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## Heats of Immersion of Uranium Oxides in Water. II. Annealing Experiments\*

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Heats of immersion of original and annealed uranium oxide samples in water were measured. Whereas the unannealed samples gave values in accordance with the already reported results, the values of annealed samples were lower. The structures were determined by the X-ray technique, and the wetting behaviour is discussed on the basis of the present knowledge of uranium oxides.

### INTRODUCTION

In the previous article on this subject<sup>1</sup>, the gradual increase of the heat of immersion values in water with increasing O/U ratio of the uranium oxide samples was reported. This increase should reflect the changes in the outermost surface layers of the oxides. Recent X-ray investigations reported by Hoekstra *et al.*<sup>2</sup> confirmed the formation of  $U_3O_7$  layer on the individual particles of  $UO_2$  in the early stage of oxidation at low temperature. It is the opinion of several authors that the more advanced the oxidation the thicker is the layer of tetragonal  $U_3O_7$ . On the other hand, Anderson<sup>3</sup> found the shape of X-ray diffraction lines to confirm his view of oxygen concentration gradient and formation of solid solution. It is further shown that  $U_3O_7$  phases are not stable when annealed and disproportionate into the cubic  $U_4O_9$  and the orthorhombic  $U_3O_8$  phases.

In order to discuss the observed increase of the heat-of-wetting values in the light of the present knowledge of the structural characteristics of uranium oxides, a new series of experiments was carried out, including annealed samples.

### EXPERIMENTAL

#### Materials

A large batch of uranium dioxide was prepared by direct reduction of the so called ammonium diuranate (ADU) with hydrogen at 600 °C. The powder was held for several hours under the protective  $CO_2$  atmosphere which was gradually replaced by air. After several weeks the O/U ratio approached the value of 2.08. From this single batch samples with different O/U ratios were prepared by low temperature oxidation between 150 °C—420 °C (Table I). Each sample was divided into three portions, two of them being annealed in evacuated sealed bulbs either at 350 °C to 400 °C for two weeks or at 750 °C to 800 °C for one week.

After the annealing and cooling periods the sealed bulbs were opened in air and definite amounts of samples were weighed into small bulbs and evacuated for

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calorimetric experiments. To check the influence of this intermediate step on the heat of wetting values, three samples (Table II, Samples B with O/U ratios 2.00, 2.34 and the last one with 2.62<sub>5</sub>) were annealed in the calorimetric bulbs and the heat values were measured directly without exposing the powders to the atmosphere. The results showed for both procedures the same tendency, *i.e.* lowering of the heat values with annealing.

### Measurements

Calorimetric measurements were carried out in water at 25°C in the same way as previously described<sup>1</sup>. A larger amount of sample, 5 to 6 g, was taken when the surface area was low. Specific surface areas were measured as before, and O/U ratios were determined in the samples already prepared for the calorimetric measurements, *i.e.* after outgassing.

X-ray diffraction data on the oxides were obtained with Cu-K radiation using a camera of 57.7 mm diameter to obtain diffraction patterns on film. A Siemens recording spectrometer was used in certain preparations when increased resolution was desired.

### RESULTS

The results of the structure determinations are given in Table I and are in accordance with the observations reported by other authors<sup>2</sup>. In the samples which were not subjected to annealing three definite structures were observed in the region between  $\text{UO}_{2.00}$  and  $\text{U}_3\text{O}_8$ : cubic, tetragonal and orthorhombic, which, however, does not necessarily excludes the presence of  $\text{U}_3\text{O}_7$  tetragonal phase<sup>2,4,5</sup>.

TABLE I  
X-ray Phase Analysis of Uranium Oxides

O/U Ratio	Oxidtn Temp. (°C)	Phases			
		Cubic a (Å) $\text{UO}_{2+x}$	$\text{U}_4\text{O}_9$	Tetragonal c/a (Å) ( $\text{U}_3\text{O}_7$ )	Orthorhombic a b c (Å) ( $\text{U}_3\text{O}_8$ )
A Sample after preparation					
2.08	—	5.466	—	—	—
2.17	150	5.460	—	—	—
2.25	240	diffuse	—	slight	—
2.34	240	—	—	1.032	detectable
2.63	420	—	—	—	6.71 3.96 4.13
B Samples annealed 14 days at 350°C — 400°C					
2.08	—	5.463	—	—	—
2.17	150	5.460	—	—	—
2.25	240	diffuse	—	1.019	—
2.34	240	—	—	1.019	slight
2.63	420	—	—	—	6.85 3.95 4.14
C Samples annealed 8 days at 750°C — 800°C					
2.08	—	5.486	5.442	—	—
2.17	150	5.467	5.442	—	—
2.25	240	—	5.441	—	detectable
2.34	240	—	5.436	—	slight
2.63	420	—	—	—	6.85 3.96 4.13

TABLE II  
*Heats of Immersion ( $\Delta H_i$ ), Specific Surface Areas ( $S$ ) and O/U Ratios  
of Original and Annealed Uranium Oxides*

O/U	$\Delta H_i$ (cal/g)	$S$ (m <sup>2</sup> /g)	$h_i$ (erg/cm <sup>2</sup> )
A Samples after preparation			
2.10	0.612	4.72	543
2.15	0.579	4.35	557
2.25 <sub>5</sub>	0.653	4.35	628
2.35	0.685	4.47	641
2.50 <sub>5</sub>	0.860	5.37	670
2.63 <sub>5</sub>	0.998	5.21	802
B Samples annealed 14 days at 350° — 400°C			
2.00*	1.105	8.96	516
2.17	0.579	4.34	558
2.26	0.590	4.65	531
3.34*	0.615	4.55	566
2.48	0.702	5.51	533
2.58	1.029	6.73	640
2.62 <sub>5</sub>	0.809	5.25	645
2.62 <sub>5</sub> *	0.597	4.70	532
C Samples annealed 8 days at 750°C — 800°C			
2.09	0.128	0.98	546
2.17	0.151	1.11	569
2.27	0.180	1.35	558
2.35	0.203	1.31	648
2.63	0.184	1.22	631

Samples annealed at 350 °C — 400 °C for two weeks did not show much change. The cubic lines were more diffuse and the tetragonal parameters corresponded to Hoekstra's  $UO_{2.3}$  structure. The  $U_4O_9$ -phase did not appear, perhaps due to the insufficient amount present to be detected by X-ray technique. Samples annealed at 750 °C — 800 °C showed absence of the tetragonal structure in accordance with its reported metastability. Up to  $U_4O_9$ , an increasing amount of the cubic  $U_4O_9$  structure was present in addition to that of  $UO_{2.00}$ . When the O/U ratio increased the increasing amount of the  $U_3O_8$  phase was detectable.

The results of wetting experiments are given in Table II. The surface area values are in accordance with the already known facts, that the low temperature oxidation up to O/U ratio of 2.33 does not influence the specific surface area, whereas the increase of the  $U_3O_8$  content causes some breaking of the particles, accompanied by the specific surface area increase. After annealing at 400 °C the areas remained essentially the same, but after annealing at 800 °C a drastic decrease of specific areas occurred due to sintering.

#### DISCUSSION

The heat-of-immersion values for the unannealed samples followed previously determined<sup>1</sup> straight line (Fig. 1, full line). Annealed samples gave

\* Samples unexposed to air (see Experimental section)

in all cases lower values. The experimental points for the annealed samples at 400 °C and 800 °C are close together.

As for the unannealed samples, the linear increase of their heat-of-wetting values with the increasing oxygen content casts some doubt as to the existence of a uniform surface layer of  $U_3O_7$ . However, the observed results cannot rule

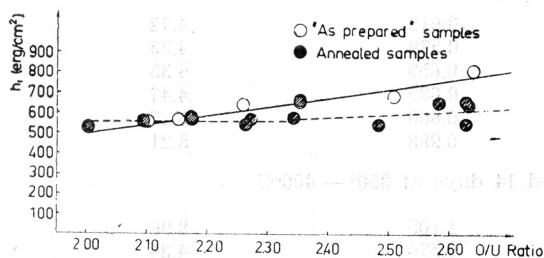


Fig. 1. Heats of wetting versus O/U ratios of »as prepared« and annealed uranium oxides.

out this possibility, since if such uniform layer existed, it should be under considerable strain due to the difference in density, as has already been pointed out by Anderson<sup>6</sup>. The strain can cause the increase of heat values.

The results of wetting of annealed samples can be reconciled with the X-ray data in the following way. On annealing, a  $U_4O_9$  cubic structure was formed on the surface of  $UO_2$ . Schaner<sup>7</sup> observed by metallographic technique the nucleation of  $U_4O_9$  phases on the boundaries of  $UO_2$  particles, which causes a release of strains in the course of annealing. Thus, the surface may behave uniformly toward wetting irrespective of the oxidation stage. The heat-of-wetting values are correspondingly the same. Oxidation beyond an O/U ratio of 2.25 caused the  $U_3O_8$  orthorhombic structure to appear. Due to the great difference in density (11 g per ccm for  $UO_2$  vs. 8.3 g per ccm for  $U_3O_8$ ) breaking of particles occurred as observed by an increase in the surface area (see Table II). Some slightly higher experimental values observed on wetting of the annealed oxides with greater O/U ratios, if not due to the scattering of the data, might reflect the presence of  $U_3O_8$ .

Another cause for lowering the heat-of-wetting values of the annealed samples might also be taken into consideration.  $UO_3$  has a heat of hydration at least 4 to 5 times higher than those of  $U_3O_8$  or  $UO_2$ . Thus even small amounts of  $UO_3$  formed during the low temperature oxidation, yet undetectable by the X-ray or the infrared technique, could greatly increase the apparent heats of immersion. Experiments are under way to check this assumption.

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### IZVLEČEK

#### Omakalne toplote uranovih oksidov v vodi. II. Poskusi s tempranjem

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Merjene so omakalne toplote tempranih in netempranih uranovih oksidov v vodi. Rezultati netempranih oksidov so v skladu z že poročanimi vrednostmi, po tempranju pa so vrednosti nižje. Kristalografske strukture so določene z rentgensko tehniko. Doseženi rezultati so primerjani z znanimi karakteristikami uranovih oksidov.

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