

KINETICS OF THERMAL DECOMPOSITION OF GELLED UO_3 MICROSPHERES

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The kinetics of decomposition of gelled UO_3 microspheres has been studied by thermal analysis (DTA and TG) and by X-ray examination. UO_3 microspheres prepared via a hydrolysis process were used in the study. The DTA and TG curves were obtained in various atmospheres at different heating rates. The activation energies for the various stages of decomposition were calculated using the Carrol and Manche method.

Spherical fuel microspheres have been proposed as the fuel material for high-temperature reactors (HTGR), light water reactors (LWR) and fast breeder reactors (FBR) [1, 2]. Dense UO_2 microspheres for reactor fuels are prepared by wet chemical processes. There are several wet chemical methods, which differ considerably from each other. They are generally known as "Sol-Gel" processes [3, 4]. They have in common the fact that a solution (feed solution: sol or broth) of uranium (uranyl nitrate) is dispersed into droplets and thereafter solidified by means of a chemical precipitation reaction. The gel particles obtained are processed into the required ceramic microspheres, mainly by heat treatment.

To achieve good spherical kernels with high density, the precipitation must always be gel-like instead of crystalline, since only a gel structure keeps the particles spherical during drying (via uniform shrinkage), whereas a crystalline precipitate results in imperfect spherical kernels.

The wet chemical processes are commonly classified into external [5] and internal gelation [6], according to the mode of precipitation.

The aim of the present work was to study the kinetics of thermal decomposition of gelled UO_3 microspheres by thermal analysis (DTA and TG) and X-ray examination.

Experimental

The UO_3 microspheres were prepared by using the hydrolysis process [7]. This process is based on the homogeneous hydrolysis of a concentrated $\text{UO}_2(\text{NO}_3)_2$ -urea solution after the addition of hexamethylenetetramine (HMTA). A concentrated uranyl nitrate solution (350 g U/l) is stabilized by urea, which forms the complex $[\text{UO}_2(\text{NH}_2\text{CONH}_2)_2]^{2+}$; the urea to uranium ratio is 2:1. This starting solution is mixed with solid HMTA at 10° until a pH of 5.5 is reached. This metastable solution is dispersed from a vibrating nozzle into hot silicone oil (90 – 95°). The droplets solidify in a few seconds, forming spherical particles. The UO_3 kernels obtained are dark-yellow and translucent. The kernels are first washed with carbon tetrachloride to remove the silicone oil from the surface, and then with hot water to remove ammonium nitrate, excess HMTA and urea. The resulting gel particles are washed five times, each for 15 min, with 3% ammonia solution at room temperature. The washed particles are dried at 70° in air for 17 hours.

Thermal analysis (DTA and TG) of the UO_3 gel microspheres was carried out with a Shimadzu thermal analyser (type DT-30) in static air and ammonia gas, in the temperature range 25 – 600° . The heating rates were 5, 10, 20 and 30 deg min^{-1} .

To determine the intermediate phases appearing on thermal decomposition, X-ray examination was carried out with a Philips diffractometer (type 1140).

The thermogravimetric curves obtained at different rates were utilized to calculate the activation energy, using the technique recommended by Carrol and Manche [8]. This technique was selected since thermogravimetric curves give more reliable results than DTA curves, and in this method the reaction rate was not considered to be proportional to the n th power of the undecomposed solid as in the case of homogeneous reactions. The latter assumption has been adopted by various authors, and the equations developed can have theoretical significance only in the cases where the value of n is 0, $1/2$, $2/3$ or 1 [9, 10].

In this method, $-dw/dt = kf(w)$, where w is the weight of the reactive portion of the sample, and k is the rate constant related to temperature by the Arrhenius equation:

$$k = Z \exp(-E/RT)$$

If the heating rate $\Phi = dT/dt$, then

$$-\frac{dw}{dT} = \frac{Z}{\Phi} \exp(E/RT) f(w)$$

$$\ln \left[\Phi \left(-\frac{dw}{dT} \right) \right] = \ln Z(f(w)) - \frac{E}{RT}$$

A plot of $\ln \Phi(-dw/dT)$ vs. $1/T$ for a given value of w , obtained at different heating rates, will lead to a value of E .

Results and discussion

The gelled UO_3 microspheres obtained by the hydrolysis process were found on X-ray analysis to have the structure $\text{UO}_3 \cdot 1/2\text{NH}_3 \cdot 3/2\text{H}_2\text{O}$, as compared with the lines given by Förthmann et al. [7].

Figure 1 shows the TG and DTA curves for the dried microspheres. They are similar to those published earlier [11]. For a heating rate of 20 deg/min (in an alumina crucible), physical water removal starts at 95° . The peak temperature at 260° corresponds to the removal of chemical water, as evidenced from weight loss calculations. These findings are in good agreement with the results published earlier [12]. The peak occurring at 320° is mainly associated with the evolution of ammonia. A final peak appears at 570° , which is due to the UO_3 — U_3O_8 conversion, as confirmed by X-ray analysis of the spheres resulting at 600° . This is in accordance with the findings of Dharwadkar et al. [13]. From weight loss calculations, the extent of reduction of the UO_3 by the released ammonia is very low (1.04%). A slight weight loss occurs above 570° , due to the U_3O_8 nonstoichiometry, as it takes the form U_3O_{8-x} .

The thermal decomposition was studied at a heating rate of 20 deg min^{-1} under static air and ammonia. It was found that the thermal decomposition under an ammonia atmosphere reduces the temperature of formation of the intermediate

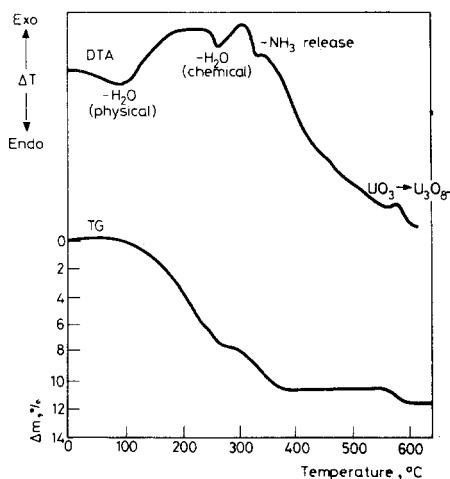


Fig. 1 DTA and TG curves for dried UO_3 gel microspheres

oxides. In static air, the first exothermic peak was at 320° , while it was at 290° in ammonia. Similarly, the last endothermic peak was at 570° in static air, while it was at 550° in ammonia. This may be because of hindered reduction in air, while ammonia helps the reduction to take place through the formation of U_3O_8 at 550° .

The previous results indicate that the thermal decomposition includes a dehydration reaction, ammonia removal to form UO_3 , and the thermal decomposition of UO_3 to U_3O_8 . The activation energies of these steps were calculated using the method mentioned above, at heating rates of 5, 10, 20 and 30 deg min^{-1} . They were found to be 166.4 kJ/mol for the dehydration step (first endothermic peak), 189.4 kJ/mol for the second step (ammonia removal), and 347.8 kJ/mol for the third step (UO_3 — U_3O_8 decomposition).

Conclusions

The present results indicate that the thermal decomposition of UO_3 microspheres takes place in three steps. In static air, physical water is evolved first, at 95° , followed by chemical water release at 260° . Ammonia is released at 320° . Finally, UO_3 decomposes at 570° . The presence of an ammonia atmosphere during the decomposition shifts the steps of ammonia release and UO_3 decomposition to oxygen-deficient U_3O_8 towards lower temperatures.

The activation energies for dehydration, ammonia release and the decomposition of UO_3 to U_3O_8 were 166.4 kJ/mol, 189.4 kJ/mol and 347.8 kJ/mol, respectively.

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References

- 1 R. L. Beaty, R. E. Norman and K. J. Note, ORNL Report-5469 (1978).
- 2 P. A. Haas, J. M. Bogvoich, A. D. Ryon and J. S. Vavruska, ORNL Report-TM-6850 (1979).
- 3 C. J. Hardy, Sol-Gel Procèsses for Ceramic Nuclear Fuels, IAEA, Vienna 1968, p. 34.
- 4 J. M. MacBride, ORNL Report-3874 (1966).
- 5 G. Brambilla, P. Gernotopulos and D. Neri, Eng. Nucl., 17 (4) (1970) 217.
- 6 Y. K. Afify, M. Sc. in nuclear engineering, Alexandria University, Alexandria, Egypt (1986).
- 7 R. Förthmann, A. Naoumidis, H. Nickel and W. Burck, Jül.Report-655 (1970).
- 8 B. Carrol and E. P. Manche, Thermochem. Acta, 3 (1972) 449.
- 9 L. Reich and S. S. Stivala, Thermochem. Acta, 34 (1979) 287.
- 10 J. M. Criado and J. Morales, Thermochem. Acta, 19 (1977) 305.
- 11 C. N. Turcanu and R. Deju, Nucl. Technology, 45 (1979) 188.
- 12 A. M. Gadalla, A. F. Bishay and Z. M. Zayed, Thermochem. Acta, 62 (1983) 217.
- 13 S. A. Dharwadkar and M. D. Karkhanavala, J. Ind. Chem. Soc., 45 (1968) 6.

Zusammenfassung — Die Kinetik der Zersetzung von Gel UO_3 Mikrokügelchen wurde mittels Thermoanalyse (DTA und TG) und Röntgenstrukturanalyse untersucht. Die in dieser Abhandlung benutzten UO_3 Mikrokügelchen wurden unter Zuhilfenahme von Hydrolyseprozessen hergestellt. Die DTA- und TG-Kurven wurden in verschiedenen Atmosphären und bei verschiedenen Aufheizgeschwindigkeiten aufgenommen. Mit der Methode von Carrol und Manche wurden die Aktivierungsenergien für die einzelnen Schritte der Zersetzung berechnet.

Резюме — Методом ДТА, ТГ и рентгеноструктурного анализа изучена кинетика разложения микросферического гелеобразного UO_3 , полученного путем гидролиза. Кривые ДТА и ТГ были измерены в различной атмосфере и при различных скоростях нагрева. Энергии активации различных стадий разложения были вычислены по методу Кэррола и Мэнча.