UNCLASSIFIED

AD 402 595

Reproduced

by the

DEFENSE DOCUMENTATION CENTER

FOR

SCIENTIFIC AND TECHNICAL INFORMATION

CAMERON STATION. ALEXANDRIA. VIRGINIA

UNCLASSIFIED

63- 9

TRANSLATION

OXIDATION OF URANIUM DIOXIDE

By

V. G. Vlasov and A. F. Bessonov

FOREIGN TECHNOLOGY
DIVISION

AIR FORCE SYSTEMS COMMAND

WRIGHT-PATTERSON AIR FORCE BASE

OHIO

TISIA
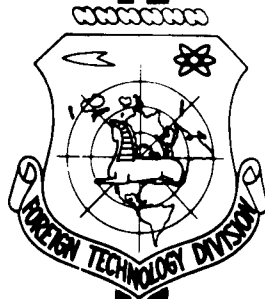
UNEDITED ROUGH DRAFT TRANSLATION

OXIDATION OF URANIUM DIOXIDE

BY: V. G. Vlasov and A. F. Bessonov

English Pages: 14

SOURCE: Russian Periodical, Izvestiya Vysshikh
Uchebnykh Zavedeniy, Tsvetnaya Metallurgiya,
Nr. 5, 1962, pp 113-122

S/149-62-0-5

PREPARED BY:

TRANSLATION DIVISION
FOREIGN TECHNOLOGY DIVISION
WP-AFB, OHIO.

Oxidation of Uranium Dioxide

by

V. G. Vlasov and A. F. Bessonov

Uranium dioxide plays an important role in the technology of obtaining metallic uranium, and is also used in role of nuclear fuel [1-3]. In reactors it functions in oxidizing-reducing conditions, and that is why the study of the oxidation process of uranium dioxide is of greater practical importance. On the other hand the reactions of UO_2 oxidation represent extremely interesting examples for studying the kinetics and mechanism of processes in solid state.

The existing viewpoints with respect to the mechanism of uranium dioxide oxidation at a temperature of over 80° and the phase conversions taking place thereat can be approximately divided into four groups:

Perio and co-workers and a number of other investigators [4-7] assume, that in the process of oxidation is rapidly formed a new phase, through which diffusion of metal cations does take place, diffusion of cations travelling to the surface. The phase conversion scheme assumed by them has the form of $UO_2 \rightarrow U_4O_9 \rightarrow U_3O_7 \rightarrow U_3O_8$;

Anderson and coworkers [8-10] assume the following scheme of phase conversions $\alpha UO_2 \rightarrow \alpha UO_{2+x} \rightarrow \beta UO_2 \rightarrow U_3O_7$; Aronson, Roof and Belle [11] evaluating the mechanism of dioxide oxidation assume the scheme $\alpha UO_2 \rightarrow \alpha UO_{2+x} \rightarrow U_3O_7 \rightarrow U_3O_8$; Blackburn and coworkers [12] assume that during the oxidation of uranium dioxide on the surface is immediately formed a tetragonal phase U_3O_7. The process is limited by oxygen diffusion through that phase. They give the following scheme of phase conversions $\alpha UO_2 \rightarrow U_3O_7 \rightarrow U_3O_8$.

In this way there is no harmony in the views pertaining to the mechanism of the

oxidation of uranium dioxide and the scheme of phase conversicns. In this connection it is necessary to further accumulate experimental data.

It is known [13-15] that, as a rule, the addition of alkali metal carbonates acceler- rates the processes of reducing with hydrogen, carbon monoxide and solid carbon.

Informations on the effect of carbonates and foreign oxides on the rate of oxida- tion of lower oxide into higher, have not been discovered in literature. The knowledge of the mechanism of effect of small additions is of absolute practical and theoret- ical importance.

In this report are given results of kinetic oxidation of uranium dioxide in various gaseous media. Simultaneously was investigated the effect of admixtures of alkali metal carbonates and ThO_2, ZrO_2 and TiO_2 oxides on the kinetic : characteristics of UO_2 oxidation process.

The properties of powderous uranium dioxide depend to a large extent upon the methods of its obtainment [2,16]. In our experiment was investigated inactive uranium dioxide, stable to air at room temperature. It was prepared by reducing uranoso-uranic oxide with hydrogen (at a pressure of 800 mm Hg) at $600°$ for a period of ten hours. After storing in open   air at room temperature   the composition of the dioxide was $UO_{2.04}$. Accuracy of determining O:U ratio was 0.01.

The investigation was made in a high vacuum installation (fig.1) having an arrange- ment for continuous control of change in weight of the batch. The installation al- lowed to create in the reaction space in any sequence a vacuum, oxidizing and reducing medium.

Additions of bicarbonates or oxides of foreign metals in the amount of 6% of uranium dioxide weight were pulverized in an agate mortar and thoroughly mixed with UO_2. The crucible with uranium dioxide batch ($\approx$ 300 mg, specific surface of powder 2,7 m^2/g) or a mixture of same with the addition was placed in the reaction tube and from the system was vacated the air at room temperature to 10^{-4} mm Hg. The batch was then dries at $120°$ until the change in weight was stopped and a residual pressure
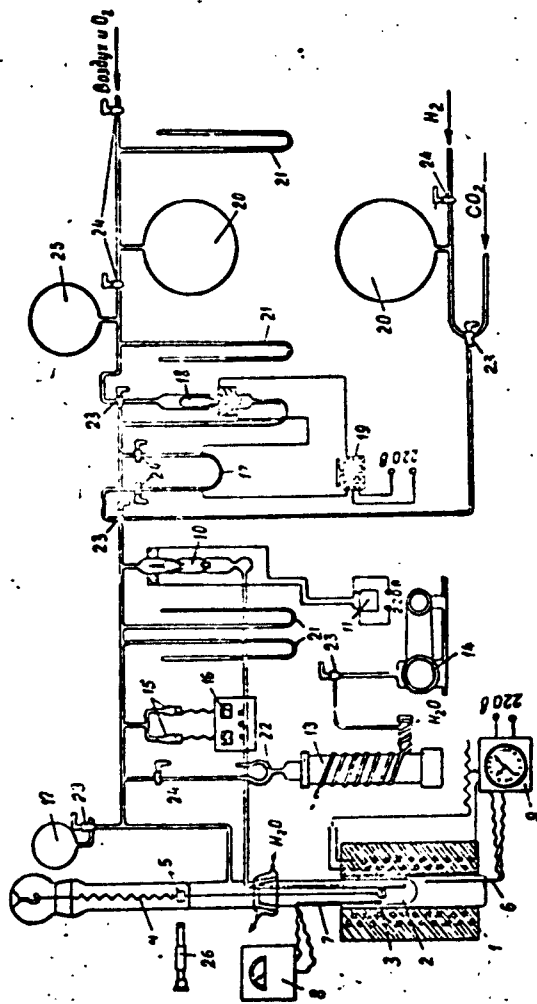
of the order of 10^{-4} mm was attained.

Fig.1. Principal scheme of experimental high vacuum installation: 1—hoisting tubular electric oven; 2—quartz reaction tube; 3— quartz crucible with batch; 4—spring indicator; 5—weight indicator and mica-screen ; 6,7—movable thermocouples to measure temperature of oven and sample; 8—millivoltmeter; 9—electron automatic potentiometer EPD-17; 10—circulation pump; 11—current circuit breaker; 12—flask for measuring volumes of system; 13—diffusion pump TSVL-100; 14—Forevacuum rotational pump RVN-20; 15—manometric tubes LM-2 and LM-2; 16—vacuummeter; 17— U-shaped pressure control tube; 18—pressure regulator; 19—lab autotransformer; 20—gas consumption flask; 21—mercury pressure gage; 22— trap (for freezing out with liquid nitrogen); 23— three-speed vacuum screen; 24—two-speed vacuum screen; 25—capacity of pressure regulator; 26—reading microscope.

After this the oven was taken out from the reaction tube , heated to given temperature and again moved into the tube. Temperature was controlled with an accuracy of $\pm 2°$.

When in the reaction space was established a given temperature, into the oven was supplied the gas-oxidizer at a certain definite pressure and the reading of weight indication time began. Pressure in the reaction space was kept constant with an accuracy of ± 0.5 mm Hg. The actual rate of the process was determined graphically by the tangent of the angle of inclination of the tangent and dependence curve of the degree of oxidation upon time. The apparent energy of activation was calculated by the Arrhenius equation. X-ray structural analysis of intermediate and finite products of oxidation was made by the Debye-Sherer method.

The effect of temperature on the kinetics of uranium dioxide oxidation with air ($p=200$ mm Hg) with oxidizer-gas circulation in the reaction space, was investigated in the range of from 165 to 800°. At 165-260° uranium dioxide oxidized into $UO_{2.36\pm0.05}$ and at 270-800° into $UO_{2.67}$ (U_3O_8). Temperatures of 260 and 800° are characteristic by the fact that after the attainment of indicated degrees of oxidation further oxidation has not taken place, in spite of the fact that the experiment continued for another 10 hrs. The results of investigations are shown in fig.2. In the range of from 165 to 200° the initial period of oxidation is quite well described by equation

$$\Delta g = k_1 \tau, \qquad 1$$

where Δg - gain in weight of batch; $\tau=$ time from beginning of experiment; k_1-constant.

Starting with a certain moment of time τ_0 the process is subjected to parabolic time law

$$\Delta g = \Delta g_0 + k_2 \sqrt{\tau}, \qquad 2$$

where Δg_0 - gain in weight of batch to the moment of time τ_0; k_2-constant.

At 270-390° on the curves in the coordinates the degree of oxidation-time exist horizontal sections at $O:U = 2.36 \pm 0.05$. On the rate/degree of oxidation dependence curves are observed several minimums: the first one at 50%, second -88%; third - 97%. Finally, approximately at 37% of oxidation the curves have weakly pronounced

inflections.

The dependence of the rate of the process upon air pressure was investigated at 340° (fig.3). In the interval of summary compositions of solid phases $UO_{2.04}$-$UO_{2.36}$± 0.05 at an air pressure of 2.5-100 mm Hg, is valid equation.

$$v = a_1 p \quad 3$$

In this zone of solid phase compositions , at pressures of 100-600 mm Hg the rate of oxidation $v = a_2 \sqrt{p}$.

At a more complete oxidation the rate/pressure dependence is observed only at values of the latter of less than 30 mm Hg.

See Attach page 5a for Figure 2

Fig.2.Oxidation isotherms of uranium dioxide with oxygen(atmospheric) At constant air pressure of 200 mm Hg).

The values of apparent energy of activation at various degrees of oxidation were:

Degree of Oxidation,%	28	37	52	54	74	88	90
Activation energy kcal/mol	34.6	27.8	43.8	27.8	34.6	45.6	39.4

The experimentally found uranium dioxide density was found to be equal to 10.8 g/cm^3, and of the lower and higher oxides, obtained as result of oxidation - 8.37 g/cm^3. The volume of lower and higher oxide in the crucible was 1.3 times great-
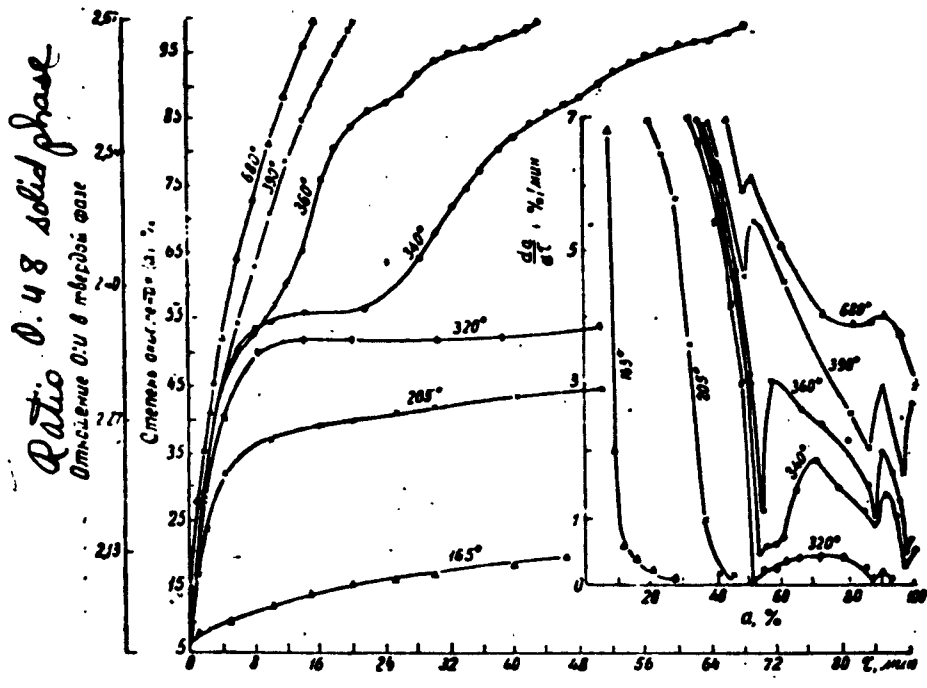
Figure 2

er than the volume of the initial dioxide.

The kinetics of UO_2 oxidation with oxygen was investigated at a range of from 125 to 330° at p_{O_2}=100 mm Hg. Results are given in fig.4. At 125-145° oxidation goes into UO_{2+x}, where $x < 0.25$. In the range from 150 to 200° is observed a sudden oxidation into $UO_{2.60}$ oxide after which the reaction is practically off. At 200-260° there is also a sudden occurrence of the process with the formation of $UO_{2.60}$ fur-

ther oxidation takes place at very low rate . In the range from 260-300° the oxidation into $UO_{2.67}$ is rapid (at 300° it is off within one minute). Oxidation of uranium dioxide, preoxidized by 15-19%, is also sudden, but the value of the jump is somewhat lower.
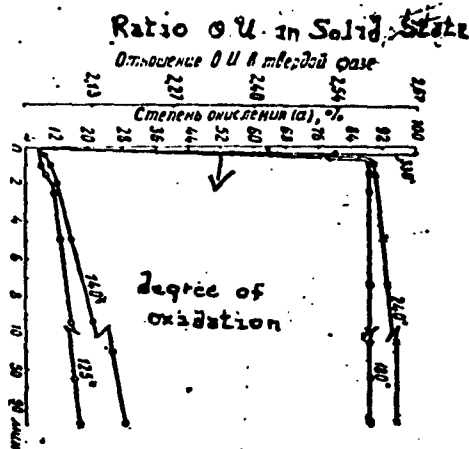

Fig.4. Dependence of the degree of uranium dioxide oxidation upon the duration of the experiment at various temperatures (Oxygen pressure 100 mm Hg).

The effect of alkali metal carbonate admixtures on the kinetic characteristics of uranium dioxide oxidation by air was investigated at 185-330°. The air pressure in all experiments was 400 mm Hg. Results are given in fig.5. At 185° the addition of K_2CO_3 reduces somewhat the rate of the process, the nature of the kinetic curve remains unchanged, just as without the addition.

At 330° additions of carbonates considerably accelerate oxidation after attaining in solid phases a ratio of O:U = 2.36 ± 0.05. Simultaneously there is a change in the nature of degree of oxidation/time dependence: the horizontal section disappears,
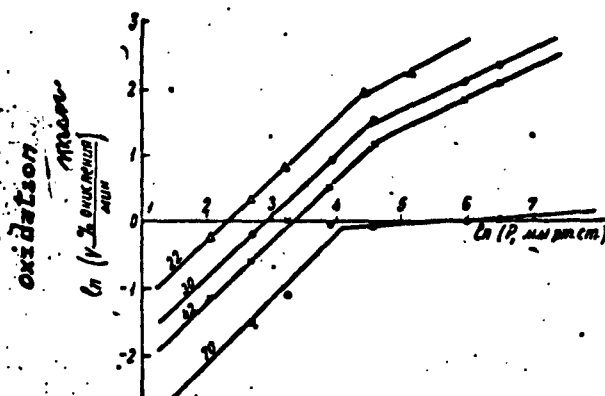
the section which occurs during oxidation without addition. The accelerating effect of carbonate additions rise in the series K_2CO_3, Na_2CO_3, Li_2CO_3.

In addition the following experiments were made. Pure uranium dioxide and dioxide with an admixture of potassium carbonate was first annealed in vacuo (10^{-4} mm Hg) at 900° for a period of two hours. Oxidation followed at 330°. In this case introduction of potassium carbonate slows down the process.

Investigated was also oxidation of uranium dioxide in presence of titanium, zirconium and thorium dioxide admixtures.

At first uranium dioxide with and without admixtures oxidized at 330° (fig.6). The rate of the process in presence of admixture rises considerably from the moment when further oxidation of the $UO_{2.36\pm 0.05}$ phase begins; the accelerating effect rises

in the following sequence: ThO_2, ZrO_2, TiO_2. In the presence of ThO_2, ZrO_2 additions there is a sharp reduction in horizontal section of the degree of oxidation curve. When TiO_2 is added this section disappears completely, and oxidation is somewhat accelerated even at O:U ratios in solid phases of less than 2.36 ± 0.005.
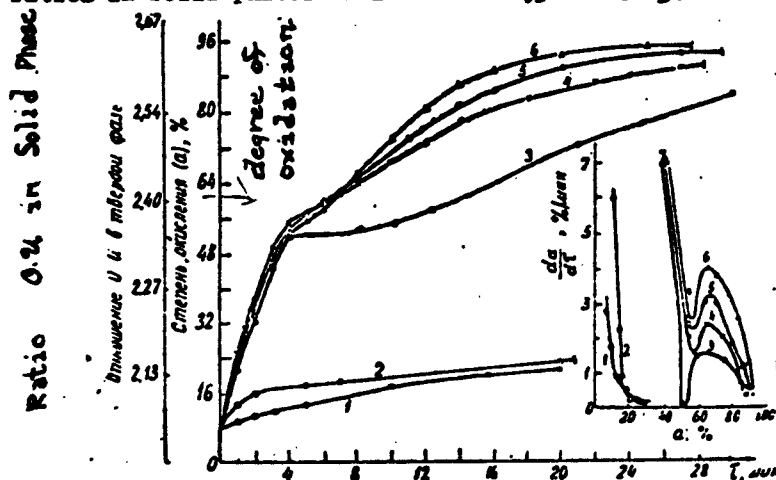
Fig.5. Isotherms of uranium dioxide oxidation with atmospheric oxygen at 185° (1 and 2) and at 330° (3-6) without additions (2 & 3) with additions: K_2CO_3 (1 & 4); Na_2CO_3 (5); Li_2CO_3(6)...

In subsequent experiments with uranium dioxide with and without admixtures the sample was first calcined (annealed) in vacuo (10^{-4} mm Hg) at 900° for a period of two hours. Oxidation was also carried out at 330°. In this case the addition of ThO_2

slows down the process of UO_2 oxidation into $UO_{2.36\pm0.05}$ and accelerates further oxidation. Addition of TiO_2 reduces somewhat the rate of the process during transformations from $UO_{2.36\pm0.05}$ to $UO_{2.67}$.
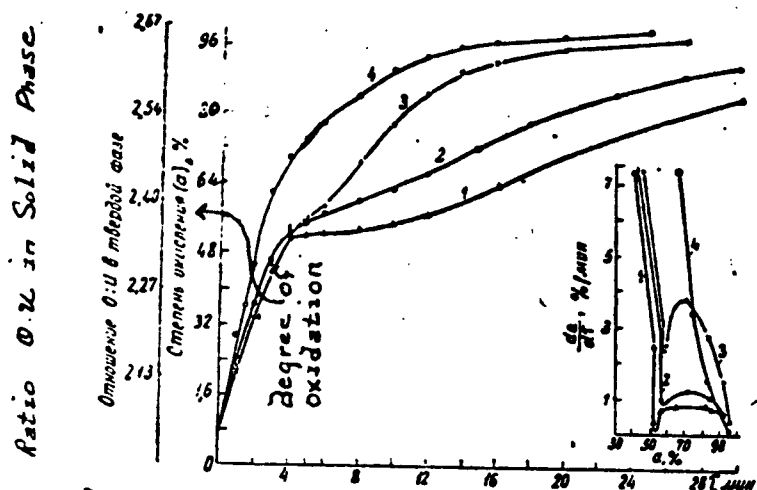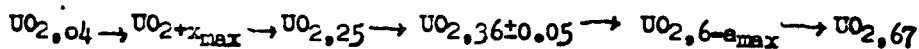

Fig.6. Isotherms of uranium dioxide oxidation with atmospheric oxygen at temperature of $330°$ without admixture (1), with admixtures: ThO_2 (2); ZrO_2(3); TiO_2(4).

Data of kinetic investigations, supplemented with results of x-ray structural analysis, allow to suggest the following scheme of phase conversions for the range of $260-390°$:

$$UO_{2.04} \longrightarrow UO_{2+x_{max}} \longrightarrow UO_{2.25} \longrightarrow UO_{2.36\pm0.05} \longrightarrow UO_{2.6-a_{max}} \longrightarrow UO_{2.67}$$

which is found to be in perfect agreement with the sequency principle of chemical conversions as stated by A.A.Baykov [17].

In the first stage of oxidation the enrichment of solid phase with oxygen takes place without phase conversions. the process develops in the presence of one condensed phase, the composition of which changes continuously from $UO_{2.04}$ to $UO_{2+x_{max}}$ (value x_{max} depends upon temperature). Further reaction with oxygen leads to origination of new phase $UO_{2.25}$ and the conversion is realized in the presence of two condensed constant composition phases. From the view point of structural changes on these stages takes place the introduction of oxygen into the cubical lattice of uranium

dioxide (orderless in first stage and ordered in second) [18-20]. The third stage of oxidation is connected with the conversion of $UO_{2.25}$ oxide into $UO_{2.36\pm0.005}$.

It is evident from the above mentioned kinetic curves (see fig.2,5,6),that there is a whole series of tetragonal phases ($UO_{2.32}$, $UO_{2.37}$, $UO_{2.41}$) which is in conformity with data of other investigators [8, 11, 12, 21 and 22]. The slight bent at a degree of oxidation $\cong 37\%$ is explained, apparently, by the fact, that the tetragonal phase originates by adding oxygen atoms into the $UO_{2.25}$ structure (U_4O_9) with considerable crystallostructural changes.

The direct proportionality of the rate of the process to pressure ($v=a_1p$) at $p = 2.5 - 100$ mm Hg points toward the Knudsen mechanism of oxygen transfer in channels of very small cross section. The appearance at pressures of over 100 mm Hg of a dependence $v = a_2\sqrt{p}$, apparently can be explained by the fact, that the oxygen molecule during conversion into condensed phase dissociates into atoms [23,24].

The physical picture of the following stages of oxidation can be given within frames of new phase nuclei formation processes and in processes of their further growth. Horizontal section on curves fig.2, 5 and 6 correspond to the induction period, the duration of which rises with /drop/ in temperature and pressure. The $UO_{2.6\pm x}$ phase forming in the process of oxidation has lower density, that is why its volume in comparison with the volume of the initial dioxide increases and it has greater porosity and better gas permeability which facilitates the delivery of oxygen to the place of reaction.

In the range of from 165 to 260° the process of oxidation corresponds to three first stages of the above described scheme , whereby the phase ratios are here less clearly expressed. Above 400° tetragonal phases become disproportioned into $UO_{2.25}$ and $UO_{2.6-x_{max}}$ [18,25] and consequently the process of uranium dioxide oxidation in the zone of from 400-800° can be represented by the following scheme

$$UO_{2.04} \longrightarrow UO_{2+x_{max}} \longrightarrow UO_{2.25} \longrightarrow UO_{2.6-x_{max}} \longrightarrow UO_{2.67} \cdot$$
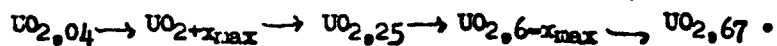
X-ray structural analysis data [26] of products of various oxidation stages

are in conformity with the proposed phase conversions schemes.

It was mentioned above that oxidation of UO_2 in an oxygen atmosphere in the range of from 150-200° transforms into $UO_{2,6\pm x}$. The thermal effect of the reaction $3UO_2 + O_2 = U_3O_8$ equals 84 kcal/mol O_2 [27]. For the purpose of comparison it can be shown that the thermal effect of reaction of carbon combustion into CO_2 equals 94 kcal/mol O_2. Because of the liberation of a considerable amount of heat during the oxidation of uranium dioxide into U_3O_8 there are local overheatings in solid phases, which causes a sharp rise in the rate of the process in these points. Thanks to this several simultaneous phase conversions are possible. When in the center of the particle develops only the first stage of oxidation total oxidation may be concluded on the surface or on account of the heat, liberating thereat, the first phase conversion etc is accelerated. This explains the sudden development of the process in the above mentioned range of temperatures. Preliminary low temperature oxidation of uranium dioxide into $UO_{2,10}$ - $UO_{2,13}$ reduces the value of the jump, since the thermal effect of transition $UO_{2,10}$ - $_{2,13} \rightarrow UO_{2,6\pm x}$ is lower than the thermal effect of conversion of $UO_{2,04} \rightarrow UO_{2,6\pm x}$.

The inhibiting effect of a K_2CO_3 addition on the process of UO_2 oxidation at 185°, apparently, can be explained by the following. At such a low temperature is highly improbable the migration of potassium ions from the crystalline lattice of carbonate into the uranium oxide lattice. At the same time the addition, being in close contact with uranium dioxide, shields a part of its surface and at the same time reduces the area for oxygen adsorption from the gaseous phase thus leading to a reduction in the summary rate of the oxidation process.

At 330° the accelerating effect of admixtures of alkali metal carbonates appears in these stages, where considerable readjustment of crystalline lattice takes place.

The second interesting fact is that in the presence of carbonates disappears the induction period during the realization of the phase conversion $UO_{2,36\pm0,05} \rightarrow UO_{2,6-x_{max}}$. It is known [25] that if in the old and new phases there are no convergent areas and

the difference in parameters is great, the new phase crystallizes independently and does not reproduce the lattice of the initial substance. The most difficult moment in this case is the formation of new phase nuclei. Exactly such a picture hase been observed in the mentioned phase conversion. The catalytic effect of carbonates is brought down to the point, that their particles appear to be crystallization centers of new phase, eliminating the induction period.

Possible is also another cause of the catalytic effect of carbonates. At 330° at points of close contact of reagents is not excluded the possibility of partial migration of metal ions from the carbonate lattice into the oxide lattice, especially since in the process of oxidation is created a metal deficiency in the oxide phase[21]. The presence of foreign ion in the lattice of the oxide causes its deformation, appearance of these or other types of distortions. The readjustment of such distorted sections into a new phase is realized easier and faster,than the sections with normal lattice.

The inhibiting effect of potassium carbonate after preliminary annealing at 900° is explained, apparently, by the fact, that at this temperature potassium carbonate decomposes with formation of K_2O with which the phase $UO_{2.6-x_{max}}$ phase nuclei originating in the process of oxidation enter into reaction forming potassium diuranate[29]. The formation of potassium diuranate is indicated by the presence of dark-orange grains in the final green-black reaction product.

When evaluating the results of the effect of additions of small amounts of foreign oxides on the kinetics of uranium dioxide oxidation it is necessary first of all to take into consideration, that binary systems,including uranium oxide, are characterized by wide zones of solid solutions , just as the uranium-oxygen system in itself. [30]. UO_2 and ThO_2 oxides have a face centered cubical lattice (structure of fluoride compounds) and as shown in report[30] they can form with each other a continuous series of solid solutions . UO_2 and ZrO_2, as established in this report, below 1900°, at a

zirconium dioxide content of less than 52% (molar) form solid solutions. Titanium dioxide does not form with uranium oxides any solid solutions nor chemical compounds.

The catalytic effect of ThO_2, ZrO_2 and TiO_2 oxides is particularly noticeable during the final stages of oxidation (see fig.6), beginning with phase conversion $UO_{2.36\pm0.05}$ $\longrightarrow UO_{2.6-x_{max}}$, i.e. when there is a substantial readjustment of crystalline lattice. Evidently, additions of mentioned oxides facilitate the formation of phase $UO_{2.6-x_{max}}$ nuclei, assuming the role of active centers. It is also known, that oxides, capable of dissolving oxygen, catalyze the reaction of oxidation[21]. Solubility of oxygen in oxides rises in the ThO_2, ZrO_2, TiO_2 series. This, most likely, explains the established by us specific effect of additions of given oxides. The inhibiting effect of thorium dioxide during the first stages of oxidation after preliminary annealing at 900° is due to the fact that at the time of annealing UO_2 and ThO_2 form a solid solution. Addition of titanium dioxide slows down in these conditions the process, because it promotes / sintering of uranium dioxide [32].

Conclusions

1. The oxidation kinetics of uranium dioxide with atmospheric oxygen in the range of from 165-800° and air pressures of 2.5 - 600 mm Hg, has been investigated. The values of apparent activation energy of the process was calculated at various stages of oxidation.

2. Investigated were the kinetic characteristics of UO_2 oxidation with pure oxygen at a range of from 125 to 330° and p_{O2}= 100 mm Hg.

3. Phase conversion schemes have been introduced during the oxidation of uranium dioxide at various temperature ranges.

4. The effect of additions of alkali metal carbonates and oxides of ThO_2, ZrO_2, TiO_2 on the kinetic characteristics of UO_2 oxidation process with air has been investigated. An explanation of thier effects is given.

Submitted: April 22, 1961

Literature

1. I.Vard. I.Johnson.Problems of Nuclear Energetics No.4,39,(1957).
2. O.Runnols. Nucleonics, 17, Nov., 104 (1959).
3. B. Goshiki. J. Ceram. Assoc., Japan, 65, 741, 289, (1957).
4. P. Perio. Bull. Soc. Chim. France 9, 840, (1954).
5. P. Perio. Mem. Pres. Soc. chim., 39, 256, (1953).
6. I.Johnson, S.Curtis; Transactions of the First International Conference on Peaceful Utilization of Atomic Energy,vol.9, rep.No.559 (1958).
7. P. Gronvold, H. Haroldson. Nature, 69, 162, (1948).
8. J. Anderson. Bull. Soc. chim. France, 2, 303, (1949).
9. J. Anderson, K.Alberman, J. chem. Soc., 9, 781, (1953).
10. J. Anderson, L. Roberts, E. Harper. J. chem. Phys., 3946, 1955.
11. S. Aronson, R. Roof, Ir. u. i. Belle. J. chem. Phys. 27, 137, (1957).
12. R. Blackburn. J. Phys. chem., 62, 8, 897, (1958).
13. F.V.Gel'd, O.A.Yesin, Doklady Akademii Nauk SSSR vol.74,ed.3.(1950)
14. F.V.Gel'd, O.A.Yesin; N.N.Serebrennikov,Trudy UPI,collection 49,61 (1954).
15. S.S.Lisnyak; C.I.Chufarov,Doklady Akad.Nauk SSSR,vol.126,ed.4,831,(1959)
16. D.Kats; Ye.Rabinovich. Chemistry of Uranium,Foreign Publication,Moscow (1954)
17. A.A.Baykov, Metallurg No.3,5 (1926)
18. G.Khukstra; S.Saygl Transactions of First International Conference on Peaceful Utilization of Atomic Energy vol.7,483 (1957)
19. R.Willardson, I.Moody, H.Goering. J. Inorg. and Nucl. chem., 6,1,19,(1958).
20. A. Arrot, J. Goldman. Phys. Rev., 108, 4, 948, (1954).
21. P. Perio. Bull. Soc. chem. France, No. 7-8, 776, (1953).
22. F. Gronvold. J. Inorg. and Nucl. chem., 1, 357, (1955).
23. R.Berrer.Diffusion in Solid Bodies,Foreign Publ.Moscow (1948)
24. K.Smittels;Gases and Metals,Metallurgizdat,Moscow-Leningrad (1940)
25. Atomic Energy 4,2,215 (1958).
26. V.N.Strekalovskiy; A.F.Bessonov; V.G.Vlasov; F.A.Sidorenko;Physics of Metals and Metallography vol. 11, ed.3,400 (1961)
27. H. Hockstra, I. Katz J. chem. Phys. 25, 6, 1089, (1956)
28. P.D.Dankov,Izvestiya Sektora Fiziko-Khimicheskogo Analiza 61,16,82,(1943)
29. K.M.Yefremova; Ye.A.Ippolitova; Yu.P.Simonov,Vik.Spitsyn,Doklady Akad.Nauk.SSSR vol.124,ed.5,1057 (1959)
30. W.Lambertson, M. Muller, F. Gunzel, J. Amer. ceram. Soc., 36, 12, 397 (1953).

31. A.Riz.Chemistry of Crystals with Defects,Foreign Publ.Moscow (1956)
32. J.Belle.Reports at the Second Geneva Conference on Peaceful Utilization of Atomic Energy,vol.6,233 (1959).

DISTRIBUTION LIST

DEPARTMENT OF DEFENSE	Nr. Copies		MAJOR AIR COMMANDS	Nr. Copies
			AFSC	
			SCFDD	1
			DDC	25
HEADQUARTERS USAF			TDBTL	5
			TDBDP	5
AFCIN-3D2	1		AEDC (AEY)	1
ARL (ARB)	1		ASD (ASYIM)	1
OTHER AGENCIES				
CIA	1			
NSA	6			
DIA	9			
AID	2			
OTS	2			
AEC	2			
PWS	1			
NASA	1			
ARMY (FSTC)	3			
NAVY	3			
NAFEC	1			
RAND	1			