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On Fabrication of UO_2 Microspheres by Internal Gelation Process

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Microspherical UO_2 kernels for HTGR coated fuel particles were fabricated by the internal gelation process in order to examine some properties of these spheres. Fabrication run was made twice, using different nozzle sizes where droplets of uranium nitrate acid containing hexamethylentetramine and urea were dropped into the warmed paraffin oil. Characterization was made on diameter, sphericity, density, grain size and crushing strength of the sphere, and comparison of surface appearance and fracture surface of the particles fabricated by this process with those by the external process (SNAM process) was made by SEM observation.

Keywords: Gelation, Fuel, Kernel, Fabrication, HTGR, Uranium Dioxide, Calcination, Uranium Nitrate

* Southwest Center for Reactor Engineering Research and Design (China)

内部ゲル化法によるUO_2微小球の製造について

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（1989年10月12日受理）

高温ガス炉被覆粒子燃料の微小UO_2核を内部ゲル代法により試作し，その粒子の特性を調べた。燃料核の製造は，硝酸ウラン溶液にヘキサメチルテトラアミと尿素を含む混合液滴を加温した流動パラフィン中に滴下する方法で行った。この試験では，異ったノズルを使って2回の製造を行った。特性試験は，直径，真球度，密度，結晶粒径及び強度について行い，また，表面及び破面についてはＳＥＭ観察を行い，外部ゲル化法による燃料核との比較を行った。

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1. Introduction

The oxide fuel kernels of the coated particles have been produced so far for use as the HTGR driver fuels by the so-called "External gelation process", which depended on the gelation of uranium nitrate droplets in conc. ammonium-hydroxide solution, forming Ammonium Diuranate, ADU, particles. The internal gelation process, which was developed in West Germany(1-3) but had not been applied for the fabrication of the kernels of the HTGR driver fuels, is based on a very fast precipitation of ADU material from a sub-stoichiometric solution. A number of papers about the internal gelation process(4-6) have been published, since this process has many advantages over the external process as follows; the process is relatively simple, thus giving a simple facility for the gelation, and properties such as density, sphericity and diameter of the kernels can be controlled more easily. Since ammonium is generated uniformly inside the droplets, therefore proceeding of uniform gelation in it, internal stress, shell structure and gradient of the properties through radius of ADU particles are not so large.

This experiment is aimed at studying each process of the internal gelation method and characterizing the particles obtained by this method for consideration on future improvement of the kernel fabrication.

2. Description of Process

A generalized flow-scheme of the process is presented in Fig. 1. A 2.3 mol/l substoichiometric solution of uranium nitrate (NO_3/U = 1.4-1.7) was prepared by dissolving U_3O_8 in a substoichiometric amount of nitric acid. During dissolving the uranium oxide, some heating was necessary for complete dissolution. The acid deficient uranium solution was mixed with urea and hexamethylentetramine(HMTA) at low temperature.

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After mixing HMTA, it was important to keep the mixed solution cool for avoiding premature solidification, because HMTA was decomposed at elevated temperature, releasing ammonia as follow[1];

$$(CH_2)_6N_4 + 6H_2O \longrightarrow 6HCHO + 4NH_3$$

The gelation proceeds in such mechanism that ammonia released by the above reaction raised pH of the droplets and solidified them. Thus, the cold solution was dropped from a nozzle of a needle into the liquid paraffin oil which was maintained in the temperature range of 85-95°C. By changing the nozzle size, diameter of the droplet, consequently, final diameter of the kernel as a result, could be controlled. In order to avoid sticking of droplets each other and of the ADU particles to the wall of the gelation column, a small amount of surfactant such as SPAN 80 was added into the paraffin oil.

Following the gelation the ADU particles were carefully washed in carbon tetrachloride to remove adhering organic liquid such as HMTA and formaldehyde. Then, the ADU particles were transferred into a dilute ammonia aqueous solution for removing NH_4NO_3, followed by ageing there for several hours. Drying the particles were made in air at 60-70°C. Two steps of heating were carried out for the dried ADU particles; firstly, calcination of the ADU particles were made in air at 300-400°C to change ADU to oxide, UO_3, followed by next heating in an oxygen free, dry mixture of 8% H_2-Ar at 1350°C for reduction and sintering of UO_2 particles.

3. Apparatus for Gelation

Fig. 2 shows the apparatus used for the gelation of the substoichiometric uranium nitrate solution which is similar to that in Southwest Center for Reactor Engineering Research and Design of China. As indicated in the figure the broth solution was stored in a storage tank which was connected to a needle by a capillary tube. The tank and the tube were cooled with water for the reason mentioned in II. Whole of the solution prepared in a beaker in advance was pumped-up to the tank once, then pressurized in the tank to make the droplets from the nozzle of the needle. Nozzle size of the needle could be changed for controlling the ADU particle diameter. Gelation column of a glass tube about 1.4 m in length was kept at 80-90°C by making a flow of warm water through outside of the column. This apparatus was equipped in a box in order to avoid uranium contamination as shown in Photo. 1.

Test runs were made twice by changing the nozzle size in order to prepare different diameter of the kernels, which are designated as CMKF-1 and CMKF-2. The conditions for the preparation are summarized in Table 1.

4. Results and Discussion

Characterization of the UO_2 particles fabricated in this experiment is summarized in Table 2. Results of kernel diameter measured by the Particle Size Analyzer(PSA)(7) gave a relation between nozzle size and final mean diameter of the UO_2 particles as shown in Fig. 3; found here was that the diameter was almost in proportion to the nozzle size. Also was evident that standard deviation of the larger particles(CMKF-2) was somewhat larger than the smaller ones(CMKF-1).

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Sphericity of the particles was measured on CMKF-1 by PSA. A good sphericity can be seen in the appearance of the particles as indicated in Photo. 2, where the particles produced by the external process is included as a reference. In the internal gelation process surface tension essentially keeps the droplets to be spherical during the gelation, whereas in the external gelation process such as SNAM process(8) the surface tension dose not affect so strongly to keep the droplets spherical during the gelation, because the solidification of the droplets starts from the surface. Comparing the particles by the external gelation process, the surface of the particles by this process is smooth.

SEM observations of the surface appearance and the fracture surface of the particles produced by the present process and the external process are shown in Photo. 3. Remarkable difference in the appearance was that the surface by the present process was characterized by the very fine feature, meanwhile the latter appearance, by the many wrinkles, supposedly introduced by shrinkage of the ADU particles during calcination. In the fracture surface of the particles UO_2 grains could be noticed, where transgranule fracture was supposedly occurred in some grains due to appearance of so many cleavage steps. This fracture mode seemed to be more remarkable in the particles by the present process. In comparison of the grain size, this in the present particles was somewhat smaller than that by the external process. In both of the particles many transgranule babbles, roughly 100 nm in diameter, were found, probably introduced during calcination. In the kernels by the present process about 1 um large voids were found, which were seemingly brought about either shrinkage of the particles during heat treatment or formation of the internal gas.

Density of the particles was measured by two methods; the one was to measure weight and volume of the particles(CMKF-1)(replacement) and the other was done by PSA method, that was to measure mean diameter of the particles(CMKF-2) by PSA, of

which weight was known. As presented in Table 2, both of the particles indicate almost the same and enough high density.

Ceramography was made on both of the particles to determine the grain size of the particles. The particles were sectioned and polished to the equator, then followed by etching in a solution of H_2O_2- H_2SO_4 . Cross sections of the particles are exhibited in Photo. 4, where grains of CMKF-1 are obviously larger than that of CMKF-2.

Crushing strength of the particles was measured on CMKF-1, which ranged between 0.8 to 2.6 kg depending on diameter of the particles as shown in Fig. 4.

5. Conclusion

The internal gelation process was examined to fabricate UO_2 particles, which were characterized in diameter, sphericity, SEM observation, density, grain size and crushing strength. Mean diameter of UO_2 particles would be proportional to the size of the nozzle. Sphericity and surface condition of the resulted particles are relatively good, comparing to the particles fabricated in SNAM method. It was confirmed that the internal gelation process could give enough high density and large strength of the UO_2 particles, of which the latter is dependent on its diameter.

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Table 1 Some technological parameters for producing kernels

Run NO.	Uranium conc. (mol/ℓ)	NO_3/U	HMTA,Urea/U	Needle size (outer diameter) (mm)	Pressure (MPa)	Drying temp. (^oC)	Reduction and sintering temp. (^oC)	Reduction and sintering atmosphere
CMKF-1	2.3	1.4	1.4	0.6	0.2	60-70	1350	8%H_2-Ar
CMKF-2	2.3	1.4	1.4	1.2	0.1	60-70	1350	8%H_2-Ar

Table 2 Performances of UO_2 kernels*

Run No.	Diameter (by PSA)			Sphericity (by PSA)	Density	Grain size	Crushing strength
	Mean value (μm)	Standard deviation (μm)	Variation (%)		(%T.D.)	(μm)	(kg)
CMKF-1	385	49.4	12.8	1.026	96 (replacement)	3.4	0.8-2.6
CMKF-2	734	77.4	10.6	-	96.7 (PSA)	4.4	-

* Natural dispersion, unclassified kernels

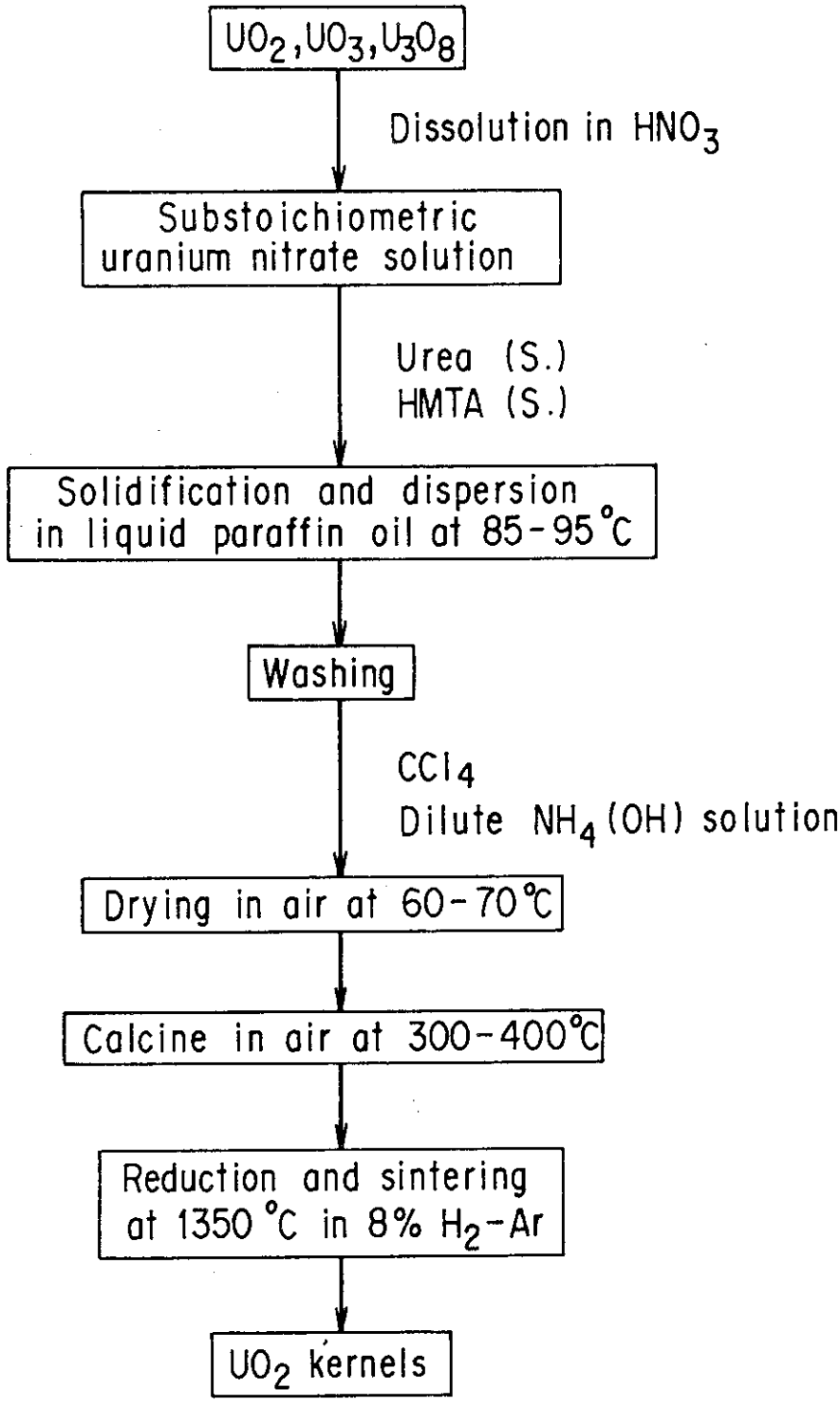
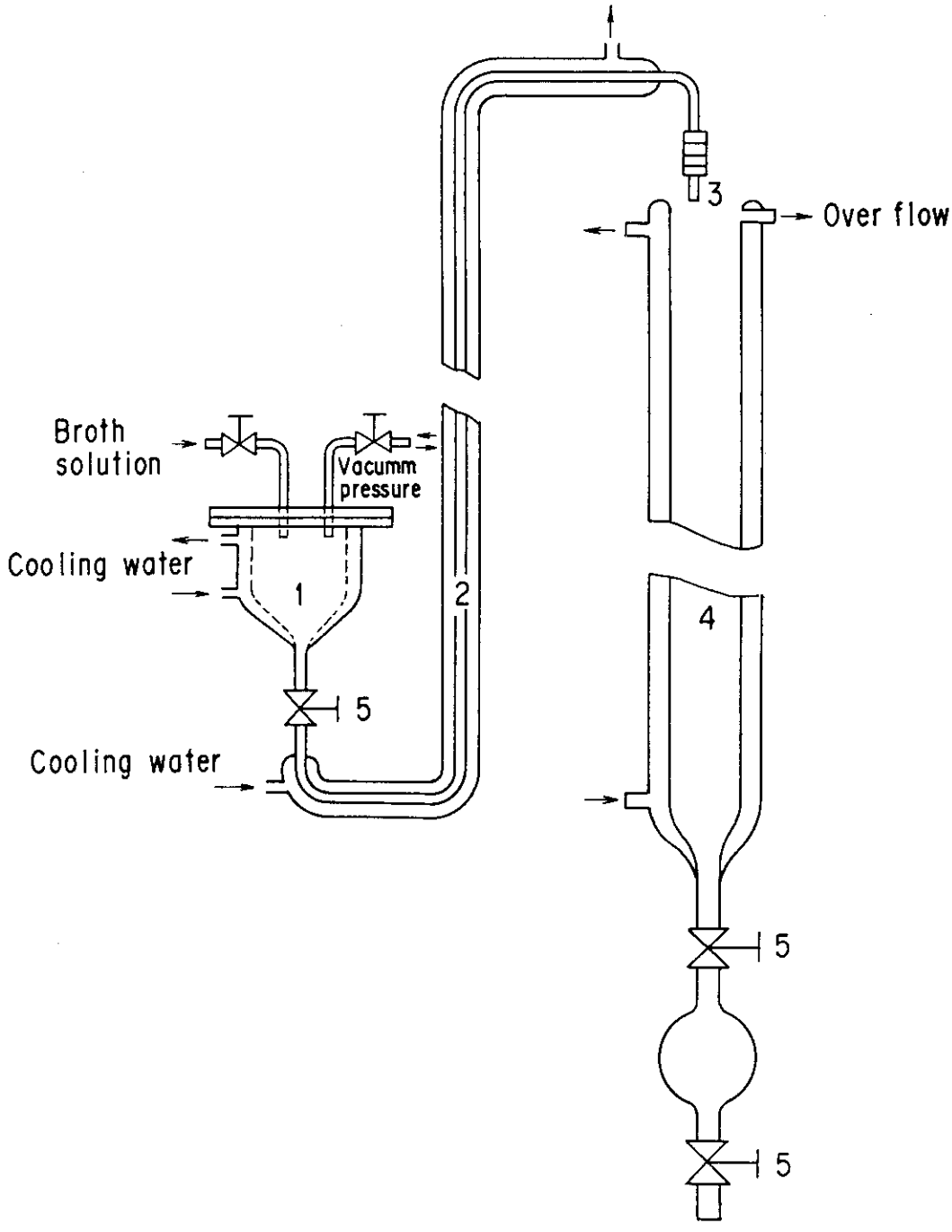


Fig. 1 Flow scheme of the present process.



1. Storage tank
2. Broth solution transport tube
3. Capillary or needle
4. Gelation column
5. Valve

Fig. 2 Apparatus used for the gelation.

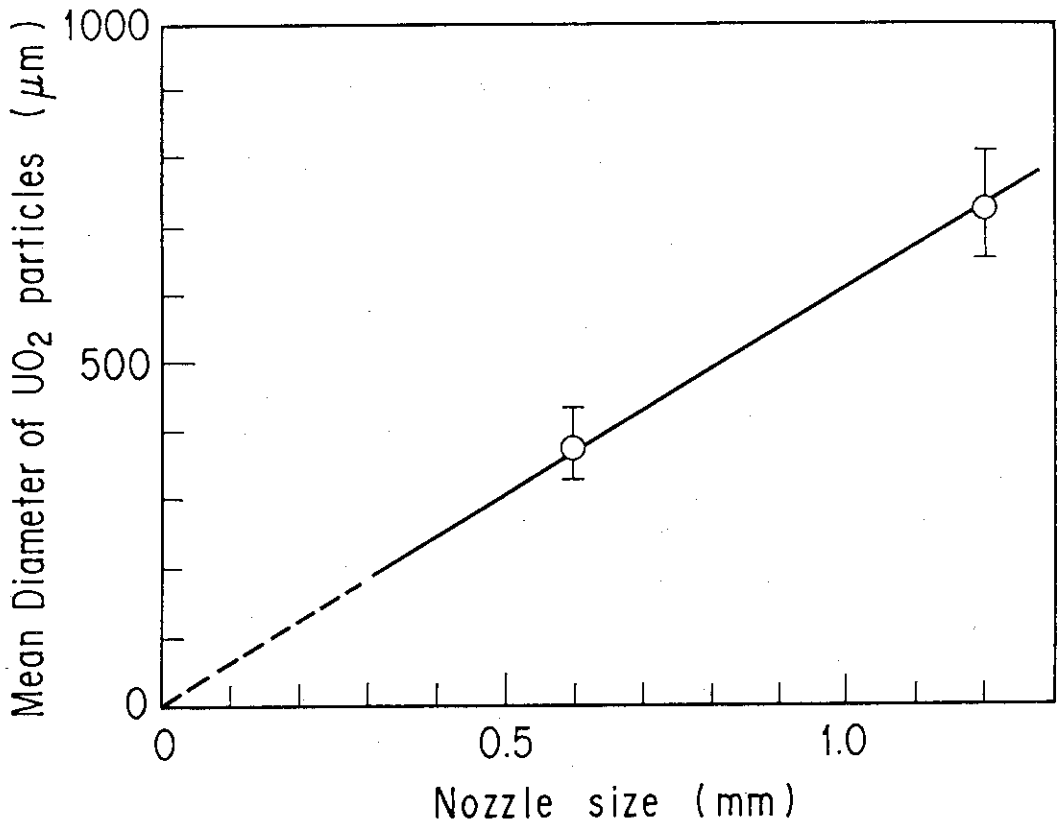


Fig. 3 Relation between mean diameter of UO_2 particles and nozzle size.

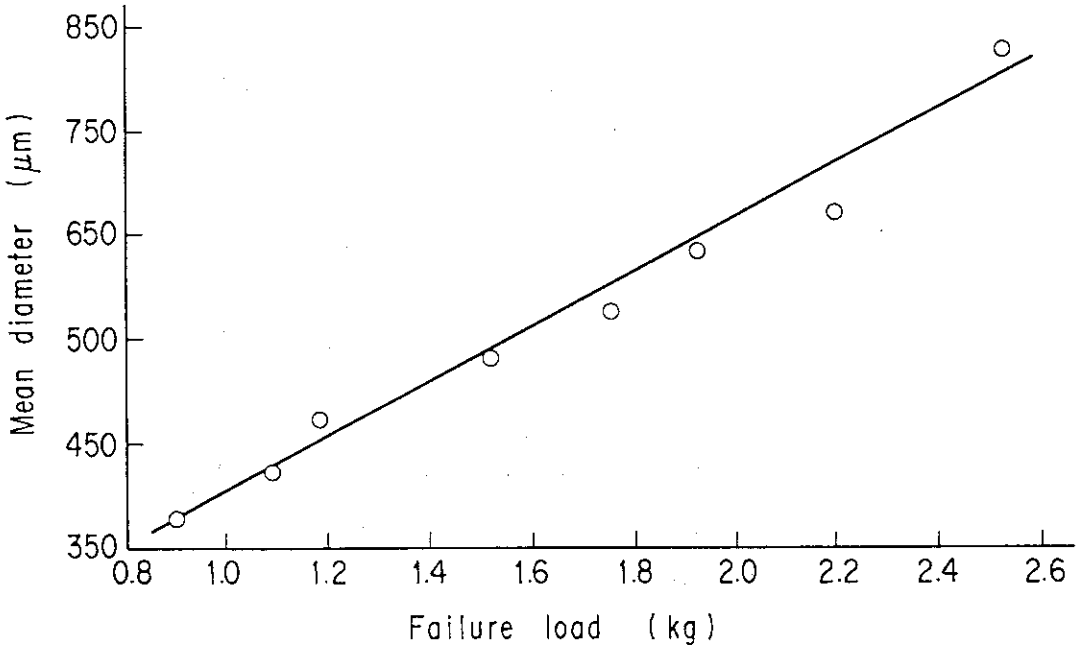


Fig. 4 Relation between mean diameter and failure load of UO_2 particles.

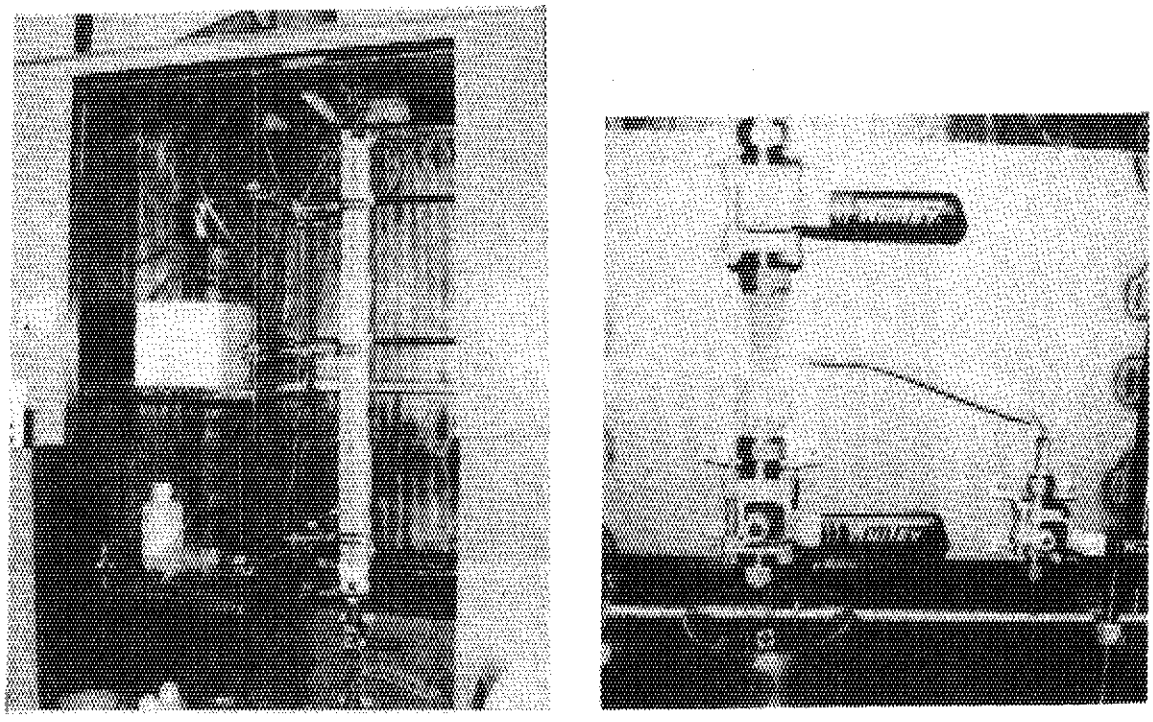


Photo. 1 Appearance of the gelation column (left)
and the bottom view of the column (right).

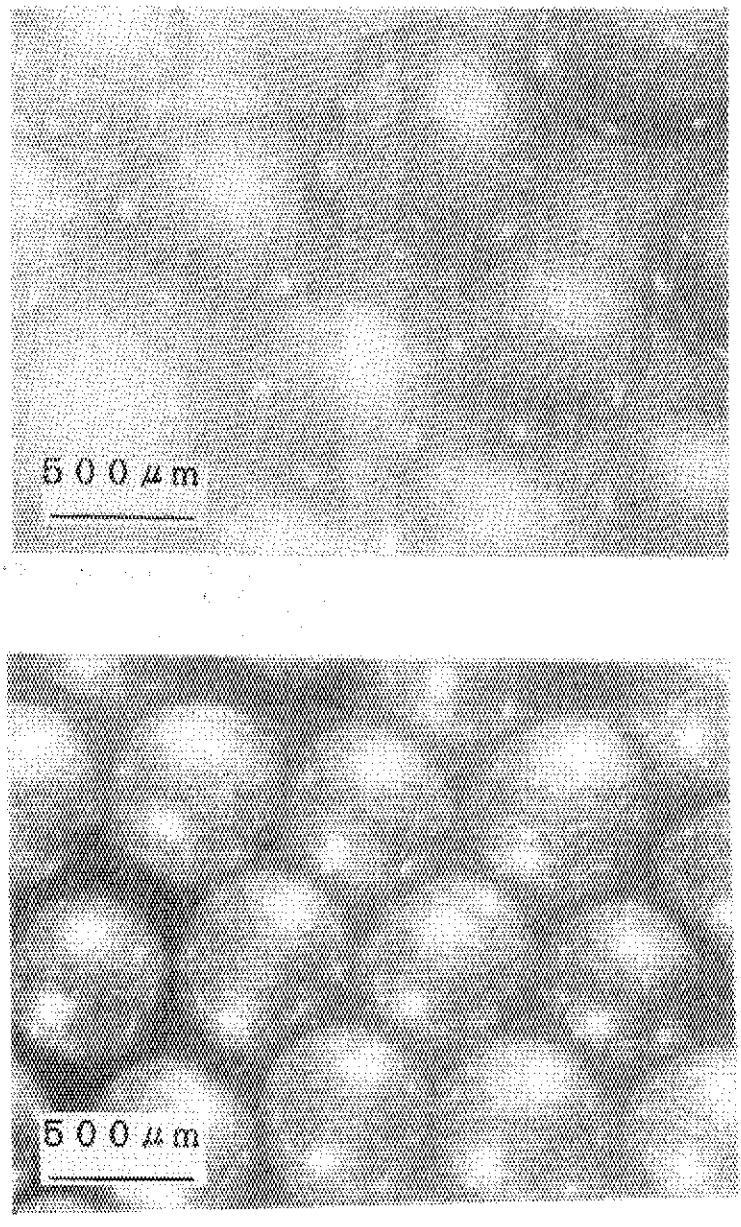
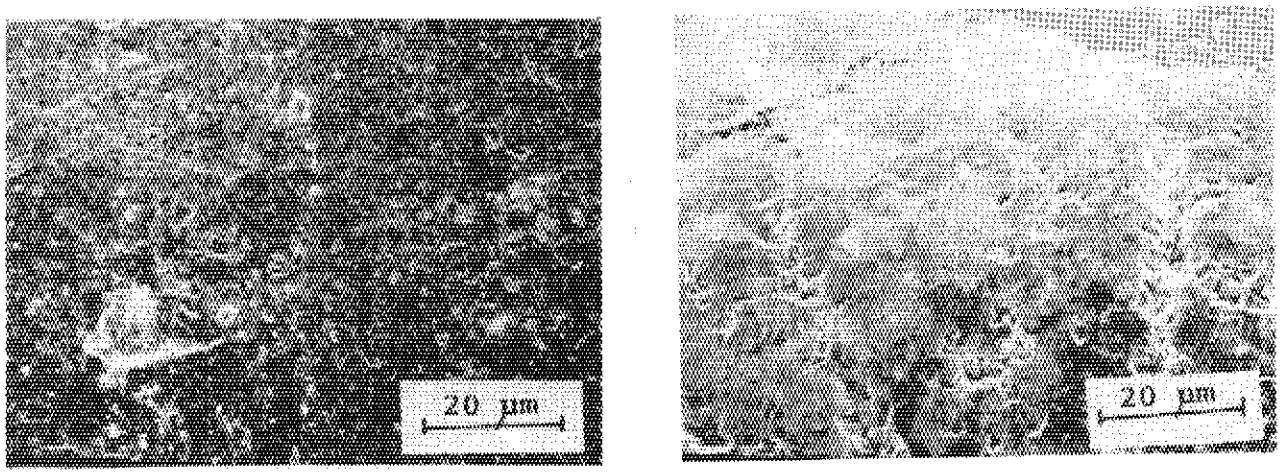
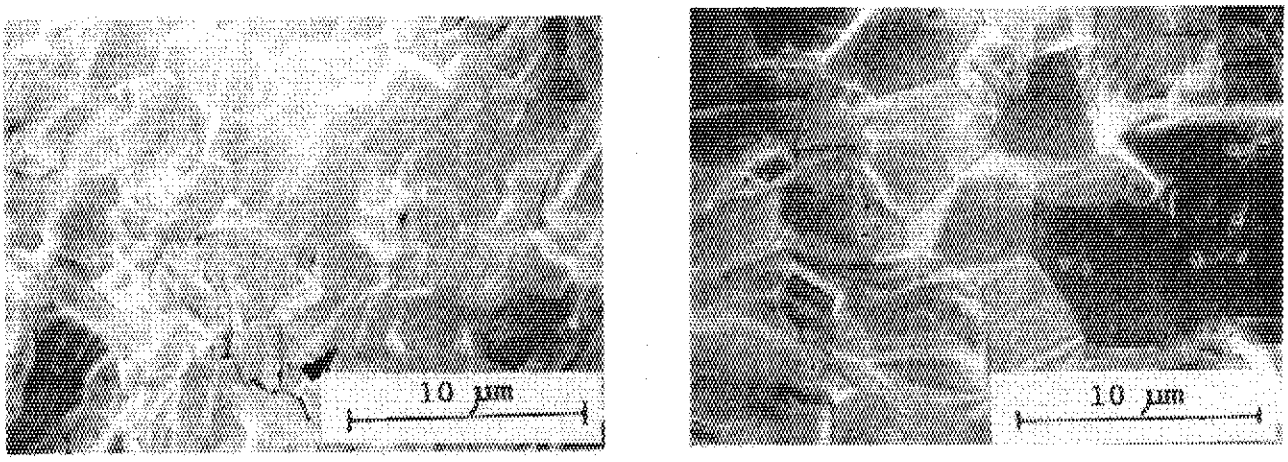


Photo. 2 Appearance of UO_2 particles fabricated by the present process (upper) and SNAM process (lower).



View of the particle surface(left: the present process, right: SNAM process).



Fractographs (left: present process, right: SNAM process)

Photo. 3 Appearance of the particle surface and the fracture surface observed by SEM.

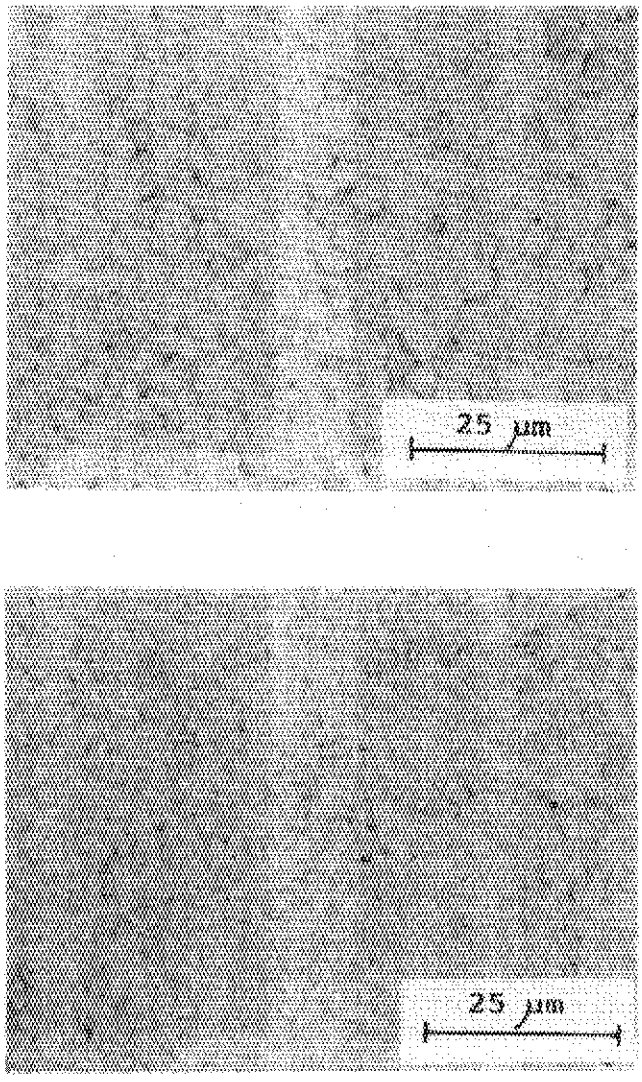


Photo. 4 Ceramographs of sectioned UO_2 particles fabricated by the present process. (upper: CMKF-1, lower: CMKF-2, refer to Tables 1 and 2.)