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Preparing UO_2 kernels by gelcasting

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Abstract A process named gel-casting has been developed for the production of dense UO_2 kernels for the high-temperature gas-cooled reactor. Compared with the sol-gel process, the green microspheres can be got by dispersing the U_3O_8 slurry in gelcasting process, which means that gelcasting is a more facilitative process with less waste in fabricating UO_2 kernels. The UO_2 kernels with the size of 500 μm, O/U≤2.01, density of 10.70 g·cm^{-3} were obtained by gel-casting process followed by heat treatment.

Key words HTR, UO_2 kernel, Gel-casting

1 Introduction

TRISO (Tri-isotropic)-coated fuel particle is widely utilized in the high temperature gas-cooled reactor (HTR). Typically, such a fuel particle is about 1 mm in diameter, with a UO_2 kernel and coating layers. Developed around 1970[1], sol-gel processes for the production of dense UO_2 kernels for HTR are based on dropping $UO_2(NO_3)_2$ solutions to precipitate UO_2^{2+} with NH_3 to produce gelled microspheres:

$$UO_2^{2+} + 2NH_4OH \rightarrow UO_3{\cdot}xH_2O{\cdot}yNH_3 + 2NH^{4+} \quad (1)$$

The reaction can be external gelation (EGU)[2] or internal gelation (IGU), as shown in Fig.1. A process known as total gelation process of uranium (TGU) was developed and chosen for the HTR-10 in China The chemical process in the TGU includes preparation of the dropping solution, dropping and gelation, washing and aging[3].

These sol-gel processes, however, share the following drawbacks: (a) the uranyl nitrate solution is prepared by dissolving nuclear grade U_3O_8 in heated nitric acid, a step producing nocuous gas NO_x; (b) a great deal of complexing agents (such as urea), and the thickener (such as polyvinyl alcohol), is added into the solution for generating homogenized uranium sol and gel, giving rise to difficulties in treatment of waste water containing the organic additives; (c) the organic additives make it difficult to control the washing and calcining steps on binder removal; and (d) large amount of waste water is produced during the steps of aging and washing.

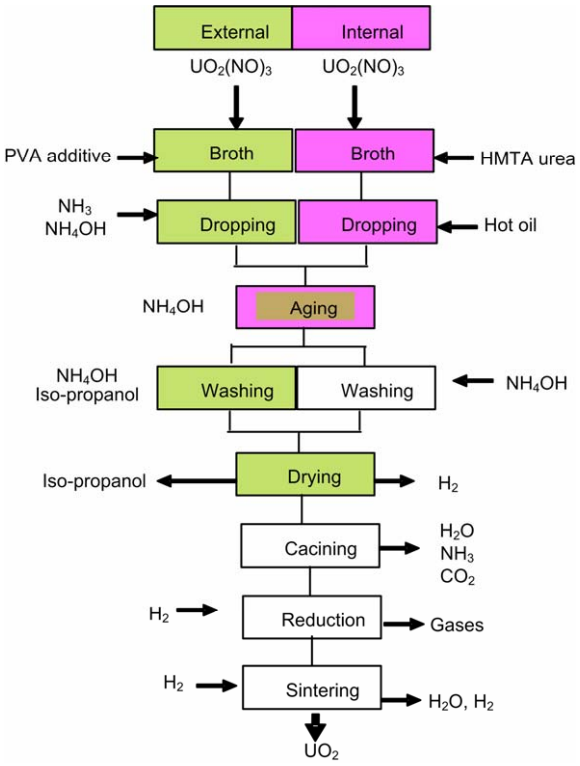

Fig.1 Flow diagram for internal and external gelation.

Gelcasting is a near-net-shape ceramic forming-technique to make high-quality complex-shaped ceramic parts. Developed by Oak Ridge National

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Laboratory for fabrication of dense ceramics[4], it combines aqueous slurry of ceramic powder and organic monomers for *in situ* polymerization of the slurry. As a low-cost high-reliability ceramic forming process, gelcasting can produce near-net-shaped ceramics. When the slurry drops are dispersed into a hot organic liquid, they become tiny spheres under the surface tension, and organic monomers in the slurry are polymerized at high temperatures to form green tiny spheres. ZrO_2 ceramic microspheres have been prepared by this gelcasting process[5].

In this paper, we report a new method for the gelcasting fabrication of UO_2 kernels. It is relatively simple, with fewer process steps and less wastes, and is suitable for automated manufacturing.

2 Chemical process development

Fig.2 shows a flowchart of the gelcasting process to make UO_2 kernels. Unlike the conventional slurry system added with catalyst, the catalyst *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TEMED) is added into the dispersing medium of hot organic liquid, where the gelation takes place and the slurry drops become green tiny spheres. This revised process is advantageous in that the slurry can be kept for much longer time and temperature of the dispersing medium can be decreased from 90℃ to 50℃.

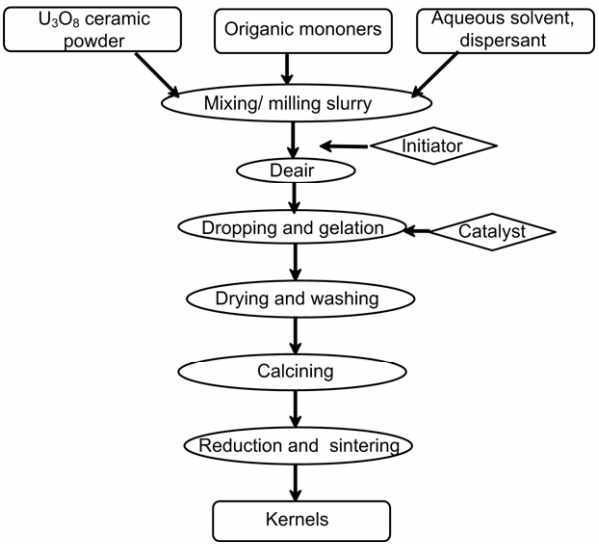

Fig.2 Flowchart of the gelcasting process fabricating UO_2 kernel.

2.1 Premix solution

The premix solution, in which the U_3O_8 ceramic powders are suspended, is the solution of acrylamide (AM) monomers with the crosslinker of N-N'-methylenebisacrylamide (MBAM). A typical premix solution contains monomers in 5–20 wt% in water, with the mass ratio of AM/MBAM ranging from 10:1 to 30:l. PAA-NH_4 is used as dispersant with the mass ratio to U_3O_8 powder being 0.2%–2%, achieved mixing the polyacrylic acid and ammonia. In a typical 50 vol% suspension of U_3O_8 ceramic powder, after drying, the polymer is less than 4 wt% of the green body.

2.2 Preparation of the dropping slurry

U_3O_8 slurry was prepared by mixing the powder in the premix solution at pH 10.5 (using ammonia) and ball-milling for about 3 h to give a well-dispersed homogeneous suspension.

The slurry was firstly degassed for 10 min and mixed with initiator. The initial is ammonium persulfate ($(NH_4)_2S_2O_3$), which contains 50 vol% ceramic suspension of 0.005–0.05 wt%.

2.3 Dropping and gelation

Dispersion of the solution into droplets was performed in air. And then the droplets entered dimethyl silicone oil at 50℃. While gelating and polymerizing *in situ*, green tiny U_3O_8 spheres formed. A typical drop formation and precipitation device in slurry processes with gelcasting is shown in Fig.3.

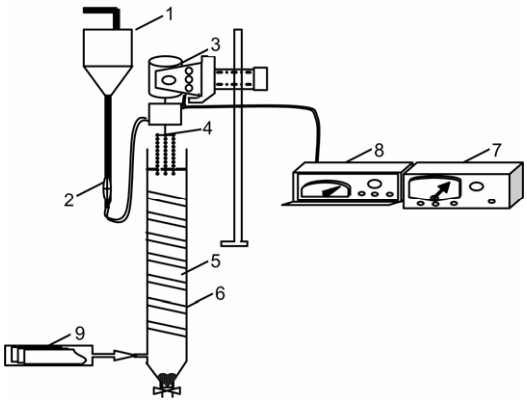

Fig.3 Laboratory-scale gelcasting apparatus arrangement for fabricating UO_2 kernel.
1, slurry storage 2, flowmeter 3, casting-dosing arrangement
4, nozzles 5, casting column 6, heat source
7, signal generator 8, power magnifier 9, air compressor

2.4 Washing and drying

The liquid desiccant drying method was used in drying gelcasting U_3O_8 ceramic spheres. The wet green spheres were immersed in an aqueous solution of PEG1000 with the containment of 60 wt% as liquid desiccant solution. After 24 h, the samples were removed from the container and washed with deionized water.

2.5 Binder burnout, reduction and sintering

After drying, the binder left in the green spheres was typically less than 4 wt%. The investigation of the binder burnout in air using thermo gravimetric and differential thermal analyses (TGA/DTA, Fig.4) showed that all the binders removed off primarily as complete combustion products, CO_2 and H_2O. The pyrolysis of the polymer in green spheres was complete at about 600℃.

The H_2-TPR (temperature programmed reduction) curves is shown in Fig.5. The H_2-TPR experiments were performed using samples of 50 mg of U_3O_8 powder (dry base), heated from room temperature to 1000ºC at 10℃/min, under a mixture of H_2/Ar (10%) with a flow rate of 50 mL/min. Hydrogen consumption was measured with a TCD (thermal conductivity detector). The reduction mainly took place at 600–1000℃.

The calcined U_3O_8 kernels were filled into the trays in portions. And then fed to the furnace and sintered at 1500℃ for 4 h in a flow of H_2/Ar (10%), according to the temperature program.

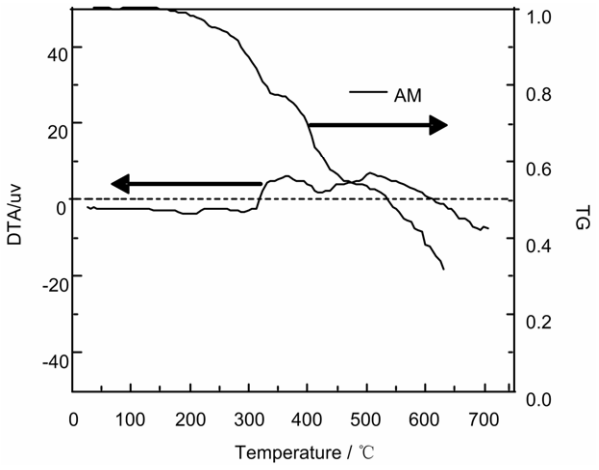

Fig.4 DTA and TG curves of AM gel.

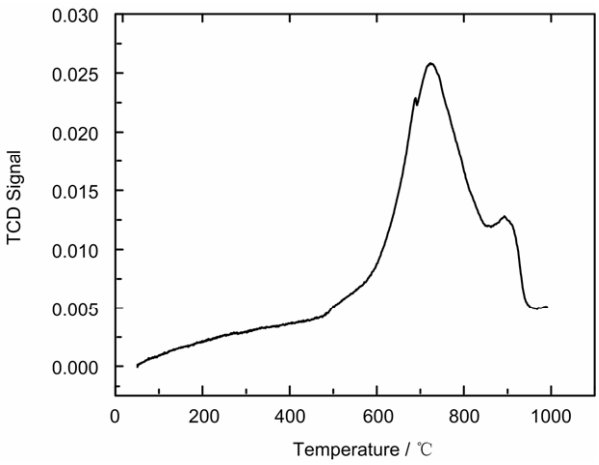

Fig.5 TPR curves of U_3O_8 spheres.

3 Results and discussion

3.1 Main characteristics of the sol-gel processes and gelcasting

3.1.1 HOBEG process

The EGU process of HOBEG has been used to manufacture UO_2 kernels by several groups[1,2]. The main chemic reactions of U in the process include:

U_3O_8 powder is dissolved in nitric acid to form a uranyl nitrate solution according to the simplified chemical reaction:

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

The uranyl nitrate solution is pre-neutralized with ammonium hydroxide to just prior to precipitation according to the following reaction:

$$2UO_2(NO_3)_2(aq)+NH_4OH(aq) \rightarrow 2UO_2(NO_3)_{1.5}(OH)_{0.5}(aq)+NH_4NO_3(aq)$$

As the reaction continues in the casting column ammonium diuranate forms inside the microspheres, with ammonium nitrate as by product:

$$2UO_2(NO_3)_{1.5}(OH)_{0.5}(aq)+2NH_4OH(aq) \rightarrow NH_4)_2U_2O_7(s) + NH_4NO_3(aq) + H_2O$$

The remaining organic additives are cracked and driven off during a gradual temperature increase. Above 400°C the ammonium diuranate is converted to UO_3:

$$(NH_4)_2U_2O_7(s)+O_2(g)\rightarrow 2UO_3(s)+2H_2O(g)+NO(g)$$

The reducing process is carried out under hydrogen atmosphere to reduce the UO_3 to UO_2:

$$UO_3(s)+H_2(g)\rightarrow UO_2(s)+H_2O(g)$$

It can be seeen that the chemic reactions in HOBEG process are complicated, and it is difficult to actualize the process. The dispersing medium, ammonia, bacomes attenuated with the gelation reaction going on. And some waste such as organic materials like urea and PVA and the by-product of gelation, NH_4NO_3 released into the ammonia, all of which ended with vast of waste water.

The U is precipited in the form of $(NH_4)_2U_2O_7$ gel. This means that fine crystal of original UO_2 and dense kernels with the density of 10.77 g/cm^3 can be obtained after sintered at a rather low temperature of 1500℃.

3.1.2 Process for HTR-10

We used the total gelation process of uranium (TGU) of HTR-10, a modified EGU process that is similar to HOBEG process. The mainly difference is that the urea serves as complexing agents reacted with uranyl nitrate in TGU, which increased the U consistency of the solution. Another difference is that hemxamethyl tetra-amine (HMTA) is used to release NH3 during the aging step, which accelerates the gelation reaction inside the spheres and the cracks are decreased.

3.1.3 Gelcasting

In gelcasting, a high solid loading ceramic slurry obtained by dispersing the powders in a pre-mixed monomer solution was cast in a mould of the desired shape. By adding an initiator the system polymerized *in situ* and green bodies of excellent mechanical property but with only a few percents of polymer could be obtained.

The valence of the raw material, U_3O_8 powder, did not change during the gelcasting process of preparing the slurry, dropping, drying and calcining. The only reaction during the reduction step is:

$$U_3O_8(s) + 8H_2(g)\rightarrow 3UO_2(s) +8H_2O(g)$$

The tendency of cracks generating decreased greatly during the drying and calcining steps because of the fewer reactions and organic aditives.

Another advantage is that after the slurry is dropped into silicone oil, the system polymerizes *in situ*, which means that little organic materials can enter the dispersing medium. Thus, the silicone oil can be reused for many times, and the waste liquid is reduced.

3.2 Controlling of the diameter of UO_2 kernels in gelcasting process

The U content of the microsphere is not changed no matter it was in U_3O_8 slurry or in UO_2 kernel. So the diameter of the final UO_2 kernels can be controlled by stabilizing the U content in gelcasting process.

Supposing radius of the final UO_2 kernels is r, the density of the UO_2 kernels is ρ, and the volume content of the slurry is V, the density of U_3O_8 powder is ρ_p, the flow amount of the slurry is L and the frequency of the vibration is f, the following equations can be got. As the mass of the U_3O_8 powder is $x=\rho_p V/(1-V+\rho_p V)$, and the dispersion relation can be described as $f(4\pi r^3\cdot\rho) = L\cdot x$, one has the frequency of the vibration

$$f=3\rho_p L /[4\pi r^3\rho(1-V+\rho_p V)].$$

For ρ, V and ρ_p are known, if the frequency of the vibration f is fixed, the UO_2 kernels with designed diameter ($2r$), could be produced by controlling the L or the f.

In the latest experiment, the diameter of the sintered UO_2 kernels was 509±13 μm, which is well satisfied with the design request of the HTR-PM (500±50 μm).

3.3 Properties of UO_2 prepared by gelcasting

Table 1 shows the properties of UO_2 kernels prepared by gelcasting and TGU, both of which were sintered at 1500℃ for 4 h. The result shows that the density of UO_2 kernels prepared by gelcasting is 10.70 g·cm^{-3}, which is less than that of TGU appreciably (10.77 g·cm^{-3}). The density could be increased when the granularity of U_3O_8 is reduced or the sintering temperature is increased. Fig.6 is the photograph of sintered UO_2 kernel by gelcasting.

Table 1 Characters of UO_2 kernel

	Density / g·cm^{-3}	Diameter / μm	O/U ratio
Sol－gel(TGU)	10.77	501	2.01
Gel－casting	10.70	509	2.01

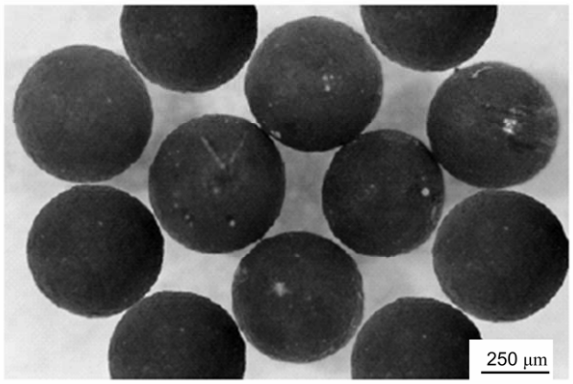

Fig.6 Photograph of sintered UO_2 kernel by gelcasting.

4 Conclusions

The feasible experiment in our laboratory indicated that properties of UO_2 kernels prepared by gelcasting could match the designed standard of HTR fairly well. Compared with sol-gel processes, gelcasting process is simpler, with few process steps and little waste material being produced. The diameter of UO_2 kernels can be controlled by the frequency of the vibration and the flow amount during dispersion step of gelcasting process. The average diameter of UO_2 kernels is 509 μm, and the density is 10.70 $g \cdot cm^{-3}$. The density could be increased when the granularity of U_3O_8 is reduced or the sintering temperature is increased.

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