

THE STUDY OF IONIC COMPOSITION OF THE “HOT” PARTICLES CONTAINING U AND Sr FORMED DUE TO THE NUCLEAR POWER PLANT ACCIDENT SIMULATION ON THE BASIS OF THE U5f-,4f-, AND Sr3p-,3d- XPS PARAMETERS

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Abstract. The XPS elemental and ionic quantitative analysis of the reactor fuel (UO₂) containing Sr before and after 6 minute heating in argon at 2300 °C as well as of the “hot” particles formed during this heating, was carried out. The heating was shown to cause Sr ions to diffuse toward the sample surface and then to sublime partially. Uranium ions of lesser than U(IV) oxidation state formally referred to as U(III) formed after such heating in reactor fuel. The condensed phase of the “hot” particles was found to consist of strontium (47 and 71 at.%) and uranium (53 and 29 at.%) ions respectively. Carbonates were formed on the surface during this process. After the Ar⁺ cleaning, the number of carbonate groups on the surface decreased significantly but the ratio U(IV)/U(VI) changed. The formation of uranyl compounds like SrUO₃, Sr₃UO₆ and SrUO₂CO₃(OH)₂ was suggested.

Introduction. To understand the processes during a nuclear power plant (NPP) accident [1], the laboratory simulation and studying of the “hot” particles formed due to the heating of the reactor fuel (UO₂) containing Sr was done. For the successful liquidation of accident consequences and rehabilitation of the environment, the data on physical and chemical states of the metal ions in the “hot” particles is critical. X-ray photoelectron spectroscopy (XPS) proved to be effective for this purpose [2]. This work presents the results of the XPS study of the initial and final products formed during the simulation of an NPP accident and of the “hot” particles from the nuclear fuel (UO₂).

Experimental. The samples to be studied were prepared as following [1]: Sample I - Initial tablet of UO₂, containing 5 weight % of Sr Ar⁺-cleaned for 5 seconds; Sample II - Sample I after 6 minute heating at 2300°C in argon; Sample III - “Hot” particles condensed on Al foil after the emission within first 30 seconds at 2300 °C; Sample IV - Sample III Ar⁺ cleaned for 30 seconds; Sample V - “Hot” particles condensed on Al foil after the emission within next 30 seconds right after Sample III at 2300 °C; Sample VI - Sample V, Ar⁺-cleaned for 30 seconds; Sample VII - UO_{2.06} [2]; Sample VIII - γ-UO₃ [2]; Sample IX - SrO [3]; Sample X - SrCO₃ [3]. XPS spectra of the studied compounds were taken with an MK II VG Scientific spectrometer using Al K_{α1,2} (hν=1486.6 eV) x-rays under ~1.3×10⁻⁷ Pa at room temperature. Overall resolution measured as the Au4f_{7/2} electron line full width half maximum (FWHM) was 1.2 eV. Electron binding energies are given relative to the E_b of the C1s electrons from

XPS spectra of uranium. The most intense line in uranium spectra is the U4f one. This spectrum consists of a spin-orbit doublet with the splitting $\Delta E_{SO}=10.8$ eV [2]. The basic U4f lines of the studied samples are complicated and can be decomposed into lines corresponding to U(IV), U(V), U(VI) etc ions. However, this requires analysis of the inner and outer VMO spectral fine structure. Unfortunately, for complex oxides it is very difficult in practice. Therefore, in this work it was supposed that the U4f spectrum consisted of two lines, which corresponded to U(IV) and U(VI) ions (380.9 eV for $UO_{2.06}$ and 382.4 eV for $\gamma-UO_3$). On the basis of the areas of these lines, the percent ionic composition was calculated (Table 1). In this approximation, the U4f spectrum of the "hot" particles containing uranium and strontium was decomposed into two spectra – one of UO_2 and the other of UO_3 (Fig.2). The sample surfaces were found to consist of 60% of U(IV) and 40% of U(VI) for sample III and of 27 at.% of U(IV) and 73 at.% of U(VI) for sample V.

Table 1. Electron binding energies (eV), ionic and elemental composition (at.%) of samples I-VI.

Sample	$E_b U_{4f_{7/2}}$, eV	Oxidation state U(N)	Ionic composition U(N), at. %	$E_b Sr_{3d_{5/2}}$, eV	Oxidation state Sr(N)	Ionic composition Sr(N)	Elemental composition, at. %	General Formula
I	380.7	U(IV)	60	132.3	SrO	61	88(U)	$U_{1.0}Sr_{0.14}O_{3.3}C_{1.1}(CO_3^{2-})_{0.17}$
	382.2	U(VI)	40	133.5	SrCO ₃	39	12(Sr)	
II	379.0	U(III)	6	132.4	SrO	44	90(U)	$U_{1.0}Sr_{0.11}O_{4.4}C_{9.0}(CO_3^{2-})_{0.2}$
	380.7	U(IV)	80	133.2	SrCO ₃	56	10(Sr)	
	382.3	U(VI)	14					
III	380.5	U(IV)	54	133.4	SrCO ₃	78	53(U)	$U_{1.0}Sr_{0.90}O_{6.0}C_{3.2}(CO_3^{2-})_{0.7}$
	381.9	U(VI)	46		Sr(OH) ₂	22	47(Sr)	
IV	380.7	U(IV)	56	133.6	SrCO ₃	9	51(U)	$U_{1.0}Sr_{0.96}O_{4.2}C_{0.6}(CO_3^{2-})_{0.09}$
	381.7	U(VI)	44		Sr(OH) ₂	91	49(Sr)	
V	380.6	U(IV)	27	133.5	SrCO ₃	58	29(U)	$U_{1.0}Sr_{2.40}O_{8.9}C_{1.5}(CO_3^{2-})_{1.4}$
	381.8	U(VI)	73		Sr(OH) ₂	42	71(Sr)	
VI	380.7	U(IV)	32	133.7	SrCO ₃	37	30(U)	$U_{1.0}Sr_{2.30}O_{8.8}C_{0.7}(CO_3^{2-})_{0.86}$
	381.7	U(VI)	68		Sr(OH) ₂	63	70(Sr)	
VII	380.9	U(IV)	84				100(U)	$UO_{2.06}$
	387.9	Sat	16					
VIII	382.4	U(VI)	85				100(U)	$\gamma-UO_3$
	386.2	Sat	15					
IX				132.4	SrO	100	100(Sr)	SrO
X				133.4	SrCO ₃	100	100(Sr)	SrCO ₃

After a 6 minute heating of the initial tablet in argon at 2300 °C, the coefficient x in UO_{2+x} decreased significantly and uranium ions of oxidation degree lesser than U(IV) formed. (Sample II). Taking into account an empirical fact that when the oxidation degree changes by 1, the corresponding binding energy, as a rule, must change by ~1 eV [5], the formation of ions formally referred to as ~U(III) was suggested.

For the U4f spectra from the "hot" particles (sample III-VI) binding energy for U4f_{7/2} electrons equals <381.8> eV on average instead $E_b U_{4f_{7/2}}=382.4$ eV for $\gamma-UO_3$. This fact and

adventitious hydrocarbons at the sample surface defined as 285.0 eV. The measurement errors of line position and widths were ± 0.1 eV, whereas relative line intensities errors were about 10%. Quantitative elemental and ionic analysis was done using the following equation: $n_i/n_j = (S_i/S_j)(k_j/k_i)$ where n_i/n_j – relative concentration of the studied atoms, S_i/S_j – relative electron line intensity (area) of the corresponding atomic shells, k_j/k_i – experimental relative sensitivity coefficient. In this work sensitivity coefficients related to carbon 1.00 (C1s), 2.8 (O1s); 5.9 (Sr3d_{5/2}), and 18.4 (U4f_{7/2}) were used.

Results and discussion. The technique of determination of physical and chemical states of radionuclides in the environment is based on both traditional spectral parameters (binding energies of inner electrons and line intensities) and fine spectral structure parameters of the inner and outer (valence) levels (intensity of the U5f electrons, inner valence molecular orbitals (IVMO) binding energies, multiplet splitting of the inner electron lines, parameters of the fine spectral structure due to the dynamic effects, relative position of shake-up satellites [2]). Such spectral data allow obtaining of the information on the physical and chemical states of radionuclides in the samples.

Low binding energy spectral region. The structure of the low energy XPS spectral region shows that the studied samples contain uranium mostly in form of UO_{2+x} , ($0 \leq x \leq 1$) (Fig. 1). On the basis of the dependence of the U5f relative intensity on the oxygen coefficient [2] the uranium ionic composition can be determined. It can be done in approximation that UO_{2+x} contains U(IV), U(V), and U(VI) ions. For instance, the U5f electron line relative intensity found as the ratio of the U5f to U4f_{7/2} areas for the "hot" particles (Sample III) was found to be 0.021 (Fig. 1). On the basis of the experimental dependence [2], complex oxide with the general formula $UO_{2.17}$ were found to form on the surface. The ionic composition of this oxide was found to be: 26% of U(IV), 67% of U(V), and 17% of U(VI). In such approximation the decomposition of the U4f line was done. It gave the same result (30% of U(IV), 65% of U(V) and 15% of U(VI)). Thus, uranyl groups were found to present on the surface of the "hot" particles (Sample III). That led to a complicated spectrum of the IVMO electrons from UO_{2+x} .

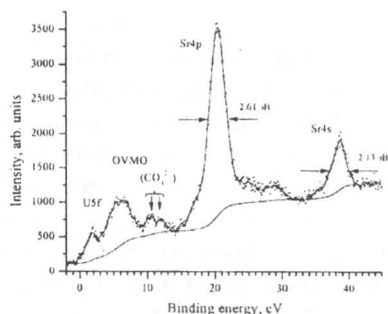


Fig. 1. X-ray photoelectron spectrum of the low-energy electrons from the "hot" particles containing U and Sr (Sample V).

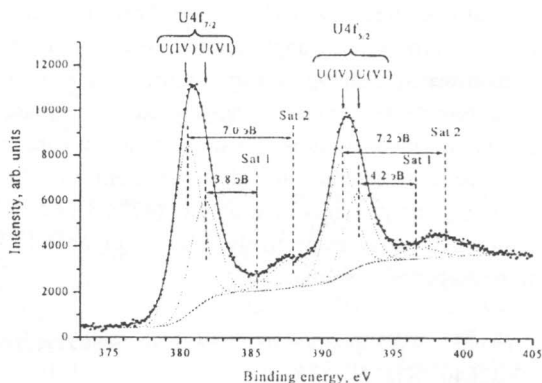


Fig. 2. X-ray photoelectron spectrum of the U4f electrons of the "hot" particles containing U and Sr (Sample IV).

the large concentration of Sr in the "hot" particles indicates to the creation of big amount of uranyl compounds like SrUO_3 , Sr_3UO_6 and $\text{SrUO}_2\text{CO}_3(\text{OH})_2$ during the heating of fuel.

XPS spectra of strontium. The surface of metallic strontium was shown to contain oxide, hydroxide, and carbonate due to the interaction with the environment: Sr(131.9 eV), SrO (132.4 eV), and SrCO_3 (133.4eV), where the $\text{Sr}3d_{5/2}$ - binding energies respectively are given in parentheses [3].

The Sr3d lines as the most intense were used for the quantitative ionic analysis. For the studied samples these lines were not always observed single (Fig.3). It indicated the presence of Sr ions of different oxidation states. For example, the Sr3d spectrum of the initial reactor fuel (Sample I) besides a doublet of strontium oxide ($E_b\text{Sr}3d_{5/2}=132.3$ eV) exhibited an extra doublet attributed to strontium carbonate ($E_b\text{Sr}3d_{5/2}=133.5$ eV). The surface contents of Sr(II) of oxide and carbonate were 61 at.% and 39 at.% respectively for this sample.

Conclusions.

In this work the XPS elemental and ionic analysis of the reactor fuel containing strontium before and after heating at 2300 °C in argon, and "hot" particles formed during the heating were carried out. The heating of the fuel was shown to cause strontium ions to diffuse toward the sample surface and sublime partially. During such heating, in the initial fuel uranium ions of oxidation degrees lesser than U(IV) (formally referred to as U(III)) were shown to form. Complex oxides UO_{2+x} ($0 \leq x \leq 1$) were found to form on the sample surface, Sr ions were shown to be Sr(II) in oxide and carbonate. Carbonates were shown to form on the sample surface. After 5 to 30 second Ar^+ cleaning, a significant decrease of the carbonate groups, decrease of U(VI)/U(IV) ratio on the surface was observed. This fact allowed a suggestion that carbonates and U(VI) ions formed on the surface due to the interaction with the environment. Condensed phase of the "hot" particles was found to consist mainly of strontium (47 and 71 at.%) and uranium (53 and 29 at.%) ions for samples III and V respectively. Uranyl compound like SrUO_3 , Sr_3UO_6 and $\text{SrUO}_2\text{CO}_3(\text{OH})_2$ were suggested to form.

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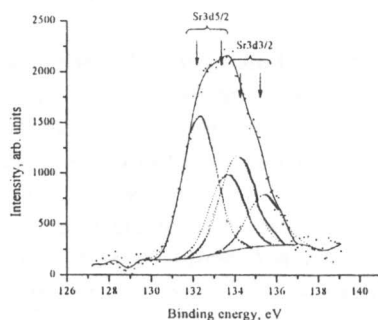


Fig.3. X-ray photoelectron spectrum of the Sr3d electrons from the reactor fuel (UO_2) containing U and Sr (Sample V).