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Original Scientific Paper

Heat of Immersion of Uranium Dioxide in Water

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Heats of immersion of UO_2 powders in water were determined by calorimetric measurements. The integral heat of immersion at 25°C was found to be 490 erg/cm^2 with an uncertainty $\pm 7\%$ for stoichiometric UO_2 . The value is linearly increasing with increasing non-stoichiometry of the powders up to $790 \text{ erg/cm}^2 \pm 7\%$ for U_3O_8 . The result is not influenced by different particle size distribution, obtained by some different methods of synthesis of UO_2 powders.

INTRODUCTION

In the past fifteen years a great number of investigators reported on physico-chemical characteristics of uranium dioxide, due to its superior performance as a fuel for nuclear power reactors. Specific surface area and surface characteristics were considered to be among the most important factors of different powders, affecting the sinterability and hereby the manufacture of nuclear fuel elements.

The scope of the present work was to determine in the calorimeter the integral heat liberated upon immersion of outgassed oxide samples with different specific surface areas and different O/U ratios in water. The method itself could be used for the determination of specific surface area of powders in general. Further, the results were expected to shed some more light on the mechanism of incorporation of non-stoichiometric oxygen into the oxide lattice. Finally, the results are of interest in view of the proposed use of water vapour to prevent the pyrophoricity of active UO_2 powders¹.

EXPERIMENTAL

Materials

Several samples were prepared by direct reduction of so-called ammonium diuranate (ADU) at 550° to 650°C in hydrogen. Resulting pyrophoric UO_2 powders with surface areas between 1.6 and $9 \text{ m}^2/\text{g}$ were held several hours in a protective CO_2 atmosphere and were afterwards exposed to air. After being in contact with atmospheric oxygen for several days, weeks or months, samples were slowly oxidized to different O/U ratios (samples No. 2, 3, 7 and 8). To reach higher O/U ratios, oxidation was carried out with a definite amount of atmospheric oxygen in a closed system at 150°C (samples No 5 to 11). U_3O_8 samples No. 12 and 13 were obtained by ignition at 600°C in air for several hours. Sample No. 5 was prepared by ignition of ADU in air to U_3O_8 and subsequent reduction to UO_2 in hydrogen at 600°C . To obtain the stoichiometric powder No. 1, the sample was transferred after reduction of ADU in hydrogen atmosphere into the bulbs which were attached to the reduction furnace. The whole system was evacuated to high vacuum and the bulbs were sealed off. Sample No. 4 was prepared by simultaneous hydrolysis and reduction of the product obtained from the reaction of UF_6 with NH_3 in gas phase.

For calorimetric measurements, definite amounts of samples (2 to 6 g) were poured into weighed pyrex bulbs, outgassed at 10^{-5} mm Hg for at least 24 hours at 300°C and sealed off on the outgassing apparatus. The outgassing temperature was accurate to $\pm 10^{\circ}\text{C}$.

Surface Area Measurements

Specific surface areas were measured with a Perkin-Elmer sorptometer² with an accuracy of $\pm 5\%$. Some values were rechecked on the standard B.E.T. apparatus and were found to be within the error of measurement.

Determination of O/U Ratios

Two methods were used: A) Oxidation to U_3O_8 with simultaneous moisture determination. The initial O/U ratio was calculated from the weight gain and it is significant to about $\pm 0.5\%$. B) Magnetic susceptibility measurements³ gave results with an accuracy of $\pm 1\%$.

Calorimeter

A thermistor calorimeter was described by Zettlemayer and coworkers⁴. The fundamental arrangement of our apparatus is similar to the instrument of Lapajne and Dolar⁵. A major modification was the use of a breaking rod for shattering the sealed evacuated sample bulbs. Some important details of the apparatus are as follows: The temperature of the closest surrounding of the calorimeter was kept constant to $\pm 0.001^{\circ}\text{C}$. The temperatures in the calorimeter were measured with thermistor C-7 (A60) (The Veco Corporation, USA). The resistance at room temperature was 2 kilohms $\pm 20\%$ and $R/R_{50} = 5.6$. The thermistor was employed in a bridge circuit, the second arm being an adjustable resistor box (Norma, Wien). The other two arms consisted of two resistors of 100 ohms each. The power was supplied to the bridge from a 6V battery over a potentiometer (6V/2V). The measuring instrument used was a portable galvanometer A 70 (Kipp-Zonen, Delft). Deviations were automatically transferred on to the chart by means of a instrument with a photocell (Nachlaufschreiber nach G. Wilhelmi, Lange, Berlin). On the chart, temperature changes of 0.0004°C within the calorimeter were detected. Since the measurements yielded total effects of 0.03°C to 0.04°C , the accuracy of measurement was within $\pm 1\%$. The calorimeter was calibrated by means of a 30 ohms manganine heater. The heater current and potential difference were determined by comparison, by means of a potentiometer (K 3, Leeds-Northrup) with a standard cell in a circuit described by Sturtevant⁶. The instrument used was a Leeds-Northrup Model 251 IV galvanometer with a sensitivity 10^{-7} A per mm of scale deflection. Oscillations of the potential differences during the heating period were less than $\pm 0.1\%$ and of the current less than $\pm 0.2\%$. The heating time was read on the automatically actuated precision timer with an accuracy of ± 0.1 sec.

Heat of Bulb Breaking

Heat effects of 0.05 to 0.2 cal due to the breaking of the bulb have been reported. Hollabaugh and Chessick⁷ found the parallel effects of evaporation and condensation of water negligible, i.e. within the error of measurements. In our experiments, the best results were obtained by tapping a breaker rod, mounted on the end with three sharp pins. The sample bulbs were accordingly pierced on three different spots simultaneously and totally shattered. The resulting heat effects were determined by several blank runs to be $0.150 \text{ cal} \pm 15\%$. A correction of 0.150 cal was applied to all measurements.

RESULTS

From the shape of the calorimetric curve (amount of heat liberated versus time) for the stoichiometric UO_2 (sample No. 1) evidence was obtained of some slow heat effect besides that of the wetting. The subsequent chemical analyses of $\text{U}^{+6}/\text{U}^{+4}$ ratio revealed the oxidation of the sample from $\text{UO}_{2.00}$ to $\text{UO}_{2.06}$. Accordingly, the experiments were repeated, using deoxygenated water and maintaining a slight overpressure of argon in the calorimeter. The fast

equilibration of the calorimetric curve and chemical analysis ($\text{UO}_{2.01} \pm 0.01$) showed that the oxidation of the former sample was due to the oxygen dissolved in water. Such effects were not observed upon immersion of non-stoichiometric oxide powders, previously exposed to the air for some time. The values of the heat effects are collected in Table I, and point to adsorption rather than chemisorption.

Several subsequent measurements of the amount of heat liberated per gram of each sample were within $\pm 5\%$ (or closer) of the mean value. Since the surface area measurements were found to be within the same limits, both values gave the uncertainty in an individual value of the heat of immersion per unit area of $\pm 7\%$.

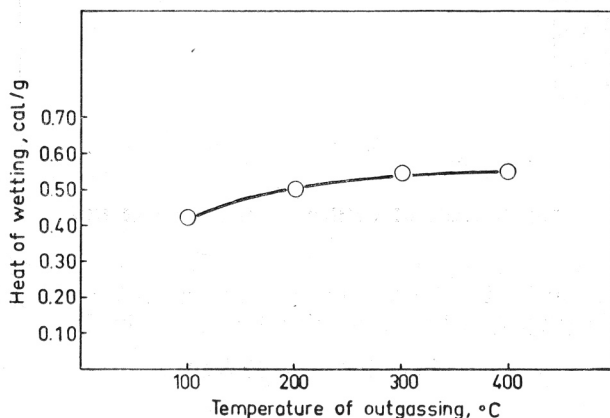


Fig. 1. Heat of wetting as influenced by outgassing temperature.

To ensure that the initial O/U ratio was not changed during the heating and outgassing, the O/U ratio of some samples was determined, after sealing off the bulbs, by magnetic susceptibility measurements. The results were equal within the error of measurement.

The strong influence of outgassing conditions upon the amount of heat liberated on wetting was noticed. The influence of outgassing temperature is shown in Fig. 1. It was further observed that the outgassing time should be at least 20 hours for active powders. Accordingly all samples were outgassed for at least 24 hours at 300°C.

DISCUSSION

Maxima were observed recently⁸ on the heat of wetting versus outgassing temperature curves of SiO_2 and TiO_2 . As it is seen from Fig. 1, the heat effects of UO_2 after a prolonged outgassing at elevated temperatures approach the steady value. Moreover, the data in Table I do not indicate any influence of particle size distribution — at least not in the region of 1.6 to 9 m^2/g — on the amount of heat liberated per unit of surface area. Deviations of heat values on an area basis with increasing specific surface area of TiO_2 samples were tentatively explained by poor crystallinity of fine particles, giving the lower heat effects. Since it is generally known that UO_2 powders

show poor crystallinity, especially in the surface phase of active powders, a linear relationship between the heat of wetting and specific surface area is to be expected.

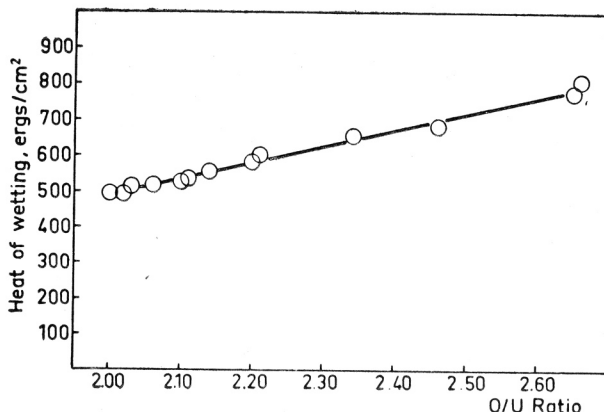


Fig. 2. Heats of wetting vs. O/U ratio of UO_2 .

A strong influence of non-stoichiometry on the heat of wetting was observed. When the heat values, expressed on an unit area basis are plotted versus O/U ratio (Fig. 2) a linear relationship is obtained:

$$h_i = 448 n - 405 \pm 10$$

where

h_i = heat of wetting at 25°C on an area basis (erg/cm²)

n = O/U ratio; $2.00 < n < 2.66$

The parameters of the equation were obtained by the least square method and the error represents the standard deviation.

TABLE I

Heats of immersion (ΔH_i), specific surface areas (S) and O/U ratios of different uranium oxide powders

Sample	ΔH_i (cal/g)	S (m ² /g)	O/U
1	1.051	8.87	2.00
2	0.803	6.80	2.02
3	0.546	4.45	2.04
4	0.205	1.66	2.06
5	0.594	4.71	2.10
6	0.522	4.06	2.11
7	1.188	8.96	2.14
8	1.119	8.15	2.20
9	0.591	4.15	2.21
10	0.458	2.94	2.34
11	0.775	4.76	2.46
12	1.061	5.74	2.65
13	0.696	3.62	2.66

On simply rearranging the equation the specific surface area S (m^2/g) of the uranium oxide powder could be calculated from the measured heat of immersion per gram, ΔH_i (cal/g) and from the determined O/U ratio:

$$S = \frac{4.183 \Delta H_i}{448 n - 405 \pm 10}$$

The method is rapid and gives a good reproducibility. Since the O/U ratio could be measured by various methods with an accuracy of $\pm 0.5\%$ or better, the precision with which the surface area can be determined depends mainly upon the accuracy of the value for the heat of wetting. The latter one is affected in several ways, through weighing, pretreatment, activation and evacuation of the samples besides that of calorimetric measurements. All these factors combined give rise to an error in the heat determination of $\pm 3\%$ to $\pm 5\%$. Accordingly, the value of the specific surface area could be expected to be correct within the same limits.

The linear increase of the heat of immersion with increasing O/U ratio should be a consequence of the structural and chemical characteristics of the surface phases of uranium oxide powders. However, it should be pointed out that all the samples were as received, active powders ($> 2 \text{ m}^2/\text{g}$), *i.e.* no attempt at equilibration has been made. To interpret the results properly, the annealed equilibrated samples were prepared and their structure was checked by the X-ray measurements. The results will be reported shortly.

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IZVLEČEK

Omakalne toplote uranovih oksidov v vodi

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Omakalne toplote praškov uranovega dioksida so merjene v kalorimetru. Integralna omakalna toplota stehiometričnega UO_2 je izmerjena 490 erg/cm^2 z negotovostjo $\pm 7\%$. Vrednost linearno narašča z naraščajočo nestihiometričnostjo praškov in doseže $790 \text{ erg/cm}^2 \pm 7\%$ pri U_3O_8 . Različna porazdelitev velikosti zrn, dobljena z različnimi metodami sinteze oksidnih praškov, ne vpliva na rezultat.

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