

SOLID-PHASE INTERACTION OF DEPLETED URANIUM TETRAFLUORIDE WITH DIFFERENT HISTORY OF PRODUCTION WITH SILICA

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The characteristics and behavior of depleted uranium tetrafluoride obtained by different methods in the process of solid-phase conversion into uranium oxides using mechano-activated crystalline and x-ray amorphous silica in oxygen-containing and inert media in the absence of mixing of the components are compared. It is found that the reactivity of depleted uranium tetrafluoride obtained by the reduction of depleted uranium hexafluoride by unsaturated organic halogen derivatives and hydrogen in a fluorohydrogen flame is actually no different, and the solid-phase reaction products UO_2 and U_3O_8 inherit the morphological features of the initial uranium tetrafluoride.

A significant amount of depleted uranium hexafluoride has been accumulated over more than a half-century of development of nuclear power and its storage in steel containers on open sites is an environmental hazard. An alternative method of storage is to convert the uranium hexafluoride into safer forms – uranium tetrafluoride or oxides.

As part of a Ministry of Education and Science Project (No. 13.G25.31.0051), the Mendeleev Russian University of Chemical Technology has developed a process for converting depleted uranium tetrafluoride obtained by reducing depleted uranium hexafluoride by unsaturated organic halogen derivatives (OTFU-1) into uranium oxides by means of mechano-activated silica. The conversion process gives a high yield of monophase uranium oxides and high-purity silicon tetrafluoride.

While studying the regularities of the solid-phase interaction in the system OTFU-1–silicon in the absence of mixing of the components, it was found that the nature of the silicon largely determines the temperature interval of the precipitation of silicon tetrafluoride [1, 2]. In terms of the effectiveness of the influence on the conversion of uranium hexafluoride into uranium oxide (rate and yield of the reaction), the forms of silicon studied form the following sequence: quartz – cristobalite – x-ray amorphous silica. It was also found that owing to the Hedvall effect – the polymorphic transition of quartz into metastable β -cristobalite – the mechano-activation of quartz, including in the presence of stimulating additives, makes it possible to lower by 150–200°C the temperature of the solid-phase conversion of OTFU-1 into uranium oxides [2–5]. The solid products obtained were comprised of multiphase nanostructured uranium oxides, which inherited the morphological features of the reagents [2].

American researchers also observed the inheritance of the morphology of one of the components of the system – depleted uranium tetrafluoride – by uranium oxide [6]: U_3O_8 particles – the products of the conversion of depleted uranium tetrafluoride (obtained by the hydrogen reduction of depleted hexafluoride) with the participation of diatomaceous earth (x-ray amorphous silica) inherited the morphological features of the initial depleted uranium tetrafluoride (spherical particles with diameter 1–10 μm). Complete conversion was attained at temperature 150°C higher than in the interaction of domestically produced tetrafluoride with x-ray amorphous silica [1].

This suggests that the production history of depleted tetrafluoride can influence the conversion and properties of the oxides obtained, since the differences in the conditions of synthesis can change its reactivity because of the granulometric composition, particle morphology, bulk density, and other properties important for the solid-phase interaction process.

Russian specialists have patented a method of obtaining depleted uranium tetrafluoride by hydrogen reduction of depleted uranium hexafluoride in a fluorohydrogen flame, but its characteristics and reactivity in solid-phase processes is unknown [7].

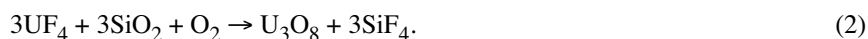
The aim of the present work was to compare the regularities of the solid-phase interaction of depleted uranium tetrafluoride of different origin with mechano-activated quartz and x-ray amorphous silica.

Experimental Part. Depleted uranium tetrafluoride OTFU-1 [3] and uranium tetrafluoride obtained at the Leading Research Institute of Chemical Technology (VNIKhT) by hydrogen reduction of depleted uranium hexafluoride in a fluorohydrogen flame on a pilot setup Mini-modul (OTFU-2) [7], quartz concentrate (quartz), and x-ray amorphous silica served as the reagents [1].

Mechano-processing (mechanoactivation) of quartz and x-ray amorphous silica were accomplished in, respectively, a Pulverisette-5 (Fritsch, Germany) planetary-centrifugal mill and a Pulverisette-9 vibrating mill (Fritsch, Germany). The granulometric composition was determined using an Analysette-22 Economy (Fritsch, Germany) laser diffraction microanalyzer and the phase composition using a D2 Phaser (Bruker, German) diffractometer. The JCPDS-PDF2 (USA) database was used to identify the phases. A Quadrasorb SI/Kr (Quantochrome, USA) setup was used to determine the specific surface area S_{sp} by means of low-temperature adsorption of nitrogen; an ULTRAPUC 1200e (Quantochrome, USA) pycnometer) was used to determine the density of the powders. A Vega 3 electron microscope (Tescan, Czechoslovakia) was used to study the morphology of the powders. Differential-thermal analysis in combination with mass-spectrometry (DRA/TG-MS) was performed on the EXSTAR TG/DATA 7300 (SII, Japan, 25°C/min) apparatus. A THERMOSTAR quadrupole mass spectrometer (Pfeiffer Vacuum, Austria) was used to determine the composition of the gaseous products released during heating.

The solid-state conversion of the depleted uranium tetrafluorides into oxides was accomplished using quartz, mechano-activated in the absence ($S_{sp} = 24.6 \text{ m}^2/\text{g}$) and presence ($S_{sp} = 15.15 \text{ m}^2/\text{g}$) of stimulating additives, as well as x-ray amorphous silica after it was mechanically processed ($S_{sp} = 102 \text{ m}^2/\text{g}$) [1, 3, 4].

The samples of depleted uranium tetrafluoride were mixed with the stoichiometric amount of silica according to the equations depending on the reaction medium:



The mixture was homogenized by short-time processing in an MM400 (German) vibrating mill and placed into corundum crucibles. The solid-phase conversion (the scheme of the apparatus is presented in [1]) was conducted in the interval 400–750°C with heating rate 10°C/min and 2 h soaking in a stream of dried air or nitrogen (flow rate 1 liter/min). After cooling, the content of the crucibles was weighed and the yield of the solid product was calculated from the equation

$$\eta = \left(\frac{\Delta m_p}{\Delta m_t} \right) 100\%, \quad (3)$$

where Δm_p is the practical mass loss of the mixture, and Δm_t is the theoretical mass loss of the mixture according to Eqs. (1) or (2).

Results and Discussion. x-Ray phase analysis showed depleted uranium tetrafluoride obtained by the reduction of depleted uranium hexafluoride by unsaturated organic halogen derivatives to be well-crystallized monophase UF_4 of the monoclinic modification (JCPDS, No. 32-1401), while the depleted uranium tetrafluoride obtained by hydrogen reduction in a fluorohydrogen flame, together with *m*- UF_4 contained a small amount (to 3%) of uranyl fluoride polyhydrate $\text{UO}_2\text{F}_2 \cdot 1.5\text{H}_2\text{O}$ (JCPDS, No. 24-1151).

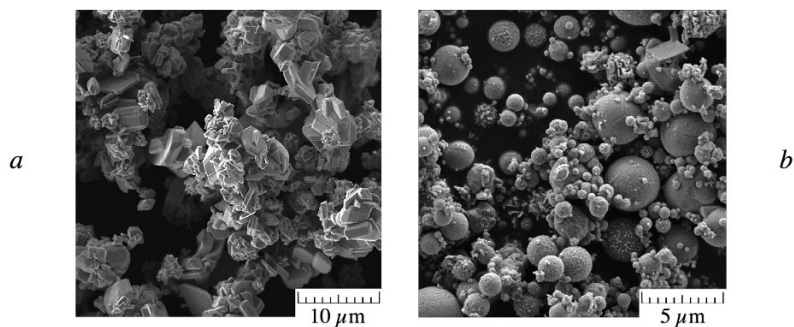


Fig. 1. Photomicrographs OTFU-1 (a) and OTFU-2 (b).

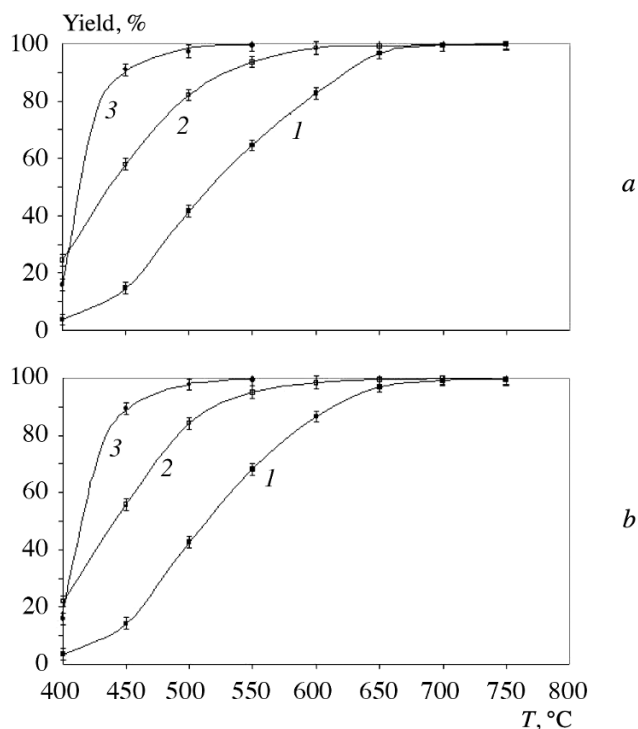


Fig. 2. Yield versus the temperature of the solid-phase interaction reaction of OTFU-1 (a) and OTFU-2 (b) in an oxygen-containing medium with mechano-activated quartz without (1) and with (2) stimulating additives and x-ray-amorphous silica (3).

The physical characteristics of the samples of depleted uranium tetrafluoride are as follows:

	OTFU-1	OTFU-2
Density, g/cm ³	6.94	7.05
Bulk density, g/cm ³	0.83	1.34
Bulk density with shaking, g/cm ³	1.52	2.02
Specific surface area, m ² /g	0.8	1.3

Comparing the characteristics of depleted uranium tetrafluoride with differing history shows that the bulk density of the depleted uranium tetrafluoride obtained by hydrogen reduction of depleted hexafluoride and the specific surface area are approximately 1.5 times greater than that reduced by unsaturated organic halogen derivatives.

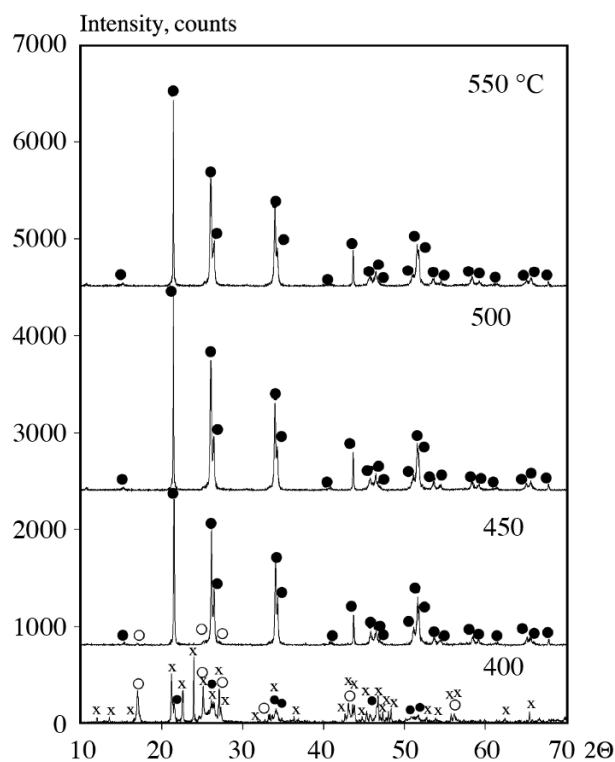


Fig. 3. Effect of the temperature on the phase composition of the products of interaction of OTFU-1 with x-ray amorphous silica in an oxygen-containing medium: ●, ○, ×) U_3O_8 , UO_2F_2 , and UF_4 , respectively.

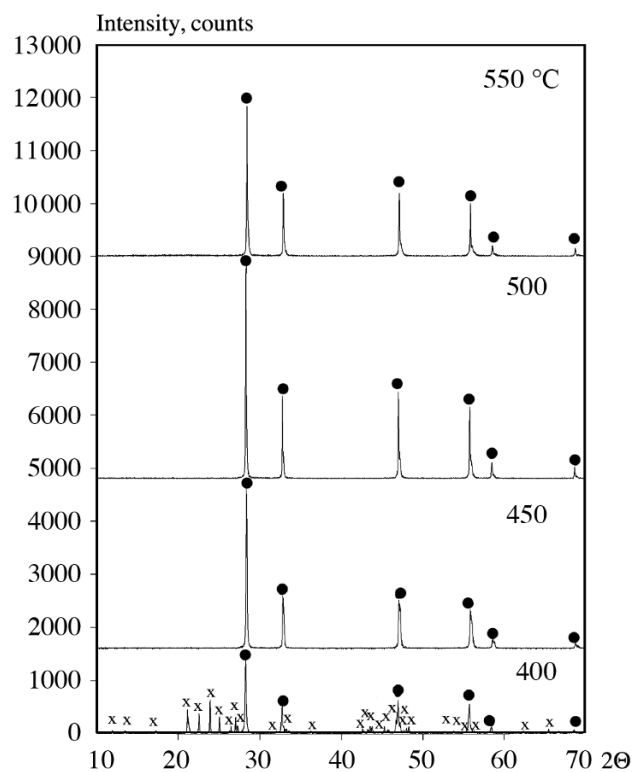


Fig. 4. Effect of the temperature on the phase composition of the products of interaction of OTFU-2 with x-ray amorphous silica in an inert medium: ●, ×) UO_2 and UF_4 , respectively.

TABLE 1. Morphology of the Conversion Products

Inheritance of morphology	Mechano-activated quartz				x-Ray amorphous silica	
	K-1		K-2			
OTFU-1						
U_3O_8	Yes		Yes		No	
Aggregates	Plate-like hexagonal	$l \sim 2-5, h$ up to 2	Plate-like hexagonal	$l \sim 2-5, h$ up to 2	Indefinite shape	d 2–10
Particles	Oval shape	d 0.05–0.25	Oval shape	d 0.05–0.25	Plate-like	$l \sim 0.4-2, h$ up to 0.4
OTFU-2						
U_3O_8	Yes		Yes		Partially	
Aggregates	Spherical	d 2–5	Spherical	d 2–5	Spherical	d 2–5
Particles	Spherical	d 0.1–0.5	Spherical	d 0.05–0.1	Plate-like	$l \sim 0.3-1, h$ up to 0.2
OTFU-1						
UO_2	No		No		No	
Aggregates	Indefinite shape	d 2–10	Indefinite shape	d 2–10	Indefinite shape	d 1–2
Particles	Spherical	d 0.3–0.7	Spherical	d 0.25–1.0	Spherical	d 0.1–0.3
OTFU-2						
UO_2	Yes		Yes		Partially	
Aggregates	Spherical	d 2–5	Spherical	d 2–5	Spherical	d 2–5
Particles	Spherical	d 0.1–0.3	Spherical	d 0.15–0.5	Spherical	d 0.05–0.1

K-1, -2 – quartz in the absence and presence of stimulating additives, respectively; l – length; h – thickness; d – particle diameter (aggregates), μm .

According to electron microscopy, the samples of depleted uranium tetrafluoride obtained by reduction of depleted uranium hexafluoride by organic halogen derivatives and by hydrogen in a fluorohydrogen flame comprise a strongly agglomerated material with different particle morphology. Thus, the agglomerates OTFU-1 (Fig. 1a) are comprised of plate-like crystals of hexagonal form up to 5 μm long and 2 μm thick, while the OTFU-2 agglomerates (Fig. 1b) are comprised of spherical particles (predominately) from 0.2 to 5 μm in size.

The DTA/TG-MS study of the solid-phase interaction in an oxygen-containing medium and in an inert medium showed that under the same conditions the reactivity of the depleted uranium tetrafluoride obtained by reduction of depleted uranium hexafluoride by unsaturated organic halogen derivatives and hydrogen in a fluorohydrogen flame differs very little, which experiments performed in a laboratory setup confirm. Curves of the yield of the solid product of the conversion reaction of OTFU-1 and OTFU-2 into uranium oxides in dried air are presented in Fig. 2. It is evident that the completeness of the conversion of both uranium tetrafluoride into U_3O_8 with the aid of silica is determined by, together with the history of the production of the latter, the isothermal soaking temperature of the mixture: x-ray amorphous SiO_2 – 500°C, quartz mechano-activated in the presence of stimulating additives – 600°C, and quartz mechano-activated in the absence of stimulating additives – 700°C.

It should be noted that the yield of the solid product of the reaction in an inert medium is attained at a lower temperature (the temperature dependence in the dried nitrogen medium is steeper) than in an oxygen-containing medium: the total conversion of both uranium tetrafluorides into UO_2 by means of the indicated reagents is observed at 450, 500, and 600°C, respectively.

The products of conversion in the oxygen-containing and inert media at the indicated temperature according to x-ray fluorescence analysis are monophase uranium octoxide U_3O_8 (JCPDS, No. 76-1850) and uranium dioxide UO_2 (JCPDS, No. 78-0664), respectively.

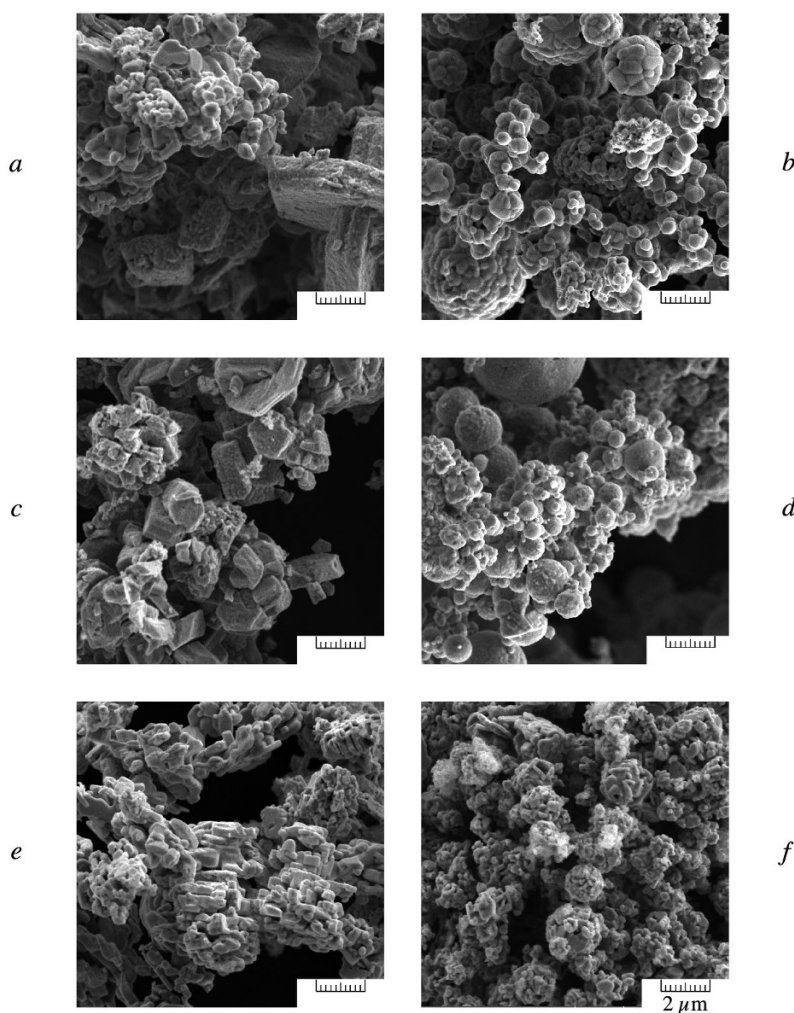


Fig. 5. Photomicrographs of U_3O_8 , obtained by the interaction of OTFU-1 (*a, c, e*) and OTFU-2 (*b, d, f*) with mechano-activated quartz without (*a, b*) and in the presence of stimulating additives (*c, d*) and with activated silica (*e, f*).

It was determined (Figs. 3 and 4) that the solid-phase interaction of both uranium tetrafluorides in an oxygen-containing medium in contrast to an inert medium proceeds via the formation of an intermediate phase of uranyl fluoride (UO_2F_2 , JCPDS, No. 75-1933), which is responsible for the difference in the yield of the solid product of the reaction (see Fig. 2).

The solid-phase interaction in the systems OTFU-1 (OTFU-2)–mechano-activated quartz is determined primarily by the content of the metastable β -cristobalite phase in silica. Comparing the content of α -cristobalite in the sample of x-ray amorphous silica and quartz, mechano-activated in the presence of stimulating additives, after their firing at 1200°C with this phase being present in the samples of quartz mechano-activated in the absence of stimulating additives showed that in the first two samples the content of α -cristobalite is close to 100% and approximately a factor of two less in the third sample.

In summary, the differences in the characteristics which are due to the production history of uranium tetrafluorides have little influence on their solid-phase interaction with mechano-activated crystalline quartz and x-ray amorphous silica.

It should be noted that according to electron microscopy the solid products of the reaction of U_3O_8 and UO_2 in some of the systems studied inherit the morphological features of the initial uranium compound to a higher degree than silicon compounds (Fig. 5). Analysis of Table 1 shows that in the solid-phase conversion by uranium oxides the form and dimensions of the particles of the initial uranium tetrafluorides are inherited only if the grain size of the solid product does not exceed $0.5\ \mu\text{m}$.

In summary, the nature of the depleted uranium tetrafluorides studied in this work has no influence on their solid-phase interaction with silica in the absence of mixing of a homogenized mixture of the components of the reaction but it does influence the morphology of the solid product of the reaction. The factors determining the solid-phase interaction are the nature of the silica and the gas medium during conversion.

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