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Effect of neutron irradiation on non-equilibrium HfB_2-B_4C composites

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Abstract. We studied the effect of neutron irradiation on composite material HfC-HfB_2-C made using rapid reactive hot pressing technology. The histograms of microhardness and results of X-ray phase analysis, obtained both before and after neutron and electron irradiation of the samples, were considered. It was found that secondary electrons make a considerable contribution at low-fluence ($\sim 10^{14}$ neutron/cm^2) neutron irradiation. A fluence range was determined at which reduction of composite material microhardness is observed.

Keywords: composite materials, HfB_2, B_4C, neutron irradiation, small-dose effect, rapid reactive hot-pressed sintering.

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1. Introduction

Synthesis of composites based on the HfB_2-B_4C system is one of the lines of development and application of neutron protector materials [1-3]. Having low specific density, these materials demonstrate large neutron capture cross-sections in the high-energy and thermal ranges and good mechanical characteristics. However, despite the above advantages, practical application of boron-containing materials is limited because of considerable gas release at transmutation of ^{10}B [2]:

$^{10}B+^{1}n \rightarrow ^{7}Li+^{4}He+2.79$ MeV,

$^{10}B+^{1}n \rightarrow 2^{4}He+^{3}H+0.23$ MeV.

In [4, 5] it was proposed to apply rapid reactive hot pressing technology with equation of reaction $2MeC+B_4C \rightarrow 2MeB_2+3C$ (Me stands for Ti, Zr or Hf) to obtain Hf-B-C-based composite with non-equilibrium phase composition related to incompleteness of the reaction process. In addition, formation of new-phase nuclei makes it possible to obtain a material with a big number of submicron grains and, correspondingly, high surface energy. The introduced composite nonequilibrium has to reduce activation threshold for the radiation-enhanced annealing (γ- and β-components), thus increasing service life of absorbing layers. To confirm experimentally the possibility of formation of Hf-B-C-based material with increased radiation resistance, we investigated the effect of neutron and electron irradiation on microhardness as well as elemental and phase composition of reactive hot-pressed composite.

The present work deals with the effects of low-fluence neutron irradiation on the composite material HfB_2-B_4C made using the reactive hot-pressed technology.

2. Experimental technique

The composite to be studied was made applying rapid reactive hot-pressed technology, using reaction $2HfC+B_4C \rightarrow 2HfB_2+3C$ with excess of hafnium carbide. Traditionally, formation of composites with similar

phase composition (but in an equilibrium state) applying non-reactive hot pressing requires 60 to 90-min aging at temperatures 2100…2200 °C. Our composite, with incompleted reaction processes, was made at a hot-pressing temperature close to 1800 °C and aging time 15 min; the pressure was 30 MPa. The structure of the composite formed represented ~1…5 μm conglomerates with residual porosity about 14% (Fig. 1). The samples under investigation were cubic (with the side 8 mm).

The neutron irradiation was made using a research nuclear pool-type reactor BBP-M, flux up to 1.2410×10^{14} neutron/(cm^2·hour). The radiation doses were from 10^{14} up to 10^{15} neutron/cm^2. After neutron irradiation of the samples, a considerable induced γ- and β-activity was observed (Fig. 2). It was related to absorption of neutrons by isotopes and further transmutations. No secondary neutron irradiation was detected.

Electron irradiation of the samples under investigation was performed at a linear accelerator ИЛУ-6 with monoenergetic (1.9 MeV) electrons. The pulse current strength was 3 mA. In the course of irradiation, the temperature was within the 60…120 °C range. The radiation dose for the samples of each set was 5×10^{15} electron/cm^2.

Microhardness of samples was measured (using Vickers method) with a microhardness meter ПМТ-3; the indentation load was 9.8 N (for 20 s). The microhardness histograms for each sample were built using uniform grouping of 200 experimental data on microhardness value.

The X-ray diffraction analysis was made with a diffractometer ДРОН-4 using $Cu_{K\alpha}$-radiation. The surface elemental analysis was made and microstructure patterns were obtained with a scanning electron microscope Carl Zeiss AG-EVO® 50 Series. Unfortunately, this procedure of elemental analysis does not enable one to determine concentration of boron and lighter elements.

3. Results and discussion

The X-ray diffraction analysis of the initial and irradiated samples did not detect essential changes either in crystal lattice periods or in quantitative phase composition (Table 1). No additional broadening of X-ray peaks corresponding to appearance of HfB_2 and HfC phases in irradiated samples related to intrinsic stresses of second-order phase transitions was observed. The results of analysis of elemental composition of the initial and irradiated samples are given in Table 2. One can see that electron irradiation (dose of 5×10^{16} electron/cm^2) as well as neutron irradiation (dose of 10^{14} neutron/cm^2) lead to variations of phase composition that do not exceed 10%. However, higher doses of neutron irradiation result in variation of phase composition that may be related to appearance of an X-ray amorphous intergranular interlayer as a separate phase.

The microhardness dependence on the irradiation dose (Fig. 3) is nonmonotonic, with a minimum near 10^{14} neutron/cm^2, after which microhardness growth is observed. The decrease of microhardness at the dose 10^{14} neutron/cm^2 is 17% of its initial value.

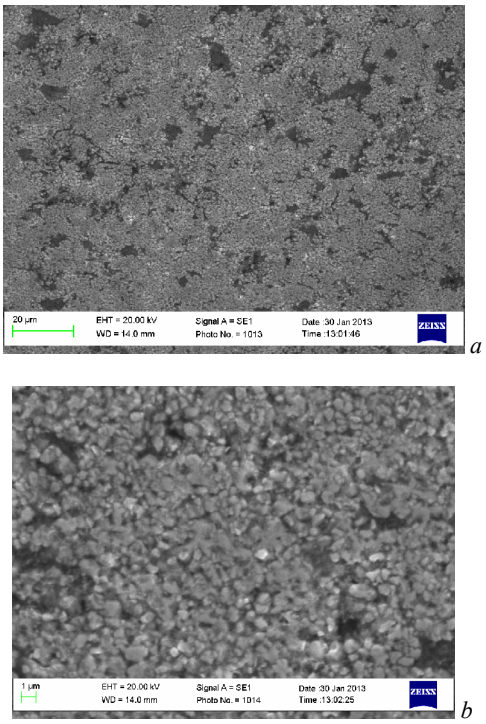

Fig. 1. Macrostructure (upper) and microstructure (lower) of reactive hot-pressed sintered HfC-HfB_2-C composite.

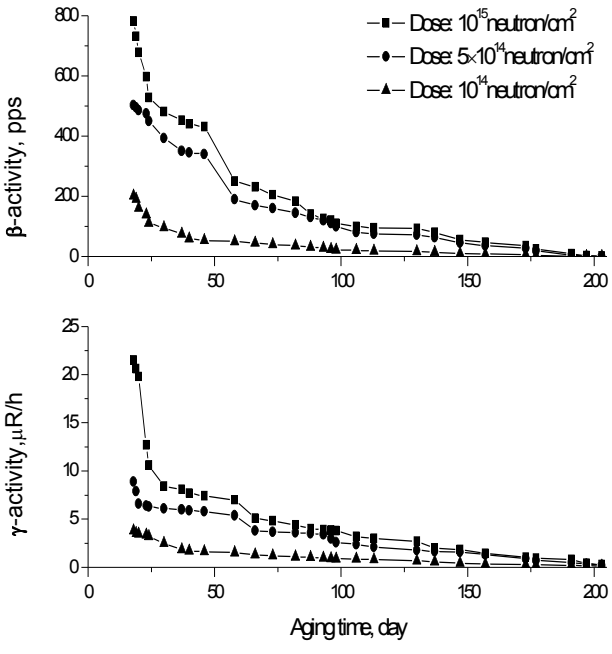

Fig. 2. Reduction of induced γ- (10^{-2} μR/hour) and β- (pulse-per-second) activity after neutron irradiation.

Table 1. Variation of crystal lattice parameters and element portions (from peak intensity) under action of neutron and electron irradiation.

Type of irradiation	Fluence, particle/cm^2	HfB_2			HfC	
		a ,Å	*c* ,Å	%	*a* ,Å	%
no irradiation	–	3.1402	3.4734	87	4.6246	13
neutron	10^{14}	3.1404	3.4731	87	4.6296	13
	5×10^{14}	3.1406	3.4732	87	4.6291	13
	10^{15}	3.1405	3.4732	87	4.6269	13
electron	5×10^{16}	3.1402	3.4734	87	4.6246	13

Table 2. Variation of elemental composition under action of neutron and electron irradiation.

Type of irradiation	Fluence, particle/cm^2	C	O	Al	Hf
		weight %	weight %	weight %	weight %
no irradiation	–	15.45	4.72	0.79	79.04
neutron	10^{14}	16.76	4.15	0.84	78.25
	5×10^{14}	22.64	3.15	0.86	73.35
	10^{15}	23.49	2.93	0.94	72.64
electron	5×10^{16}	15.42	4.69	0.81	79.08

The experimentally obtained microhardness value was 4 GPa (Fig. 3), while the tabular values for the appropriate materials are tens of GPa. In accordance with the model approaches [6], if pore size is below that of indentation pit, then porosity will result in a shift of microhardness distribution towards lower values of microhardness, without considerable distortion of the distribution itself.

In the framework of approach [6], appearance of Gaussian distortion at microhardness of 4…5 GPa (Fig. 3) cannot be related to any of the available phases. At the same time, our composite material differs from that considered in [6] by presence of nonequilibrium states near the grain boundaries that are characterized with increased concentration of impurity atoms (which is related to incompleteness of their removal because of small duration of aging at synthesis).

The mechanism of the effect of neutron irradiation on material may involve the following three constituents. The first one is formation of defect clusters in the phase grains under action of neutrons, thus leading to structure degradation. The second constituent is formation of point defects under action of secondary electron irradiation. And the third constituent is defect annealing (i.e., exclusion of defects from the grain bulk to the grain boundary and intergranular space) and proceeding of reactions between phases near the intergranular boundaries under action of secondary electrons whose energies are less than the knock-out defect formation energy. Contrary to the approach [6], nonequilibrium of composite material must delay appearance of the second and third mechanism constituents because of energy losses for phase transformations and proceeding of HfB_2 formation near the grain boundaries.

So, we believe that departure of the microhardness distribution for synthesized materials from the classic one is due to contacting grain surfaces reactively formed in the course of compaction. They are characterized by increased concentration of impurity atoms because of incomplete removal of them due to a small period of holding at a temperature of synthesis. Since neutron irradiation forms defect clusters and serves as a source of secondary electron irradiation, we made additional treatment of check sample with electron irradiation to separate the above mechanisms and verify that statement.

Contrary to neutron irradiation, electron irradiation can produce point defects only. As electron energy is reduced down to 0.25 MeV, all the electron energy goes to material (without production of radiation defects) and can serve for activation of radiation annealing of non-reacted remains of the initial phases. Therefore, the microhardness distribution shifts towards the 4…5 GPa region via increasing intergranular cohesion, and its half-width is below the values obtained after neutron irradiation.

A comparison between the cases of neutron and electron irradiation (see Fig. 3) shows that both lead to reduction of impurity concentration near the grain boundaries and, as a result, to changing the profile of microhardness distribution to that characteristic of nonreactive pressed composite of the system under investigation. At low doses of neutron irradiation, we observe transition of microhardness histograms to the Gaussian with the minimum near 3 GPa. Further irradiation results in growth of concentration of radiation defect clusters and, correspondingly, increase of the peak half-width accompanied with the mean value shifting towards high microhardness values.

Our hypothesis is confirmed by the fact that the crystallographic parameters of the HfC and HfB_2 phases as well as their interrelations do not change essentially

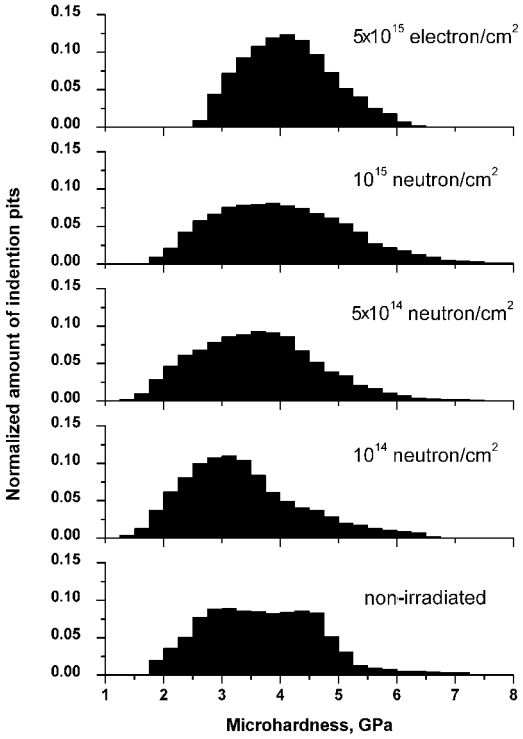

Fig. 3. Variation of microhardness of the investigated material under action of neutron and electron irradiation.

under action of neutron and electron radiation. So, one can assume that radiation-induced variations of microhardness are related to x-ray amorphous components of the composite. In our case, this component is nanosize remains of reacting components and reaction products.

4. Conclusions

We showed experimentally variation of mechanical characteristics of the composite material Hf-B-C subjected to action of low-dose neutron irradiation, while the crystallographic characteristics remained unchanged. For the material prepared using the reactive hot pressing technique, a region of microhardness reduction was determined.

A model is proposed for the effect of neutron irradiation on reactively-presses composite materials This model makes it possible to take into account the features of structural transformations of intergranular inclusions formed in the course of phase formation. As a result, the mean value of microhardness decreases and histogram of microhardness distribution changes at rather low irradiation doses (about 10^{14} neutron/cm^2).

An assumption is suggested concerning essential effect of secondary electron radiation in the course of low-fluence neutron irradiation of composite material. This assumption is supported by the results of electron irradiation of the material under investigation in the energy range that corresponds to secondary β-radiation.

The above features are promising for development of materials intended for transport and storage of radioactive waste and sources of neutron radiation.

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