Journal of Thermal Analysis, Vol. 44 (1995) 1439-1448

DETERMINATION OF SPECIFIC SURFACE AREA OF URANIUM OXIDE POWDERS USING DIFFERENTIAL THERMAL ANALYSIS TECHNIQUE

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(Received January 2, 1994; in revised form May 10, 1994)

Abstract

The two step oxidation of UO_{2+x} and reduction of U_3O_8 powders observed during Differential Thermal Analysis (DTA) has been exploited to determine their Specific Surface Areas (SSAs). The results obtained by this method have been compared with the Braunauer, Emmett and Teller (BET) method and are found to be in good agreement in the SSA range of 2–4 m^2/gm in the case of UO_{2+x} obtained from ADU route and 4–8 m^2/gm in the case of AUC route. A precision of ±0.1 m^2/gm is obtained. The maximum temperature of oxidation and reduction of these oxides are dependent upon their preparative routes such as Ammonium Diuranate (ADU) and Ammonium Uranyl Carbonate (AUC).

Keywords: DTA, specific surface areas, uranium oxide

Introduction

The Specific Surface Area (SSA) of UO_{2+x} powders is a key guiding parameter for sintering of oxide powders to get sintered UO_2 fuel pellets to be used in Nuclear Power Reactors [1, 2]. Uranium Oxide powders are obtained mainly by ADU and sometimes by AUC route. The O/U ratio, Average Particle Size (APS), SSA are important parameters for sintering of the oxides. An O/U ratio of 2.04 to 2.15, SSA of 2.4 to 2.8 m^2/gm and APS in the range 0.8 to 1 micron are the specifications for obtaining flawless, sintered UO_2 fuel pellets. However in case of AUC route the SSA is in the range of 6 to 8 m^2/gm [3]. APS is also higher than that of ADU route UO_2 powder. Investigations on sintering behav-

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0368–4466/95/ $ 4.00

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iour of ADU derived UO_2 powders with surface area falling below 2.2 m^2/gm and above 3.0 m^2/gm have revealed that the sintered pellets deviate from specifications for low surface area powders and pressing and microstructural defects for high surface area powders [4] and any variation in surface area value of more than ±0.5 m^2/gm results in microstructural faults and inhomoginities [5]. This necessitates determination of SSA of powders on routine basis during fuel fabrication.

The BET method is an age old method for the determination of SSA for powders based on adsorption of N_2 gas by the sample at liquid nitrogen temperature (~77 K). However this method requires large sample size, liquid nitrogen, identical containers for sample and reference etc. Also there is a basic assumption in this method that the adsorption isotherm is of Langmuir type i.e., there is a monomolecular layer of N_2 gas adsorbed by the sample. This demands prior removal of any volatile material such as moisture and adsorbed air from the sample.

Oxidation of UO_{2+x} powders using DTA technique has been extensively studied [6–10]. It has been reported that the oxidation of UO_{2+x} powder takes place in two stages corresponding to exothermal peaks of (1) $UO_{2+x} \rightarrow U_3O_7$ and (2) $U_3O_7 \rightarrow U_3O_8$ and the difference between the temperature of these two peaks depends on specific surface area of the powders [11].

Further the U_3O_8 powders obtained as an intermediate product during the uranium conversion process can also be studied for their thermal behaviour during reduction and utilize the data for their SSA determination.

In addition to this, it is worth studying the variation in oxidation temperature of UO_{2+x} powders obtained from different preparative routes namely Ammonium Diuranate (ADU) and Ammonium Uranyl Carbonate (AUC). Therefore, efforts have been made to extend DTA to study the oxidation of UO_{2+x} and reduction of U_3O_8 for the determination of SSA of these powders as an alternate method.

Experimental

For the purpose of establishing the calibration graph, U_3O_8 powders of varying SSAs were prepared starting from uranyl nitrate pure solution (UNPS) of ≈80 g/l concentration at 60°C, by slow addition of ammonium hydroxide solution (≈10N), drying the resulting ADU at 110°C and calcining it at different temperatures. These U_3O_8 powders of different surface areas were reduced in H_2 atmosphere at 625°C to get UO_{2+x} powders of different specific surface areas. The SSA of UO_{2+x} and U_3O_8 powders were determined by BET method, and these powders of known SSA were used for drawing the calibration graphs of oxidation and reduction respectively using DTA technique.

Similarly, AUC was prepared by addition of Ammonium bicarbonate solution to ADU slurry at 50°C and washing the precipitate with methanol. The AUC is dried at room temperature and calcined at different temperatures to get U_3O_8 powders of varying specific surface areas. These U_3O_8 powders were reduced in H_2 gas at 600°C to get UO_{2+x} powders of different specific surface areas. The SSA of these UO_{2+x} and U_3O_8 powders were determined by BET method. These powders of known SSA were used for drawing calibration graph using DTA technique.

Oxidation and reduction of UO_{2+x} and U_3O_8 powders respectively were carried out using SETARAM TAG-24 Symmetrical Thermal Analyser (2 furnaces model). Alumina crucibles were used as sample holders and Pt/Pt-Rh 30%/6% as thermocouple. The differential thermocouple emf was recorded on EPSON PCe printer controlled by G11 universal controller with chosen 200 μV Full Scale Detection for differential temperature.

In the case of oxidation of UO_{2+x} powders, the samples were heated in static air to 800°C from ambient temperature with a heating rate of 10 deg·min^{-1}, whereas in the case of reduction of U_3O_8 powders, first the furnace chamber was evacuated to 1 Pa then filled with H_2 gas. The samples were then heated to 700°C with a heating rate of 10 deg·min^{-1}, and the thermoanalytical curves were recorded.

Results and discussion

The dynamic DTA of oxidation of UO_{2+x} and reduction of U_3O_8 are shown in Figs 1 and 2 respectively. It is evident that the oxidation of UO_{2+x} powders

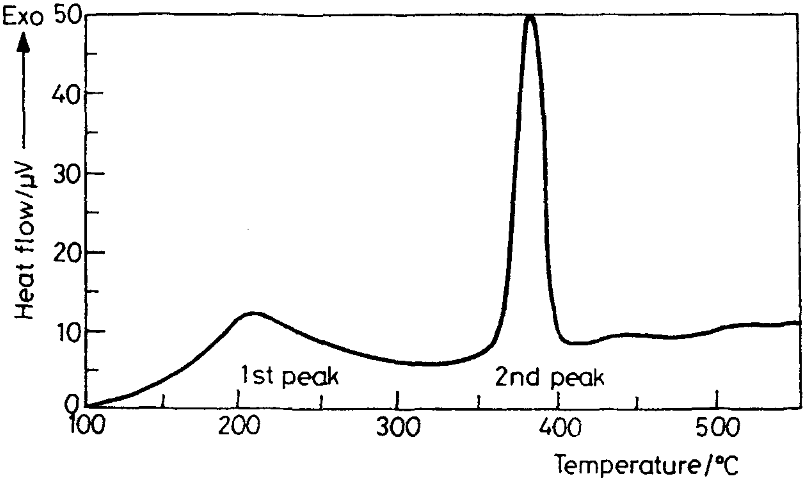

Fig. 1 DTA curve of UO_{2+x} oxidation

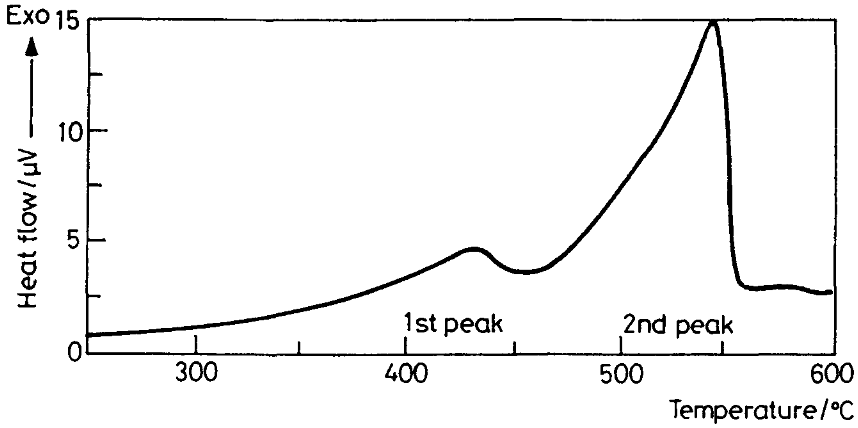

Fig. 2 DTA curve of U_3O_8 reduction

Table 1 O/U ratio of 1st peak product of UO_{2+x} oxidation

Sample	O/U ratio
AUC-5	2.289
AUC-6	2.332
AUC-8	2.342
AUC-11	2.338
AUC-9	2.361

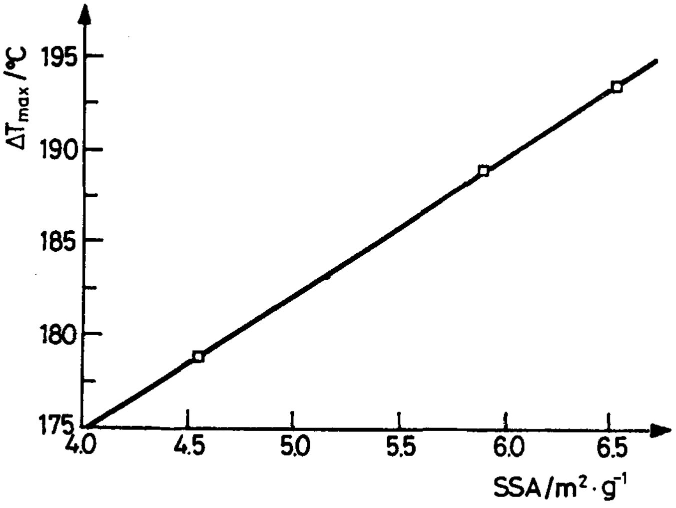

Fig. 3 Calibration graph of AUC route UO_{2+x} powders

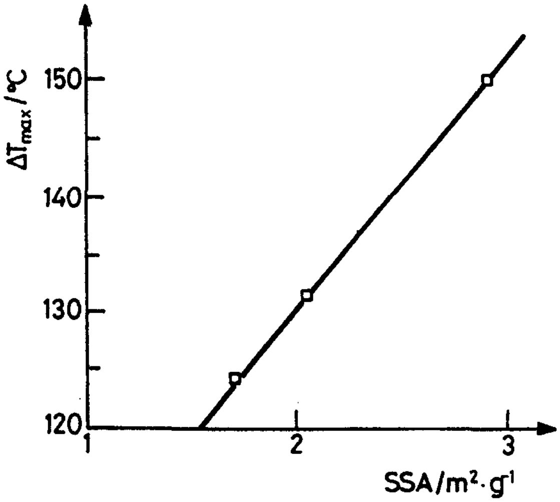

Fig. 4 Calibration graph of ADU route UO_{2+x} powders

is a two step process passing through an intermediate state of U_3O_7. The two exothermal peaks relate to (1) $UO_{2+x} \rightarrow U_3O_7$ and (2) $U_3O_7 \rightarrow U_3O_8$. The intermediate state was analysed for O/U ratio and was found to be around 2.33 as presented in Table 1 indicating a composition of U_3O_7. As can be seen from Figs 3 and 4, that both in the case of AUC and ADU route powders, there exists a linear relationship between the SSA of UO_{2+x} and the difference in temperature (ΔT_{max}) of two exothermic peaks. It has been observed that the calibration curve is linear in the range of SSA of 2 to 4 m^2/gm and 4 to 8 m^2/gm for ADU and AUC derived UO_2 powders respectively which is the normal range of SSA required for a sinterable powder. Hence DTA method serves the purpose for the determination of SSA on a routine basis as it compares well with BET method in the range of interest. The precision in SSA of two methods is shown in Table 2. A precision of ± 0.1 m^2/gm at 95% confidence level is obtained in both

Table 2 Precision of BET and DTA methods of UO_{2+x} sample code CFFP-839

Max. temp. of oxidation of 1st peak/ °C	Max. temp. of oxidation of 2nd peak/ °C	Difference in temperature of two peaks ΔT_{max}/°C	SSA/m²·g	
			DTA value	BET value
234.7	383.5	148.8	2.90	2.85
232.5	384.5	151.8	3.00	2.88
233.0	383.8	150.8	2.95	2.80
233.8	383.8	150.0	2.90	2.79

the cases in spite of a variation of ±1°C in ΔT_{max}. Tables 3 and 4 compare the SSA values of AUC and ADU route UO_{2+x} powders respectively, obtained by BET and DTA methods. It can be seen that there is a good agreement.

Table 3 Comparison of SSA values obtained by BET and DTA methods of AUC route UO_{2+x} powders

Sample	Max. temp. of oxidation 1st peak/ °C	Max. temp. of oxidation 2nd peak/ °C	Difference in temperatures of two peaks ΔT_{max}/°C	SSA/m²·g	
				BET value	DTA value
AUC-5	198.7	389.1	190.4	5.89	6.05
AUC-6	206.8	385.3	178.5	4.69	4.55
AUC-7	206.2	384.5	178.3	4.22	4.40
AUC-8	195.6	387.6	192.0	6.21	6.30
AUC-9	211.0	382.5	171.5	3.97	3.55
AUC-10	205.2	382.7	177.5	4.66	4.40
AUC-11	210.0	391.4	181.4	4.92	4.90

Table 4 Comparison of SSA values obtained by BET and DTA methods of ADU route UO_{2+x} powders

Sample	Max. temp. of oxidation 1st peak/ °C	Max. temp. of oxidation 2nd peak/ °C	Difference in temperatures of two peaks ΔT_{max}/°C	SSA/m²·g	
				BET value	DTA value
ADU-1	223.0	381.7	158.7	3.47	3.35
ADU-2	233.8	379.9	146.1	2.77	2.75
ADU-3	244.2	385.5	140.8	2.68	2.50
ADU-4	225.6	384.3	158.7	3.30	3.08
ADU-5	234.7	383.5	148.8	2.85	2.90
ADU-6	230.4	381.7	151.3	2.91	2.95
ADU-7	231.2	380.2	149.0	2.79	2.85
ADU-8	229.9	379.7	149.8	2.70	2.90

In the case of reduction of U_3O_8 powders we get two exothermic peaks which can be expressed as (1) $U_3O_8 \rightarrow U_2O_{5+\delta}$ (2) $U_2O_{5+\delta} \rightarrow UO_2$. The O/U ratio of intermediate phase has been found to be around 2.590, which confirms to $U_2O_{5+\delta}$ [12–14], as can be seen from Table 5.

Table 5 O/U ratio of 1st peak product of U_3O_8 reduction

Sample	O/U ratio
ADU-9	2.593
ADU-10	2.589
ADU-11	2.582
ADU-11	2.582
ADU-14	2.590

Again, in the case of reduction of U_3O_8 powders prepared by both routes there exists a linear relationship between SSA and the temperature of reduction to UO_2, as can be seen from Figs 5 and 6. Table 6 and Table 7 compare the SSA values of U_3O_8 powders from AUC and ADU routes respectively obtained by BET and DTA methods.

Another interesting observation is that the difference in temperature of two exothermic peaks of oxidation of UO_{2+x} depends upon the route of preparation of these oxides. A ΔT_{max} in the case of oxidation of UO_{2+x} from ADU route is 150°C whereas through AUC route it is 180°C. The temperature of the second exothermic peak of oxidation is essentially same in both the cases but differs considerably in the first exothermic peak of oxidation. This may be attributed to the difference in surface area because after first oxidation peak there will be some sintering due to exothermic reaction and surface area for all samples may become comparable thereby not affecting the second peak temperature.

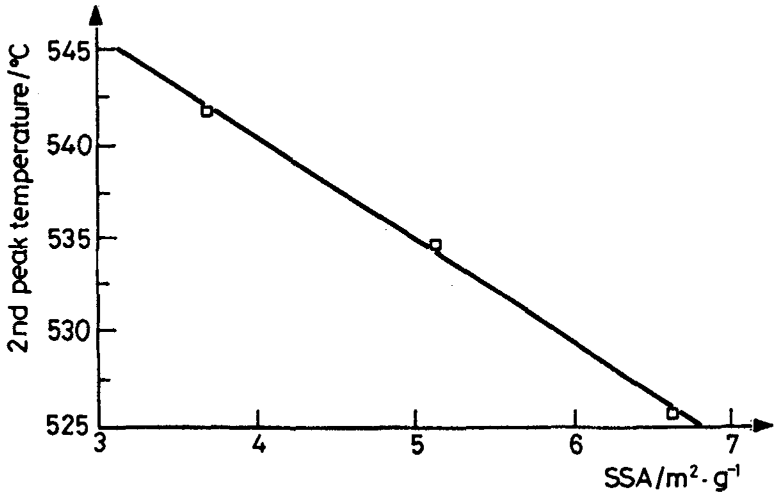

Fig. 5 Calibration graph of AUC route U_3O_8 powders

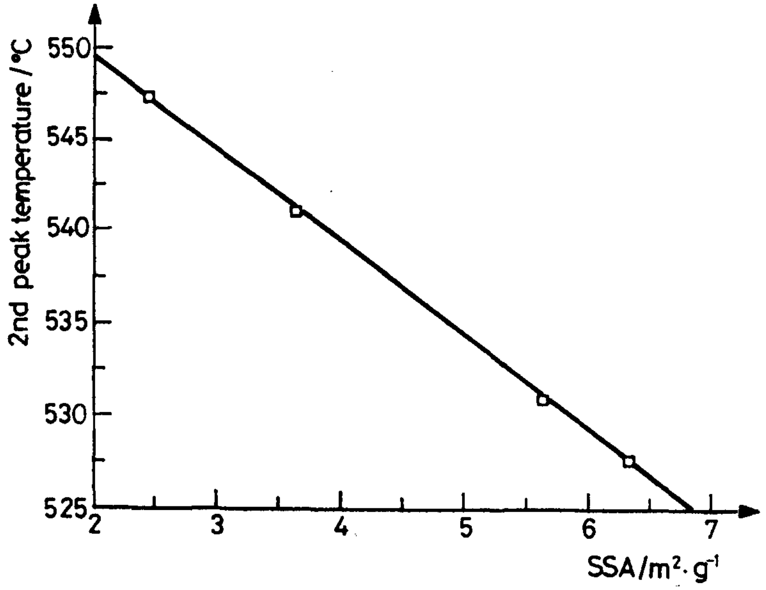

Fig. 6 Calibration graph of ADU route U_3O_8 powders

Table 6 Comparison of SSA values obtained by BET and DTA of AUC route U_3O_8 powders

Sample	2nd peak	SSA/m^2·g	
	T/°C	BET value	DTA value
AUC-17	526.0	6.64	6.50
AUC-18	531.6	5.45	5.50
AUC-19	530.8	5.62	5.60
AUC-20	522.5	7.21	7.15
AUC-21	522.0	7.32	7.25
AUC-22	522.4	7.18	7.20
AUC-23	524.0	6.87	6.95
AUC-24	537.9	4.49	4.30

The behaviour of U_3O_8 reduction prepared from different routes are similar as the particles were calcined during its preparation. Further it can be seen from Fig. 7, the DTA curve for the oxidation of UO_{2+x} powder, that the U_3O_7 peak is broader where SSA is less. This indicates that the bigger particle size of the powder is responsible for the broadening of the peak.

Table 7 Comparison of BET and DTA methods SSA values of ADU route U_3O_8 powders

Sample	2nd peak	SSA/m^2·g	
	T/°C	BET value	DTA value
ADU-20	545.1	2.79	2.75
ADU-21	538.2	4.22	4.15
ADU-22	544.6	2.99	2.90
ADU-23	547.2	2.70	2.50
ADU-24	544.0	3.02	3.00
ADU-25	543.0	3.24	3.20
ADU-26	541.6	3.46	3.35
ADU-27	540.0	3.76	3.75
ADU-28	536.5	4.38	4.45
ADU-29	544.0	3.00	2.95

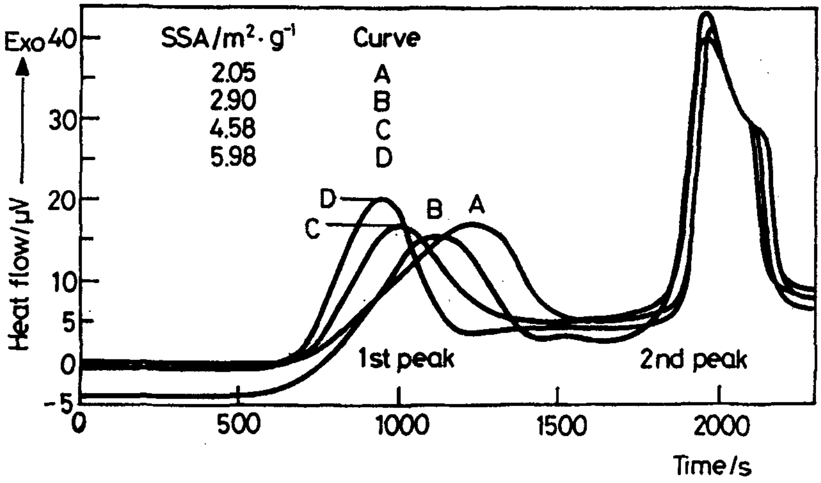

Fig. 7 Variation of DTA curve shape with SSA of UO_{2+x} powders

Conclusions

It can be concluded that DTA can be used for the determination of SSA of UO_{2+x} and U_3O_8 powders with reasonable precision and accuracy in the range of SSA which are adequate for the optimum conditions of a sinterable powder for production of UO_2 fuel pellets.

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The authors wish to express their thanks to Shri V. A. Chandramouli, Ex-Deputy Chief Executive (QA), for his keen interest and constant encouragement during this work. The authors also wish to thank Shri H. R. Ravindra and Shri B. N. Murthy scientific officers, for their technical disscussion. The authors also wish to thank Shri B. V. V. Ramana for typing the manuscript.

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Zusammenfassung — Die bei der DTA beobachtete zweistufige Oxidation von UO_{2+x} und die Reduktion von U_3O_8-Pulvern wurde zur Bestimmung der spezifischen Oberfläche genutzt. Die mittels dieser Methode erzielten Resultate wurden mit der Methode von Braunauer, Emmett und Teller (BET) verglichen, wobei man eine gute Übereinstimmung für den Bereich der spezifischen Oberfläche fand: 2–4 m^2/g im Falle von UO_{2+x} (erhalten über den ADU-Weg) und 4–8 m^2/g (erhalten über den ACU-Weg). Die erzielte Genauigkeit beträgt ±0.1 m^2/g. Die maximale Temperatur für Oxidation und Reduktion dieser Oxide hängt von deren Herstellungsweg: über Ammoniumdiuranat (ADU) oder Ammoniumuranylkarbonat (ACU).