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EFFECTS OF DRYING CONDITIONS ON THERMAL DECOMPOSITION BEHAVIOUR OF UO_3 GEL MICROSPHERES

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The effects of the drying conditions on the thermal behaviour of UO_3 gel microspheres were studied by TG, DTA and X-ray examination. The effects of drying with air, steam or alcohol on the crystal structure and crystallite size were also studied. The results indicate that the thermal decomposition of UO_3 gel microspheres involves five steps: the first two for dehydration, the third for ammonia release, the fourth for ammonia oxidation, and the last one for UO_3 recrystallization. It was also found that the crystal growth varied from 110 Å after air drying to 512 Å and 496 Å after steam and alcohol treatment, respectively.

Uranium dioxide microspheres are being considered as fuel material for use in different types of nuclear reactors. For the application of UO_2 microspheres in light water reactor (LWR) and fast breeder reactor (FBR) fuel elements, fuel pins containing vibro-compacted microspheres (sphere-pac) are suitable [1, 2]. For high-temperature gas-cooled reactor (HTGR) application, fuel is also needed in the form of microspheres for coated fuel particles [3].

For the fabrication of UO_2 microspheres, several wet chemical processes have been reported [4–6]. They are generally termed sol-gel [2, 7] and gelation processes [8, 9]. The gelation processes are commonly classified into external [10] and internal [11] gelation, depending on the mode of precipitation.

According to Haas et al. [12] and Förthmann et al. [3], the composition of the gel microspheres prepared by the hydrolysis process is $UO_3 \cdot xNH_3 \cdot yH_2O$, where the values of x and y depend on the preparation conditions.

The aim of the present investigation is to study the effects of the conditions of drying gelled microspheres on their thermal decomposition behaviour, by means of thermal analysis (TG and DTA) and X-ray diffraction.

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Experimental

Preparation of UO_3 gel microspheres

The UO_3 gel microspheres were prepared by the hydrolysis process [11]. The uranium feed solution was prepared by dissolving urea in a highly concentrated uranyl nitrate solution (about 500 g U/l) and adding solid hexamethylenetetramine (HMTA) at temperatures below $+10°$ until a pH of 5.5 was reached. This metastable solution was dispersed into droplets from a vibrating nozzle into hot silicone oil (90–95°). The droplets solidified in a few seconds, forming spherical kernels. The obtained UO_3 kernels were deep-orange and translucent. The kernels were first washed with CCl_4 to remove the silicone oil from the surface, then washed with dilute ammonia solution (3%) four times, each for 15 minutes at room temperature, to remove ammonium nitrate, excess HMTA and urea.

The washed microspheres were dried by using three different methods: oven air drying, steam drying and alcoholic dehydration.

For oven air drying, experiments were conducted at room temperature (20°), 70° and 140°.

For steam drying, experiments were carried out by passing a flow of steam over the samples. Microspheres were placed in a heated tube at 240° and drying was continued for 1, 2 or 4 h.

For alcoholic dehydration of gel microspheres, three types of alcohols were used: ethanol, *n*-butanol and isopropanol.

Techniques

Thermal analysis (TG and DTA) of gelled microspheres dried by different methods was carried out using a Shimadzu DT–30 thermal analyser in static air, in the temperature range 25–600°. The heating rate was 10 deg min^{-1}.

An X-ray investigation of the gelled microspheres was performed with a Philips 1140 diffractometer. 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° in 2 min.

The mean crystallite size was determined from the X-ray diffraction broadening using the Scherrer equation, $D = K\lambda/\beta \cos\theta$ [3], where K is a constant approximating to unity; its value is 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 $K = 0.89$.

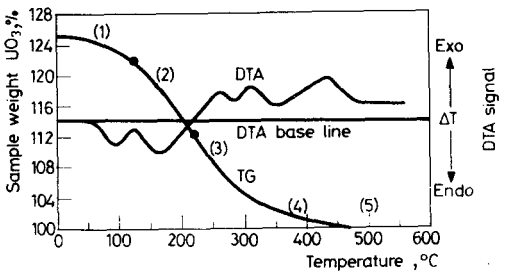

Fig. 1 DTA and TG curves for ammonia washed microspheres and dried at RT (20 °C) for 36 hours. (1): UO_3 + adsorbed H_2O + crystalline $H_2O + NH_3$. (2): UO_3 + Crystalline $H_2O + NH_3$. (3): UO_3 + part of crystalline $H_2O + NH_3$. (4): UO_3 + part of crystalline H_2O. (5): UO_3

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

Results and discussion

Thermal behaviour of UO_3 gel microspheres

Figure 1 shows the TG and DTA curves for microspheres dried in air at room temperature (20°). The TG curve reveals five temperature zones, where weight loss appears together with two characteristic levels for the resulting oxides. In the first part of the decomposition, three successive domains can be observed, where the weight losses are only limited by small inflections, without clear-cut steps due to the gradual elimination of water and ammonia. The second part of the decomposition differs from the first by the appearance of a characteristic anhydrous UO_3 level, as well as a reduction process involving oxygen loss and U_3O_8 formation, that represent a slightly slopping level.

A series of endothermic and exothermic effects appear in the DTA curve. The first of the two endothermic steps, at about 100°, is characteristic of the removal of adsorbed water; the second step, at 160°, is characteristic of the partial removal of constitution water. There are three exothermic steps. The first step, at 250°, is characteristic of the removal of incorporated ammonia. The second step, at 300°, is characteristic of ammonia oxidation by oxygen present in the furnace atmosphere. The third step, at 440°, is attributed to UO_3 recrystallization due to slow dehydration. These results are in good agreement with those of Spacu [14] and Turcanu et al. [15]. The interpretation of the TG curves leads to the suggested formula $UO_3 \cdot 1.93NH_3 \cdot 1.34H_2O$ for the air-dried microspheres,

$UO_3 \cdot 1.52NH_3 \cdot 0.71H_2O$ for the steam-dried microspheres and $UO_3 \cdot 1.27NH_3 \cdot 0.32H_2O$ for the alcohol-dehydrated microspheres.

Effects of drying conditions

i) Air drying

The DTA curves of microspheres dried at room temperature (20°), 70° and 140° are given in Figs 2A, B and C, respectively. It is seen that the retained water is released in two stages. DTA curves A and B show that the retained water is in the form of surface and crystalline water, and the peaks reach their maximum at 100° and 170°, respectively. DTA curve C indicates that the incorporated water is in the form of crystalline water and is released in two steps, at 200° and 265°, respectively. It is also seen that drying at 140° results in shifts of the exothermic peaks of ammonia removal and ammonia oxidation to higher temperatures than those for the samples dried at 20° and 70°. This effect can be attributed to the closing of the pores during drying as a result of the shrinking of the microspheres.

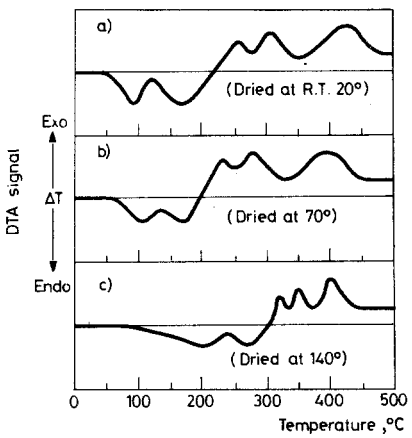

Fig. 2 Differential thermal analysis of ammonia washed UO_3 microspheres dried in oven air at different temperatures

Figure 3 shows the effects of the drying temperature on the retained ammonia. It is observed that increase of the drying temperature from 20° up to 70° has no effect on the ammonia content. Increase of the drying temperature from 70° to 140° results in a decrease from 2.0 to 1.7 mole ammonia per mole U.

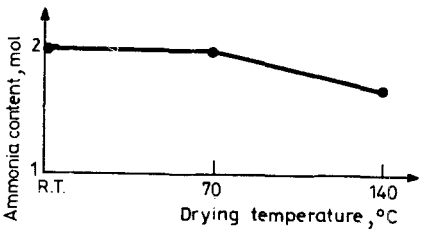

Fig. 3 Effect of drying temperature on ammonia content

ii) Steam drying

Figure 4 shows the DTA curves of microspheres dried with steam for 1, 2 or 4 h. It is seen that the retained water is released in one step, at 120°, which indicates that the incorporated water is in the form of crystalline water. This could be due to evaporation of the surface water during drying. It is also observed that the first exothermic peak, which is characteristic of ammonia release, shifts from 235° to 250° with increase of the drying time from 1 h to 2 h, and disappears after drying for 4 h. This result indicates that the release and oxidation of ammonia occur simultaneously; the peak has its maximum at 300°.

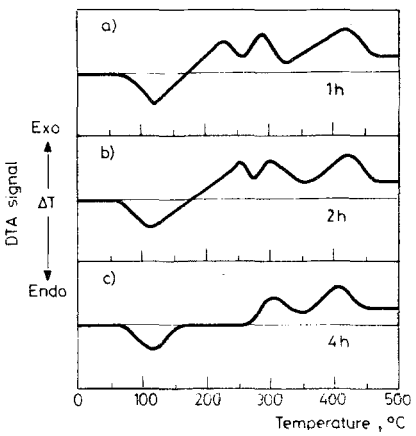

Fig. 4 Differential thermal analysis of microspheres dried in a flowing steam for different time

The effect of the time of drying with steam on the retained ammonia content is shown in Fig. 5. The retained ammonia decreases from 1.5 to 0.5 mole per mole U on increase of the drying time from 1 h to 4 h. This can be attributed to transfer of the retained ammonia to the flowing steam as a result of the concentration gradient.

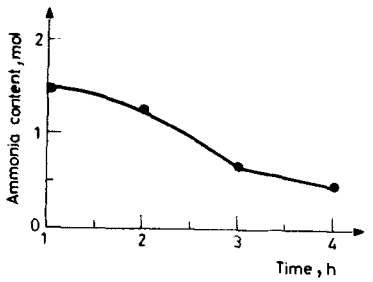

Fig. 5 Effect of steam drying time on ammonia content

iii) Alcoholic dehydration

The DTA curves of microspheres dehydrated by using *n*-butanol, isopropanol and ethanol are shown in Fig. 6. It is seen that the second stage, characteristic of the partial removal of crystalline water, has disappeared. This can be attributed to the ability of alcohols to extract water from the microspheres. It is also observed that the type of the alcohol has no effect on the three exothermic peaks.

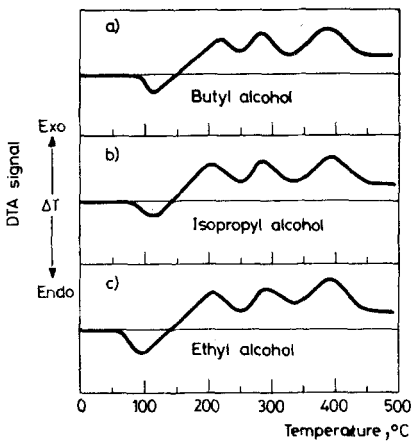

Fig. 6 Differential thermal analysis of microspheres dehydrated by different alcohol

The retained ammonia content of the microspheres dehydrated with isopropanol, ethanol and *n*-butanol is 1.7, 1.4 and 1.0 mole per mole U, respectively, as shown in Fig. 7. It is observed that microspheres dehydrated with alcohols contain lower amounts of retained ammonia than air-dried microspheres (see Fig. 3), This result can be accounted for by the extraction of a large part of the crystalline water by the alcohols, which leads to porous microspheres. Consequently, the retained ammonia can easily be released at room temperature.

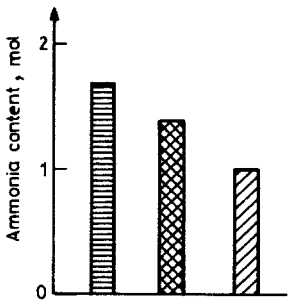

Fig. 7 Effect of alcohol type on the ammonia content. ▤ isopropyl alcohol; ▩ Ethylalcohol; ▨ *n*-butyl alcohol

X-ray diffraction analysis

X-ray examination of microspheres air-dried at 70° indicates a crystallite size of 110 Å. Steam drying of gel microspheres for 1 h results in a crystallite size of 512 Å, whereas alcoholic dehydration with *n*-butanol leads to a crystallite size of 496 Å. These results might be due to a decrease in the concentration of OH^- ions inside the microspheres, through extraction by the alcohol or diffusion into the flowing steam. Consequently, the pH inside the microspheres decreases and leads to crystal growth. These results are in agreement with those of Naefe et al. [10].

The X-ray diffraction data obtained for air-dried microspheres (70°) and steam-dried microspheres (4 h) are given in Tables 1 and 2, respectively. These data agree

Table 1 X-Ray diffraction pattern of air dried gel microspheres with corresponding reflections observed by Lloyd et al. (type 2)

Obs.		Lloyd et al.	
I/I_0	d (Å)	I/I_0	d (Å)
60	7.43	m	7.54
100	3.52	vs	3.54
80	3.24	vs	3.24
80	3.19	vs	3.2
50	3.04		
10	2.84	m	2.83
30	2.01	m	2.04
25	1.97	m	1.99
25	1.95		

vs = very strong, m = medium

Table 2 X-Ray diffraction pattern of steam dried gel microspheres with corresponding reflections observed by Debets et al. (type 3)

Obs.		Debets et al.	
I/I_0	d (Å)	I/I_0	d (Å)
100	7.30	100	7.25
13	3.73		
20	3.60	22	3.63
50	3.50	60	3.52
80	3.17	70	3.17
15	2.56		
20	2.51	18	2.53
11	2.30	3	2.31
20	2.04	10	2.03
20	2.02		
16	1.95	11	1.96

with those obtained for UO_3 gel microspheres of type 2 ($UO_3 \cdot 1/4NH_3 \cdot 7/4H_2O$) and type 3 ($UO_3 \cdot 1/2NH_3 \cdot 3/2H_2O$) by Lloyd et al. [16] and Debets et al. [17].

Conclusion

The present results indicate that the thermal decomposition of UO_3 gel microspheres depends on the drying conditions. The dehydration peak temperatures were below 250° for air-dried microspheres, and 120° for steam-dried or alcohol-dehydrated microspheres. The peak temperatures for ammonia removal were 250–300°, 220–300° and 200° for air drying, steam drying and alcoholic dehydration, respectively. It was found that the method of drying has no effect on the peak temperatures of ammonia oxidation and UO_3 recrystallization. These peaks were 290° and 395°, respectively.

Crystal growth was observed from 110 Å for air-dried microspheres to 512 Å and 496 Å for steam-dried and alcohol-dehydrated microspheres, respectively.

The retained ammonia content depends on the drying time for steam drying and on the type of alcohol used for alcoholic dehydration.

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Zusammenfassung — Die Effekte der Trocknungsbedingungen auf das thermische Verhalten von UO_3-Gelmikrokugeln wurden mittels TG, DTA und Röntgenanalyse untersucht. Ebenfalls wurden die Auswirkungen der Trocknung mit Luft, Dampf und Alkohol auf die Kristallstruktur und die Kristallitgröße untersucht. Die Ergebnisse deuten darauf hin, daß die thermische Zersetzung der UO_3-Gelmikrokugeln in 5 Schritten verläuft: die ersten zwei sind Dehydratisierungsprozessen, der dritte der Freisetzung und der vierte der Oxydation von Ammoniak und der letzte der Rekristallisation des UO_3 zuzuschreiben. Die Kristallitgröße variiert zwischen 110 Å nach Lufttrocknung und 512 bzw. 496 Å nach Trocknung mit Dampf bzw. Alkohol.

Резюме — Методом ТГ, ДТА и рентгеноструктурного анализа изучено термическое поведение микросферических гелей UO_3 в зависимости от условий их сушки. Исследовано также влияние высушивания гелей воздухом, паром или спиртом на кристаллическую структуру и размеры кристаллитов UO_3. Результаты показали, что термическое разложение микросферического геля UO_3 включает пять стадий: первые две стадии — дегидратация, третья стадия — выделение аммиака, четвертая — окисление аммиака и последняя стадия — рекристаллизация UO_3. Показано, что рост кристаллов изменяется от 110 Å после высушивания воздухом до 512 и 496 Å после обработки их, соответственно, паром и спиртом.