THE FORMATION OF COMPLEX CHEMICAL COMPOUNDS IN THE SPENT FUEL AND THEIR INFLUENCE ON SEPARATION PROCESSES

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(Received April 18, 2017)

Some problems on formation of the complex chemical compounds (uranate, zirconate, etc.) in the fuel rods during irradiation and in oxidative reactions are considered. Complex compounds influence the separation processes at magnetoplasma reprocessing of spent nuclear fuel (SNF). The variant of the experimental setup for simulating the processes of formation of complex compounds in the SNF is proposed.

PACS: 03.65.Pm, 03.65.Ge, 61.80.Mk

1. INTRODUCTION

It is known that in a number of reactors about 95% U-238 and 5% of fissile U-235 in the form of oxides is loaded. At U and Pu fission and subsequent radioactive decay of the fission products (FPs) a large number of new chemical elements is formed. In addition, for each fission two atoms of oxygen release in the oxide fuel, which can participate in different chemical reactions, producing a complex oxide compound. In [1] some of the physicochemical processes on formation of complex compounds in the fuel rods at deceleration of the multi-charged FP ions in the UO_2 target were considered. It is pointed there that within the potential well (Fig.1,a) FP ion transfers energy to the molecules of the target, which, in turn, dissociate and ionize. The electrons of the neighboring molecules attract potential well of the FP ion and the oxygen ions are repelled (Fig.1,b). Lattice vibrations stimulate the diffusion of oxygen, which in the form of atoms and ions diffuses much faster than O_2 and can oxidize the UO_2, forming, for example, U_3O_8. However, at irradiation of fuel elements in stationary conditions, a significant consumption of oxygen goes to the oxidation of FPs [2]. Sr, Y, Zr, Nb, Ba, and rare earth elements oxidize unlike Kr, Xe and noble metals. Fission products of Ru, Rh, Pd form with fuel the intermetallics. The fuel rods contain metal precipitations of Mo, Cu and the noble metals. Mo, Cs, Te, I, can be presented both elements and oxides. Available significant amount of Ce, Nd, Zr, W, Mo and Cs form the oxides in fuel. ZrO_2 dissolves in UO_2, mainly in the form of solid solutions. In addition, Ba, Sr and Zr can form chemical compounds of so-called "gray phase" – zirconate of barium and strontium: $SrZr0_3$, $BaZr0_3$, etc. Metal and oxidized fission products form a system of complex compounds (uranates, plutonates, oxitellurides, zirconates, etc.) Direct research in the spent fuel is difficult for several reasons, therefore it is proposed to simulate experimentally physicochemical processes of complex compounds formation in the fuel elements. Bombardment of the target using materials-simulators (e.g., BaO, and, possibly, UO_2 using U-238) by multiply charged ions of the elements, present in the SNF in significant quantities (Zr_{n+}, Nd_{n+}, etc.) is offered. The energy of a beam is 1 MeV, that corresponds the energy of the FPs near the end of deceleration track (Fig.1,c).

The principal scheme of experimental setup is presented in Fig.2. It is assumed that from the exit of ion source –1 multi-charged ions penetrate into the target – 2 to a few monolayers, forming a new chemical bonds, that is, at deceleration upon collision with the target complex oxides can be formed. A standard volume – surface analysis to determine composition and structure of a bombardment area can be applied. An alternative method is the analysis of ablative torches, generated by electron beams or lasers. Plasma of ablative torches may be partially ionized, Ti 0.5...3 eV$\ll$5...8 eV=E_{dis} (dissociation energy of the complex oxides). The particle flux of ablative torch enter the ion source – 4, where the main ionizing processes of complex compounds take place in a gas plasma ($ne \sim 10^{13}$ $10^{14}\,cm^3$, $Te \approx 3...5\,eV$). The magnetic focusing system focuses the ion beam. Accelerated molecular ions through the gap gain to the mass-analyzer – 5.

In [1] it is indicated that the presence of complex compounds formed in SNF introduces certain difficulties in the purification of nuclear fuel from the FPs.

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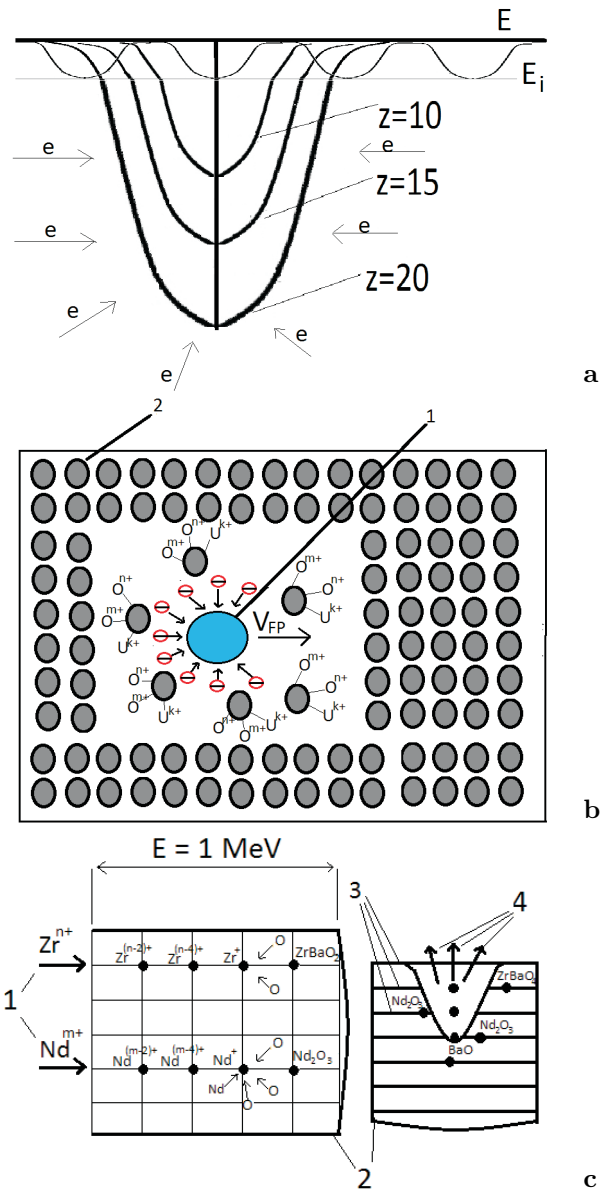

Fig.1. *Schematic view of: a)– potential well of the multi-charged FP ion in the UO_2 lattice; b) – movement of multi-charged FP ion (2) in the UO_2 lattice (1); c) – complex compound formation: multi-charged ion beam of $\sim 1\,MeV$ decelerate (1) upon collision the target (2), and, in the monolayers (3) form chemical compounds, which under laser or electron irradiation are derived from the ablative torch (4)*

In particular, when studying cesium removal from SNF at induction heating to $2300°C$ [3, 4] it was shown that the complex oxides can form in the fuel. Mathematical modeling of heat treatment in $O_2/Ar/N_2$ atmosphere of irradiated fuel shows the possibility of ternary compounds formation: Cs_2MoO_4, $Cs_2U_4O_{12}$, Cs_2ZrO_3, $SrZrO_3$, $SrMoO_4$, $BaMoO_3$, $BaZrO_3$, $BaUO_3$, $Ba_2U_2O_7$, Ba_3UO_6 – mostly in grey phase. To reduce their quantities the possibility of reducing the amount of oxygen when adding hydrogen was considered. The results of experimental studies with irradiated fuel have shown that temperature for release of cesium compounds is higher than temperature of cesium removal. In addition, it was found that there was a dependence on the chemical formula of cesium compounds and the structure of the fuel.

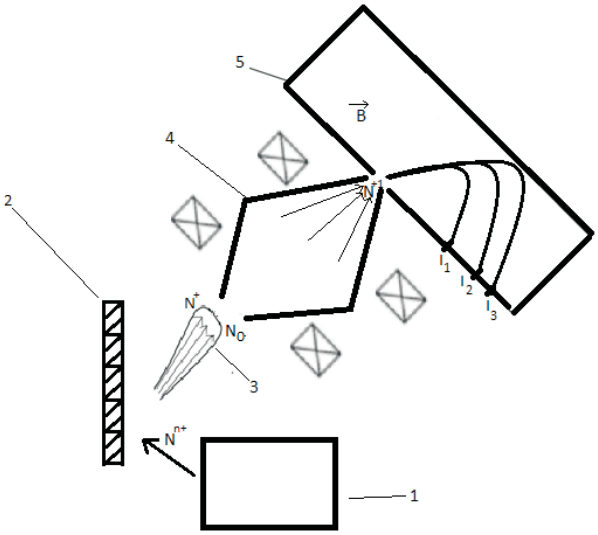

Fig.2. *Schematic view of experimental setup: 1 – source of multi-charged ions; 2 – target of the metallic oxides to form the complex compounds; 3 – ablative torch; 4 – source of molecular ions; 5 – mass-analyzer*

In plasma separation of spent nuclear fuel a variety of molecular ions (in particular, with masses exceeding the mass of UO_2) complicates the processes of mass-separation and deposition on the respective collectors. For higher quality removal FPs from irradiated fuel in a rotating plasma [5,6] additional collector [1] is provided. Another difficulty is the lack of information on physical values for different oxides, in particular, the ionization cross-sections of uranium and lanthanide oxides. To estimate these values calculation of ionization cross-sections by the Thomson formula and extrapolation according to the known cross-sections of alkali metals was carried out.

$$\sigma_i = 4\pi a_0^2 (R_y/I)^2 (I/E - I^2/E^2)\,, \qquad (1)$$

σ_i – ionization cross-section , E – energy of the incident electron, I – ionization potential, R_y – ionization potential of a hydrogen atom, a_0 – Bohr radius. Fig.3 shows the estimated and extrapolated data of ionization cross-section (σ_i) in dependence of electron energy for some oxides, present in SNF.

2. CONCLUSIONS

The presence of complex oxide compounds in the SNF complicates the processes of magnetoplasma reprocessing, reduces fission product removal from spent oxide fuel, and hence impact on the environment. The variant of experimental setup for studies of physicochemical processes on forming complex oxides in SNF is proposed, where modeling of chemical compounds formation at deceleration of the multicharged ions upon collision the target of metallic oxides and determining of a number of physical-chemical values are expected.

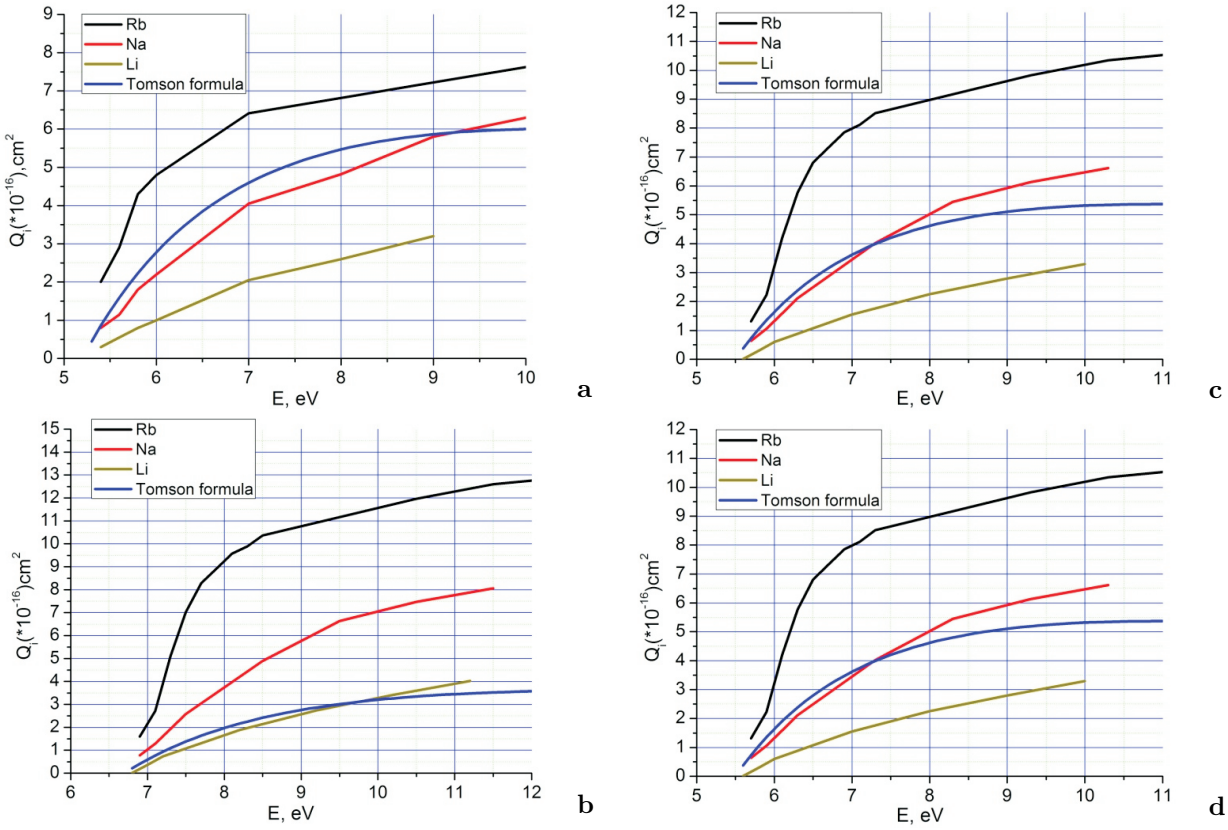

Fig.3. *Extrapolated and calculated values of ionization cross-sections for some of the oxides, present in SNF The estimated value generally is between extrapolated values. Obtaining of new experimental data on the formation of complex oxides present in SNF will allow to clarify the values of ionization cross-sections of:* ***a*** *–* UO_2*;* ***b*** *–* ZrO_2*;* ***c*** *–* Nd_2O_3*;* ***d*** *–* La_2O_3

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ОБРАЗОВАНИЕ СЛОЖНЫХ ХИМИЧЕСКИХ СОЕДИНЕНИЙ В ОЯТ И ИХ ВЛИЯНИЕ НА СЕПАРАЦИОННЫЕ ПРОЦЕССЫ

В. Б. Юферов, В. В. Катречко, В. О. Ильичева, С. В. Шарый, А. С. Свичкарь, М. О. Швец, И. В. Буравилов, С. Н. Хижняк

Рассмотрены некоторые проблемы, связанные с образованием сложных соединений (уранаты, цирконаты и др.) в ТВЭЛ-ах при облучении и в окислительных реакциях, которые влияют на сепарационные процессы при магнитоплазменной переработке ОЯТ. Предложен вариант экспериментальной установки для имитации процессов образования сложных соединений в ОЯТ.

УТВОРЕННЯ СКЛАДНИХ ХІМІЧНИХ СПОЛУК В ВЯП ТА ЇХ ВПЛИВ НА СЕПАРАЦІЙНІ ПРОЦЕСИ

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Розглянуто деякі проблеми, пов'язані з утворенням складних сполук (уранати, цирконати та ін.) у ТВЕЛ-ах при опроміненні та в окисних реакціях, які впливають на сепараційні процеси при магніто-плазмовій переробці ВЯП. Запропоновано варіант експериментальної установки для імітації процесів утворення складних сполук у ВЯП.