Development of Thermo Chemical Stable Matrices with the Purpose Transuranium Elements Immobilization

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ABSTRACT

The most suitable material for actinides immobilization is the crystalline ceramics. At the same time it is very tempting to apply for synthesis of compound suitable for being used as the materials for long-term storage or final disposal, the fission products, which are abundant in irradiated fuel itself and capable of producing slightly-soluble compounds with the most hazardous nuclides.

The object of this work was to conduct experimental study on synthesis matrices on the base of 'reactor' palladium for immobilization of long-lived transuranium elements **(**TUE) It may be suggested that the incorporation of radioactive element oxides into Pd-based matrix would allow obtaining a material of lower leach rate which would be perfectly suitable for save long-term storage.

In the paper the results of experiments on synthesis of matrices with metal oxides on palladium base are presented. Physicochemical characteristics (mechanical strength, data on leach rate et alias) are also presented. Calculation of neutron physical characteristic of Pd-based matrix (from the point of view the behavior under irradiation) has been executed.

INTRODUCTION

When choosing the materials suitable for HLW safe removal from biosphere, the particular attention is paid to their chemical stability. By now numerous litterature data are available concerning the synthesis of a large range of various materials, the major part of references being concerned with zirconium-based products [1-3].

It is worth mentioning that zirconium is one of fission products and it is accumulated in the fuel in large amounts. This phenomenon precludes from using such fission zirconium for the purposes of synthesis of mineral-like matrices that would meet all requirements for safe HLW immobilization. Fission products, which are abundant in irradiated fuel and capable to produce slightly soluble compounds with the most harmful nuclides, are very tenting to be used for synthesizing of the materials suitable for radionuclides long-term storage or final disposal.

Along with zirconium, the other elements, such as molybdenum, platinum group metals are found in the fuel and are thought to be used for synthesis of various compounds of short-lived (Cs, Sr) or long-lived (TUE) radionuclides [4].

The most special palladium feature which differs this element from the other platinoides is its capacity to be dissolved into nitric acid. Therefore, if in the future the materials on Pd-base would be used for TUE immobilization and long-term storage, a simple dissolution of these mateials in nitric acid followed by extraction recovery of target elements (americium , curium…) would be sufficient in case of TUE recovery need. (That is why the use of palladium as target material for these element transmutation is of special interest).

A target for transmutation may be made of individual TUE compound without use of any matrix material. TUE is most commonly mixed with matrix material and mono- or two-phase targets are prepared. It is rather complicated to select unambiguously appropriated chemical form for TUE and matrix material. So, for instance, when choosing TUE chemical forms, a number of their physico-chemical characteristics (melting point, decomposition point, density, thermal conductivity, resistance to thermal and radiation fields) should be taken into consideration. Currently such data are not available yet.

On this basis, the object of this work was to carry out a study on synthesis matrices on the base of 'reactor' palladium for immobilization of long-lived TUE radionuclides. In authors opinion incorporation of radionuclides TUE oxides into metal palladium matrix would allow to get a material with low lixiviation rate and suitable for a safe long-term storage. Such materials may be also used as the targets for radionuclides transmutation as well.

RESULTS OF EXPERIMENTS AND DISCUSSION

In the first phase of the study the experiments were carried out on palladium powder pressing. The goal of these studies was to find out the effect of binding agent should be added on mechanical strength of pressed pellets. The solution of paraffin in heptane was used as a binder. Binder's mass was 0.2-3.0% of metal palladium powder mass. The pellets obtained by cold pressing in steel molds were subjected to a heat treatment in a muffle furnace. The mechanical strength of the specimens so obtained was further analyzed. Taking into consideration the appearance of the specimens and their sizes the following mechanical testing techniques were selected:

- Vickers hardness determination (acc. to Russian State Standard GOST 2999-75 [5]), loading = 1 kgf;
- Loading through compression up to maximum possible force.

The results of these experiments allow making the following conclusions:

The comparison of the specimens being produced when using various amounts of binder did not reveal any significant differences.
B Among all tested techniques for powder compacting the heat-treatment at 1000^{o}C only has led to a plastic deformation of the specimen. In the other cases the pellets underwent a brittle fracture through disintegration into powder. The appearance of the pellet after mechanical test is shown in Fig. 1

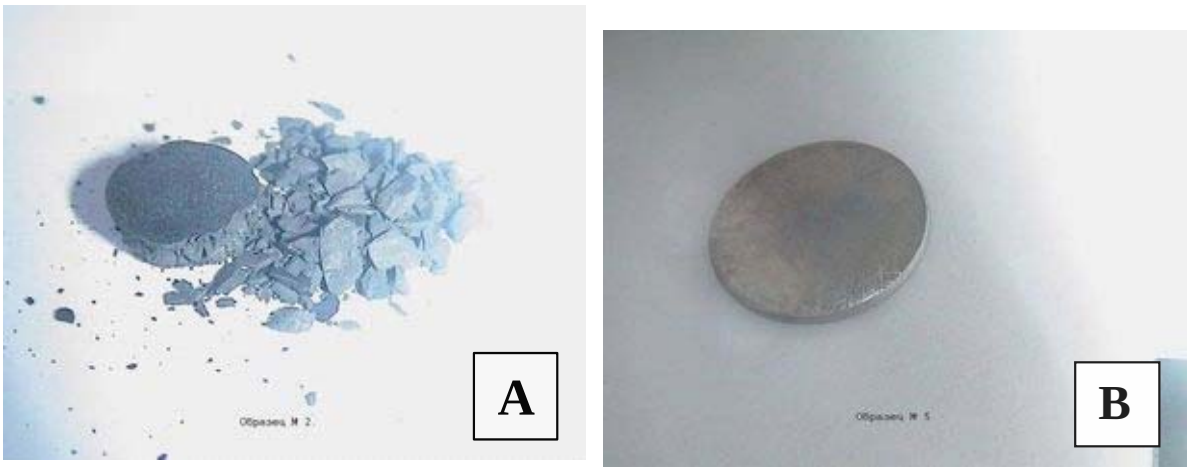

Fig. 1. The appearance of the pellets being pressed from metal palladium powder and further tested for strength. Pellet production technique: (A) - pressing with the adding of binding agent (1% solution of paraffin in heptane); (B) - pressing with no binder, followed by sintering at 1000°C.

In the next stage of our studies the experiments on Pd- and Eu_2O_3-based product synthesis were conducted. The powders of metal palladium and europium oxide, obtained by oxalate precipitation technique followed by precipitate calcination, were use as initial materials. (The powders of metal palladium and europium oxide are the system with practically identical dispersity ($D_{av.} \sim 0.35\mu$).) The apparatus used to study the process of Pd-based pellets preparation was comprised of the following units: press, HF generator, fore vacuum chamber and a pump station. (The press-molds were made of graphite AG-1500.)

Weighted portion (3-4 g) of working mixture (metal palladium and europium or uranium oxides) was poured into press-mold (mold-mortise diameter = 11 mm). The mold was inserted inside the inductor. The chamber was evacuated by means of fore pump and further filled with argon. Powder pressing was conducted for 1 hour at given temperature and pressure. Determination of pellet elemental composition was carried out by electron-probe microanalysis technique, which is based on comparison of characteristic X-ray spectra of the specimen to be analyzed with those of references of known compositions. This technique sensitivity is about 0.5 mass. %. Specimen's characteristics are presented in Tables I-II.

Table I. The Results of X-ray Diffraction Analysis for Specimens No. 200 and 210 (Polished Surface).

Phases	Analysis area, % (No. 200)-				Analysis area, % (No. 210)			
	Average, %	A	B	C	Average, %	A	B	C
Eu_2O_3	55	0 - 5	98	80 - 70	75*	0 - 5	95 - 90	55
Pd	40	100 - 95	1 - 4	0 - 10	20	100 - 95	5 - 10	5
X	~ 5	0	0	20	~ 3	0	0	40

* - monoclinic modification

Table II. The Results of X-ray Morphological Analysis for Specimens No 200 and 210 (Polished Surface).

No. 200	Al	S	Cl	Pd	Eu	No. 210	Al	S	Cl	Pd	Eu
Average**	0.7	0.6	0.3	40.6	57.6	Average	0.5	0.3	0.4	17.9	70.9
A	0	1	0	95 - 100	5 - 0	A	0	0.6	0.3	97.4	2.5
B	0.9	0	0	1 - 4	84	B	0.8	0	0	6 - 12	78.4
C*	0.3	0.3	1	0 - 10	55 - 70	C*	0	0	2	0 - 10	30 - 50

* - the phase non-identified by X-ray analysis.
** - measurement area ~ 5 mm^2

At micrographs obtained three phase (A, B, C) were clearly seen which are non-uniformly distributed throughout the pellet surface. The data given in Table I show that the phase A comprises mainly metal palladium whereas the phase B is constituted of europium oxide. The phase C is the most likely to be a solid solution of Pd- Eu_2O_3 and an X-ray amorphous substance (the most likely – carbon of graphite press-mold) [4]. Europium oxide and palladium contents were consistent with composition of initial mixture being pressed. The appearance of the pellets obtained by the hot pressing of metal palladium and europium oxide mixture is shown in Fig.2.

In the next stage of our studies we obtained under analogous conditions several specimens of metalloceramic compositions made of palladium and mixture of uranium and cerium oxides.

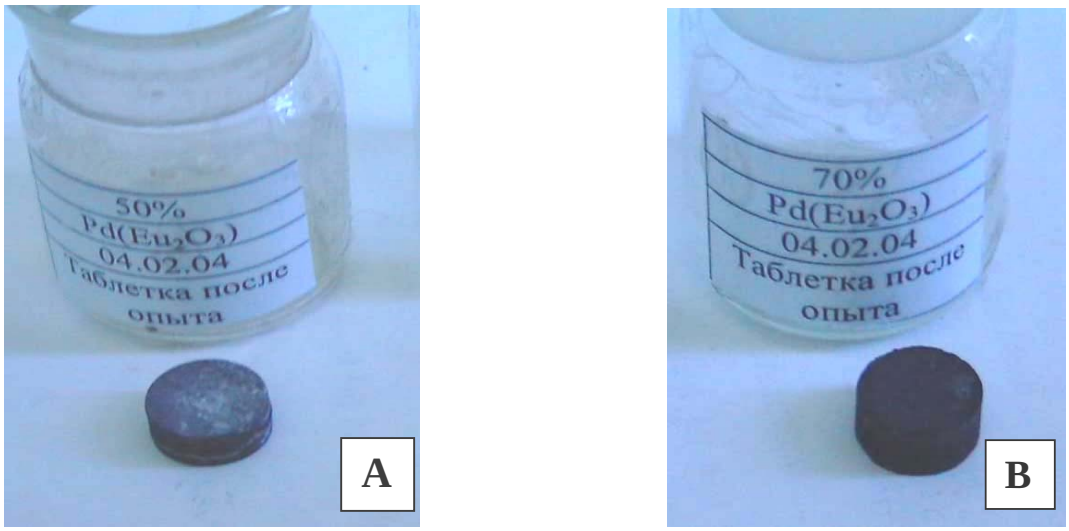

Fig.2. Specimens of palladium-containing matrix compositions with the content of Eu_2O_3 – 50% (A) and 70% (B).

The leach rate was determined for all specimens. These tests were conducted in distillated water, room temperature.

The results of leach rate estimation are given in Table III.

Table III. The Leach Rate of Europium and Uranium from Pd-base Metalloceramic Compositions.

Pellet composition.	The leach rate of europium and uranium (R).					
	t, days	R, $kg/m^2 \cdot day$	t, days	R, $kg/m^2 \cdot day$	t, days	R, $kg/m^2 \cdot day$
Pd -50% (Eu_2O_3)	30	$4.4 \cdot 10^{-7}$	60	$7.8 \cdot 10^{-7}$	202	$1.4 \cdot 10^{-4}$
Pd -70% (Eu_2O_3)	30	$4.8 \cdot 10^{-9}$	60	$5.1 \cdot 10^{-9}$	223	$5 \cdot 10^{-6}$
Pd -50% (UO_2 -Ce_2O_3)	197	$2.9 \cdot 10^{-5}$	435	$1.5 \cdot 10^{-5}$	515	$1.4 \cdot 10^{-5}$
Pd -% 75% (UO_2 -Ce_2O_3	197	$2.2 \cdot 10^{-5}$	435	$2.1 \cdot 10^{-5}$	515	$2 \cdot 10^{-5}$

Also we had executed the calculation of neutron physical characteristic of Pd-based matrix (from the point of view the behavior under irradiation) has been executed. One of essential criterion for selection of matrices suitable for TPE transmutation is a low absorbability of neutrons by these materials for prevention of the losses of neutrons needed for transmutation.

It was experimentally shown that oxide matrices MgO, $MgAl_2O_4$, $Y_3Al_5O_{12}$ absorb neutron one hundredth as actively as TPE. Nitride matrices, such as TiN, VN, NbN, AlN are also much weaker neutron absorbers than TPE. Metal matrices are more powerful neutron absorbers than ceramic materials. To illustrate, Mo and W offer the absorbability, which is similar to that of TPE, and vanadium – to that of FP. Matrix irradiation should not be accompanied by generation of long-lived products of activation. It was shown that the matrices based on Mg- and Al-containing compounds generate under irradiation stable or short-lived nuclides, which are neither gamma-rays emitters nor radiotoxic species [6].

There is only one radioactive nuclide of palladium in spent nuclear fuel: Pd-107 which has a half-life of $6{,}5 \cdot 10^5$ years and decays with radiation of soft beta rays of 35 keV. One of possible "reactor" palladium usage that waives an radioactivity objection connected with its radioactivity is palladium usage as a basis for making containers and targets for long-term storage long-lived radioactive materials and irradiation in reactor (transmutation). (Melting temperature (1552° C), mechanical strength and also chemical inertness permit to use palladium as target's material.)

While estimation Pd container's neutron physical characteristic from the point of view the opportunity of using for intrareactor it should be noted the following: Container not must insert fair quantities of distortion in neutron flow in reactor channel. The data for palladium isotopic composition in spent fuel and neutron-absorption cross-sections are presented in Table IV below. (Data of JENDL 3.3. library have been used.)

Table IV. Content of Palladium Isotopes in Spent Nuclear Fuel.

Nuclide mass	Half-life	Content in spent fuel after 30 years, (%, weight)	Neutron-absorption cross-sections, barns		
			Thermal neutrons	Intermediate neutrons	Fast neutrons
Pd-102	Stable	0.0	2.97	19.5	0.11
Pd-104	Stable	15,8	0.46	21.9	0.077
Pd-105	Stable	27,5	17.9	96.7	0.12
Pd-106	Stable	26,4	0.27	9.3	0.073
Pd-107	$6{,}5 \cdot 10^5$ years	15,9	1.8	112.2	0.122
Pd-108	Stable	10,9	7.6	252.1	0.054
Pd-110	Stable	3,6	0.2	2.81	0.028

Neutron-absorption cross-sections of Pd are notably higher in comparison with constructional materials of reactor active zone (zirconium iron or nickel). However container's influence isn't catastrophically and neutron flow reduction in immediate vicinity will average about 15 – 20 %. While palladium irradiation some long-lived nuclides (silver, gadolinium) could be accumulated. According rough estimate during one year of irradiation it could be accumulated about 0.1% atoms of silver and gadolinium that give a few curies per gram of palladium. So neutron physical characteristic of Pd are severely limited but inestimable advantage connected with simple reprocessing of Pd-based targets after irradiation (TPE transmutation) give grounds to consider this material as very promising.

CONCLUSION

The concept of HLW management adopted in majority of the countries is based on the multi-barrier principle of radiological-safety protection. Accordingly to this principle the radionuclides isolation is ensured by a complex system of engineering and natural barriers.
It's necessary to immobilize the wastes in matrices stables to lixiviation for an unlimited period of storage. The indispensable requirements concerning the materials selected for long-lived radionuclides fixation are their radiation and thermal stability and high mechanical strength. The most suitable material for actinides immobilization is the crystalline ceramics. Unlike the glass, where the radionuclides distribution in material is quite homogeneous, the HLW components occupy well-determined sites in these ceramic materials crystalline lattice. With a rare exception, the wastes composition complexity results in necessity to use a polyphase ceramics presenting a varied stability of different phases and no uniformity of radionuclides distribution in these phases. But it worth noting that when using crystalline ceramics it would be very difficult to put into practice of crystalline material dissolution process in case of TUE recovery need.

In this case the use of 'reactor' palladium as a material for TUE immobilization seems to be quite justified. Neutron physical characteristic of Pd-based matrix as material for targets (during transmutation) could be quite acceptable. The studies are being conducted now in searching for optimum conditions of pressing and addition protective coating application.

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