

## INFLUENCE OF MoO<sub>3</sub> AND HfO<sub>2</sub> PARTICLE SIZE ON THE PHASE COMPOSITION AND DENSITY OF DYSPROSIUM HAFNATE PELLETS

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The results of studies of the influence of the MoO<sub>3</sub> alloying additive, as well as HfO<sub>2</sub> with different particle sizes on the phase composition and density of dysprosium hafnate pellets are presented. It is shown that the use of coarse HfO<sub>2</sub> powder (ГФО-2 grade) with particles size from 1 to 100 μm does not lead to the achievement of high density of sintered pellets and the completeness of the dysprosium hafnate synthesis, since dysprosium oxide remains in the synthesized material at sintering temperature of 1650°C. The use of HfO<sub>2</sub> manufactured by China Rare Metal Material with a crystallite size near 22 nm leads to an increase in the sintered pellets density (8.2...8.3) g/cm<sup>3</sup>. The doping of MoO<sub>3</sub> in the amount of 2.5 wt%. promotes the intensification of synthesis process with the formation of a single-phase fluorite structure at a temperature of 1450°C, but does not increase the density of sintered pellets.

*Keywords:* dysprosium hafnate, density, powder, pellet, phase

Dysprosium hafnate (Dy<sub>2</sub>O<sub>3</sub>-HfO<sub>2</sub>) is a promising material for control components of VVER and PWR reactors. Due to its high physical efficiency of neutron absorption and significant radiation resistance, this material can be used to develop absorber rod designs with increased long-term operation and reliability. The main requirement for the structural and phase state of dysprosium hafnate pellets is the absence of initial oxides due to their insufficient radiation and corrosion resistance. It is desirable to achieve the highest possible density of pellets since this characteristic affects the physical efficiency of neutron absorption. In addition, previous studies have shown that high density of dysprosium hafnate pellets increases their strength and corrosion resistance in the VVER-1000 coolant environment.

The main aim of this work is to study the effect of hafnium oxide particle size and molybdenum oxide as a doping additive on the characteristics of the dysprosium hafnate pellets during sintering in air atmosphere, such as phase composition and density.

The following oxides were used as starting materials:

- 1) Dy<sub>2</sub>O<sub>3</sub>, (99.5%), China Rare Metal Material co., Ltd. (CRMM);
- 2) HfO<sub>2</sub> (ГФО-2, ZrO<sub>2</sub>+HfO<sub>2</sub> 99.5%), ТУ 48-4-201-72;
- 3) HfO<sub>2</sub> (nano, ZrO<sub>2</sub>+HfO<sub>2</sub> ≥99.95%, Zr<0.23%) (CRMM);
- 4) MoO<sub>3</sub> (ЧДА, 99.9%), ТУ 6-09-44-71-77.

Varying different grades of initial HfO<sub>2</sub> and doping additive MoO<sub>3</sub> gave the following powder compositions (batches, charges) for the synthesis of dysprosium hafnate (Table 1).

Table 1. Compositions of dysprosium hafnate

Batch	Composition, wt. %	Composition, mol. %
HD1	63.9%Dy <sub>2</sub> O <sub>3</sub> +36.1%HfO <sub>2</sub> (ГФО-2)	50%Dy <sub>2</sub> O <sub>3</sub> +50%HfO <sub>2</sub>
HD2	63.9%Dy <sub>2</sub> O <sub>3</sub> +36.1%HfO <sub>2</sub> (CRMM)	
HDM3	62.4%Dy <sub>2</sub> O <sub>3</sub> +35.1%HfO <sub>2</sub> (ГФО-2)+2.5%MoO <sub>3</sub>	47.5%Dy <sub>2</sub> O <sub>3</sub> +
HDM4	62.4%Dy <sub>2</sub> O <sub>3</sub> +35.1%HfO <sub>2</sub> (CRMM)+2.5%MoO <sub>3</sub>	47.5%HfO <sub>2</sub> +5%MoO <sub>3</sub>

Manufacturing of dysprosium hafnate pellets included the following technological operations:

- 1) mixing of the starting powders and plastifyser - polyethylene glycol (PEG-400) in distilled water in a planetary mill "Pulverisette 6" (Fritch, Germany) using WC milling balls;
- 2) drying the powder mixture to a final moisture content of less than 0.5%;
- 3) pressing pellets with a diameter of 8.55 mm in a steel mould at a pressure of 200 MPa;
- 4) sintering at 1450°C for 3 hours and at 1650°C for 3 and 6 hours in an furnace (HT 16/17 P470 Naberterm GmbH, Germany).

According to the results of scanning electron microscopy HfO<sub>2</sub> (ГФО-2) is a coarse powder with elongated fragmented particles ranging in size from 1 to 100 μm.

Dy<sub>2</sub>O<sub>3</sub> (CRMM) is fine-dispersed powder with fragmented particles ranging in size from 1 to 5 μm.

MoO<sub>3</sub> powder is coarse with fragmented particles ranging in size from 1 to 40 μm.

According to the X-ray diffraction analysis the crystallite size (or coherent scattering domains size CSD) of HfO<sub>2</sub> (CRMM) is equal to  $L=22$  nm and the microstrain is  $\varepsilon=2.37 \cdot 10^{-3}$ .

The study of dysprosium hafnate pellets of batch HD1 showed that after sintering at 1450°C the formation of two solid solutions based on the structure of dysprosium hafnate with different lattice parameters  $a = 0.5209$  nm and  $a = 0.525$  nm was observed. We marked them as Hf<sub>1-x</sub>Dy<sub>x</sub>O<sub>y</sub>-1 and Hf<sub>1-x</sub>Dy<sub>x</sub>O<sub>y</sub>-2.

Dysprosium oxide and cubic hafnium oxide were also present. The density of the pellets was  $5.8 \text{ g/cm}^3$ . When the sintering temperature was increased to  $1650 \text{ }^\circ\text{C}$ , the content of  $\text{Dy}_2\text{O}_3$  decreased to 9.6 wt.% and  $\text{Hf}_{1-x}\text{Dy}_x\text{O}_y-1$  to 3.3 wt.%, while the content of  $\text{Hf}_{1-x}\text{Dy}_x\text{O}_y-2$ , on the contrary, increased to 87.1% wt. The density of the pellets increased to  $6.3 \text{ g/cm}^3$ . After 6 hours of exposure at a sintering temperature of  $1650 \text{ }^\circ\text{C}$ , there was a slight increase in the density of pellets up to  $6.6 \text{ g/cm}^3$ , but the material remained three-phase: two fluorite type solid solutions  $\text{Hf}_{1-x}\text{Dy}_x\text{O}_y-2$  (93.9% wt.),  $\text{Hf}_{1-x}\text{Dy}_x\text{O}_y-1$  (2.0 wt.%) and  $\text{Dy}_2\text{O}_3$  (4.1 wt.%). The trend of decreasing the content of  $\text{Hf}_{1-x}\text{Dy}_x\text{O}_y-1$  and  $\text{Dy}_2\text{O}_3$  and increasing the content of  $\text{Hf}_{1-x}\text{Dy}_x\text{O}_y-2$  continued.

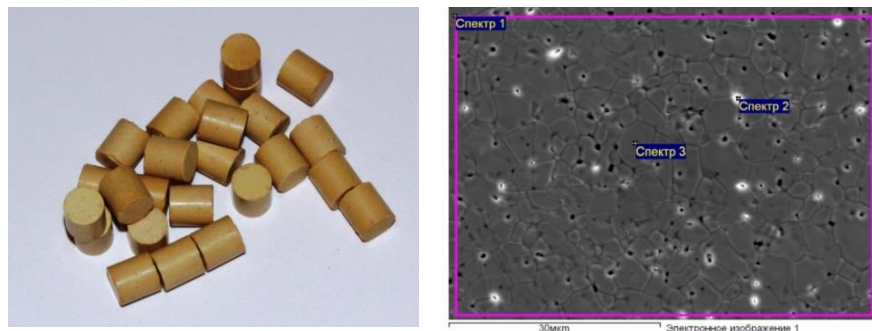
The study of dysprosium hafnate pellets of batch HD2 showed that at  $1450^\circ\text{C}$ , the formation of two solid solutions of dysprosium hafnate  $\text{Hf}_{1-x}\text{Dy}_x\text{O}_y-1$  (9.2 wt.%) and  $\text{Hf}_{1-x}\text{Dy}_x\text{O}_y-2$  (74.1 wt.%) was observed. The sample also contained dysprosium oxide (16.7 wt.%). The density of the tablets was  $7.1 \text{ g/cm}^3$ . When the pellets were sintered at  $1650 \text{ }^\circ\text{C}$  for 6 hours, the content of  $\text{Dy}_2\text{O}_3$  decreased to 10.9 wt.% and  $\text{Hf}_{1-x}\text{Dy}_x\text{O}_y-1$  to 12.5 wt.%, but the content of  $\text{Hf}_{1-x}\text{Dy}_x\text{O}_y-2$  increased to 76.6 wt.%. The density of the pellets increased to  $8.2 \text{ g/cm}^3$ . With an increase in sintering time up to 6 hours at  $1650 \text{ }^\circ\text{C}$ , there was a slight increase in the density of the pellets to  $8.3 \text{ g/cm}^3$ . The material remains three-phase: it contains two phases of the fluorite type  $\text{Hf}_{1-x}\text{Dy}_x\text{O}_y-2$  (82.3 wt.%),  $\text{Hf}_{1-x}\text{Dy}_x\text{O}_y-1$  (13.9 wt.%) and  $\text{Dy}_2\text{O}_3$  (3.8 wt.%).

The study of dysprosium hafnate pellets of batch HDM3 synthesized at  $1450^\circ\text{C}$  showed that the material was two-phase and consisted of fluorite-type  $\text{Hf}_{1-x}\text{Dy}_x\text{O}_y-2$  (98.0 wt.%) and  $\text{Dy}_2\text{O}_3$  (in amount of 2.0 wt.%). The density of the pellets was  $5.5 \text{ g/cm}^3$ . With a further increase in temperature to  $1650^\circ\text{C}$ , the material became single-phase and had a fluorite-type structure. The density of the pellets increased to  $6.1 \text{ g/cm}^3$ . When the sintering time was increased to 6 hours, the density of the pellets increased to  $6.2 \text{ g/cm}^3$ .

The study of dysprosium hafnate pellets of the HDM4 batch showed the following. The material synthesized at  $1450 \text{ }^\circ\text{C}$  was single-phase with a fluorite structure of  $\text{Hf}_{1-x}\text{Dy}_x\text{O}_y-2$ . The density of the pellets was  $5.7 \text{ g/cm}^3$ . With an increase in temperature to  $1650^\circ\text{C}$ , the material did not change its phase composition. The density of the pellets increased to  $6.2 \text{ g/cm}^3$ . When the sintering time was increased to 6 hours, the density of the pellets increased to  $6.3 \text{ g/cm}^3$ .

The study of the characteristics of dysprosium hafnate pellets of batch HD1, which were manufactured according to the technological scheme, including the preliminary synthesis of dysprosium hafnate at  $1450 \text{ }^\circ\text{C}$ , grinding of powders in a planetary mill, drying, pressing and sintering of pellets, showed the following. The pellets were characterized by a density of  $(8.0..8.3) \text{ g/cm}^3$  and a single-phase fluorite structure  $\text{Hf}_{1-x}\text{Dy}_x\text{O}_y-2$  with lattice parameter of  $a = 0.52581 \text{ nm}$ . The content of the main elements in the integral calculation along

the sample plane is: Dy-55.1 wt.% and Hf-30.5 wt.% (Fig. 1, Spectrum 1), and in local areas the content of these elements is quite close to the integral value of the content and was: Dy-55.3 wt.% and Hf-30.4 wt.% (Fig. 1, Spectrum 2) and Dy-54.9 wt.% and Hf-31.6 wt.% (Fig. 1, Spectrum 3). The microstructure of the pellets is characterized by a fine-grained structure with a grain size of (2...5)  $\mu\text{m}$  and a uniform distribution of spherical pores with a size of to 1  $\mu\text{m}$ .



Element	Spectrum 1		Spectrum 2		Spectrum 3	
	wt.%	at.%	wt.%	at.%	wt.%	at.%
Dy	55,1	24,1	55,3	24,2	54,0	23,6
Hf	30,5	12,1	30,4	12,5	31,6	12,6
O	14,4	63,8	14,4	63,3	14,4	63,9

Fig. 1. Appearance, microstructure and elemental composition of dysprosium hafnate pellets of batch HD1 with density (8.0...8.3)  $\text{g}/\text{cm}^3$ .

Thus, results of the research will be used to develop a laboratory technology for the manufacturing of dense dysprosium hafnate pellets with a single-phase fluorite structure, which is currently being developed on the basis of the equipment of the NFC STE of NSC KIPT.