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TRANSLATION

OXIDATION OF URANIUM DIOXIDE

By

V. G. Vlasov and A. F. Bessonov

FOREIGN TECHNOLOGY DIVISION

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OXIDATION OF URANIUM DIOXIDE

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

English Pages: 14

Oxidation of Uranium Dioxide

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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 the 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 UO₂ 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 800°C 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 \( \text{UO}_2 \rightarrow \text{U}_4\text{O}_9 \rightarrow \text{U}_3\text{O}_7 \rightarrow \text{U}_3\text{O}_8 \).

Anderson and coworkers [8-10] assume the following scheme of phase conversions: \( \text{UO}_2 \rightarrow \alpha \text{UO}_2\alpha \rightarrow \beta \text{UO}_2 \rightarrow \text{U}_3\text{O}_7 \). Aronson, Roof and Bells [11] evaluating the mechanism of dioxide oxidation assume the scheme \( \alpha \text{UO}_2 \rightarrow \alpha \text{UO}_2\alpha \rightarrow \alpha \text{U}_3\text{O}_7 \rightarrow \text{U}_3\text{O}_8 \). Blackburn and coworkers [12] assume that during the oxidation of uranium dioxide on the surface is immediately formed a tetragonal phase \( \text{U}_3\text{O}_7 \). The process is limited by oxygen diffusion through that phase. They give the following scheme of phase conversions: \( \alpha \text{UO}_2 \rightarrow \text{U}_3\text{O}_7 \rightarrow \text{U}_3\text{O}_8 \).

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 conversions. 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 accelerates the processes of reducing with hydrogen, carbon monoxide and solid carbon.

Informations on the effect of carbonates and foreign oxides on the rate of oxidation 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 theoretical 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 ThO₂, ZrO₂ and TiO₂ oxides on the kinetic characteristics of UO₂ oxidation process.

The properties of powder 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 uranous-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 UO₂.04. Accuracy of determining O/U ratio was 0.01.

The investigation was made in a high vacuum installation (fig.1) having an arrangement for continuous control of change in weight of the batch. The installation allowed 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 UO₂. The crucible with uranium dioxide batch (∼ 300 mg, specific surface of powder 2.7 m²/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 dried at 120° until the change in weight was stopped and a residual pressure
of the order of 10^{-4} \text{ 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 EFD-17; 10-circulation pump; 11-current circuit breaker; 12-flask for measuring volumes of system; 13-diffusion pump TSVL-100; 14-Prevacuum rotational pump RYN-20; 15-monovacric tubes LM-2 and LM-2; 16-vacuometer; 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 ± 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 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-Scherer 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 UO₂,₃6±0.05 and at 270-800° into UO₂,₆₇ (U₂O₇). 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

\[ \Delta g = k_1 \gamma \]

where \( \Delta g \) - gain in weight of batch; \( \gamma \) - time from beginning of experiment; \( k_1 \) - constant.

Starting with a certain moment of time \( \gamma_0 \) the process is subjected to parabolic time law

\[ \Delta g = \Delta g_0 + k_2 \sqrt{\gamma} \]

where \( \Delta g_0 \) - gain in weight of batch to the moment of time \( \gamma_0 \); \( k_2 \) - constant.

At 270-390° on the curves in the coordinates the degree of oxidation-time exist horizontal sections at \( \Delta g = 2.36 \pm 0.05 \). On the rate/degree of oxidation dependence curves are observed several minima: the first one at 50%, second - 95%; third - 97%. Finally, approximately at 37% of oxidation the curves have weakly pronounced
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 $\text{UO}_2.04-\text{UO}_2.36 \pm 0.05$ at an air pressure of 2.5-100 mm Hg, is valid equation

$$v = a \cdot p$$

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:

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<th>Degree of Oxidation, %</th>
<th>28</th>
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<th>52</th>
<th>54</th>
<th>74</th>
<th>88</th>
<th>90</th>
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<td>Activation energy, kJ/mol</td>
<td>34.6</td>
<td>27.8</td>
<td>43.8</td>
<td>27.8</td>
<td>34.6</td>
<td>45.6</td>
<td>39.4</td>
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The experimentally found uranium dioxide density was found to be equal to 10.3 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-
or than the volume of the initial dioxide.

The kinetics of UO₂ oxidation with oxygen was investigated at a range of from 125 to 330° at pO₂=100 mm Hg. Results are given in fig. 4. At 125-145° oxidation goes into UO₂⁺ₓ where x < 0.5. In the range from 150° to 200° is observed a sudden oxidation into UO₂⁺₆₀ oxide after which the reaction is practically off. At 200-260° there is also a sudden occurrence of uranium dioxide upon the concentration of atmospheric oxygen at 340°. Numbers on curves designate percentage of oxidation.

In the range from 260° to 300° the oxidation into UO₂⁺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.

The effect of alkali metal carbonate admixtures on the kinetic characteristics of uranium dioxide oxidation by air was investigated at 125-330°. The air pressure in all experiments was 400 mm Hg. Results are given in fig. 5. At 185° the addition of K₂CO₃ 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 0₂U = 2.35 ± 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$_2$CO$_3$, Na$_2$CO$_3$, Li$_2$CO$_3$.

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°C for a period of two hours. Oxidation followed at 330°C. 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°C (fig.6). The rate of the process in presence of admixture rises considerably from the moment when further oxidation of the UO$_2$+$0.05$ phase begins; the accelerating effect rises in the following sequence: ThO$_2$, ZrO$_2$, TiO$_2$. In the presence of ThO$_2$, ThO$_2$ 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 ratio in solid phases of less than 2.36 ± 0.005.

In subsequent experiments with uranium dioxide with and without admixtures the sample was first calcined (annealed) in vacuo (10$^{-4}$ mm Hg) at 900°C for a period of two hours. Oxidation was also carried out at 330°C. In this case the addition of ThO$_2$.
slows down the process of $UO_2$ oxidation into $UO_2,36\pm 0,05$ and accelerates further oxidation. Addition of $TiO_2$ reduces somewhat the rate of the process during transformations from $UO_2,36\pm 0,05$ to $UO_2,67$.

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°:

$$UO_2,04 \rightarrow UO_2 + x_{max} \rightarrow UO_2,25 \rightarrow UO_2,36\pm 0,05 \rightarrow UO_2,6 - x_{max} \rightarrow UO_2,67$$

which is found to be in perfect agreement with the sequence 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 viewpoint of structural changes on these stages takes place the introduction of oxygen into the cubic lattice of uranium.

PTD-77-63-102/1-2
diode (orderless in first stage and ordered in second) \([18-20]\). The third stage of oxidation is connected with the conversion of \(\text{UO}_2.25\) oxide into \(\text{UO}_2.36\pm 0.005\).

It is evident from the above mentioned kinetic curves (see fig.5, 6), that there is a whole series of tetragonal phases (\(\text{UO}_2.32\), \(\text{UO}_2.37\), \(\text{UO}_2.41\)) which is in conformity with data of other investigators \([8, 11, 12, 21\) and 22\]. The slight bent at a degree of oxidation \(\approx 37\%\) is explained, apparently, by the fact, that the tetragonal phase originates by adding oxygen atoms into the \(\text{UO}_2.25\) structure \((\text{U}_4\text{O}_9)\) with considerable crystallostructural changes.

The direct proportionality of the rate of the process to pressure \((v=ap)\) at \(p = 2.5 - 100 \text{ mm Hg}\) 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 \(1/T\) in temperature and pressure. The \(\text{UO}_2.6\) 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 \(\text{UO}_2.25\) and \(\text{UO}_2.6\) \([18, 25]\) and consequently the process of uranium dioxide oxidation in the zone of from 400-800° can be represented by the following scheme:

\[
\text{UO}_2.34 \rightarrow \text{UO}_2 + \text{X}_{\text{MAX}} \rightarrow \text{UO}_2.25 \rightarrow \text{UO}_2.6\text{X}_{\text{MAX}} \rightarrow \text{UO}_2.67.
\]

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\textsubscript{2} in an oxygen atmosphere in the range of from 150-200\degree C transforms into UO\textsubscript{2}6\textsubscript{x}. The thermal effect of the reaction 3UO\textsubscript{2} + O\textsubscript{2} = U\textsubscript{3}O\textsubscript{6} equals 84 kcal/mol O\textsubscript{2}\[27\]. For the purpose of comparison it can be shown that the thermal effect of reaction of carbon combustion into CO\textsubscript{2} equals 94 kcal/mol O\textsubscript{2}. Because of the liberation of a considerable amount of heat during the oxidation of uranium dioxide into U\textsubscript{3}O\textsubscript{6} 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 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\textsubscript{2},10 - UO\textsubscript{2},13 reduces the value of the jump, since the thermal effect of transition UO\textsubscript{2},10 = 2.13 → UO\textsubscript{2},6\textsubscript{x} is lower than the thermal effect of conversion of UO\textsubscript{2},04 → UO\textsubscript{2},6\textsubscript{x}.

The inhibiting effect of a K\textsubscript{2}CO\textsubscript{3} addition on the process of UO\textsubscript{2} oxidation at 185\degree C, 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\degree C 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\textsubscript{2},6\textsubscript{2}O\textsubscript{0},05 → UO\textsubscript{2},6-x\textsubscript{max}. It is known\[28\] 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 have 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 500°
is explained, apparently, by the fact, that at this temperature potassium carbonate
decomposes with formation of \( K_2O \) with which the phase \( UO_2(\cdot\cdot\cdot) \) phase nuclei origi-
nating in the process of oxidation enter into reaction forming potassium diuranate[25].
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 character-
ized by wide zones of solid solutions, just as the uranium-oxygen system in itself.
[20]. \( UO_2 \) and \( ThO_2 \) oxides have a face centered cubical lattice (structure of fluoride
compounds) and as shown in report[25] 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 ThO₂, ZrO₂, and TiO₂ oxides is particularly noticeable during the final stages of oxidation (see Fig. 6), beginning with phase conversion UO₂₂₆₋₀₅ → UO₂₋ₓ_max, i.e., when there is a substantial readjustment of crystalline lattice. Evidently, additions of mentioned oxides facilitate the formation of phase UO₂₋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 ThO₂, ZrO₂, TiO₂ 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 UO₂ and ThO₂ 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 UO₂ 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 ThO₂, ZrO₂, TiO₂ on the kinetic characteristics of UO₂ oxidation process with air has been investigated. An explanation of their effects is given.

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Literature

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