ml was successfully prepared and gelled into microspheres with a microwave heating device. The third new technique was applied to aging effectively the gel microspheres; they were rinsed by flowing hot NH_4NO_3 solution. This aged the gel microspheres enough to be easily dried. The dried ones were sintered to UO_2 microspheres with high density around 98% TD.

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