Preparation and properties of composite material based on hafnium diboride and aluminum

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***Abstract* — Hafnium diboride (HfB_2) in aluminum matrix (Al) material was prepared by diffusion sintering of a mixture of hafnium diboride and aluminum micropowders. The effect of the hafnium diboride content (HfB_2) in the aluminum matrix (Al) on sintering characteristics and properties of the samples is presented. The effect of microwave activation of the aluminum powders has been established. The diffusion sintering behavior was concluded. The material properties and structure were defined.**

Keywords: ceramics, aluminum, hafnium diboride, microwave activation, diffusion sintering.

I. INTRODUCTION

Due to the nuclear industry development the new materials design process is a crucial task to protect against ionizing radiation and neutrons [1]. New materials that can absorb or scatter ionizing radiation, at the same time having a low density and mass-dimensional characteristics of the final products are needed to be design. Moreover, using of lead screens and their subsequent disposal are a complex environmental problem; therefore, replacing such screens with new materials makes it possible to solve not only technical problems, but also to improve the environmental situation [2].

Hafnium diboride (HfB_2) should be noticed as a perspective material because of its nucleus high neutron capture cross section and scattering properties of boron nucleus. Aluminum has a relatively low density and low induced radioactivity [3]. Hafnium diboride physicochemical and radiation properties are well–studied, it is also known that it has high strength covalent bonding and low self-diffusion coefficient which indicates the need for high temperatures and pressure to create a strong non-porous structure. HfB_2 is a ceramic material, which suggests its fragility [4, 5]. Taking into consideration the known features of sintering ceramic materials with aluminum, leading to low-strength crack-sensitive systems (different thermal expansion coefficients of metals and ceramics, thermal stresses at the metal-ceramic interface) it was decided to create a system based on microwave radiation activated aluminum micropowder. Microwave effect on metal powders is known to an increase in the oxidation heat affect and a decrease in the oxidation onset temperature [6]. Microwave effect also leads to an increase of the aluminum nanopowder reserve energy, which is the result of the double electric layer formation and stabilization. Thereby microwave emission leads to a change in the substructural characteristics of metal-containing high-energy materials and results in an increase in the micro-stress in the metal component of aluminum particles [7].

Solid phase sintering was chosen because, in addition to the required lower energy costs, this solid phase interaction process is a diffusion process. A metal layer deposited on ceramics partially oxidized from the side facing the ceramics. The metal crystal lattice in the surface layer varies, at the same time, the chemically reorganized cells are not separated from the internal cells with the original crystal structure [8].

The aim of the work was to carry out exploratory researches of hafnium diboride diffusion (solid phase) sintering using microwave activated aluminum micropowder.

II. EXPERIMENTAL TECHNIQUES AND POWDER CHARACTERISTICS

To prepare material by diffusion sintering, mixtures of HfB2 and Al micropowders were prepared by heating. Information about the initial micropowders are given in table 1.

TABLE I. INITIAL POWDERS

HfB_2	TU No 6-09-03-418-76; particle shape is irregular; particle size – 40 μm
Al	ASD – 6M produced by OOO «SUAL-PM» (Shelekhov): the average surface diameter of the powder particles is 2.3 μm, the shape of the particles is close to spherical. The powder was produced by spraying molten aluminum in a chamber with a special atmosphere [9, 10]. The aluminum content in the powder after storage in conditionally sealed containers is 86 wt. %

The powder was irradiated according to the conditions and methods described in [6]. Figure 1 shows the thermograms of the initial (a) and irradiated aluminum powder (b).

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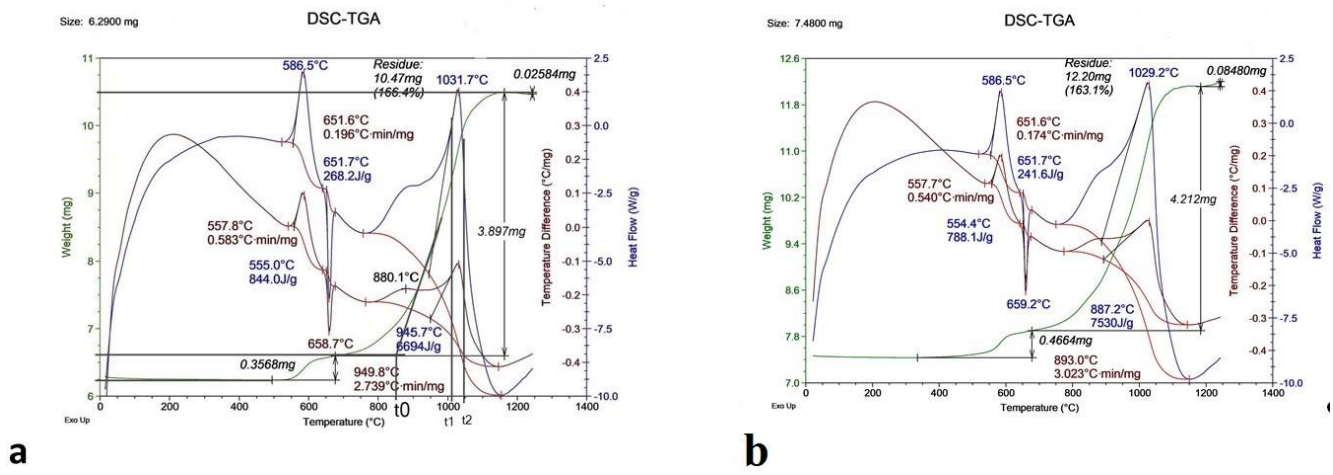

Fig. 1. Thermograms of aluminum powder ASD-6M: a - thermogram of the initial powder; b - powder thermogram after microwave irradiation

To prepare material samples HfB_2: Al mixtures were used, the composition and mass of which are presented in table 2. Similar mixtures were obtained on the basis of microwave irradiated aluminum [11, 12]. Tungsten nanopowder (W) was added to sample 4 in order to increase the sample adsorbing ability since W possesses high shielding properties due to high x-ray density. In addition, W is characterized by extremely high melting point, good machinability and high corrosive resistance [13, 14].

The initial and the microwave irradiated micropowders were checked for pyrophorosity by determining four activity parameters [6]. After the powder irradiating, its oxidation onset temperature decreased by almost 100 °C, remaining above 400 °C (Fig. 1), i.e. microwave radiation does not give a pyrophorous property to the previously passivated powder [15, 16].

TABLE II. COMPOSITION OF MIXTURES OF POWDERS HfB_2 AND AL

Item No	HfB_2 content, wt. %	Al content, wt. %	The additive nanopowder W content, wt. %	The mixture mass, g.
1	90	10	0	5.5
2	50	50	0	10.0
3	10	90	0	9.5
4	50	20	30	8.0

The powders sample weights were mixed by grinding them on the tracing paper with a cork wrapped in tracing paper until a uniform color was obtained. The resulting mixtures were pressed using a hydraulic press. Compacting pressure - 1.5 MPa. Compressed tablets sintering was carried out in a muffle furnace at 550 °C in an anoxic environment for 4 hours.

X-ray phase analysis (XRD) of sintered samples was performed using a Diffrey-401 diffractometer (X-ray tube radiation F_{K_α}, λ = 1.93 Å).

III. EXPERIMENTAL RESULTS

Figure 2 shows photographs of the obtained samples. Initial aluminum based samples have splits and cracks. Microwave-irradiated aluminum based samples are characterized by higher mechanical characteristics. According to the obtained results, the sintered samples phase composition is consistent (table 1) with the data of table 2 and 3: the composition of the sintered samples corresponds to the additivity concept. The results of the XRD are given in tables 3 and 4.

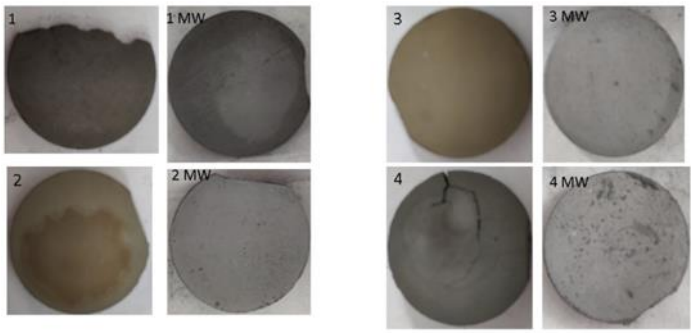

Fig. 2. Photos of the samples: 1,2,3,4 - samples of the corresponding composition based on the initial aluminum powder and 1 MW, 2 MW, 3 MW, 4 MW - samples of the corresponding compositions based on microwave-activated aluminum

TABLE III. SINTERED SAMPLES PHASE COMPOSITION OF MATERIAL BASED ON HfB_2 AND INITIAL ALUMINUM

Item No	HfB_2 content, wt. %	Al content, wt. %	The additive nanopowder W content, wt. %	The mixture mass, g.
1	90	10	0	5.5
2	50	50	0	10.0
3	10	90	0	9.5
4	50	20	30	8.0

TABLE IV. SINTERED SAMPLES PHASE COMPOSITION OF MATERIAL BASED ON HFB2 AND MICROWAVE IRRADIATED ALUMINUM

Item No	HfB_2 content, rel. %	Al content, rel. %	Sintering products contents, rel. %
1	97	3	0
2	75	25	0
3	48	52	0
4	68	13	18 (B2O3)

Boron oxidized to B_2O_3 was found on the sample surface. Al_2O_3 on the surface was not detected. According to the XRD results, there are significant differences in the composition of samples 3 and 4 (tables 2 and 3). For sample 3 the differences can be explained by the structure homogeneity imperfection,

when most of the aluminum is in the sample surface layer. For sample 4 the difference in the content of sintering products is related to the oxidation possibility of the additive (W) in the presence of sample defects noted for samples based on initial aluminum (there is a cleavage and crack in the sample volume).

The apparent density of samples without taking into account closed and open pores was measured in this work [17, 18]. The apparent density of initial Al based samples are given in table 5, microwave-activated Al based samples in table 6.

TABLE V. THE APPARENT DENSITY OF HfB_2 BASED SAMPLES AND INITIAL AL POWDER

Characteristics	Item No (tab. 2)			
	1	*2*	*3*	*4*
Density ρ, g/cm3	1.97	2.05	2.36	2.79
Shrinkage,%	-0.41	-0.23	-0.50	-3.95

TABLE VI. THE APPARENT DENSITY OF HfB_2 BASED SAMPLES AND MICROWAVE-ACTIVATED AL POWDER

Characteristics	Item No (tab. 2)			
	1	*2*	*3*	*4*
Density ρ, g/cm3	3.98	1.94	1.97	3.14
Shrinkage,%	-0.31	-0.35	-0.35	-0.31

There are a high porosity and negative shrinkage for all samples, which indicate oxidation processes. At the same time, comparing the obtained data, it can be said that the microwave-activated Al based samples structure is more stable.

Figure 3 shows photographs obtained using scanning electron microscopy (SEM).

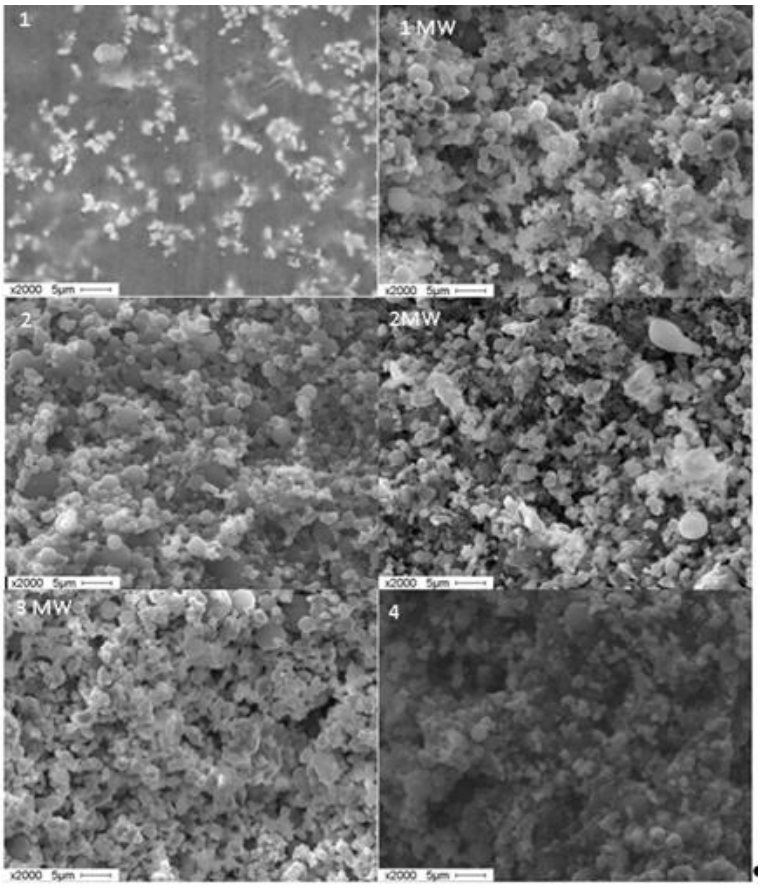

Fig. 3. Samples photos obtained by diffusion sintering: 1,2,4 are photographs of the initial aluminum powder based samples respectively; 1 MW, 2 MW, 3 MW - photographs of the microwave-activated aluminum powder based samples respectively

In photo 1 (Fig. 3) spherical particles with an average size of 2.1 μm are observed, while in photo 1 MW a specific geometric shape is not observed and particle size is about 2.5 μm. The high light areas are hafnium diboride particles, characterized by a higher density and occupy about 11% of the volume in photograph 1 and about 28% in photograph 1 MW. Fragments are combined into associations, which indicates partial sintering. According to microanalysis, there are aluminum atoms in sample 1 detected by the electrons emission from the Kα orbitals at their mass ratio of 74.01%, and hafnium atoms in a mass ratio of 25.99% by electrons emission from the L orbitals. There are aluminum atoms in sample 1 MW detected by the electrons emission from the K orbitals at their mass ratio of 79.47 %, and hafnium atoms in a mass ratio of 20.53 % by electrons emission from the L orbitals. Boron atoms were not detected, since its content in

the sample is below the microscope detection limit. For samples 2 and 2 MW, the average grain size is 2 and 2.6 μm, respectively. The mass ratio of aluminum and hafnium in the sample is 2 61.92 % and 38.02%, respectively. For sample 2 MW is 67.05 % and 32.95%. Boron atoms were also not detected. In sample 3 MW, the average grain size is 2.5 μm, the mass fraction of aluminum is 28.4%, the mass fraction of hafnium is 71.6%., The tungsten content is defined as 26.1 wt. % in sample 4, the hafnium content is 40.84 wt. %. The images determine structure of the samples as porous.

According to additionally carried out experiments using a spectrophotometer, the aluminum nanopowders burning samples emission spectra were recorded [19].

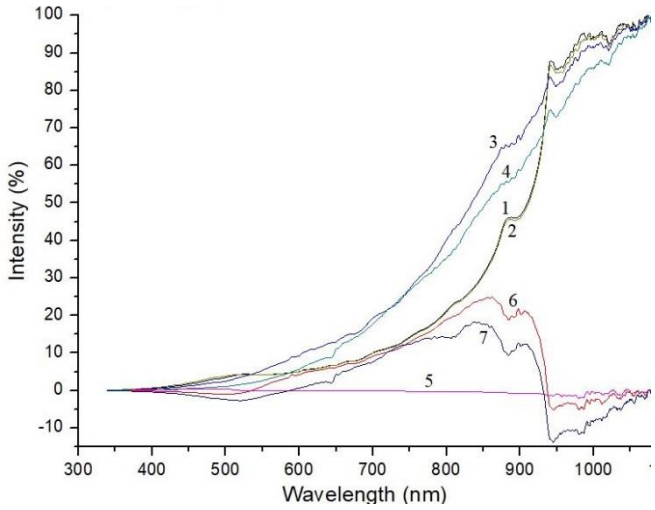

Fig. 4. Aluminum powders emission spectra: 1 – Initial aluminum powder; 2 - Microwave-activated aluminum powder; 3 - Irradiated by 4 MeV electron beam (dose 31 x-ray); 4 - Irradiated by 7 MeV electron beam (dose 100 x-ray);
Difference spectra: 5 – Microwave-activated aluminum nanopowder and initial aluminum nanopowder; 6 – Irradiated by electron beam (dose 31 X-ray) aluminum nanopowder and initial aluminum nanopowder; 7 – Irradiated by electron beam (dose 100 X-ray) aluminum nanopowder and initial aluminum nanopowder

Microwave-activated aluminum nanopowder during combustion emits a difference spectrum (spectrum 5), as well as an internal nanopowder. At the same time, the irradiated by electron beam aluminum nanopowder has an additional emission band in the range of 600–950 nm (difference spectra 6 and 7), which significantly improves the combustion characteristics of such aluminum in comparison with unirradiated powders [20, 21].

IV. Conclusions

1. The method of diffusion sintering of a ceramic material in an aluminum matrix was tested in this paper. It was concluded that the obtained samples properties are not correspond to the required strength properties of the material. Nevertheless, it is noted that microwave-activated aluminum based samples have better sintering properties and a complete structure in general.

2. Due to the insufficient hardness of the obtained compact samples, this sintering method can be recommended for the material used to fill hollow protective partitions manufacturing.

Acknowledgment

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