

## Specific surface area determination by TG/DSC

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### Abstract

The specific surface area is an important feature, greatly affecting the sintering behavior of ceramics and metallic powders. It is usually reported as a BET measurement. Similarly, for  $\text{UO}_2$  powders, the stoichiometric O/U ratio also has an influence on the sinterability and can be measured by thermogravimetry.

The aim of this work is to report the influence of both the BET specific surface area and O/U ratio over thermal analysis results for  $\text{UO}_2$  powders (obtained by the wet route, i.e., AUC powders reduced in a fluidized bed). The TG and DSC curves for oxidation in air of  $\text{UO}_2$  powders, in the 25–800°C range, are investigated for several BET and O/U ratio values. It was found that, as the BET values increase, the first oxidation peak is shifted to lower temperatures, while the second oxidation peak is shifted to higher temperatures. It was also found that O/U ratio rises both the temperatures, remaining the difference between them constant. These results allow to build calibration curves for peak positions (temperatures) versus BET values. As a conclusion, BET values for a given powder can be estimated by its peak positions obtained in a thermal analysis.

X-ray analysis was used to identify the intermediary and final phases of  $\text{UO}_2$  oxidation, as well to determine the crystallite size. The last appears to have no influence in the peak temperatures. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** DSC; Powder; Surface area;  $\text{UO}_2$ ; X-ray diffraction

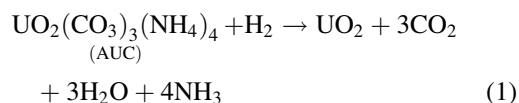
### 1. Introduction

One of the most important ceramic powder properties is the specific surface area which gives an approach on the sintering behavior. Although the crystallite size is said to be the governing factor for sintering, one can compare powders in terms of its specific surface area if they come from the same process route at the same plant [1].

The uranium dioxide is a non-stoichiometric oxide exhibiting high reactivity with oxygen or air. It can be readily oxidized to  $\text{U}_3\text{O}_8$  through a two-step reaction.

In order to achieve uranium dioxide pellets complying with the specification, besides surface area, the original powders must hold a set of several determinate properties, such as bulk and tap densities, oxygen to uranium stoichiometric ratio (O/U ratio), water and impurities content, powder flowability, etc.

The Materials Laboratory from Brazilian Navy Technological Center at Sao Paulo produces  $\text{UO}_2$  powders by ammonium uranyl carbonate (AUC) reduction in  $\text{H}_2$ /steam atmosphere at a fluidized-bed reactor. The general chemical reaction occurring during the reduction can be written as:



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The process is carried at temperatures between 550° and 650°C over several process steps where the gas flows are changed, including a pyrohydrolysis step with superheated water vapor. After the reduction, the  $\text{UO}_2$  powder undergo a controlled limited oxidation (passivating) to achieve stability in air. Depending on process parameters, such as reduction temperatures, pyrohydrolysis and passivating conditions, the  $\text{UO}_2$  powder results with different specific surface areas and O/U ratios. The control of powder properties is done by conventional methods, say BET for specific surface area and gravimetric for O/U ratio.

The BET method has been also carried out by the measurement of the  $\text{N}_2$  mass loss at vacuum microbalances [2,3]. The surface reactivity of some materials has been studied using TG/DTA non-isothermal analysis [4].

The proposition of this work is to design a new method based on simultaneous thermal analysis that could evaluate the BET, O/U ratio, water and uranium content in a single analysis. This seems to be an advance in characterization methods for  $\text{UO}_2$  or other ceramic and metallic powders since the conventional gravimetric and BET methods are hard and time-consuming.

## 2. Experimental

The  $\text{UO}_2$  samples were withdrawn from fluidized-bed experimental production lots, chosen to be dis-

tributed at BET values between 3 and 9  $\text{m}^2/\text{g}$ . One 1.37  $\text{m}^2/\text{g}$  powder obtained from AUC static bed reduction under pure hydrogen at 500°C was also included. The specific surface areas were measured for each powder by BET method (Ströhlein Areameter II). The crystallite sizes were evaluated by step scanning diffraction X-ray profile employing a Philips PW3710 Diffractometer equipped with a  $\text{CuK}_{\alpha 1}$  tube, operated at 40 kV and 40 mA. An Philips software allows the crystallite size determination through the comparison of profile lines broadening related to a standard material (Si). For this purpose, the Scherrer's relationship was utilized [5].

The TG and DSC curves for  $\text{UO}_2$  samples oxidation were carried out by Netzsch STA-409EP simultaneous thermal analyser up to 800°C at 10°C/min under a 150 cc/min synthetic air flow. The sample masses of  $80 \pm 1$  mg were placed in platinum covered crucibles, an empty crucible being the reference. For buoyancy correction,  $\text{U}_3\text{O}_8$  was used in amounts corresponding to the same volume. This last uranium oxide was chosen for reference material due its high density and inertness at oxygen bearing atmospheres.

## 3. Results and discussion

Fig. 1 is a typical TG/DSC simultaneous curve against the temperature for  $\text{UO}_2$  powder. As can be seen, the oxidation consists of two steps, being the first

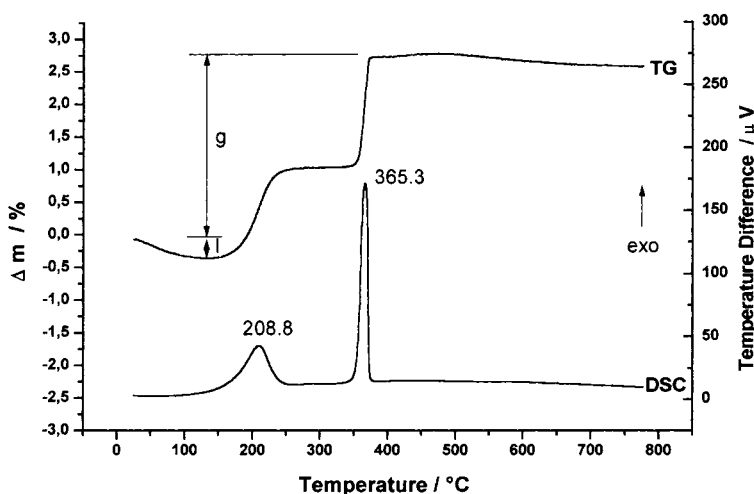


Fig. 1. Typical TG/DSC curve for  $\text{UO}_2$  oxidation in air.

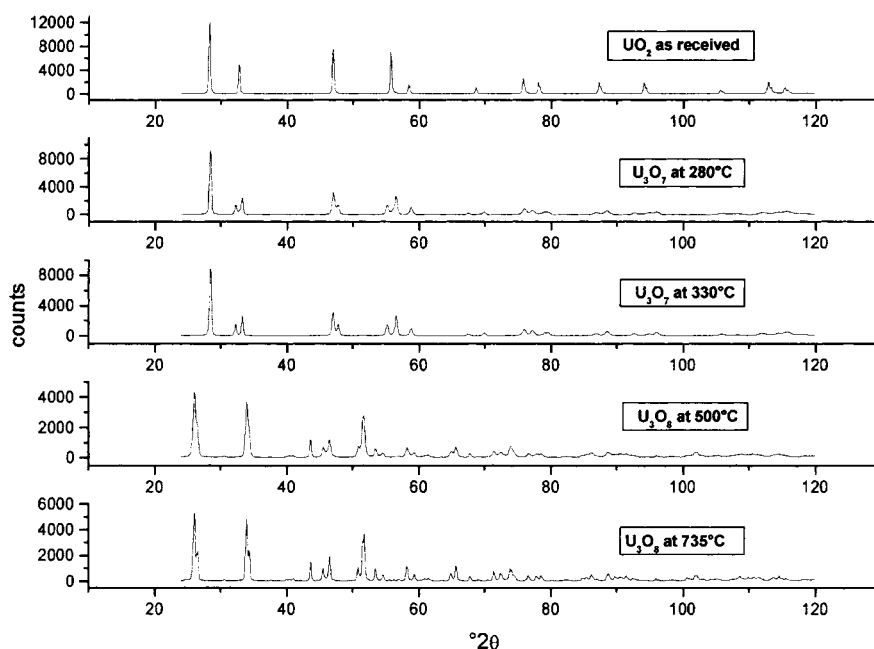


Fig. 2. Phase evolution X-ray profiles during  $\text{UO}_2$  oxidation in air.

weight loss (1) the water and volatile impurities. The O/U stoichiometric ratio was calculated by the equation:

$$\text{O/U} = 2.6667 - 17.5439 \times \frac{g + 1/100}{1 + g/100} \quad (2)$$

The impurity oxides correction was not introduced since the results vary little (total impurities <200 ppm).

The intermediate and final compounds were identified by stopping the thermal analysis at the respectively first and second plateaus and submitting the almost quenched samples to X-ray diffraction analysis. Fig. 2 shows the phase evolution during oxidation from  $\text{UO}_2$  to  $\text{U}_3\text{O}_8$  according to X-ray analysis.

Beginning with  $\text{UO}_2$  (cubic), as the temperature increases, the first plateau was identified as  $\text{U}_3\text{O}_7$  intermediate oxide (tetragonal) and the final phase as  $\text{U}_3\text{O}_8$  (orthorhombic). The first plateau was scanned for diffraction line profiles at two temperatures (280°, 330°C) to verify a small increase in DSC signal. According to measured full width at half maximum (FWHM), the 330°C line profiles were sharper than at 280°C which means higher crystallinity (Fig. 2). The second and final plateaus were also scanned at 500° and 735°C since the TG signal changes over this temperature range. However, as the X-ray profiles

were similar, the signal shift was attributed to buoyancy effects, despite the  $\text{U}_3\text{O}_8$  line profiles at 735°C have been sharper than at 500°C, again suggesting higher crystallinity.

Since the oxidation process depends on surface area for oxygen absorption, as expected the higher powder BET value the lower the oxidation temperature related parameters. The comparison of four samples with BET values ranging from 1.37 to 9 m<sup>2</sup>/g is shown in Fig. 3.

It can be seen that the first DSC peak shift to lower temperatures and the second peak shift to higher temperatures as the powder surface area increases. These effects have been explained in terms of defect structure [6], since the higher the defect concentration, the higher the interstitial volume for oxygen accommodation, leading to lower first temperature oxidation. Also, a higher defect concentration enhances the formation of an intermediate oxide,  $\text{U}_3\text{O}_{7+x}$ , with greater oxygen excess, which hinders the oxygen atoms rearrangement needed to form the  $\text{U}_3\text{O}_8$  nuclei, delaying the second oxidation. The intermediate oxide formed with the higher BET powders would then be more stably related to oxidation. It has to be pointed out that one could not note a higher first TG plateau

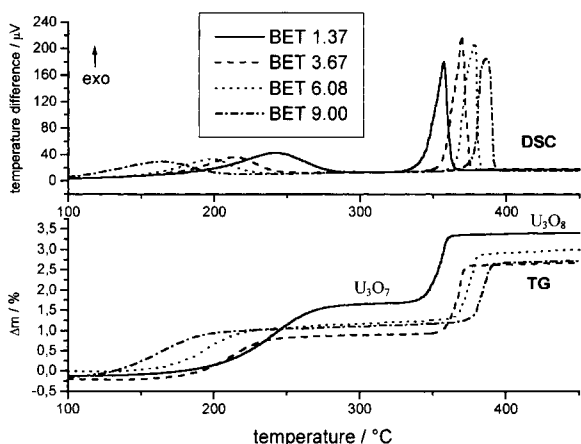


Fig. 3. Comparison of four TG/DSC runs in air flow.

level at higher BET powders because they start from different O/U ratios, being the greater the mass gain as the smaller the O/U ratio is.

Table 1 shows the studied samples named by its BET values with their respective DSC peak temperatures, calculated O/U ratios and crystallite sizes. Examining the DTG plots it was found that the temperature values were almost the same as DSC peaks. Also, the DSC plots do not give any further information for this work purpose. Other parameters like onset temperatures were not found to be suitable for this study since two overlapped reactions can be

Table 1

Sample experimental data on thermal analysis and X-ray diffraction

BET/ (m <sup>2</sup> /g)	O/U ratio	DSC			Crystallite size/nm
		1st peak/°C	2nd peak/°C	2nd– 1st/°C	
1.37	2.07	240.8	357.8	117	86.2
3.67	2.17	214.5	370.6	156.1	84.5
3.70	2.13	208.8	365.3	156.5	60.7
3.93	2.12	199.9	360.3	160.4	—
4.24	2.15	204.3	370.6	166.3	126.0
4.30	2.10	197.5	363.1	165.6	—
4.40	2.12	195.7	362.4	166.7	—
4.68	2.13	203.3	380.9	177.6	97.5
4.80	2.09	195.1	366.6	171.5	—
5.00	2.12	192.8	364.0	171.2	—
6.08	2.15	197.0	379.3	182.3	—
6.17	2.20	192.0	380.7	188.7	46.0
6.94	2.19	194.0	381.3	187.3	105.0
9.00	2.18	163.1	383.8	220.6	—

present at the beginning of the first peak, i.e., water loss and oxidation.

Fig. 4 is a plot including the first and second DSC peak temperatures for each powders as a function of specific surface area (BET). The scattering of data is more pronounced for the second peak temperature than for the first. A better way to visualize the dependence is to consider the difference between the two temperatures, plotted at the same graphic with respect

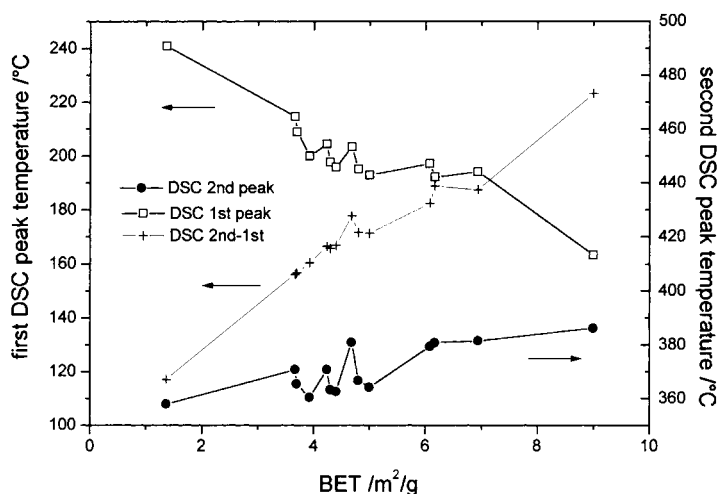


Fig. 4. DSC peak temperatures for  $\text{UO}_2$  oxidation under synthetic air flow.

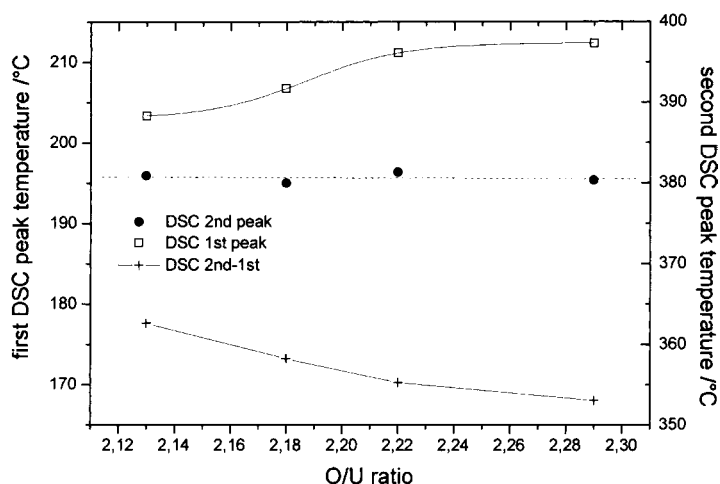


Fig. 5.  $\text{UO}_2$  oxidation temperatures as a function of O/U ratio.

to the left axis. The trace is nearly linear, denoting the scattering being mainly attributed to the inherent changes of the conditions in a thermal analysis. However, there remained deviating points which can be ascribed to unlike starting O/U ratios.

The crystallite size does not appear to affect the DSC peak temperatures, suggesting the diffusion through crystallite boundaries has no influence in the oxidation mechanism. Similarly, for  $\text{UO}_2$  pellets, it has been shown that there is no preferential diffusion through grain boundaries [7].

To investigate the dependence of the oxidation temperatures on O/U ratio, the same powder was submitted to oxidation at  $150^\circ\text{C}$  for different durations of time at the thermal analyser before heating. Since at this temperature level the powder does not change its BET [8], the result is the same surface area powders with different O/U ratios. For this experiment, the programmed heating cycle was as follows: first heating to  $150^\circ\text{C}$  at  $10^\circ\text{C}/\text{min}$ ; static segment at  $150^\circ\text{C}$  for 5, 10 and 30 min; followed by cooling to  $30^\circ\text{C}$  for 1.5 h; and, finally, the full heating to  $800^\circ\text{C}$  at  $10^\circ\text{C}/\text{min}$ . Fig. 5 shows the peak temperatures plot against the O/U ratio.

Although the second peak temperature remains unchanged, the first peak temperature increases as the O/U rises, but the dependence is stronger for smaller O/U ratio values, say, up to 2.21. Thus, the difference between the two temperatures decreases as the O/U ratio increases.

The prime objective of this work is to build a chart where, given a temperature values from a powder TG/DSC analysis, one could determine the specific surface area. Since the temperatures obtained above have shown dependence with powder BET and O/U values, the investigation of the influenced of the last into actual produced  $\text{UO}_2$  powders is needed. Accordingly, it is better to group the powder samples (Table 1) by its O/U values.

Fig. 6 is a plot of grouped samples where can be seen that both the first and second peak temperatures rise for O/U ratio from 2.10 to 2.15, remaining almost unchanged for O/U from 2.15 to 2.19. The first DSC peak increase confirms the results shown in Fig. 5, but the second peak temperature increase is in contradiction to these results, where they were constant. The fact is that the original powder lots are somewhat different, with respect to oxidation behavior, from the powder oxidized at the thermogravimetric apparatus. One possibility is the formation of early  $\text{U}_3\text{O}_8$  nuclei during the static segment into the instrument and, since the second step oxidation is controlled by the rate of nucleation [6,8], the second peak temperatures have remained constant in the experiment as shown in Fig. 5. The increase of the second peaks in the direct heating (Fig. 6) can also be explained by the excess of oxygen atoms which delay the oxidation.

The proposed chart achieved by this work, i.e., the specific surface area versus the difference between the two-oxidation steps, is plotted in Fig. 7. It should be

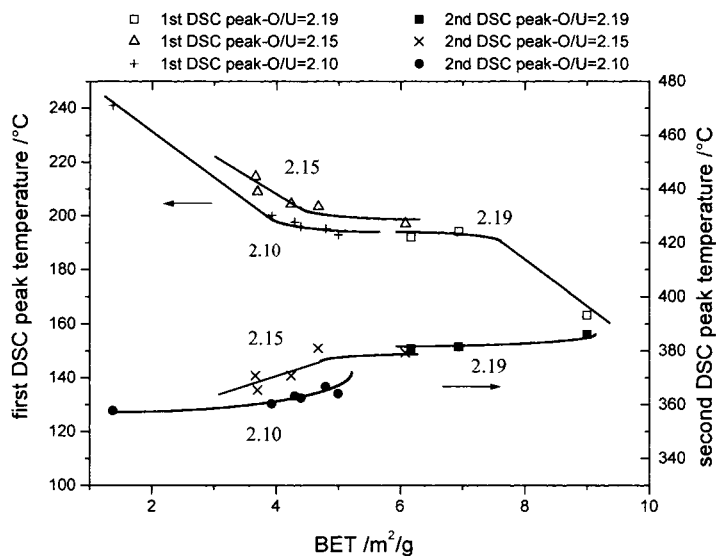


Fig. 6. Oxidation temperatures for  $\text{UO}_2$  samples by O/U ratios.

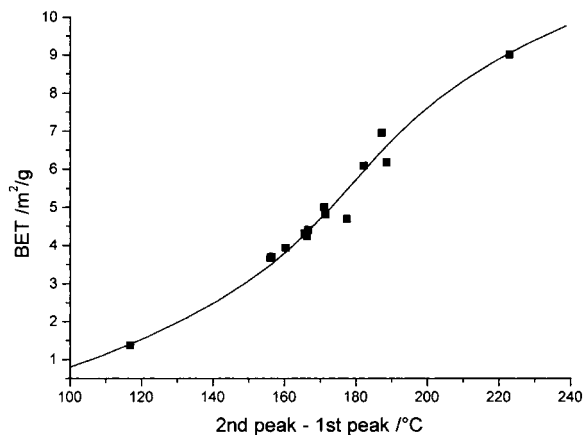


Fig. 7. Chart for specific surface area determination through oxidation temperatures at a TG/DSC apparatus.

noted in Fig. 6 that both temperatures increase with the O/U ratio at the approximately same amounts. Then the difference between the two temperatures is unaffected by the O/U ratio, allowing the chart without correction factors or several iso-O/U traces. The chart is valid for 80 mg  $\text{UO}_2$  powder samples, oxidized at a minimum of  $600^{\circ}\text{C}$  at  $10^{\circ}\text{C}/\text{min}$ , in covered platinum crucibles, under 150 cc/min synthetic air flow, with empty crucible used as the reference.

The same approach can be held with other kinds of powder lots from production or manufacturing plants, especially metallic powders that always undergo oxidation in air. It is also possible to use this work principles to some ceramic powders which react with a gas, such as  $\text{B}_4\text{C}$ .

For  $\text{UO}_2$  powder, the advantage grows in the sense that it can evaluate the O/U ratio, the uranium and water contents and the specific surface area in a single thermal analysis, spending not more than an hour and a few milligrams of radioactive material.

#### 4. Conclusions

1. The proposed method for specific surface area evaluation of a powder, based on reaction temperatures measured at a simultaneous TG/DSC or DSC only apparatus is feasible, leading to confident results, the only requirement being the powder shall react with a gas.
2. Both the DSC peak temperatures for  $\text{UO}_2$  oxidation shift as the powder specific surface area increases: the first peak shifts to lower and the second peak to higher temperatures.
3. The best way to build a calibration chart for  $\text{UO}_2$  surface area is to consider the difference between the two temperature peaks for the two-step oxida-

tion, since it is unaffected by the O/U stoichiometric ratio.

4. The powder crystallite size does not seem to affect the oxidation peak temperatures.

## References

- [1] H.G. Riella, L.G. Martinez, K. Imakuma, *J. Nucl. Mat.* 153 (1988) 71.
- [2] A.W. Czanderna, *Thermochimica Acta* 24 (1978) 345.
- [3] E. Robens, G. Walter, *Thermochimica Acta* 9 (1974) 23.
- [4] T. Ishii, *Thermochimica Acta* 200 (1992) 355.
- [5] A. Guinier, *X-Ray Diffraction*, W.H. Freeman and Company, 1963.
- [6] R. Furuichi, T. Ishii, T. Nakane, *Thermochimica Acta* 33 (1979) 51.
- [7] A.C.S. Sabioni, F. Millot, W.B. Ferraz, IV CGEN, 1996, Rio de Janeiro, Brasil.
- [8] J. Belle, *Uranium Dioxide – Properties and Nuclear Applications*, Chap. 8, U.S. Atomic Energy Commission, 1961.