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Mechanocomposites for Polymer Materials of Radiation Protection

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Abstract

Mechanochemical formation of composites Fe/TiB_2, W/TiB_2, Fe/B_4C and W/B_4C was investigated. These composites may be used as fillers for ultra-high molecular weight polyethylene intended for protection from neutron and γ-radiation. Mechanochemical synthesis of the composites was carried out in a planetary ball mill with water cooling in the atmosphere of argon. The phase composition, structural and morphological characteristics of the composites, and their thermal stability were studied by means of a set of physicochemical methods (X-ray phase analysis, scanning electron microscopy, thermal analysis). It is demonstrated that the composites Fe/TiB_2, W/TiB_2, Fe/B_4C and W/B_4C are formed during mechanical activation. They are composed of particles 0.5–1.0 μm in size, their shapes being close to spherical. The particles are agglomerated into larger formations 30–50 μm in size. The resulting composites exhibit thermal stability under heating to ~800 °C.

Keywords: mechanochemical synthesis, composites, iron, tungsten, boron carbide, titanium diboride

INTRODUCTION

Materials for radiation protection involved in the operation under stationary conditions of atomic power plants, storage sites for radioactive substances and wastes are known since the middle of the XX century. These materials include heavy concrete, metals (tungsten, lead, steel) and pseudo-alloys (tungsten with copper, iron and nickel) [1–5]. At present, plastic composite polymer materials are under intense development for use in atomic and space industry [6–12].

The introduction of fine fillers into polymeric matrixes allows solving the problems of the efficiency of protection from multifactor ionizing radiation.

For example, the presence of light elements (hydrogen-containing substances, graphite, boron carbide) in the materials used as a protection from neutron and γ-radiation is necessary for moderation of fast and intermediate neutrons during elastic scattering, heavy elements with large atomic mass (tungsten, iron, molybdenum, zirconium, titanium, *etc.*) are necessary for moderation of fast neutrons in the process of inelastic scattering and weakening of capture gamma radiation, while the elements with the high effective cross-section, such as boron, are necessary for the absorption of thermal neutrons.

A promising approach combining the preparation of fine powders of filler materials with the formation of composites based on polymers is me-

chanical activation (MA). Under the conditions of intense shock-and-shear deformations, the processes that take place in the materials include mixing, dispersing with the formation of a large contact surface, and physicochemical interactions, which promotes changes in the initial structural state of the materials and causes the formation of the composite structure [13, 14].

The goal of the present work was to obtain fine composites Fe/TiB_2, W/TiB_2, Fe/B_4C and W/B_4C by means of MA.

EXPERIMENTAL

The powders of carbonyl iron, tungsten, titanium diboride TiB_2 and boron carbide B_4C were used in the work. The ratio of the components in the systems M–TiB_2 or M–B_4C (M = Fe, W) was 50 : 50 mass %.

Fine powders of the composites were obtained by means of MA of the mixtures of initial powders in a high-energy ball planetary mill AGO-2 with water cooling [15] in the argon atmosphere. Vial volume was 250 cm^3, ball diameter 5 mm, the mass of balls loaded into the mill was 200 g, the mass of the sample under treatment was 10 g, the rate of vial rotation around a common axis was ~1000 r.p.m., the MA duration of the samples was 2 min.

X-ray diffraction studies were carried out using a D8 Advance diffractometer (Bruker, Germany) with the characteristic radiation Cu$K_{\alpha 1}$ (λ = 1.5406 Å). Calculations and refinement of the profile and structural parameters were carried out using TOPAS software.

The morphological characteristics of mechanocomposites were determined with the help of scanning electron microscopy (SEM) using a TM 1000 instrument (Hitachi, Japan).

The thermal stability of the composites was studied by means of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) with a STA 449 F/1/1 JUPITER thermal analyzer (Netzsch, Germany) in the atmosphere of argon.

RESULTS AND DISCUSSION

Mechanocomposites Fe/TiB_2 and W/TiB_2

Mechanical activation of the systems Fe–TiB_2 and W–TiB_2 for 2 min leads to a strong decrease in the size of TiB_2 crystallites from 3000 to 100–125 nm (Table 1), however, its crystal structure does not change (Fig. 1, *a, b*). According to the results of X-ray phase analysis (XPA), only Fe/TiB_2 and W/TiB_2 mechanocomposites are formed in the systems during MA. In the systems with iron, lattice parameters of the components increase substantially in comparison with the initials, which may be due to high microstrains, while in the systems with tungsten they remain practically unchanged (see Table 1).

According to SEM data, Fe/TiB_2 composite particles up to 20 μm in size, consisting of smaller particles ~1 μm, are observed in the mechanically activated Fe–TiB_2 system (Fig. 2, *a*). In the system W–TiB_2 the particles of W/TiB_2 composites are present after MA; they are agglomerates with a size from ~10.5 to 15 μm consisting of smaller (~1 μm) particles with nearly spherical shape (Fig. 2, *b*).

The high thermal stability of carbides and borides should promote an increase in the thermal stability of polymer composites modified with these compounds. Thermal stability of composites

TABLE 1

Composition and structural characteristics of initial TiB_2, Fe, W and the systems Fe–TiB_2, W–TiB_2 after MA for 2 min in the atmosphere of Ar

Chemical composition	Phase composition	Crystal structure	Lattice parameters, nm	Crystallite size, nm
TiB_2 (initial)	TiB_2	*P6/mmm*	*a* = 0.3031 *c* = 0.3229	3000
Fe (initial)	Fe	*Im-3m*	*a* = 0.2867	85
W (initial)	W	*Im-3m*	*a* = 0.3164	520
Fe–TiB_2, MA	TiB_2	$P6_3/mmc$	*a* = 0.3038 *c* = 0.3237	125
	Fe	*Im-3m*	*a* = 0.2879	44
W–TiB_2, MA	TiB_2	*P6/mmm*	*a* = 0.3030 *c* = 0.3227	110
	W	*Im-3m*	*a* = 0.3165	60

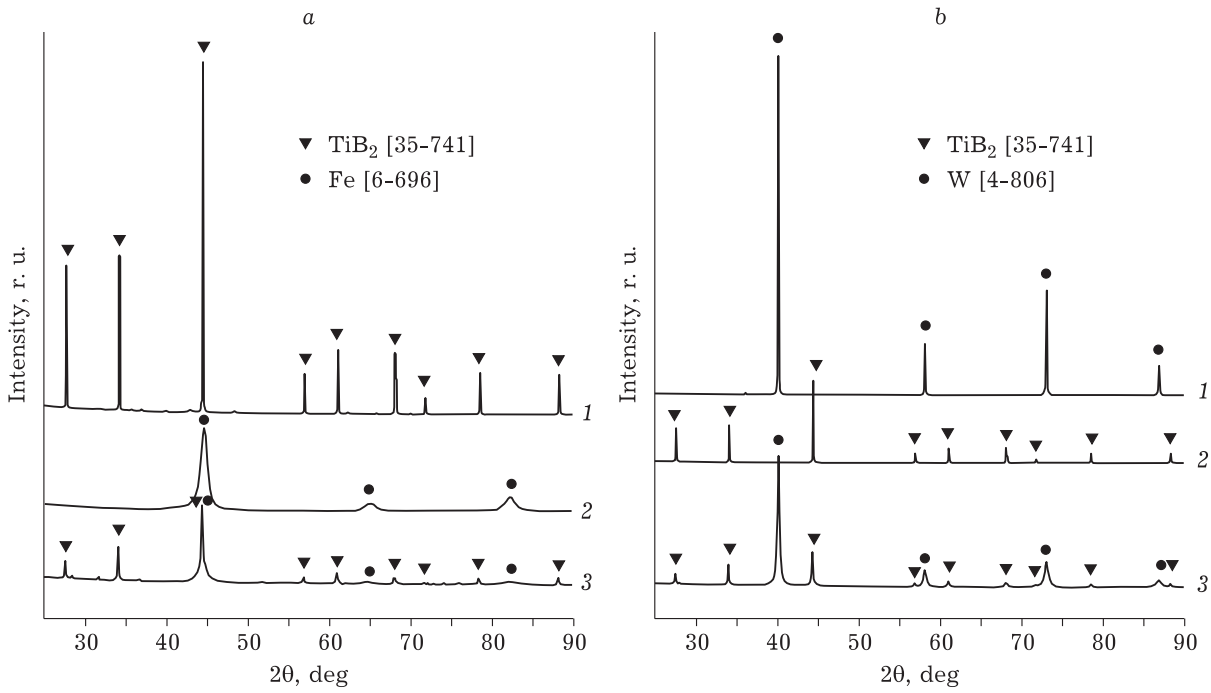

Fig. 1. Diffraction patterns: *a* – initial TiB_2(*1*), Fe (*2*) and Fe–TiB_2 system obtained after MA (*3*); *b* – initial W (*1*), TiB_2 (*2*) and W–TiB_2 system obtained after MA (*3*). Here and in Fig. 2–4: MA for 2 min in the Ar atmosphere.

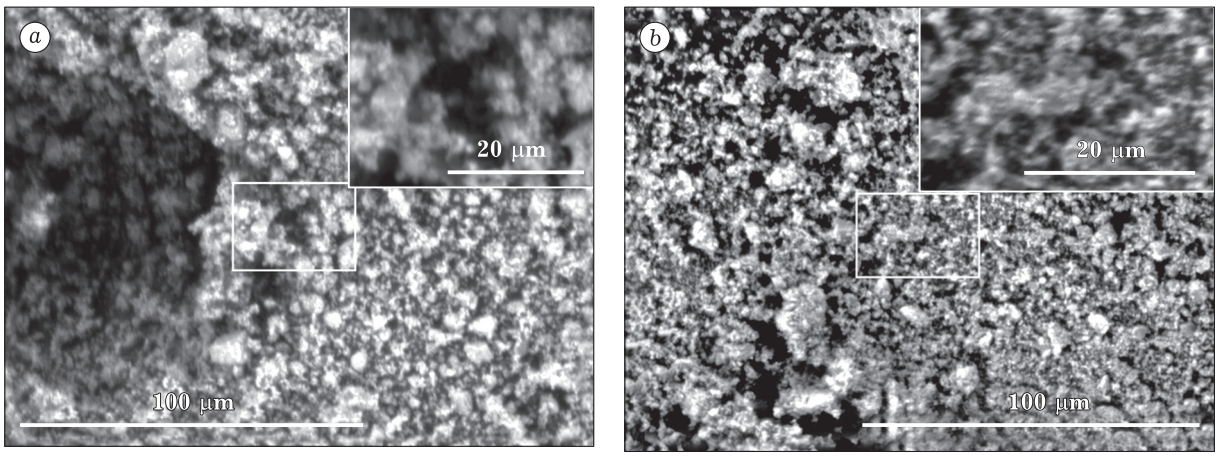

Fig. 2. SEM images of particles in the systems Fe–TiB_2 (*a*) and W–TiB_2 (*b*) after MA. For MA conditions, see Fig. 1.

Fe/TiB_2 and W/TiB_2 obtained by means of MA was confirmed by thermographic studies. For example, the composites are stable under heating in the atmosphere of argon within the temperature range from 40 to ~800 °C (Fig. 3).

Mechanocomposites Fe/B_4C и W/B_4C

As a result of MA of the systems Fe–B_4C and W–B_4C, the size of B_4C crystallites decreases, but their crystal structure remains the same (Fig. 4). Chemical interaction takes place in the system Fe–B_4C during MA; as a result, in addition to Fe/B_4C mechanocomposites, boron carbides of complicated composition are formed. In the system W–B_4C, only W/B_4C mechanocomposite is formed.

The parameters of Fe and W lattices in mechanically activated systems Fe–B_4C and W– B_4C remain practically the same in comparison with the initial components (Table 2).

Electron microscopic analysis of the activated Fe–B_4C powders showed that Fe/B_4C composites are agglomerates up to 50 μm in size, composed of smaller particles (~0.5 μm).

In the activated system W–B_4C, composite W/B_4C particles up to 30 μm in size are formed;

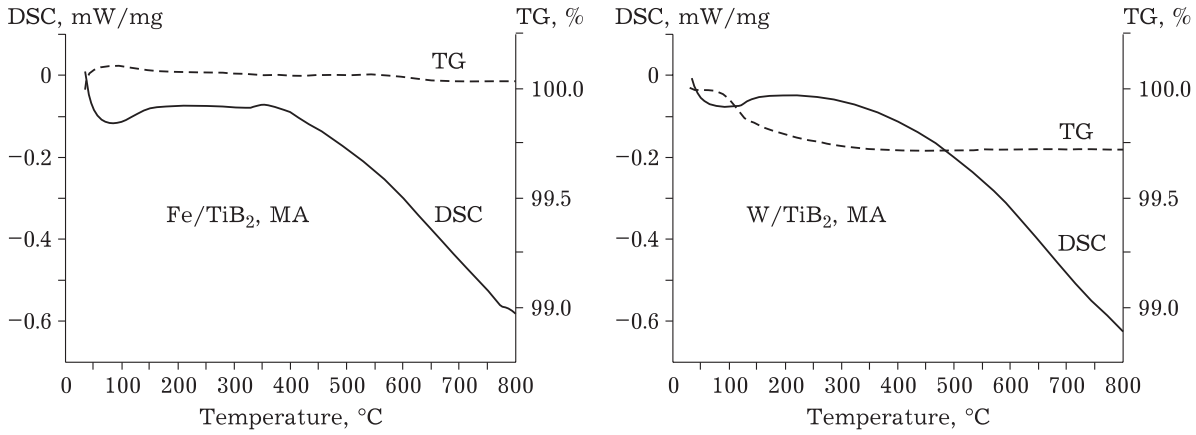

Fig. 3. Data of the differential thermal analysis for mechanocomposites of the systems Fe–TiB_2 (*a*) and W–TiB_2 (*b*) after MA. For MA conditions, see Fig. 1.

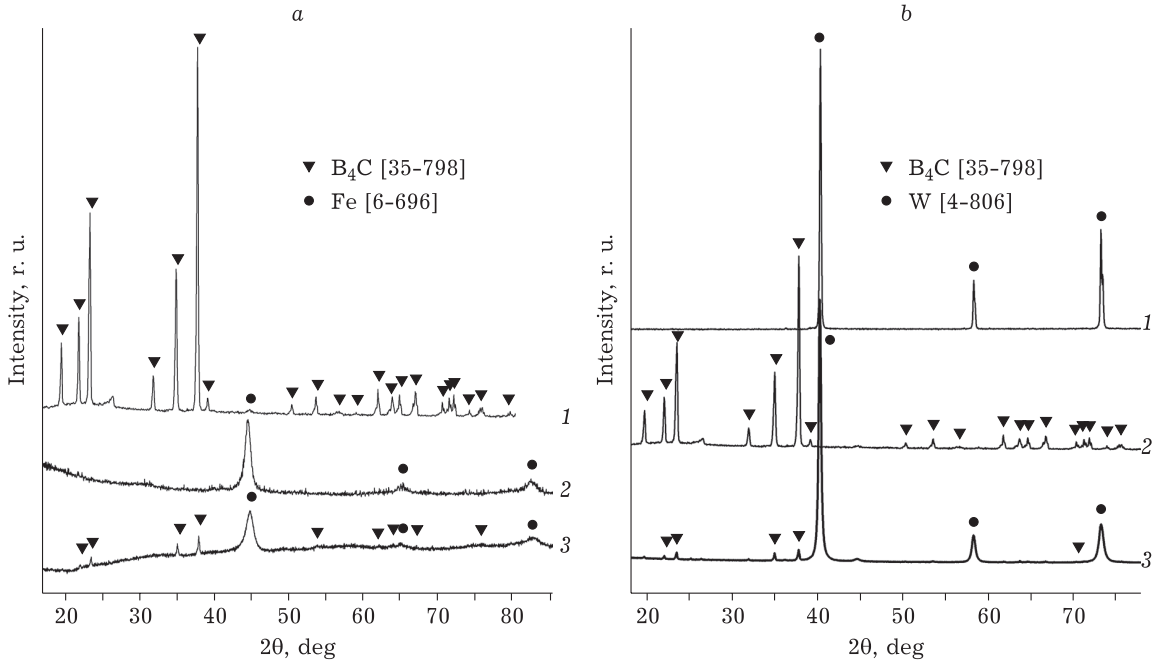

Fig. 4. Diffraction patterns: *a* – initial B_4C (*1*), Fe (*2*), the system Fe–B_4C after MA (*3*); *b* – initial W (*1*), B_4C (*2*), the system W–B_4C after MA (*3*). For MA conditions, see Fig. 1.

TABLE 2

Composition and structural characteristics of initial B_4C and the systems Fe–B_4C, W–B_4C after MA for 2 min in the atmosphere of Ar

Chemical composition	Phase composition	Crystal structure	Lattice parameters, nm	Crystallite size, nm
B_4C (initial)	B_4C	*R*-3*m*	*a* = 0.5628 *c* = 1.2110	70
	$C_{1.48}B_{13.77}$	*R*-3*m*	*a* = 0.5650 *c* = 1.2157	40
Fe–B_4C, MA	$C_{36}B_{11.4}$	*R*-3*m*	*a* = 0.5589 *c* = 1.1991	55
	Fe	*Im*-3*m*	*a* = 0.2866	55
W–B_4C, MA	B_4C	*R*-3*m*	*a* = 0.5601 *c* = 1.2080	30
	W	*Im*-3*m*	*a* = 0.3165	92

they are agglomerates consisted of smaller particles (~1 μm), and their shape is close to spherical.

CONCLUSION

Finely dispersed composites Fe/TiB_2, W/TiB_2, Fe/B_4C and W/B_4C were formed by means of MA in a ball planetary mill. These composites are agglomerates (30–50 μm) consisted of the particles ~0.5–1.0 μm in size, their shape is close to spherical. The obtained composites are thermally stable in the argon atmosphere under heating to ~800 °C.

The studied fine dispersed composites are proposed for use as the polymer composite materials for radiation protection from neutron and gamma radiation.

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