

ПРОБЛЕМЫ ЯДЕРНОЙ, РАДИАЦИОННОЙ
И ЭКОЛОГИЧЕСКОЙ БЕЗОПАСНОСТИ

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МАТРИЧНАЯ ФОРМА ПЕРОВСКИТА С ИСПОЛЬЗОВАНИЕМ
ТЕХНОЛОГИИ САМОРАСПРОСТРАНЯЮЩЕГОСЯ
ВЫСОКОТЕМПЕРАТУРНОГО СИНТЕЗА (СВС) ДЛЯ
ИММОБИЛИЗАЦИИ ВЫСОКОАКТИВНЫХ РАДИОАКТИВНЫХ
ОТХОДОВ (ВАО)

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Синрок признан в качестве вторичного отхода для захоронения высокоактивных радиоактивных отходов (ВАО). В этом исследовании один из самых изученных синрок-минералов, перовскит (CaTiO_3), был получен путем самораспространяющегося высокотемпературного синтеза (СВС). Nd_2O_3 и Al_2O_3 были использованы в качестве окислителей, с Ni в качестве восстановителя. Перовскит в этом случае был успешно синтезирован. Синтезированные образцы легко затвердевали с желаемой плотностью и твердостью по Виккерсу.

Ключевые слова: технология СВС, матричная форма перовскита, CaTiO_3 , радиоактивные отходы высокого уровня.

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1. Introduction

The immobilization of high-level waste (HLW) radionuclides from the reprocessing of spent nuclear fuel from commercial or military reactors is an international challenge that has occupied much attention over many decades. At present, vitrification of borosilicate and phosphate glasses is the exclusive approach for industrial scale application of HLW management. However, the low solubility of minor actinides in glass matrix and the metastable nature of glasses are the major limitations. Synroc waste forms, which are mainly composed of multiple mineral phases such as zirconolite ($\text{CaZrTi}_2\text{O}_7$), pyrochlore ($\text{A}_2\text{B}_2\text{O}_6\text{X}$), perovskite (CaTiO_3), hollandite ($\text{BaAl}_2\text{Ti}_6\text{O}_{16}$), rutile (TiO_2), spinel (AB_2O_4), nepheline ($\text{KNa}_3(\text{AlSiO}_4)_4$) etc., were recognized as promising host materials for HLW immobilization. From isomorphism substitution theory, radioactive nuclides can be incorporated into the lattice structure of above-mentioned mineral phases, which significantly promote the long-term stability and safety for HLW disposal.

In the Synroc family, perovskite is an important component phase. The majority of chemical elements from the periodic table can form ABX_3 compounds with the perovskite structure. The diversity of chemical elements, which form perovskite structures, their ability to create cation- or anion-deficient structures, and a rich variety of distorted perovskite structures lead to an extremely broad range of physical properties. Because of this, the perovskite structure is often called the 'inorganic chameleon'. Ferro- nad piezoelectricity, high electronic and ionic conductivity, diverse magnetism, and colossal magnetoresistive effects, paraelectricity and superconductivity, all of these phenomena are known to occur in perovskite-type compounds.

However, in previous studies, perovskite waste forms were mainly synthesized from two approaches: (1) high temperature solid state reaction, (2) liquid phase synthesis.

Meanwhile, compulsive densification processes, such as hot pressing (HP) or hot-isostatic pressing (HIP), must be incorporated to get highly compacted specimens. Muthuraman et al. Have proposed a novel synthesis approach, self-propagating high-temperature synthesis (SHS), for the management of nuclear wastes. As an exothermic chemical reaction, the combustion of SHS reactants can be sustainably propagated after ignition. Compared with conventional solid state reaction process, SHS leads to high temperature and high reaction speed, as well as low energy consumption, low cost, simplified equipment requirement and convenient handling. However, the generated high temperature and high reaction speed in SHS reaction cause this process hardly be controlled, which may be a crucial limitation for industrial application of this technique. On the other hand, SHS reaction usually results in porous materials because of the high reaction speed and lack of compression process.

In this paper, the main goal is that using SHS technology to create immobilization solidified body - NdAlO₃ and analyze the sample component.

2. Experimental details

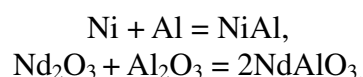
As initial components in the synthesis of matrix material by the SHS method, commercially manufactured powders of aluminum oxide, neodymium oxide, aluminum, nickel were used:

- neodymium oxide, grade x.h., TU 48-4-186-72;
- aluminum oxide GOST 8136 grade AOA-2;
- Nickel grade PNK-OT1;
- aluminum grade PA-4.

In accordance with the following exothermic reaction:



The process of formation of the final components should be of a two-stage nature and proceed along the following reaction channels:



Synthesis of materials by the SHS method in this work included the following stages:

- mixing the powders of the starting reagents according to the stoichiometric calculation according to the corresponding reaction equation (2.1) with the addition of a different amount of the Nd₂O₃-Al₂O₃ additive in a cubic mixer;
- drying of the initial burden of reagents in a vacuum;
- pressing the initial mixture of reagents into cylindrical tablets;
- implementation of the SHS process in a laboratory installation and obtaining samples of functional materials;
- processing of obtained samples.
- Mixing of powders of the initial reagents was carried out in a cubic mixer AR 403 All-Purpose Equipment (Germany), which is a hollow rotating cube with three stainless steel rods (rice), designed to enhance mixing of the components of the mixture, for 30 minutes.



Fig. 1.1 Cubic Mixer ERWEKA

After mixing, the initial charge was dried under a vacuum for 3 hours at a temperature of the order of 400 K (Fig.).

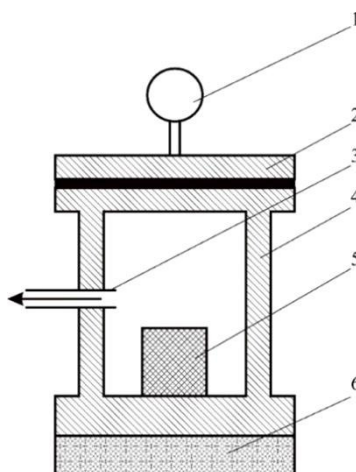


Fig. 1.2 Diagram of installation for vacuum drying: 1 - manometer; 2 - the camera cover; 3 - fitting; 4 - steel chamber; 5 - cuvette with charge; 6 - heating element

Pressing of the initial charge was carried out using a hydraulic laboratory press PGL-12 (maximum pressure of 50 MPa per surface area of 30 cm²), designed specifically for equipping the production analytical and research laboratories. The charge of reagents was pressed into cylindrical samples with a diameter of 30 mm and a height of 12-15 mm at different pressures - 15, 20, 25, 30 and 40 MPa, in order to obtain samples of different density.

Metal molds are made of tool steel. The pressing time was 30 minutes.

The synthesis was carried out under the conditions of a technical vacuum at the experimental stand of pyrometric studies of the regularities of the SHS process, including the SHS reactor (Fig. Heating of the sample and initiation of the synthesis reaction were carried out using a tungsten filament connected to a linear current converter. The temperature regimes were recorded with the help of tungsten-rhenium thermocouples connected to a multichannel pulse counter Aries SI8, with data recording by a personal computer.

In this experiment the equipment was not closed under vacuum, which means that the temperature at which the reaction occurred was higher than the temperature in the vacuum.

- Measured temperature: 1000 C
- Vacuum temperature (usual): 800 C – Using about 0,9 kgf/cm³

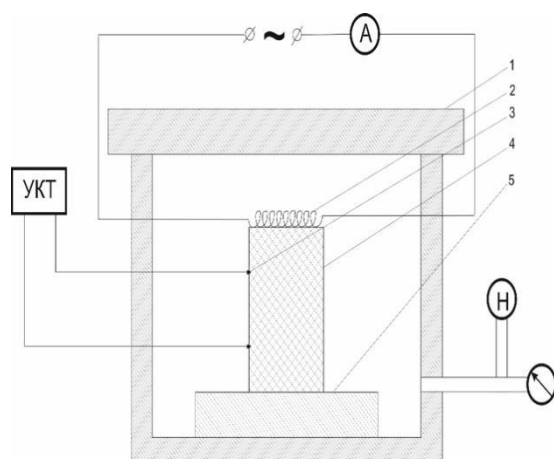


Fig. 1.3 The scheme of the experimental setup for the production of SHS materials: 1 – the reactor cover; 2 – tungsten filament; 3 – thermocouple; 4 – synthesized sample; 5 – fireproof stand

If the vacuum is not realized, there will be impurities in the atmospheric air that can react with the elements and influence the result of the experiment. Just like the energy that is lost by convection into the air.

Important indications for a quality experiment:

Suitable pressure, dust quality, heating temperature, temperature / cooling time.

The final sample should have a good aspect and don't have any bubble in the surface.

After this process, the pellet is sent to an x-ray analysis laboratory where it is analyzed and the composition is described.

Results and discussions

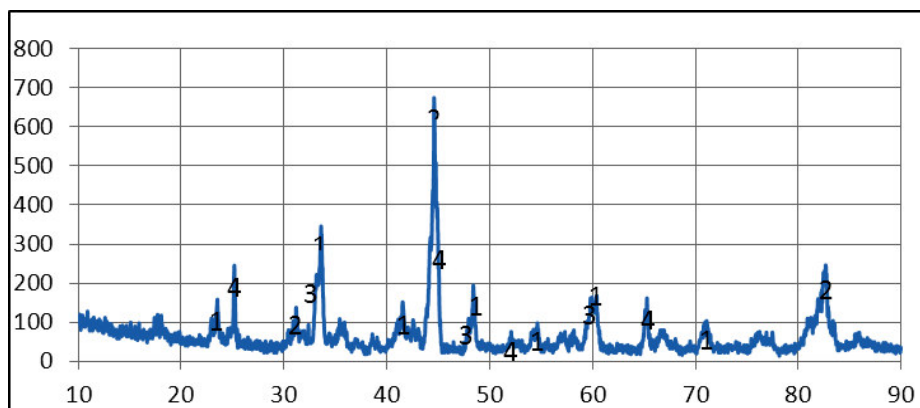


Fig. 2.1 The XRD pattern of the sample

Tab. 2.1 The mass percentage of composition

Composition	Mass percentage
NdAlO ₃	10.1%
NiAl	56.5%
NdAl ₂	9.4%
Ni ₂ Al ₃	23.9%

The products of SHS reaction were analyzed with the XRD pattern presented in Figure 2.1 and Table. The phase composition conforms to the original phase, we obtained the perovskite phase as NdAlO_3 . Besides it, there are some other phases, like NiAl , NdAl_2 and Ni_2Al_3 . The diffraction peak of Nd_2O_3 completely disappeared in the sample, indicating that Nd^{3+} has been solidified in the crystal lattice of NdAlO_3 .

3. Conclusion

In order to create NdAlO_3 , SHS technology was adopted. SHS technology, is the technology that using a large amount of heat released by the chemical reaction to maintain its own reaction to obtain a new material with the specified composition and structure. According to the XRD pattern shows, we obtained NdAlO_3 , and there is no Nd_2O_3 , it means that Nd^{3+} has been solidified in the crystal lattice of NdAlO_3 . However the final product has a big part of NdAl , these are not the target products. We need to adjust the more suitable experimental conditions to conduct experiment, such as pressure for powder, cooling process etc.

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Perovskite Matrix Form by Using SHS Technology for Immobilization HLW

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Abstract – Synroc is recognized as the second generation waste form for the disposal of high-level radioactive waste (HLW). In this research, one of the mostly studied Synroc minerals, perovskite (CaTiO_3), was prepared by self-propagating high-temperature synthesis (SHS). Nd_2O_3 and Al_2O_3 were employed as the oxidants with Ni as the reductant. Perovskite was successfully synthesized. The as-synthesized samples were readily solidified with desirable density and Vickers hardness.

Keywords: SHS technology, perovskite matrix form, CaTiO_3 , high level radioactive waste.