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Abstract

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On the Study of the Conditions for the Formation of Various Modifications of Uranium Trioxide

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One amorphous and five crystalline modifications of uranium trioxide are known (hexagonal α-, monoclinic γ-, cubic δ-UO_3, as well as β- and ε-UO_3, whose unit cells have not been established) ([1,2]). Oxidation of uranium oxide-oxide at elevated oxygen pressures in the temperature range 450–700° yields α-, β-, and γ-UO_3. The conditions for formation of the α- and β-phases from U_3O_8 have not been sufficiently clarified. The δ-UO_3 phase was obtained as a result of the thermal decomposition of uranyl hydroxide β-$UO_2(OH)_2$ ([3]). Oxidation of U_3O_8 by ozone, nitrogen dioxide, or atomic oxygen at temperatures of 200–350° gives ε-UO_3. Thermal decomposition of some compounds of hexavalent uranium ($UO_4 \cdot 2H_2O$, $(NH_4)_2U_2O_7 \cdot nH_2O$, $UO_3 \cdot 2H_2O$) usually leads to the formation of amorphous UO_3, but in some cases crystalline α-, β-, or γ-phases, respectively, may be obtained ([4,1]).

The aim of our work was to determine the conditions of formation and stability of various modifications of UO_3. The oxidation of uranium oxide-oxide was studied over a wide range of temperatures and oxygen pressures; the interaction of various oxidants (ozone, nitrogen dioxide, oxygen under pressure) with the defective hexagonal phase α-UO_{3-x}* formed upon heating amorphous uranium trioxide UO_3 (A) to 525° in air was also investigated. In addition, the crystallization of amorphous trioxide and the thermal decomposition of uranyl hydroxide α-$UO_2(OH)_2$**, as well as ammonium diuranate $(NH_4)_2U_2O_7 \cdot nH_2O$, were investigated. Amorphous trioxide was obtained by calcining uranium peroxide dihydrate (400°), ammonium diuranate by the action of an excess of ammonia on a solution of uranyl nitrate, and α-uranyl hydroxide by heating UO_3 (A) or $UO_3 \cdot 2H_2O$ with water at a temperature of 250° in an autoclave.

The data obtained (Table 1) show that oxidation of U_3O_8 to α-UO_{3-x} proceeds much more rapidly than further oxidation of the latter to UO_3. Thus, in experiment No. 6, after 30 hours at a temperature of 500–550° and an oxygen pressure of 90 atm, all U_3O_8 was oxidized, whereas α-UO_{3-x} was one of the principal phases; in experiment No. 16, after 80 h under the same conditions, the initial α-UO_{3-x} partially remained unchanged. This conclusion agrees with the observation ([2]) of the low reactivity of $UO_{2.9}$ oxide.

The phase obtained from U_3O_8 at low temperatures is ε-UO_3. It is formed in experiments with oxygen under pressure below 440–450°, and in experiments with ozone or nitrogen dioxide below 350°. The formation of ε-UO_3 upon oxidation of U_3O_8 under oxygen pressure had not previously been detected.

The first bright lines of the X-ray diffraction pattern of ε-UO_3 correspond to the 001, 110, and 200 lines of uranium oxide-oxide; the remaining U_3O_8 lines are split in the Debye pattern of ε-UO_3. Using the principle of homology, it was possible to index all lines of ε-UO_3 in a triclinic cell with parameters $a = 4.002$; $b = 3.841$; $c = 4.165$ Å; $\alpha = 98°17'$; $\beta = 90°33'$; $\gamma = 120°28'$; $z = 1$; $\rho_{\text{X-ray}} = 8.73$; $\rho_{\text{pycn}} = 8.54$ ([1]). The values of the parameters a, b, and γ are very close to their values for U_3O_8 in the corresponding aspect, and the distortion of the cell is expressed only in the deviation of the angles α and β from 90°.

* $x \approx 0.1$.

** Rhombic, $a = 10.23$; $b = 6.89$; $c = 4.28$ Å.

Table 1

Results of phase and chemical analysis of uranium trioxide obtained by various methods

No.	Starting substance	Treatment method	Time, h	Composition of oxide obtained*	Phase composition: main phase	Phase composition: impurities
1	U_3O_8	NO_2, 300°	15	–	ε-UO_3	α-UO_{3-x}
2	U_3O_8	O_3, 250—350°	5	$UO_{2.98}$	ε-UO_3	U_3O_8 possibly; α-UO_{2-x}
3	U_3O_8	O_3, 350°; 150°	3; 30	$UO_{3.03}$	ε-UO_3	α-UO_{3-x} (traces)
4	U_3O_8	55 atm O_2, 650°	5	$UO_{2.86}$	γ-UO_3, U_3O_8	none
5	U_3O_8	100 atm O_2, 680—700°	20	$UO_{3.00}$	γ-UO_3	none
6	U_3O_8	90 atm O_2, 500—550°	30	$UO_{2.97}$	α-UO_3, α-UO_{3-x}	β-UO_3, γ-UO_3
7	U_3O_8	230 atm O_2, 450—470°	320	$UO_{3.00}$	α-UO_3	β-UO_3, γ-UO_3

No.	Starting substance	Treatment method	Time, h	Composition of oxide obtained*	Phase composition: main phase	Phase composition: impurities
8	U_3O_8	120 atm O_2, 450°	60	$UO_{2.98}$	α-UO_3, α-UO_3-x	β-UO_3, γ-UO_3, U_3O_8
9	U_3O_8	230 atm O_2, 420—440°	220	$UO_{2.99}$	ε-UO_3	β-UO_3, γ-UO_2
10	U_3O_8	250 atm O_2, 410—430°	210	$UO_{3.00}$	ε-UO_3	β-UO_3, γ-UO_3
11	α-UO_3-x	NO_2, 325°	5	–	α-UO_3-x	not identified
12	α-UO_3-x	NO_2, 450°	5	–	α-UO_3-x	none
13	α-UO_3-x	NO_2, 450°	25	–	ε-UO_3	α-UO_3-x
14	α-UO_3-x	O_3, 250—350°	5	$UO_{2.99}$	α-UO_3	none
15	α-UO_3-x	O_3, 250°; 20	25; 25	$UO_{2.98}$	α-UO_3	none
16	α-UO_3-x	115 atm O_2, 500—550°	80	$UO_{2.97}$	α-UO_3	α-UO_3-x, β-UO_3, γ-UO_3
17	UO_3 (A)	270 atm O_2, 490°	120	$UO_{3.00}$	γ-UO_3	none
18	UO_3 (A), UO_3-x	270 atm O_2, 480—500°	120	$UO_{3.00}$	α-UO_3	γ-UO_3, α-UO_3-x
19	α-$UO_2(OH)_2$	370° slow heating; 400°	200; 240	$UO_{3.00}$	α-UO_3	none
20	$(NH_4)_2U_2O_7$ nH_2O	Rapid heating to 500°	15	–	β-UO_3	α-UO_3-x or U_3O_8
21	$(NH_4)_2U_2O_7$ nH_2O	Slow heating to 400°	100	–	UO_3 (A)	none

No.	Starting substance	Treatment method	Time, h	Composition of oxide obtained*	Phase composition: main phase	Phase composition: impurities
22	$(NH_4)_2U_2O_7 \cdot nH_2O$	250°; same, 350°; same, 400°; same, 500°; same, 520°	24; 48; 24; 48; 24	–	UO_3 (A)	none
23	$(NH_4)_2U_2O_7 \cdot nH_2O$	Slow heating to 700°	4	–	U_3O_8	γ-UO_3

* The chemical composition of preparations containing significant impurities of bound nitrogen or water is not given.

Upon oxidation of U_3O_8 or α-UO_{3-x} under oxygen pressure in the temperature range 450—550°, the principal phase obtained is α-UO_3. In all our experiments the β-phase was not formed as the principal one, but was present together with the γ-phase as an impurity to the ε- or α-modification (except experiment No. 18). In experiment No. 18 (starting substance—a mixture of UO_3 (A) and α-UO_{3-x}), β-UO_3 was not detected; possibly it was present in an amount below the sensitivity limit of X-ray phase analysis, since from UO_3 (A) under analogous conditions pure γ-UO_3 is formed (experiment No. 17). This latter fact is not consistent with the literature data ([1]), where formation of α-UO_3 was noted. In experiments with increased oxygen pressure, formation of the γ-phase was observed over the entire temperature range studied, and not only above 550°, as indicated in ([1]).

From consideration of the results obtained, it may be concluded that the formation of one or another modification of uranium trioxide is influenced by the structure of the starting substance, the calcination temperature, and, in the case of thermal decomposition, also the rate of heating. Thus, upon slow decomposition of ammonium diuranate (experiments Nos. 21 and 22) an amorphous phase is formed, whereas as a result of comparatively rapid heating (experiment No. 20) β-UO_3 is formed, owing to the closeness of its structure to the structure of the starting uranate.

Most of the lines of the roentgenogram of β-UO_3, including all the strong lines, could be indexed in a rhombic subcell with parameters $a =$

$= 6.866 \pm 0.003$ Å, $b = 3.906 \pm 0.001$ Å; $c = 7.14 \pm 0.004$ Å, which is close to the parameters of ammonium diuranate $a = 4.03\sqrt{3}$ Å, $c = 7.25$ Å. The parameters of the true unit cell of β-UO_3 could not be established.

The thermal decomposition of α-$UO_2(OH)_2$ was carried out at a temperature of 370–400°. Under these conditions the formation of γ-UO_3 was to be expected ([3]). In our experiment α-UO_3 was obtained, which can also be explained by the difference in the rate of heating.

Oxidation of uranium dioxide usually is accompanied by the formation of ε-UO_3 below 450° and α-UO_3 in the interval 450–550°. This is probably explained by the phase transformation of uranium dioxide in the interval 400–500° ([5]). ε-UO_3 has a distorted U_3O_8 structure and therefore forms below the temperature of transition of U_3O_8 to the hexagonal modification, whereas from hexagonal U_3O_8 and UO_{3-x} hexagonal α-UO_3 is obtained. Amorphous uranium trioxide crystallizes with formation of γ-UO_3, if decomposition to UO_{3-x} does not occur.

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Note: Figure translations are in progress. See original paper for figures.