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Fabrication of Carbon-dispersed UO_3 Microspheres by an Internal Gelation

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Abstract

An internal gelation process was adopted for the fabrication of carbon-dispersed UO_3 microspheres which will be fed to the fabrication for uranium nitride microsphere fuels by the carbothermic reduction. For investigating the proper process conditions, a composition range of feed solution for preparing good UO_3 gel spheres was firstly defined by observing the gelation behavior. Within the defined solution compositions, carbon-dispersed microspheres were prepared and carbon distribution in microspheres were observed by SEM. The results showed that production of good carbon-dispersed microspheres was possible, and the most of carbon were evenly distributed in the microspheres although large carbon-rich aggregates were sparsely existent.

1. Introduction

Such MX-type(M=U, Pu; X=C, N) fuels as carbide and nitride are

considered as advanced nuclear fuels for liquid metal reactors[1-2] due to their higher breeding ratio and shorter doubling time compared with the oxide fuel. Nitride fuel is particularly more attractive because of its compatibility with the existing reprocessing techniques; besides, its fabrication can take place in existing oxide fuel facilities. Presently, the fabrication of nitride fuel pellets is mainly based on the carbothermic reduction of the oxide powder in nitrogen, and the conventional powder-pellet route[3]. As an alternative method, the sol-gel process has been studied[4]. By this method the process can be simplified and the radioactive dust problem can be avoided. It also readily gives a homogeneous mixed nitride and allows remotely controlled operations. For the homogeneous nitride fuel, the internal gelation process is adopted for the preparation of microspheres[5]. In this process homogeneous gelation can be achieved by the internal supply of ammonia from the thermal decomposition of premixed hexamethylenetetramine. This homogeneity may be an important advantage for the gelation of carbon-dispersed microsphers.

The purpose of this study is to investigate the proper conditions in the internal gelation process for preparing homogeneously carbon-dispersed UO_3 microspheres which is required for the fabrication of good-quality nitride microspheres.

2. Experimental

2.1 Observation of gelation behavior

An acid-deficient uranyl nitrate solution (ADUN; uranium concentration 3.0 mol/l, and nitrate/uranium mole ratio 1.55) was prepared by dissolving U_3O_8 powders in nitric acid. A solution of 3 mol/l hexamethylenetetramine(HMTA) and 3 mol/l urea as a gelation agent was prepared by dissolving solid HMTA in a urea solution. Both of the ADUN and (HMTA+urea) solutions were cooled to 0℃ and then mixed to various uranium concentrations and (HMTA,

urea)/uranium mole ratios. One drop (~0.01 ml) of the feed solution was charged into a polyethylene minivial and soon the minivial was dipped in the hot water bath heated to 90℃ for 3 min to obtain gel. After cooling and then drying in the ambient atmosphere without washing, the appearance of the gel in the minivial was visually inspected.

2.2 Preparation of carbon-dispersed microspheres

The carbon-dispersed feed solution having a carbon/uranium mole ratio of 2.5 was prepared by mixing carbon black powder "N326" in the ADUN solution and dispersing them with an ultrasonic vibrator. The "N326" carbon black has the average particle size of 28 nm and the specific surface area of 84 m^2/g[6].

Gelation was carried out in the column tube of silicone oil which was heated to 90℃ with hot water circulating in the outer tube. About 1 ml of the feed solution was dropped into the hot silicone oil with a syringe having a nozzle size of 0.3 mm I.D × 0.7 mm O.D.

Gel microspheres were washed with carbon tetrachloride (CCl_4) and aged in a 3 mol/l NH_4OH solution for 20 h. Thereafter they were washed with flowing 0.05 mol/l NH_4OH solution at a rate about 35 ml/h for 7 h. The washed gel microspheres were dried in the room atmosphere for 1 day. The dried microspheres were calcined at 500℃ for 1 h in Ar atmosphere.

In order to investigate the carbon distribution in UO_3 matrix, a scanning electron microscope (SEM, JEOL JSM-5300) was used for the observation of the fractured surfaces of the calcined microspheres.

3. Results and discussion

3.1 Gelation behavior

Proper compositions for gelation were investigated by using carbon-free feed

solutions. Three types of gel formation behavior were observed. At high uranium concentrations and low(HMTA, urea)/uranium mole ratios, the dried gel was cracked and fractured. The feed compositions with low uranium concentrations and high (HMTA, urea)/uranium mole ratios gave a crack-free gel having a smooth surface. In the present experiment good quality gel was obtained within the compositions ranging from 0.7 to 1.1 mol-U/l. Similar gelation behavior of uranyl nitrate solutions was observed by Vaidya et. al.[7] although the evaluation method was different from ours. They recommended the feed compositions ranging within the shaded area in Fig. 1 for an actual microsphere gelation using a hot silicone oil column.

3.2 Gelation of carbon-dispersed microspheres

A series of experiments for preparing carbon-dispersed microspheres were conducted within the defined range in the section 3.1. Smooth gel microspheres could be obtained, though clogging of the nozzle occurred at the highest uranium concentration of 1.3 mol/l. Photo. 1 shows carbon-dispersed microspheres calcined at 500℃ in Ar atmosphere for 1 h. The feed solutions of 1.05 and 0.7 mol-U/l yielded microspheres with a good sphericity and smooth surface, but fine cracks were occasionally observed. Microspheres prepared from the 1.3 mol-U/l solution cracked.

3.3 Distribution of carbon in microspheres

Photo. 2 shows fractured surfaces of carbon-dispersed microspheres calcined at 500℃ in Ar atmosphere. There was no difference in appearance among the different feed compositions. Black coarse(max. 30 μm) inclusions were distributed in all the cases. They were confirmed to be carbon-rich aggregates. It is desirable that the size of dispersed carbon aggregates is as small as possible. However, it may be considered that homogeneous distribution of carbon particles of a few μm or smaller will be sufficient for the carbothermic

reduction of (UO_3+C) into UN. Therefore, if the large aggregates were eliminated, the present distribution of carbon would be accepted.

4. Conclusion

For investigating the proper process conditions for homogeneous carbon dispersion in UO_3 microspheres, a composition range of feed solution for obtaining good UO_3 gel was defined. And carbon-dispersed microspheres were prepared in the defined range and analyzed for the appearance and the distribution of carbon in microspheres.

(1) The proper compositions for carbon-free UO_3 gel formation were defined as a range from 0.7 to 1.1 mol/l of uranium.

(2) Carbon-dispersed microspheres with C/U ratio of 2.5 were successfully prepared by the internal gelation process.

(3) Although large carbon-rich aggregates distributed sparsely on the fractured surface, the carbon distribution in the microspheres was generally uniform.

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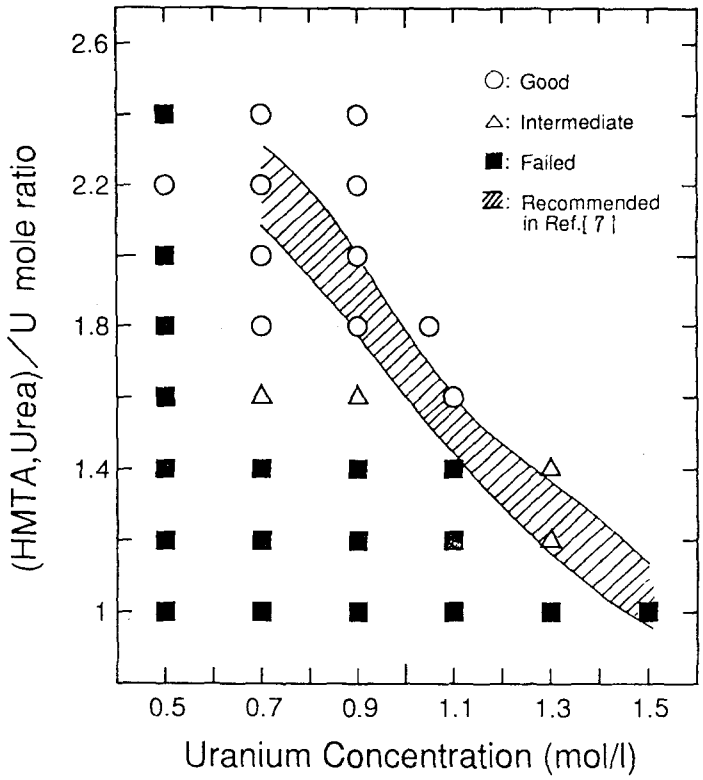

Fig. 1 Gelation field diagram ; the shaded area is a range of optimum compositions observed by V.N.Vaidya et. al.

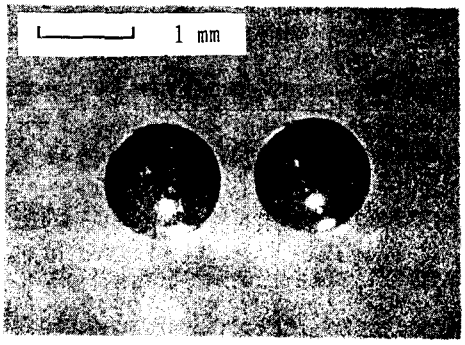

Photo. 1 Appearance of calcined microspheres.

Photo. 2 SEM micrographs of calcined microspheres.