Effect of the Compaction Pressure and Ni Content on the Modified Aluminum-Based Perovskite Synthesis Designed to Immobilize the Radioactive Waste in Combustion Mode

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Abstract. The article deals with the synthesis of perovskite-like ceramics matrix material for immobilization of radioactive waste by SHS method. The dependence of the compaction pressure on the synthesis of the samples was established. Synthesis conditions for the matrix with the desired properties of the composition were determined that is acceptable for reliable isolation of radionuclides throughout the long-term storage of waste. The maximum amount of aluminum perovskite is observed when the initial mixture compaction pressure equal to 30 MPa and 25% wt. nickel.

1. Introduction

Nuclear industry is inevitably associated with the ecologically hazardous nuclear waste accumulation [1, 2]. The issue of the treatment of high-level waste (HLW), formed during the processing of irradiated nuclear fuel is considered to be far more complicated. This waste has a complex chemical composition which depends on the reactor type, exposure time, processing technology, etc.

The traditional way of HLW isolation from the biosphere is their immobilization in phosphate and borosilicate glasses of different composition. However, glass does not completely satisfy the requirements to the matrices for the preservation of long-lived radionuclides for a long period of time [3].

Along with the improvement of glasses material necessary for long-term HLW disposal in the geological environment, various types of ceramics based on the unique rock-forming minerals with high chemical, thermal and radiation stability are being developed [4]. The basic idea of this method - the inclusion of chemically bound active atoms of radionuclides and toxic waste components in the form of a solid solution into the crystal lattice of the minerals' matrix similar to the stable natural minerals, where such radionuclides exist for thousands of years with the levels of radioactivity or toxicity hundreds of times smaller than if they were in free or mechanically blocked state [5-8]. Nowadays over 20 compounds differing in capacitance depending on the elements mentioned, chemical and radioactive strength were proposed. These compounds include zircon, zirconolite, perovskite, yttrium-aluminum garnet (IAG), britholite, monazite, pyrochlore.

The analysis of the known studies in matrix immobilization showed that the main reasons hindering wide practical application of the methods, are the complexity and high cost of technologies (mixtures heated to temperatures of 1300-2000° C, the need for more sophisticated technological operations to eliminate such accompanying processes as dust and gas formation, foaming, samples compaction, etc.).

High-level waste disposal by means of a spontaneous metallothermic process with the SHS in durable synthetic mineral-like matrix is the most economical and simple way of HLW isolation from the environment. This out-of-furnace method has almost no energy costs for the refractory materials synthesis, a short time of the SHS-product formation and the absence of sophisticated equipment that facilitates the work with high-level materials in a hot cell and makes it safer [9, 10].

Thus the aim of this study was to obtain a matrix material based on a modified perovskite of ABO_3 (A = Me^{3+}, B = Al) type by SHS method. The neodymium oxide was used as a trivalent radioactive waste simulator due to the similarity in ionic radii of actinides and neodymium [11-13].

2. Methods and experiments

SHS-based materials synthesis included the following steps:
– mixing powders of initial reagents according to the stoichiometric calculation for the corresponding reaction equations;
– drying the initial mixture of reactants in a technical vacuum;
- mixing in a cubic mixer;
- compressing the initial reactants mixture into cylindrical pellets of different diameter and height with variations in material density values in samples obtained by changing the pressure;
- running the SHS process in a laboratory facility and obtaining functional materials samples.

To prepare the mixture we used industrially manufactured PA-4 aluminum powders and neodymium oxide with a chemical purity grade TU 48 – 4 – 186 – 72.

The initial mixture was prepared for the exothermic reactions (1):

$$Al + Nd_2O_3 = Al_2O_3 + Nd, \qquad (1)$$
$$Al_2O_3 + Nd_2O_3 = 2NdAlO_3.$$
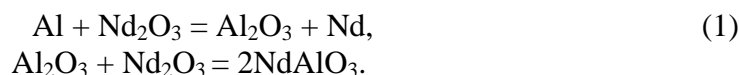
Initial reagents powders have been mixed in a cubic mixer AR 403 All-Purpose Equipment (Germany), which is a hollow rotating cube with three stainless steel rods, designed to enhance the mixing of the blend components.

After mixing and vacuum drying the resulting mixture was compressed into cylindrical samples 30 mm in diameter and 12-15 mm in height at different pressures – 15, 20, 25, 30, 35 and 40 MPa, to obtain samples of different density.

Pressing the initial mixture was performed using a hydraulic press PGL-12 (maximum pressure 50 MPa to 30 cm^2 surface). Metal molds were made of tool steel. Duration of pressing - 15 min.

The synthesis was carried out on the test bench for pyrometric studies of SHS laws, including a SHS reactor.

The phase compositions of the synthesized compound have been determined using a diffractometer Rigaku D / Max-2200 (CuKα radiation, a step 0.02, 1 second exposure).

3. Results and discussions

By heating the initial sample to a temperature of about 500-600 K (depending on the preparation of the initial mixture of components), the combustion wave was initiated at the ends' edges that spread over the sample volume. In this process the temperature increased rapidly, then stabilized, and burning continued almost isothermally under the temperature of 1000-1250 K. After the passage of the combustion wave along the sample volume, it cooled down to ambient temperature of the medium.

The study of the described system showed that sustainable propagation of the combustion wave is observed in the cases where the value of the system pressure equals 15 ... 30 MPa for all values of preheat temperature. However, when the initial mixture pressure is approximately 35 MPa and higher there was a significant increase in the specific energy release of the reactions occurring per unit volume of the sample; thus leading to the thermomechanical destruction of the samples samples during synthesis.

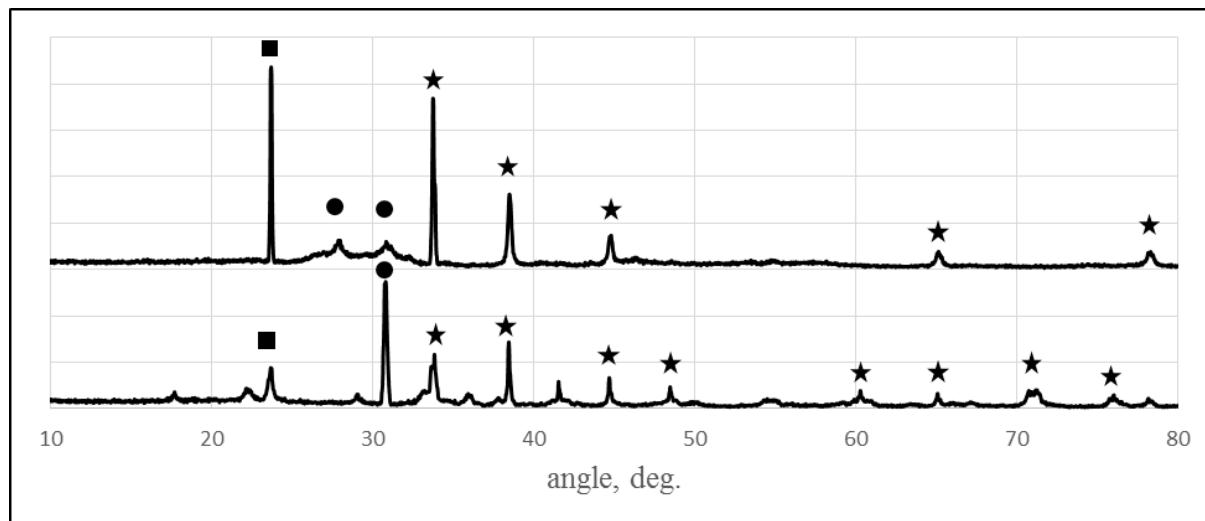Figure 1 shows an X-ray phase analysis of the samples obtained the compaction pressure of 25 and 30 MPa.

Figure 1. X-ray phase analysis of the samples obtained the compaction pressure of 25 (lower) and 30 MPa (upper), where ■ − $NdAlO_3$, ● − Nd_2O_3, ★ − Al.

Phase composition was the following:
− phase composition of the sample (% by weight) with the compaction pressure 25 MPa: 63.2% Al, 24.6% Nd_2O_3, 12.2% $NdAlO_3$;
− phase composition of the sample (% by weight) with the compaction pressure 30 MPa: 69.1% Al, 19.6% Nd_2O_3, 11.3% $NdAlO_3$.

The X-ray phase analysis shows that most part of Al left unreacted and the presence of the desired perovskite-like phase is only about 10% by weight in samples subjected to synthesis. Most likely, this phenomenon can be explained by the insufficient temperature growth in the synthesis of the final product and it is necessary to increase the total heat impact required for the reaction. This means that the process temperature must be increased so that the temperature conditions throughout the entire volume of the sample would allow to complete the SHS.

As it was previously noted, increasing the sample compaction pressure higher than 35 MPa leads to thermo-mechanical degradation, therefore, it is necessary to look for other ways to control the SHS process.

One solution to this problem could be the introduction of the stoichiometric reactive additives to the initial reactants mixture, which react exothermically with the components of the mixture during the synthesis, thereby increasing the total heat effect of SHS.

As a required additive we selected c.p. PNA OT1 Ni powder. Adding nickel involves the formation of the following phases: NiAl; Ni_2Al_3; $NiAl_3$. Ni2Al3 and $NiAl_3$ phases, in contrast to the negative component NiAl, should provide a high strength characteristics, because have irregular crystal lattice structures, which are more resistant to mechanical stress [14].

To obtain the result, which is the most appropriate to the characteristics, the samples with various contents of Ni (10 ... 30 wt.%) and compaction pressure (15 ... 30 MPa) were prepared.

Experiments have shown that the combustion temperature depends on the nickel additive amount in the initial mixture of reactants. Thus, when the content of additional components in a sample is about 25% wt. there is a significant increase in temperature (up to 2700 K) of the process; in case of 30% wt. − thermochemical degradation of the sample during synthesis for any stoichiometry considered due to significant heat release of the reactions in the mixture.

Figure 2 is shows a X-ray pattern of the samples containing 20% wt. of additives:

- phase composition of the sample (% wt.) with the compaction pressure 15 MPa: 59.3% Ni_2Al_3, 4.6% $NdAlO_3$, 9.9% NiAl, 22.5% Al;
- phase composition of the sample (% wt.) with the compaction pressure 25 MPa: 43.1% Ni_2Al_3, 10.2% $NdAlO_3$, 21.1% NiAl, 23.7% Al.
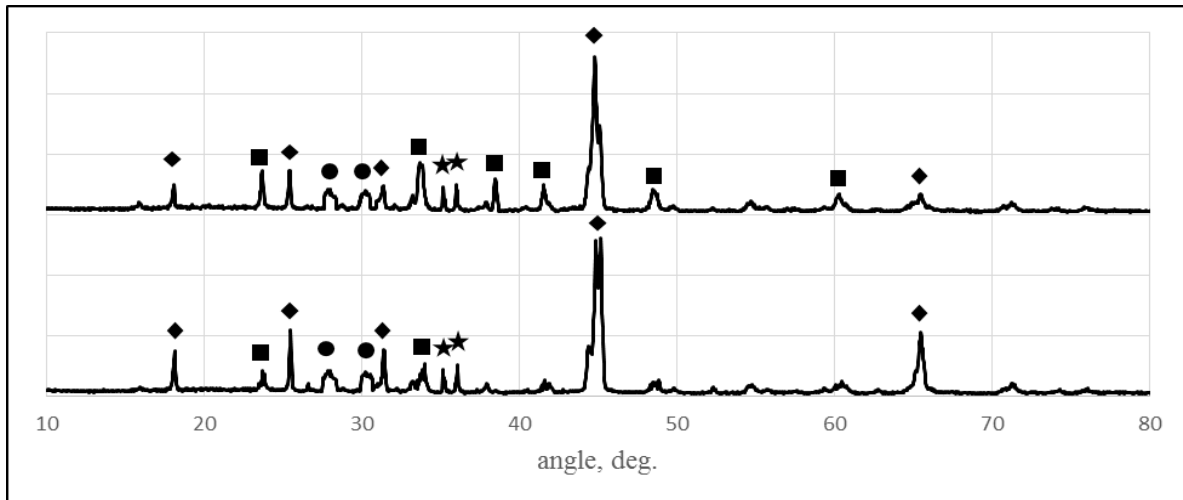

Figure 2. X-ray phase analysis of the samples obtained the compaction pressure of 15 (lower) and 25 MPa (upper), where ■ − $NdAlO_3$, ♦ − Ni_2Al_3, ▲ − $NiAl_3$, ● − Nd_2O_3, ★ − Al.

As a result of the nickel additive use, most of unreacted aluminum entered into the exothermic reaction with the further the formation of the nickel aluminide phases, wherein phase formation shifted towards lower formation of perovskite phase. According to [15] aluminum perovskite formation depending on the stoichiometric mixture ratio starts from 1100 K, therefore, it can be assumed that the SHS does not involve higher temperatures.

Figure 3 is shows a X-ray pattern of the samples containing 25% wt. of additives:
- phase composition of the sample (% wt.) with the compaction pressure 20 MPa: 27.6% $NdAlO_3$, 36.9% Ni_2Al_3, 31.6% $NiAl_3$, 3.2% Nd_2O_3;
- phase composition of the sample (% wt.) with the compaction pressure 25 MPa: 39.9% $NdAlO_3$, 56.5% Ni_2Al_3, 3.6% Nd_2O_3;
- phase composition of the sample (% wt.) with the compaction pressure 30 MPa: 48.4% $NdAlO_3$, 46.8% Ni_2Al_3, 4.8% Nd_2O_3.
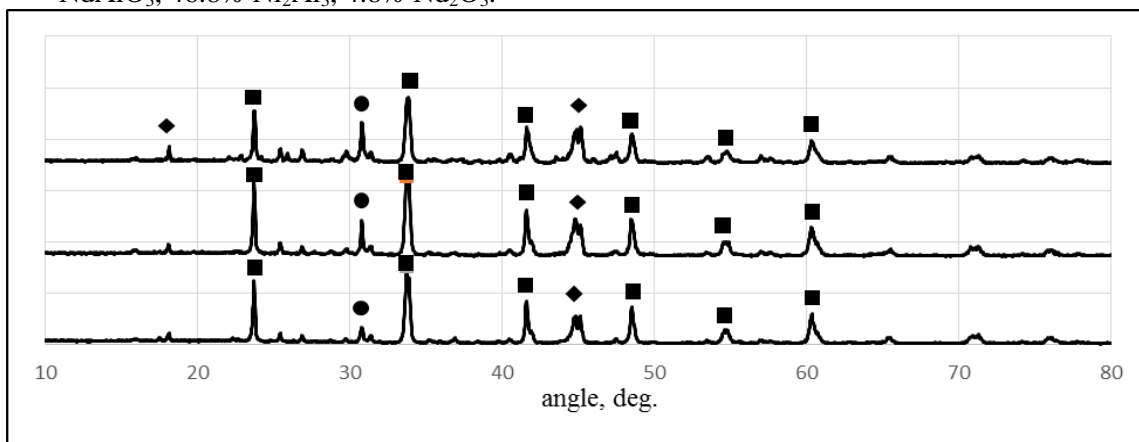

Figure 3. X-ray phase analysis of the samples obtained the compaction pressure of 20 (lower), 25 (middle) и 30 MPa (upper), where ■ − $NdAlO_3$, ♦ − Ni_2Al_3, ▲ − $NiAl_3$, ● − Nd_2O_3.

Thus, by increasing the content of additives amounts up to 25% wt. and compressing pressure of 30 MPa, the content of the modified aluminum-based perovskite based in the samples reaches almost 50 wt.%, and the amount of unreacted neodymium oxide is less than 5% wt.

4. Conclusions
Thus, results of the accomplished studies allowed to certify the following:

1) In the synthesis of matrix material, there is a lack of reaction energy yield for the $NdAlO_3$ formation according to reactions 1, therefore, it is necessary to use additives which increase the energy yield to ensure complete interaction between initial components

2) It is established that the samples obtained by compression of the mixture with the addition of Ni samples at the compaction pressure increased from 15 to 30 MPa experience the phase shift towards the final product formation due to the higher energy yield.

3) The maximum amount of aluminum perovskite is observed when the initial mixture compaction pressure equal to 30 MPa and 25% wt. nickel.

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