FORMATION OF DIBORIDES OF GROUPS IV–VI TRANSITION METALS DURING MECHANOCHEMICAL SYNTHESIS

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Fine powders of diborides of groups IV–VI transition metals (TiB_2, HfB_2, NbB_2, TaB_2, CrB_2, Mo_2B_5, and W_2B_5) were produced by mechanochemical synthesis and low-temperature heat treatment of activated charges. The particle size of the powders was ≤ 1 μm. It is revealed that processes of formation of diborides of groups IV–VI transition metals differ within period and group. Diborides Ti and Nb formed discontinuously. Diborides Hf and Ta formed after the formation of lower boride phases, whereas higher borides Cr, Mo, and W formed in almost a single-phase state only after a low-temperature treatment of preliminarily mechanoactivated charges. The differences were analyzed from the point of view of the donor-acceptor capacity of the atoms of boron and diboride-forming transition metals.

Keywords: *fine powder, diboride of transition metals, mechanochemical synthesis, donor-acceptor capability.*

INTRODUCTION

Due to their high hardness, heat resistance, refractoriness, durability, and un-reactiveness, borides of groups IV–VI transition metals are used either independently or as components of composite materials intended to resist high temperatures, high mechanical stresses, and corrosive media. In particular, TiB_2, ZrB_2, CrB_2 are used in cutting-tool, wear-resistant, oxidation-resistant, and creep-resistant alloys and in protective coatings. The resistance of these borides to molten aluminum, copper, iron, and steel allows producing a variety of melting crucibles, thermocouple tubes, and special drills. Molybdenum boride Mo_2B_5 is used in radio engineering. Studying and designing processes for the synthesis of borides are of scientific and applied interest [1].

A common method to produce refractory borides is synthesis from elements in normal conditions at temperatures 1600–1700°C accompanied by intensive heat liberation, resulting in the formation of strong cakes that should be thoroughly ground [2].

To obtain fine and nano-dispersed powders of refractory compounds, the reaction should be run at low temperatures in conditions that are far from equilibrium. Mechanochemical synthesis and mechanical activation followed by low-temperature synthesis have become very popular recently. Mechanical synthesis produces solid-phase compounds. High-energy milling causes plastic deformation of and structural defects in the original material. Such a maximally disordered structure relaxes, forming a new phase. The energy barrier is created by the interatomic

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interaction between the original components and, therefore, depends on their electronic structure and the type of chemical bond in the substances formed [3, 4].

The mechanochemical synthesis of transition-metal boride powders is addressed in [5–16], where various approaches to describing the formation of boride phases are discussed: structural correspondence of metal and its boride [7], special selection of conditions for mechanical synthesis [5]; diffusion mechanism of the processes [6, 10], etc.

The purpose of this study is (i) to obtain fine diborides of groups IV–VI transition metals by mechanochemical synthesis of elements, (ii) to identify the differences in their formation, and (iii) to discuss these differences in terms of electronic structure of the metals and boron atoms.

MATERIALS AND EXPERIMENTAL PROCEDURE

Borides TiB_2, HfB_2, NbB_2, TaB_2, CrB_2, Mo_2B_5, and W_2B_5 were produced in the same conditions of high-energy milling. Commercial metal powders and amorphous boron with a purity of 99.8% and a particle size of ~1 μm were used as original agents.

Characteristics of the Original Metal Powders

Metal, grade	Specific surface area, m^2/g
Titanium PTE	1.4
Hafnium GFN-1	0.7
Niobium PNB-1	0.4
Tantalum TaPA.	0.9
Chrome PKh-1	0.2
Molybdenum MPCh	0.4
Tungsten PV1.	1.2

The mechanical treatment of Me–B mixtures intended for producing diboride and Me_2B_5 phases in the relevant systems was performed in an AIR planetary mill with a centrifugal acceleration of 25g in steel drums with steel balls charged with boron to reduce the iron ground. The ball-to-powder weight ratio was 20 : 1; with a ball diameter of 9.5 mm and degree of mill fill 1 : 3. The mechanical treatment was carried out in argon for 2 min, followed by cooling for 5 min. The total treatment time was 5, 10, 15, 30, and 60 min. After 30 min of mechanical activation in the conditions indicated above, the powder mixtures were subject to heat treatment in an SShV vacuum furnace at 1000°C for 1 h.

The results of mechanical synthesis were analyzed using a DRON-3 diffractometer. The specific surface area was determined by thermal desorption of nitrogen. The morphology and particle size were studied using a Jeol Superprobe 733 scanning electron microscope.

EXPERIMENTAL RESULTS

Mechanical Synthesis of Diborides of Group IV Metals. After high-energy milling of a mixture of titanium and boron powders for 5 min, the products of mechanical synthesis contain original α-Ti with hardly changed lattice periods and a small amount of titanium diboride. Milling for 10 min results in a single-phase product—the X-ray pattern shows only the reflection lines of hexagonal TiB_2 (Table 1; Fig. 1).

These results are in agreement with the data in [5], where the formation of titanium diboride is considered to be "explosive" synthesis.

The structure HfB_2 forms after 10 min of milling of an Hf–B powder mixture. The high intensity of the reflection from the plane (100) may indicate that the diboride forms across this plane. In addition to the main phase HfB_2, the products have a trimetric boride phase HfB that, according to [2], is stabilized by gas admixtures such as nitrogen and oxygen. Being metastable, this phase could be formed in non-equilibrium conditions of mechanochemical

TABLE 1. Specific Surface Area and XRD Results for Mechanosynthesis Products

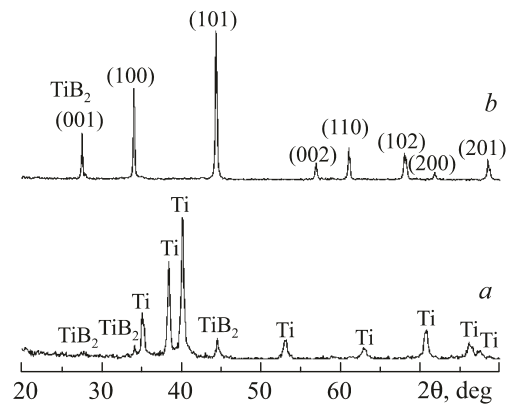| Original powder mixture	Duration of mechanical treatment, min	Specific surface area, m^2/g	XRD results	
			Phase composition	Lattice periods, nm
Ti + 2B	5	4.8	α-Ti	$a = 0.2958, c = 0.4684$
			TiB_2	–
	10	2.7	TiB_2	$a = 0.3035, c = 0.3101$
Hf + 2B	10	2.7	HfB_2	$a = 0.3122, c = 0.3484$
			HfB	–
	30	2.2	HfB_2	$a = 0.3138, c = 0.3455$
			HfB	–
	60	2.7	HfB_2	$a = 0.3154, c = 0.3462$
Nb + 2B	5	2.6	Nb	$a = 0.3298$
	10	2.7	Nb	$a = 0.3310$
	15	3.8	NbB_2	$a = 0.3103, c = 0.3267$
	30	5.3	NbB_2	$a = 0.3123, c = 0.3221$
Ta + 2B	5	2.3	Ta	–
	10	2.4	Ta	$a = 0.3353$
	15	2.1	Ta	–
	30	3.0	TaB_2	$a = 0.3099, c = 0.3227$
			Ta_3B_4, Ta_2B	–
	60	2.8	TaB_2	$a = 0.3106, c = 0.3222$
Cr + 2B	5	1.9	Cr	$a = 0.2868$
	15	2.5	Cr	$a = 0.2868$
	30	2.3	Cr	$a = 0.2879$
	60	3.1	Cr	$a = 0.2878$
			CrB_2	$a = 0.2950, c = 0.3111$
2Mo + 5B	5	2.3	Mo	$a = 0.3147$
	15	3.6	Mo	$a = 0.3149$
	30	2.5	Mo	$a = 0.3150$
	60	2.6	Mo	$a = 0.3157$
W + 2B	5	4.5	W	$a = 0.3151$
	15	3.8	W	$a = 0.3157$
	30	3.2	W	$a = 0.3158$
	60	3.6	W	$a = 0.3169$

Fig. 1. X-ray pattern of products resulting from TiB_2 mechanochemical synthesis after 5 (*a*) and 10 min (*b*) of milling of the original powder mixture
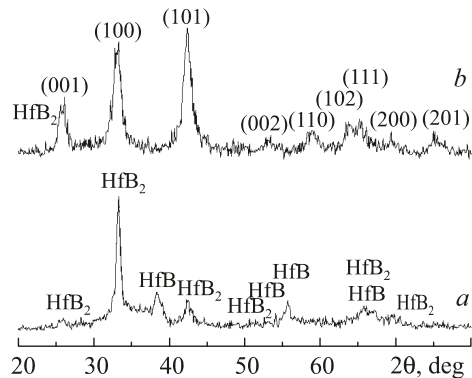
Fig. 2. X-ray pattern of products resulting from HfB_2 mechanochemical synthesis after 10 (*a*) and 60 min (*b*) of milling of the original powder mixture

synthesis. Also, the phase HfB is still present after 30 min of mechanical treatment. A single-phase HfB_2 composition powder is also observed after 60 min of mechanical treatment (Fig. 2; Table 1). Unlike TiB_2, hafnium diboride forms for a longer time and after the formation of boride phase HfB.

Mechanical Synthesis of Diborides of Group V Metals. According to the X-ray analysis, after 5 and 10 min of treatment of the original mixtures Nb–B and Ta–B, the powders contain only the original metals Nb and Ta, respectively. If the mechanical treatment of Nb–B mixture is performed for 15 min, the X-ray patters show all reflection lines of hexagonal NbB_2 (Fig. 3). After 30 min of mechanical treatment, all X-ray reflection lines are broader, which may result from the deformation and dispersion of niobium diboride. At the same time, the specific surface area increases up to 5.3 m^2/g (Table 1).

During 10 and 15 min of high-energy milling of Ta–B mixture, the metal tantalum remains and its lines are broader. Should the milling time is increased up to 30 min, a mixture of boride phases Ta_2B, Ta_3B_4, and TaB_2 appears in the reaction products. After 60 min of milling, a single-phase powder of hexagonal tantalum diboride TaB_2 forms (Table 1).

Mechanical Synthesis of Diborides of Group VI Metals. The formation of boride phases during mechanical treatment of mixtures of group VI metals (Cr, Mo, W) with boron is very complicated.

After 60-min mechanical treatment of the mixture Cr–B, along with reflection lines of the main phase (metallic chromium), the X-ray patterns display weak lines of chromium boride of the CrB_2 composition (Table 1). The study of the phase formation in mechanically activated system Cr–B in [6] has established that no boride phases form during mechanical activation in conditions similar to our experimental procedure. However, they did form after subsequent heat treatment of the activated charge.
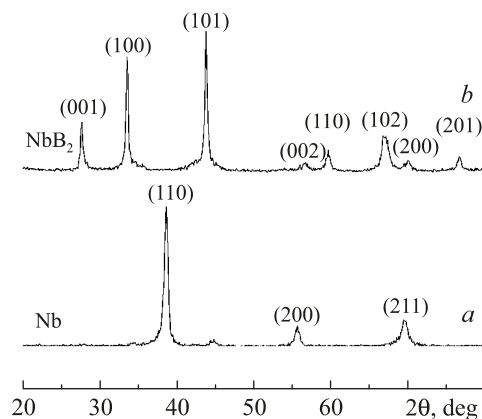

Fig. 3. X-ray pattern of products resulting from NbB_2 mechanochemical synthesis after 10 (*a*) and 15 min (*b*) of treatment of the original powder mixture

TABLE 2. Mechanically Activated Mixtures Cr–B, Mo–B, and W–B: Temperature, Time, and Results of Low-Temperature Treatment

Original mixture	Heat treatment temperature, °C	Heat treatment duration, h	Specific surface area, m^2/g	Phase composition as per XRD
Cr + 2B	800	2	2.9	CrB_2, CrB, Cr_5B_3
	900	2	2.3	CrB_2, CrB, Cr_5B_3
	1000	1	2.2	CrB_2, Cr_3B_4 (traces)
2Mo + 5B	1000	1	2.3	Mo_2B_5, Mo_2B (traces)
2W + 5B	1000	1	2.8	W_2B_5, WB (traces)

During mechanical treatment in the systems Mo–B and W–B, boride phases did not form. However, the lattice periods of metals increased for both systems with increasing the duration of mechanical treatment from 5 to 60 min (Table 1). This, apparently, results from the dissolution of boron atoms in the metal lattice in the special conditions of high-energy milling.

Low-Temperature Treatment of Activated Powder Mixtures. Since it is not possible to produce boride phases of chromium, molybdenum, and tungsten by mechanochemical synthesis, the mixtures Cr–B, Mo–B, and W–B (preliminarily milled for 30 min) were subjected to a low-temperature treatment in vacuum. The optimum temperature (1000°C) and holding time (1 h) were chosen based on the results of heat treatment of chromium diboride (Table 2). Table 2 shows that the powders consist of higher boride phases with a small admixture of lower borides. All powders were produced at temperatures lower by 500–600°C than the temperature of conventional synthesis of borides, which promoted their fineness. However, the boride CrB_2 produced is not a phase of stoichiometric composition, but is located in the homogeneity range of the phase CrB_2, as confirmed by the value of its interplanar spacings.

According to an electron-microscopic analysis, the products of mechanochemical synthesis of TiB_2, HfB_2, NbB_2, and TaB_2, and powders produced by heat treatment widely vary in particle size. The powders are composed of particles ≤1 μm that make agglomerates of 5–20 μm in size, which explains their small specific surface area. Figure 4 shows micrographs of the single-phase powders TiB_2, HfB_2, and NbB_2 produced by mechanochemical synthesis.

DISCUSSION OF THE RESULTS

The study on the mechanochemical synthesis of diborides of groups IV–VI transition metals has revealed differences in formation under the same conditions of high-energy milling. The difference in the time and way the compounds form is observed within both period and group of metals. Titanium and niobium diborides are formed
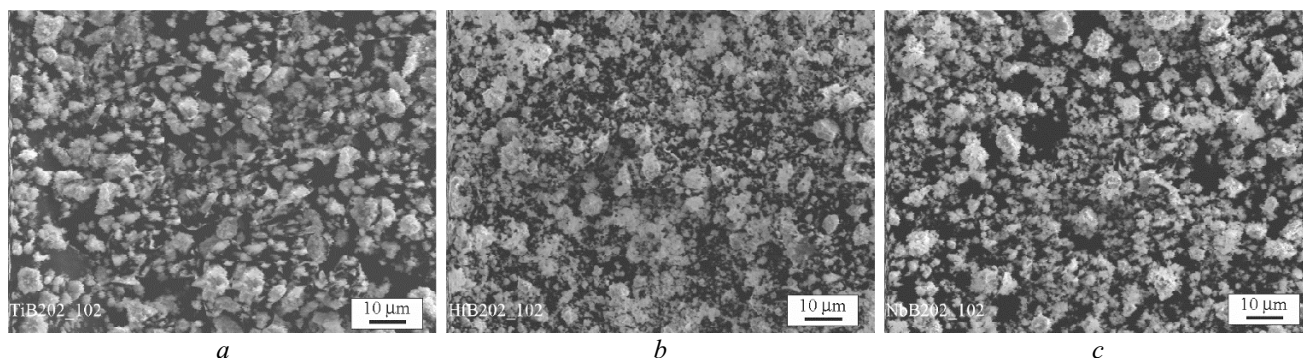

a   *b*   *c*

Fig. 4. Micrographs of particles of mechanically synthesized single-phase powders TiB_2 (*a*), HfB_2 (*b*), and NbB_2 (*c*)

easily and quickly, which is in good agreement with published data. Hafnium and tantalum diborides are formed after the formation of lower boride phases, while higher borides of chromium, molybdenum, and tungsten (not resulting from the mechanical treatment) are formed only after additional low-temperature heat treatment of preliminarily mechanically activated original charges .

It can be assumed that the difference in diboride formation results from the electronic structure of metals and boron.

During boride formation, the electron interaction of boron atoms in the boric sublattice (whose structure becomes more complex with increasing B/Me atomic ratio) is essential. Having one unpaired electron in the outer electronic shell, the boron is seeking to form stable *sp*-states, utilizing both its own valence electrons and electrons of the partner. In diborides, boron forms graphite-like layers with strong covalent bond between the atoms and acts as an electron acceptor [17]. The charge state of boron and metals in borides was assessed using X-ray photoelectron spectroscopy [18].

Interacting with boron during diboride formation, groups IV–VI transition metals transfer their *d*-electrons for the formation of the Me–B bond and strengthening of the B–B bonds, which is confirmed by the study of the magnetic and electromagnetic properties of diborides [2]. However, the donor-capacity of these metals decreases with higher energy stability of *d*-phases resulting from the increase in the number of electrons in the *d*-orbitals and their principal quantum number [19]. This is also witnessed by the increased electronic work function of metals during transition from titanium to niobium and chromium, for which it makes 3.84, 3.95, and 4.5 eV, respectively [20]. Quantum-mechanical calculations of the diboride electronic structure made it possible to evaluate the transfer of electrons from the shells of isolated atoms to the orbitals of their compounds and B–B bond energy in the diboride structure:

Results of Quantum-Mechanical Calculations of Diboride Electronic Structure [17]

Filling of *d*-states, %		Energy of B–B bond, eV
Ti. 43	TiB_2. . . . . .21.1	TiB_2. . . . . 443.5
V. 81	VB_2. . . . . 56.8	VB_2. . . . . 412.5
Cr. 84	CrB_2. . . . . 79.5	CrB_2. . . . . 358.3

The above results allow examining the differences in the diboride formation from the point of view of donor-acceptor capacity of metals and boron.

Thus, during mechanochemical synthesis, titanium having with two electrons in the *d*-shell and tending to d^0-configuration easily transfers its electrons to boron, which promotes its intensive interaction with boron and formation of diboride.

Hafnium is in the same group with titanium, but in a lower period. This hampers the transition of electrons to the outer electronic shell, complicating its interaction with boron during the formation of the diboride phase, which is manifested as longer mechanical synthesis.

Niobium and tantalum (group V metals) demonstrate a lower donor capacity than the group IV metals. Therefore, to form diborides, a higher energy of mechanical activation should be accumulated to break through the energy barrier of the interatomic interaction of the original components. This is also manifested aslonger mechanical synthesis and additional formation (in the case of TaB_2) of lower borides.

Among the metals under consideration, chromium, molybdenum, and tungsten possess the lowest donor capacity due to the presence of a stable half-filled *d*-shell. Under normal conditions, there are no diborides at all in the systems Mo–B and W–B, in which the most likely boride phases are Me_2B_5. Due to the insufficient donor capacity of chromium, molybdenum, and tungsten and, therefore, low reactivity with boron, we failed to obtain higher boride phases during high-energy milling: the energy of mechanical activation was not enough. To obtain boride phases, preliminarily activated original charges should be subjected to heat treatment. To obtain CrB_2, Mo_2B_5, and W_2B_5 composition borides, a heat treatment at 1000°C for 1 h turned out to be sufficient. These results are consistent with the published data [6, 11].

CONCLUSIONS

Fine powders TiB_2, HfB_2, NbB_2, and TaB_2 with a grain size of ≤ 1 μm have been produced by mechanochemical synthesis.

To produce powders of boride phases CrB_2, Mo_2B_5, and W_2B_5, a low-temperature treatment of preliminarily mechanoactiated charges was required. A heat treatment at temperatures lower by 500–600°C than the temperature of conventional synthesis of borides ensures their fineness.

Differences in periods and groups during the formation of diborides of groups IV–VI transition metals have been revealed: diborides TiB_2 and NbB_2 form discontinuously, while diborides HfB_2 and TaB_2 form after the formation of lower boride phases, whereas higher borides Cr, Mo, and W form in almost a single-phase state only after an additional low-temperature treatment of preliminarily mechanoactiated charges. The established differences have been discussed from the point of view of the donor-acceptor capacity of atoms of transition metals and boron.

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