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Immobilization of plutonium dioxide into borobasalt, pyroxene and andradite compositions

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The immobilization of plutonium-containing wastes into stable solid compositions is one of the problems to be solved in the disposal of radioactive wastes.

This paper presents the data on the synthesis of plutonium-containing materials based on borobasalt, pyroxene, and andradite compositions in the muffle furnace and by the cold crucible induction melter (CCIM) method. Compositions containing up to 4.6-5.7 wt% plutonium oxide were obtained in laboratory facilities installed in glove boxes. Comparison studies of the materials synthesized in the muffle furnace and CCIM demonstrate the advantages of using the CCIM method. The distribution of components in the materials synthesized were investigated, and certain of their physicochemical properties determined.

KEYWORDS: *immobilization, plutonium, glass-like compositions, mineral-like compositions, distribution*

I. Introduction

The progress of nuclear power engineering and nuclear technology as a whole is associated with solving the problems of the nuclear fuel cycle, including the disposal of radioactive wastes with long-lived nuclides that require long-term and safe storage.

The works on the choice, preparation with the use of the cold crucible induction melter (CCIM) technology, and investigation of materials that are most suitable for immobilizing plutonium-containing wastes of different origin have been carried out at the All-Russian Scientific Research Institute of Inorganic Materials (VNIINM) in the framework of the agreements with Lawrence Livermore National Laboratory (LLNL, USA) on the material and technical support.

The paper presents the data on the synthesis of plutonium-containing materials based on borobasalt (Bz), pyroxene (JED), and andradite (A) compositions in a muffle furnace and a CCIM.

II. Preparation of Vitreous and Mineral-Like Compositions

Based on analysis of compositions of the possible plutonium-containing wastes, the borobasalt vitreous matrices and also pyroxene and ferrosilicate (andradite) compositions were chosen as matrix materials for the immobilization.

Plutonium-containing vitreous borobasalt compositions (Table 1) were prepared in laboratory facilities [alundum crucibles in muffle furnaces (Fig. 1a) and CCIM (Fig. 1b)] installed in glove boxes. The materials were synthesized by melting of mixtures of a previously prepared borobasalt glass frit and the plutonium oxide (PuO_2) at a temperature of 1200 - 1300°C for 1 - 3 h.

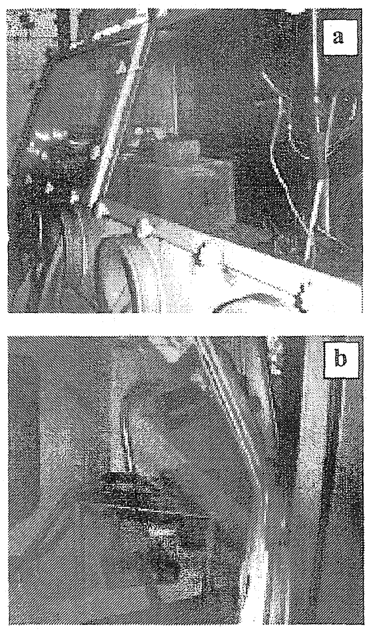

Fig.1 Glove boxes with (a) muffle furnace and (b) CCIM.

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Table 1 Calculated compositions of synthesized borobasalt materials

Oxide	Oxide content, wt %	
	Bz-Pu-5	Bz-Na-Pu-5*
Na_2O	1,9	5,7
MgO	4,9	2,9
Al_2O_3	8,1	9,6
SiO_2	28,9	33,7
K_2O	0,3	0,9
CaO	16,6	14,4
TiO_2	0,5	0,9
MnO	0,1	0
Fe_2O_3	5,8	5,7
B_2O_3	27,9	22,2
PuO_2	5,0	4,0

** – Calculations were carried out for the preparation of 150 g of melted material block.*

Plutonium-containing compositions of the pyroxene and andradite types (Table 2) were prepared in the laboratory CCIM facilities (Fig. 1b). The materials were synthesized by melting of mixtures of a previously prepared matrix frit and the plutonium oxide (PuO_2) at a temperature of 1500 - 1600°C for 0.5 - 1 h.

Table 2 Compositions of materials synthesized in CCIM

Oxide	Oxide content, wt %							
	GED-F		GED-Pu		A-F		A-Pu	
	calcd	as-an	calcd	as-an	calcd	as-an	calcd	as-an
SiO_2	42,0	55,0	40,1	n/a	38,0	50,6	35,9	n/a
MgO	16,0	9,0	15,3	n/a	8,0	6,8	7,6	n/a
Al_2O_3	8,0	9,5	7,6	n/a	12,0	14,6	11,3	n/a
CaO	14,0	11,0	13,4	n/a	11,0	8,1	10,4	n/a
Fe_2O_3	12,0	8,0	11,4	n/a	26,0	15,9	24,6	n/a
NiO	-	-	-	-	1,0	0,4	0,9	n/a
Cr_2O_3	-	-	-	-	2,0	1,8	1,9	n/a
MnO_2	-	-	-	-	2,0	1,8	1,9	n/a
Na_2O	8,0	7,5	7,6	n/a	-	-	-	-
PuO_2	-	-	4,6	4,6	-	-	5,5	5,7

JED block - 130 g, A block - 110g, n/a – not analyzed

III. Investigation of Prepared Materials

1. Borobasalt compositions

Pu containing borobasalt composition Bz-Pu-5 as muffle furnace synthesized is a vitreous material, whole bulk glass contains dispersed crystalline particles consisting PuO_2 that are undissolved or recrystallized in molten (fig. 2). The solubility of plutonium in the muffle furnace synthesized Bz-Pu-5 is ~ 3.5 wt.% plutonium dioxide (fig. 3, table 3). Excess plutonium basically sediments at the bottom of a glass log to form a crystalline phase layer (figs. 2, 3a, 3b) Individual crystalline particles (fig. 3c) as well as their aggregates are also available within a glass log. The borobasalt material Bz-Na-Pu-5, as CCIM synthesized in homogeneous glass with uniformly distributed plutonium at the average content of 5,6 wt.% (fig. 4, table 4).

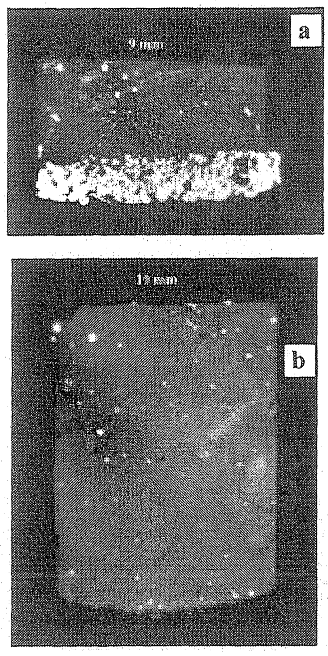

Fig.2 Radiographic images of Bz-Pu-5 samples taken from (a) bottom and (b) central parts of glass block.

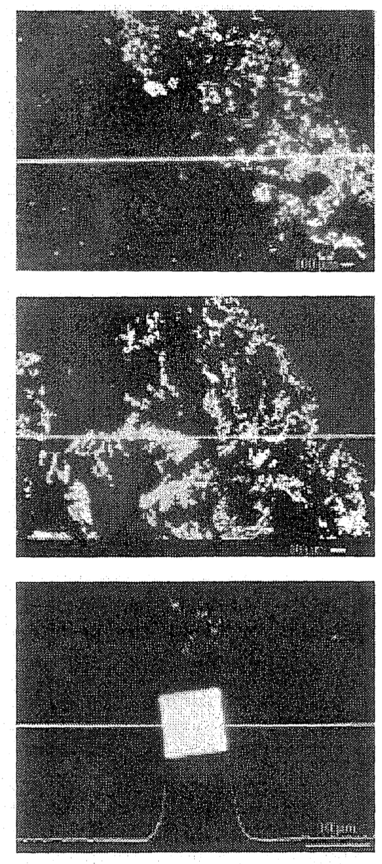

Fig.3 SEM (reflection electrons) images of Bz-Pu-5 samples.

Table 3 Data of profile probing for the Bz-Pu-5 composition
(Fig. 3a; probing step, 500 μm)

Point of probing	Plutonium content, wt % PuO_2
1	0.9
2	10.17
3	4.79
4	1.85
5	2.20
6	3.27
7	3.06
8	2.66
9	3.76
10	3.40
11	3.23

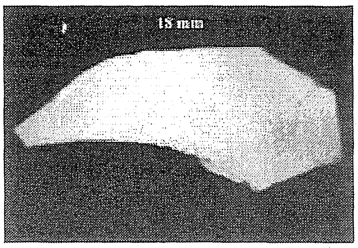

Fig.4 Radiographic image of the central part of Bz-Na-Pu-5 block.

Table 4 Data of profile probing for the Bz-Na-Pu-5 composition
(Fig. 4; probing step, 500 μm)

Point of probing	Plutonium content, wt % PuO_2
1	5.29
2	5.60
3	5.61
4	5.38
5	5.40
6	5.68
7	5.56
8	5.70
9	5.64
10	5.60

2. Mineral-like compositions

The investigation of the samples of the plutonium-containing pyroxene composition JED-Pu synthesized in the CCIM demonstrated that plutonium is uniformly distributed over the glass in the upper and central zones of the block. Its average content (the mass of the operating volume block is about 130 g) is equal to 4.6 wt % PuO_2 (Fig. 5a, Table 5).

In the plutonium-containing garnet composition A-Pu synthesized in the CCIM, plutonium is also uniformly distributed in the upper and central zones of the block, in which its average content (the mass of the operating volume block is about 100 g) is equal to 5.7 wt % PuO_2 (Fig. 5b, Table 6).

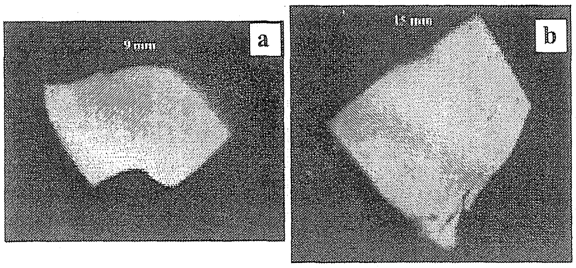

Fig.5 Radiographic images of (a) JED-Pu and (b) A-Pu samples.

Table 5 Data of profile probing for the JED-Pu composition
(probing step, 500 μm)

Point of probing	Plutonium content, wt % PuO_2
1	4.6
2	4.4
3	4.6
4	4.8
5	4.6
6	4.4
7	4.3
8	4.6
9	4.5
10	4.5
11	4.7
12	4.8

Table 6 As-analyzed plutonium contents in samples of the A-Pu composition
(gamma spectrometry)

Point of probing	Plutonium content, wt % PuO_2
1	6.4
2	5.5
3	5.1
4	6.1
5	5.8
6	5.5
7	5.3
8	6.1
9	5.7
10	5.7
11	5.8
12	5.3

IV Conclusion

The examinations of the synthesized materials implemented by the methods of optical and electron microscopy, radiometry, alpha-radiography and X-ray phase analysis demonstrate that the process of induction melting in "cold" crucible used to immobilize radwaste results in homogeneous materials (logs) with uniformly distributed plutonium.