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THERMAL AND X-RAY ANALYSIS STUDIES OF UO_3 GEL MICROSPHERES

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The thermal decomposition behaviour of UO_3 gel microspheres has been studied. Thermal analysis involved DTA, TG, DTG and X-ray examination.

The effects of washing the UO_3 gel microspheres with hot water and with ammonia solution were investigated, as were the effects of soaking the microspheres in ammonia solution before or after washing on the crystallite size.

The results indicate that the thermal decomposition of UO_3 gel microspheres includes five steps: the first two for dehydration, the third for ammonia removal, the fourth for ammonia oxidation and the last step for UO_3 recrystallization.

This paper describes a study of the thermal analysis and X-ray diffraction of UO_3 gel microspheres prepared by hydrolysis [1]. Hydrolysis is one of several sol-gel processes [2–4] which have been developed for the fabrication of UO_3 microspheres can be used as fuel kernels in coated particle fuel for high-temperature gas cooled reactors. For the application of UO_3 microspheres in light water and fast breeder reactor fuel elements, two different fuel forms are being considered. Sphere-pack fuel rods are formed by the vibrocompactions of microspheres and pelletizing of the microspheres.

Hydrolysis is a very simple process based on the rapid solidification of droplets from a fairly concentrated uranyl nitrate solution (about 1.4 *M*) containing urea and hexamethylenetetramine at temperatures of about 90° in silicone oil. The resulting microspheres are deep-orange and fully transparent. After washing in CCl_4 to remove silicone oil, the kernels are either washed with hot water for 10 min at 95° or with 3% ammonia solution for 2 hours at 25°. Hot water-washed microspheres are opaque and yellow, while ammonia-washed microspheres are transparent and orange.

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For a more detailed study of the solidification process, the influence of the soaking time of the microspheres in ammonia solution before or after the washing step has been investigated by thermal analysis and X-ray diffraction.

Experimental

Materials

The UO_3 gel microspheres were prepared by the hydrolysis process and soaked in 3% ammonia solution for 6, 12 or 24 hours before or after washing.

Equipment and procedure

The experiments in this work were mainly carried out on a Shimadzu thermal analyser (type DT–30) in air, in the temperature range 25–500°. The heating rate was 10 deg/min.

X-ray investigation of the gelled UO_3 microspheres was performed with a Philips diffractometer (type 1140). The patterns were run with Cu as target and Ni as filter (λ = 1.54178 Å), at 40 KV and 30 mA, with a scanning speed of 2 deg/min.

The mean crystallite size was determined from X-ray diffraction broadening using the Scherrer equation $D = K\lambda/\beta \cos\theta$ [5], where K is a constant approximating to unity, related both to the crystallite shape and to the way in which β and D are defined. β is the width of a powder reflection free from all broadening due to the experimental method employed in observing it. Most investigators define β as the angular width at half maximum intensity. Bragg gave a simplified derivation for the Scherrer equation and found that $K = 0.89$.

In this work, the pure diffraction width β was obtained from the experimentally observed breadth B of a diffraction line by subtracting from it the breadth b of a line produced under similar conditions with a crystallite size of about 1000 Å.

Results and discussion

Figure 1 shows the DTA curves for microspheres soaked for 6 or 24 hours before or after washing. These curves reveal a series of endothermic and exothermic effects. The endothermic effect appears in two steps; the first step, at about 150°, is characteristic of the removal of adsorbed water, and the second step, at 200°, is characteristic of the partial removal of constitution water. On the other hand, the exothermic effect appears in three steps. The first step, at $220 \pm 5°$, is characteristic of the removal of incorporated ammonia. The second step, at $280 \pm 7°$, is

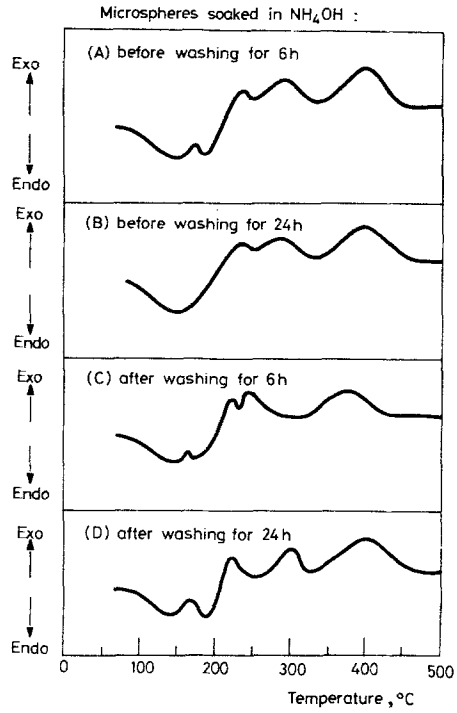

Fig. 1 Differential thermal analysis of UO_3 microspheres soaked in ammonia solution before and after washing. *A:* Microspheres soaked in NH_4OH before washing for 6 h. *B:* Microspheres soaked in NH_4OH before washing for 24 h. *C:* Microspheres soaked in NH_4OH after washing for 6 h. *D:* Microspheres soaked in NH_4OH after washing for 24 h

characteristic of ammonia oxidation by oxygen present in the furnace atmosphere. The third step, at $395 \pm 5°$, is attributed to UO_3 recrystallization due to slow dehydration. These results are in good agreement with those of Spacu et al. [6] and Turcanu et al. [7]. According to Haas et al. [8] and Förtmann [9], UO_3 gel microspheres have compositions of the form $UO_3 \cdot xNH_3 \cdot yH_2O$, where the values of x and y depend on the preparation conditions. The interpretation of the TG curves leads to a suggested formula, $UO_3 \cdot 1.73NH_3 \cdot 0.8H_2O$ for the microspheres soaked before washing, and $UO_3 \cdot 2.33NH_3 \cdot 1.66H_2O$ for the microspheres soaked after washing.

It is seen from DTA curves *A* and *B* that the retained water is released in two steps and in one step in the case of soaking for 6 and 24 hours, respectively, before washing. The peaks are maximized at temperatures higher than 100°, which indicates that the retained water is in the form of crystalline water. It is also observed that increase of the soaking time has no effect on the exothermic decomposition. DTA curves *C* and *D* show that the retained water is released in two

stages and that the peaks are maximized at temperatures higher than 100°, which indicates that the incorporated water is in the form of crystalline water. It is also observed that the ammonia incorporated when the microspheres are soaked after washing is released at lower temperatures than that incorporated when the microspheres are soaked before washing.

Figure 2 shows the effect of the soaking time before or after washing on the retained ammonia. It is seen that soaking the microspheres for up to 12 hours has no effect on the ammonia content in either case. Increase of the soaking time from 12 to 24 hours results in a decrease of the ammonia content from 1.75 mole to 1.1 mole for soaking before washing, and its increase from 2.5 mole to 2.9 mole for soaking after washing.

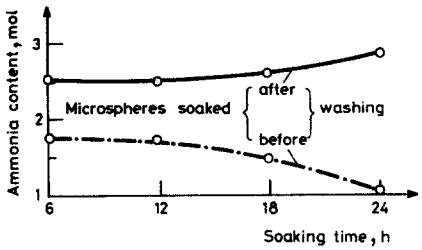

Fig. 2 Effect of soaking time in ammonia solution on ammonia content. —— Microspheres soaked after washing. ——Microspheres soaked before washing

It was found that soaking of UO_3 gel microspheres for 12 hours in ammonia solution before washing results in a crystallite size of 85 Å, while soaking after washing leads to crystal growth, up to a size of 155 Å. This can be due to the fixation of nitrate ions through their reaction with ammonia solution during the soaking process. As the soaking solution is unchanged and unstirred, the concentration of NO_3^- reaches equilibrium with the ammonia solution surrounding the microspheres. Accordingly, the concentration of NO_3^- ions increases inside the microspheres and promotes the nucleation process, which in turn leads to grains with smaller crystallite size.

During the washing process, the concentration of NO_3^- ions inside the microspheres decreases due to the leaching effect of washing. During the soaking step, ammonia solution fills the pores resulting from the diffusion of NH_4NO_3 to the washing solution. This results in a greater replacement of OH^- ions and consequently in a decrease in the pH inside the microspheres, which leads to crystal growth. These results are in agreement with those of Naefe et al. [10].

Conclusions

The results indicate that the thermal decomposition of UO_3 gel microspheres includes a dehydration reaction, ammonia removal, ammonia oxidation and UO_3 recrystallization. The peak temperatures were below 200° for the dehydration reaction, $220 \pm 5°$ for ammonia removal, $280 \pm 7°$ for ammonia oxidation and $395 \pm 5°$ for UO_3 recrystallization. It was also found that soaking of the microspheres in 3% ammonia solution after washing results in crystal growth (155 Å), while soaking before washing results in nucleation and consequently in a smaller crystallite size (85 Å).

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Zusammenfassung — Die thermische Zersetzung von UO_3-Gelmikrokugeln wurde mittels DTA, TG, DTG und Röntgendiffraktometrie untersucht. Die Auswirkungen des Waschens der UO_3-Gelmikrokugeln mit heißem Wasser und mit Ammoniaklösungen sowie der Einfluß des Wässerns der Mikrokugeln vor und nach dem Waschen mit Ammoniaklösungen auf die Kristallitgröße wurden untersucht. Die thermische Zersetzung der UO_3-Gelmikrokugeln verläuft in 5 Schritten: in den ersten beiden erfolgt die Dehydratisierung, im dritten die Abgabe und im vierten die Oxydation von Ammoniak und schließlich im letzten Schritt die Rekristallisation von UO_3.

Резюме — Методом ДТА, ТГ, ДТГ и рентгенографии изучено термическое разложение микросферического геля $ЫО_3$. Исследовано как влияние промывки геля горячей водой и раствором аммиака, так и вымачиванием его в растворе аммиака перед или после промывания геля до размера кристаллитов. Полученные результаты показали, что термическое разложение микросферического геля $ЫО_3$ включает пять стадий, из которых первые две являются стадиями дегидратации, третья — выделение аммиака, четвертая — окисление аммиака, а последняя — рекристаллизация $ЫО_3$.