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Mechanochemical Technology of Borane Compounds and Their Application

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Abstract

Results of the investigation of mechanochemical reactions of the synthesis of diborane (6) B_2H_6 from M^*BH_4 (M^* = Li, Na, K) and halides of polyvalent metals MX_n, adducts of BH_3 borane with nitrogen-containing organic Lewis bases (L) of the L ×BH_3 type, borazine $H_3B_3N_3H_3$ from M^*BH_4 and NH_4Cl, tetrahydroborates of transition metals $M(BH_4)_n$ (M = Zr, Hf, U, Ti) from MX_n and M^*BH_4 are generalized. Reactions were performed under mechanical activation of mixtures of crystalline reactants in vacuum ball mills in the absence of solvents. Rotary and vibratory mechanical activators were used. The listed reactions can serve as the basis for mechanochemical technologies. Technological aspects of the application of borane compounds are considered.

INTRODUCTION

Chemistry of boranes and their derivatives is an intensively developing area of modern inorganic chemistry. Novelty, unusual properties and structural forms, valuable functional characteristics of the compounds of these classes make this area interesting from the viewpoints of comprehensive and applied approaches. Mechanical engineering, technologies of electronics, inorganic and organic synthesis, metallurgy, catalysis, production of heat-proof polymers, technologies of the deposition of layers and coatings onto metals, medicine, analytical chemistry comprise an incomplete list of areas in which boron hydrides and their derivatives are applied or their application is reasonable [1–5]. A necessary condition for technological application of a class of compounds is the availability of effective methods to obtain these compounds.

Traditional methods of the synthesis of boranes and their derivatives are based on reactions that are carried out in pure polar organic solvents like esters, amines, *etc.* [6, 7]. Inevitable operations include solvent preparation and purification, separation of the target substances from reaction media and by-products. There are also problems connected with the protection of environment from waste products formed during production. Full technological cycles of obtaining the substances of classes under consideration are complicated. These difficulties can be eliminated in some cases by using solid-phase mechanochemical synthesis. The term «mechanochemical synthesis» implies reactions between crystalline substances under mechanical action on their mixtures, *i. e.*, under the mechanical activation (MA). An appropriate definition of the subject of mechanochemistry given in the review [8] can be cited: “Reaction occurring during the action of deformation, friction of cleavage of solids are considered as mechanochemical phenomena”. The recent decade was remarkable for extremely intensive development of mechanochemistry. Attention should be paid to a large number of original investigations, reviews and monographs published within these years [8–13], as well as the proceedings of scientific conferences dedicated to this subject [14–16].

The earliest publications on mechanochemical reactions in the chemistry of boranes are those of the scientists from the USA [17, 18]. The authors of [17] report the synthesis of $NaBH_4$ from solid NaH and B_2O_3 under MA:

$$4NaH(s) + 2B_2O_3(s) = NaBH_4(s) + 3NaBO_2(s)$$

The reaction was carried out by attrition of the reaction mixture with steel balls in a rotating tightly closed tube.

Another reaction [18] conducted under MA is the synthesis of zirconium tetrahydroborate:

$$ZrCl_4(s) + 4LiBH_4(s) = Zr(BH_4)_4 \text{ (liq, g)} + 4LiCl(s)$$

In this reaction, the salts of Zr and Li are transformed into non-ionic volatile compound $Zr(BH_4)_4$ which exists in liquid phase (liq) and in vapour (g) under the synthesis conditions (near room temperature), because its melting point is 28.7 °C and boiling point ~123 °C. Our work of many years was dedicated to mechanochemical reactions of the synthesis of diborane (6) B_2H_6 and a series of the simplest borane derivatives; our investigations showed that it was quite possible to carry out the processes of this kind, while the synthesis processes involving MA are very efficient and possess substantial advantages over the traditional liquid-phase methods. Results of the initial stage of investigations are published in [19].

Later generalizing works were published [20, 21]. These works sum up the results of investigations into the solid-phase reactions of the following types: 1) the synthesis of B_2H_6 from MBH_4 (M = Li, Na, K) and halides of polyvalent metals MX_n; 2) synthesis of the adducts of borane BH_3 with organic nitrogen-containing Lewis bases (L), with hydrazine, giving $L \times BH_3$, from MBH_4 and corresponding halide salts $L \times HX$ (where X is halide); 3) synthesis of borazine (borazole), a heterocyclic boron-nitrogen compound $H_3B_3N_3H_3$, from MBH_4 and ammonium halides NH_4X; 4) synthesis of volatile covalent Zr(IV), Hf(IV), Ti(III), U(IV) tetrahydroborates $M(BH_4)_n$ from halides of these metals and MBH_4; 5) synthesis of metal carborane cluster closo-$SnB_9C_2H_{11}$ *via* two consequent mechanochemical reactions from the salts with nido-$B_9C_2H_{12}^-$ anion, $SnCl_2$ and NaH.

Reactions are performed in tightly closed ball mills of rotary or vibratory action. The first four reactions among those listed above can be the basis for obtaining technically valuable products. The 5th synthesis gives a complicated metal carborane cluster [22]. This fact showed the possibility to use MA in the synthesis of cluster structures, which was confirmed and developed in later studies in application to the clusters of transition metals [23–25]. Principal data on the first four mechanochemical reactions are presented in [20, 21]. However, the technological aspect and apparatus were described only briefly. Aspects of the technical application of borane compounds obtained with the help of MA are not considered. Meanwhile, it is the development of simple and efficient mechanochemical synthesis methods that builds up the basis for wide technological application of the series of compounds under investigation. The goal of the present work is to compensate this lack of information. Mechanochemical synthesis methods can help creating simple compact production directly at the consumption sites using a sort of local generators of volatile compounds.

MECHANOCHEMICAL METHODS OF THE SYNTHESIS OF DIBORANE (6) AND BORON HYDRIDE DERIVATIVES

Synthesis of diborane (6)

The synthesis of B_2H_6 is performed under MA *via* the interacion of anhydrous halides of polyvalent metals MX_n with tetrahydroborates of alkali metals M^*BH_4 (M^* = Li, Na, K):

$$MX_n(s) + nM^*BH_4(s) = n/2B_2H_6(g) + n/2H_2 + M + nM^*X \quad (1)$$

M = Cu, Zn, Sn, Pb, Cr, Cd, Ge.

In practice, it is more reasonable to use chlorides MCl_n and $NaBH_4$. An important version of the reaction (1) is the process

$$SnCl_2(s) + 2NaBH_4(s) = B_2H_6(g) + H_2 + Sn + 2NaCl \quad (2)$$

Technical details of its performance are published in [26]. Of interest is also the reaction of I_2 with M^*BH_4 [27]:

$$I_2 + 2M^*BH_4 = B_2H_6 + H_2 + 2M^*I \quad (3)$$

The general equation of the reaction (1) provides a wide choice of versions using different MX_n. When choosing the working version, one should take account of the hygroscopic proper-

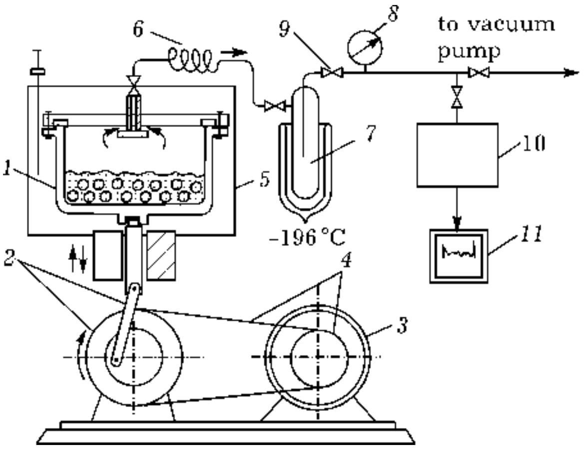


Fig. 1. A schematic of ball vibratory mill with eccentric crank drive. For designations, see text.

ties of MX_n, toxicity of M and its compounds, possibility to recover M from reaction products in the form of anhydrous MX_n for repeated use. The most favourable version may be the synthesis according equation (2) using $SnCl_2$. Tin is not toxic, relatively easily available, metal tin simply is transformed into non-hygroscopic $SnCl_2$ according to [28]. Because of this, a mechanochemical generator of B_2H_6 and the corresponding technological cycle have been proposed on the basis of the reaction (2) [26]. This does not exclude the possibility to use other MX_n, in particular CuCl, CuI [29].

A vibratory ball mill (Fig. 1) was used to study mechanochemical reactions and to perform syntheses. A tightly closed reaction chamber *1* of the mill with ball load and a mixture of reagents to be activated is driven to a vertical vibrational movement by an eccentric system of crank gear *2* equipped with electric motor *3* and V-belt transmission *4*. The frequency of transmission rotation is adjusted by changing the diameters of pulleys at the constant rotation frequency of the motor shaft *3*. The frequency of vibrations of the chamber (f) is thus adjusted. Changing the length of eccentric, one can change the amplitude (A). The reaction chamber of the mill is placed into air thermostat *5* and connected with a flexible spiral copper tube *6* to the cooled condenser trap *7* in which the volatile reaction products are collected. The pressure in the system is measured with a manometer *8*; gas flows are governed by vacuum bellows valves *9*. An automatic gas-meter set-up *10*, *11* is used to observe the processes during MA. This set-up allows determining the dependence of gas evolution on time (t) and other technological parameters. In experiments, molar ratios (n) in the mixtures under activation were varied, as well as the volumes of mill chambers (V_m), ball masses (m_b), their diameter (d_b), t, f, A, temperature t. The described experimental set-up turned out to be very useful to study the above-listed reactions including those of B_2H_6 synthesis. The samples of the obtained reaction products were investigated by means of elemental analysis, IR spectroscopy, mass spectrometry.

Typical conditions under which the reactions were investigated and syntheses were performed: $V_m = 100$ cm^3, $m_b = 100$ g, $d_b = 6$ mm, $f = 23$ Hz, $A = 6$ mm, mass of reaction mixture loaded into the mill 3–4 g. The amount of the formed B_2H_6 was determined gravimetrically measuring the mass of boron on the walls of quartz tube when the gas sample was heated to 700 ℃. Figure 2 shows the dependence of B_2H_6 yield in reaction (2) on MA time (t) and the nature of MBH_4 at the molar ratio of reactants $[MBH_4] : [SnCl_2] = 2$. A 86–95 % yield of B_2H_6 was achieved at t » 2 h, which is quite satisfactory for preparative and technological syntheses. Large-scale synthesis of B_2H_6 was carried out in a reactor with $V_m = 0.5$ l, $m_b =$

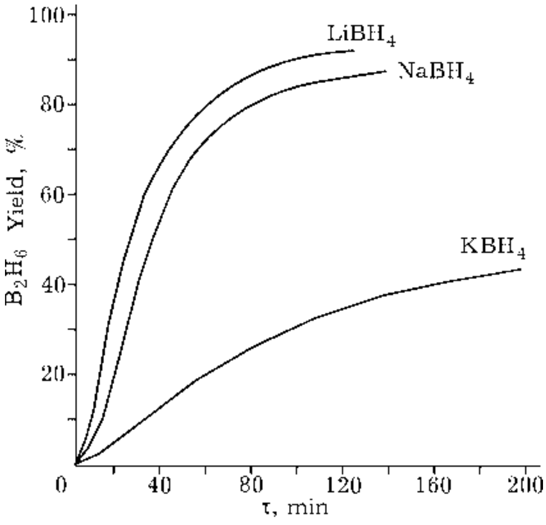


Fig. 2. Dependence of B_2H_6 yield in reaction (2) on MA time and MBH_4 nature.

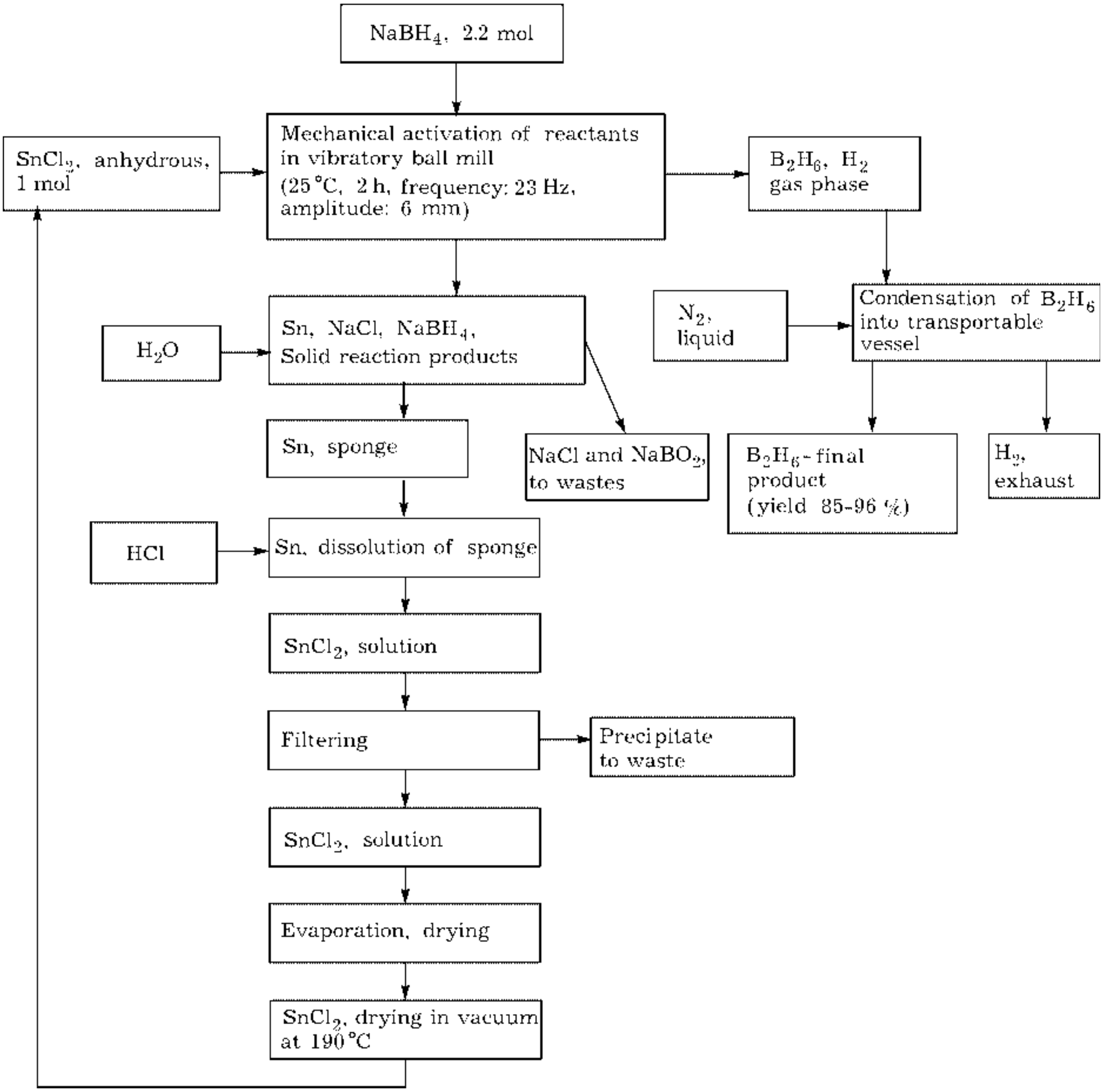


Fig. 3. Operational flowchart of the technology of B_2H_6 obtaining according to reaction (2).

400–600 g at f = 23 Hz and A = 6 mm. Having loaded $NaBH_4$ 6.39 g, $SnCl_2$ 11.63 g, n = 2.2–2.8, t = 30–40 min, we obtained 1260 cm^3 B_2H_6, which corresponds to the 91.4 % yield with respect to $SnCl_2$. Figure 3 shows the operation scheme of the technological process of obtaining B_2H_6 by the reaction (2). This process is a closed one with respect to Sn consumption; components to be consumed include $NaBH_4$, hydrochloric acid, liquid N_2 (cooling agent), H_2O. Wastes include H_2 and NaCl. Taking these quite favourable circumstances into account, we may consider this process to be the basis for local generators of pure diborane (6).

Synthesis of borane adducts L ×BH_3

The BH_3 borane has a vacant hybrid *sp* atomic orbital at the B atom. Hence, this molecule is an electron pair acceptor, *i. e.* a Lewis acid which is able to interact with the Lewis bases L, electron pair donors. The adducts of the L ×BH_3 type are formed in this interaction if L is organic nitrogen-containing base or NH_3, N_2H_4, *etc.* The L ×BH_3 adducts, some of which are rather stable and water-soluble, are used as stereo-selective reducing agents in organic and inorganic syntheses [30, 31]. The application of L ×BH_3 in chemical nickel- and cobaltcoating processes is also known [3]. A confirmation of wide practical use of these products may be the fact that not less than 27 compounds of the L ×BH_3 type are listed in the catalogues of reagents supplied by Aldrich (USA), the largest world's company. It is demonstrated in the monograph [7] that L ×BH_3 compounds re usually obtained by the interaction between B_2H_6 and L, or by substituting L from other adducts, or by the reactions of MBH_4 with halide salts L ×HX in organic solvent. For example, the authors of [33] demonstrated that $(CH_3)_3N$ ×BH_3 is formed with a high yield in the reaction between $LiBH_4$ and $(CH_3)_3N$ ×HCl in diethyl ether. Reactions of this type form the basis for the general principle of L ×BH_3 synthesis, first of all alkyl amino boranes R_3N × BH_3 [34]. These syntheses usually involve $LiBH_4$ since it is soluble in ether and similar solvents; $NaBH_4$ and KBH_4 are not used for this purpose.

We demonstrated that mechanochemical solid-phase syntheses of L ×BH_3 with organic nitrogen-containing bases L can be carried out quite easily; they are simpler, rather efficient and allow using $NaBH_4$ or KBH_4 [20, 21]. Reactions are described with an equation

$$MBH_4(s) + L \times HCl(s) = L \times BH_3 + MCl + H_2 \qquad (4)$$

Here M = Li, Na, K; L = $(CH_3)_3N$, $(C_2H_5)_3N$, $(CH_3)_2HN$, $(C_2H_5)_2HN$, $(C_4H_9)_2HN$, $(C_6H_5{-}CH_2)_3N$, C_5H_5N. Reactions of this type were carried out in a vibratory reactor (see Fig. 1). Information concerning the effect of MA conditions and other parameters on the reaction was obtained from the data on H_2 gas evolution. Large-scale syntheses of volatile $(CH_3)_3N$ ×BH_3 and $(C_2H_5)N$ ×BH_3 were performed in tightly closed rotary ball mills with periodic removal of the formed H_2, followed by evaporation in vacuum from the reaction volume into the cooled condensing traps. Non-volatile L ×BH_3 were extracted from reaction mixture by hydrocarbons (benzene, hexane); after this, solvents were evaporated by distillation. Typical results of syntheses are shown in Table 1. The results on gas meter investigation of the reactions were published in [19, 35–41]. The data shown in Table 1 suggest that L ×BH_3 can be successfully synthesized mechanochemically from MBH_4 and L ×HCl with 45–89 % yields. Technically important $(CH_3)_3$ ×BH_3 and $(C_2H_5)N$ ×BH_3 can be quite satisfactorily synthesized using $NaBH_4$ and KBH_4. However, mechanochemical method turned out to be unsuitable for the synthesis of monoalkyl aminoboranes RNH_2 ×BH_3. In particular, the interaction of $(CH_3)NH_2$ ×HCl with MBH_4 under MA results in the formation of complicated mixtures containing $(CH_3)_3NH_2$ ×BH_3 along with large amount of its decomposition products and by-products.

Mechanochemical synthesis of hydrazine-bis-borane N_2H_4 ×$2BH_3$ [36, 42] was carried out using the reaction

$$N_2H_4 \times 2HCl + 2MBH_4 = N_2H_4 \times 2BH_3 + 2H_2 + 2MCl \qquad (5)$$

Nonvolatile N_2H_4 ×$2BH_3$ was isolated by extraction with tetrahydrofuran. Yields of 70–80 % were achieved in the vibratory reactor (see Fig. 1) at V_m = 100 cm^3, f = 23 Hz, A = 6 mm, t = 40 min. Hydrazine-bis-borane is interesting from the viewpoint of its applications because its pyrolysis results in fine pure boron nitride used in oxygen-free ceramics.

The synthesis of $H_3B_3N_3H_3$ borazine

Borazine (or borazole) is a heterocyclic boron-nitrogen compound $H_3B_3N_3H_3$. It is of interest for some branches of technology. This substance is an ideal initial material to obtain boron nitride BN as powder, layers or coatings deposited from gas phase (borazine melting point is −58 °C, its boiling point is 55 °C) [43]. Because of this, technological development of the processes of obtaining BN-based materials is determined by the creation of efficient methods of borazine synthesis and development of procedures to handle it. In fact, only one method to synthesize $H_3B_3N_3H_3$ is considered in literature. It is based on the reduction of B-trichloroborazine by $LiBH_4$, $NaBH_4$, $LiAlH_4$ or LiH in diglyme with tributylamine and ether added [44, 45]. The necessary $B_3Cl_3N_3H_3$ is obtained by the reaction of BCl_3 with NH_4Cl in chlorobenzene solution. Borazine is isolated from solution by vacuum distillation and purified by rectifying.

We developed a mechanochemical method of the synthesis of borazine on the basis of

TABLE 1

Mechanochemical synthesis of L ×BH_3 using the reaction (4)

Experiment No.	Reactor type and other features	Starting reactants		Reactant mass, g		n*	t, °C at MA	t, h	Yield of R_3N ×BH_3	
		MBH_4	R_3N ×HCl	MBH_4	R_3N ×HCl				g	%
1	Rotary ball mill, V_m = 2.5 l	$NaBH_4$	$(CH_3)_3N$ ×HCl	36.4	91.5	1.00	25	5	55.0	78.7
2	The same	»	»	52.2	144.0	0.91	70	6	87.0	86.7
3	»	»	$(C_2H_5)_3N$ ×HCl	120.0	400.0	1.09	25	4	290.0	86.7
4	»	»	»	145.0	500.0	1.05	25	4	355.0	84.9
5	»	»	»	145.0	420.0	1.25	70	3	290.1	82.6
6	»	KBH_4	$(C_2H_5)_3N$ ×HCl	55.4	137.0	1.00	90	6	85.0	74.0
7	»	»	»	97.0	238.2	1.01	90	6	164.1	82.5
8	Vibratory reactor (see Fig. 1), V_m = 90 ml, f = 23 Hz, A = 12 mm	$LiBH_4$	$(CH_3)_2NH$ ×HCl	0.66	2.55	0.97	25	1.5	1.20	67.2
9	The same	$NaBH_4$	»	1.99	3.46	1.20	25	1.2	1.12	45.0
10	»	KBH_4	»	4.54	3.60	1.91	25	1.5	1.21	46.4
11	The same, as in Exp. 8 L ×BH_3 isolation with benzene	$NaBH_4$	$(C_7H_7)_3N$ ×HCl tribenzylamine ×HCl	0.11	1.57	0.60	25	6	0.49	73.0
12	The same	$LiBH_4$	C_2H_5N ×HCl	2.10	5.50	2.0	25	2	3.82	86.5
13	»	$NaBH_4$	»	3.11	4.85	2.0	25	2	3.21	82.5
14	»	KBH_4	»	3.12	3.62	1.9	25	2	2.60	89.0

*[MBH_4] : [L × HCl] molar ratio in reaction mixture.

the reaction between $NaBH_4$ and NH_4Cl at 190–250 °C [46–48]:

$$3NaBH_4(s) + 3NH_4Cl(s) = H_3B_3N_3H_3\ (g) + 3NaCl + 9H_2 \quad (6)$$

The design of apparatus in which the reaction (6) is conducted under MA is described in [46, 47]. The synthesis of borazine according to the reaction (6) has several specific features: 1) borazine is formed in mixture with large amount of hydrogen (9 moles of H_2 per one mole of $H_3B_3N_3H_3$); 2) initial substances and final products are light-weighed powders noticeably carried away with gas flow; 3) borazine is an easily hydrolyzed and oxidized substance, so its contact with air and water should be excluded.

It is difficult to perform MA at high temperatures in a tightly closed reactor providing at the same time removal of the formed gaseous products. Because of this, the version was realized involving preliminary MA of a mixture of $NaBH_4$ with NH_4Cl in a chamber of the rotary ball mill [48]. In this version, the consequent stages of the complex reaction (6) are involved. The first stage occurs under MA and is not connected with gas evolution:

$$NaBH_4 + NH_4Cl = NH_4BH_4 + NaCl\ (25\ °C)$$

Subsequent stages are connected with the transformation of NH_4BH_4 into borazine; they proceed at temperature increased from 25 to 240 °C. They do not require MA and can be performed in an immobile reactor, which simplifies heating and removal of gases from it. These stages follow the scheme [20, 21]:

NH_4BH_4 ® $H_2B(NH_3)_2BH_4$ (s) + H_2

$H_2B(NH_3)_2BH_4$ (s) ® $H_3B_3N_3H_3$ (g) + $(BHNH)_n$ + H_2 (g), t » 120–240 °C.

A set-up shown schematically in Fig. 4 was applied to perform the synthesis according to this principle. The synthesis was carried out in reactor *1* which was a tightly closed ball mill with V_m = 7 l and diameter 15 cm, filled to 25 % of the volume with steel balls (d_b = 12 mm). $NaBH_4$ and NH_4Cl were loaded into the reactor, then the reactor was sealed with a flange cap, evacuated, and put into operation to treat the mixture mechanically by rotating the apparatus. After MA, the reactor was tightly connected to the vacuum system. A filter for rough purification of the exhaust gases from dust *3* is mounted on the cap of the reactor. The filter is filled with steel balls *4* 5 mm in diameter; the released gases pass through it. The activated mixture in the reactor was heated with an aluminium unit *6* equipped with thermocouple *5* mounted at the controllable electric heater 7. Fine purification of gases from dust was performed by passing them through a multilayered grid filter *8*. Borazine was condensed from a mixture with H_2 in a cooled condenser

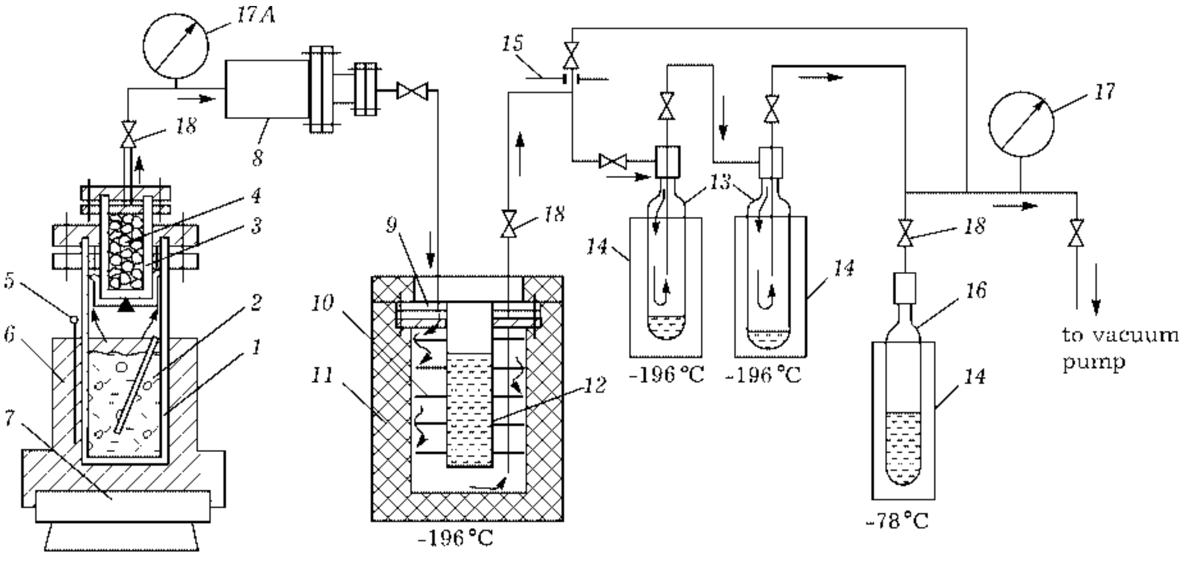


Fig. 4. A scheme of the set-up for borazine synthesis according to reaction (6). For designations, see text.

9 at aluminium discs *10* cooled with liquid nitrogen *12*. Condenser was thermally isolated with foam plastic *11*. After the condensation in *9*, *10* was finished, $H_3B_3N_3H_3$ was re-condensed into cooled traps $_{13}$ from which it was finally distilled into the detachable ampoule *16*. Glass traps and the ampoule were cooled with liquid nitrogen or dry ice placed in the Dewar vessels *14*. Pressure in the system was measured with manometers *17*. Vacuum system was maintained with the help of the bellows valves *18*. The best results were obtained under the following conditions: a) the composition of the reaction mixture: $NaBH_4$ 250 g, NH_4Cl 500 g, molar ratio $[NH_4Cl] : [NaBH_4] = 1.5$; b) MA mode: $\tau = 2.5$ h, $t \sim 25$ °C, airless medium; c) conditions of the reaction (6) itself: reactor temperature raise from 135 to 240 °C for 30 min, release of the formed vapour and gas into the cooled condenser. The yield of $H_3B_3N_3H_3$ was 50–51 g, which is 29–30 % of the amount of $NaBH_4$.

Thus obtained borazine was used in the production of thin film capacitors with BN insulating films formed by plasmachemical decomposition of $H_3B_3N_3H_3$ vapour.

Synthesis of volatile tetrahydroborates of transition metals

Tetrahydroborates of transition metals and aluminium are the simplest metal borane compounds of the general formula $M(BH_4)_n$, where M = Al(III), Ti(III), Zr(IV), Hf(IV), Th(IV), U(III), U(IV), Pa(IV), Np(IV), Pu(IV), Zn(II), Cd(II), Ln(III). The chemistry of $M(BH_4)_n$ and problems of the synthesis of these compounds were discussed in a series of reviews [20, 21, 49–51]. Physical properties and type of $M-BH_4$ bonds allow us to relate these species to typically non-ionic compounds. They possess noticeable volatility, melt at not very high temperatures, some of them are soluble in nonpolar organic solvents. The $M-BH_4$ covalent bonds occur as bridging three-centre M–H–B–H bonds of different dentate state [52]. Thanks to these features and high reactivity, $M(BH_4)_n$ are promising for use in catalytic hydrogenation and polymerization, in the deposition of boride layers on surfaces by means of thermal decomposition of vapour or by electrolysis [3, 5, 18, 53]. We demonstrated that solid-phase mechanochemical reactions involving metal chlorides, $LiBH_4$ and $NaBH_4$ are quite applicable to the synthesis of $Zr(BH_4)_4$, $Hf(BH_4)_4$, $U(BH_4)_4$, $Ti(BH_4)_3$, $Zn(BH_4)_2$, $Cd(BH_4)_2$ [54–58]. Among the listed $M(BH_4)_n$, the most interesting ones are $Zr(BH_4)_4$ and $Hf(BH_4)_4$. Because of this, the synthesis of these compounds by mechanical activation was the subject of more detailed investigations [54, 55]. Investigated were reactions:

$$MCl_4(s) + 4M^*BH_4(s) = M(BH_4)_4(liq, g) + 4M^*Cl(s) \quad (7)$$

where M = Zr, Hf; M* = Li, Na. Reactions of this type are not accompanied by substantial gas evolution. Because of this, they were conducted in tightly closed rotary ball mills; after MA, their chambers were connected to the systems of cooled trapping ampoules into which the formed $Zr(BH_4)_4$ and $Hf(BH_4)_4$ were distilled by evaporation in vacuum, since their saturated vapour pressure at 25 °C is 14.9 and 15.0 mm Hg, respectively. Table 2 shows the data on the synthesis of $M(BH_4)_4$ in different reactors at varied reaction mixture compositions. One can see that the synthesis of $Zr(BH_4)_4$ using $LiBH_4$ under MA proceeds rather rapidly at 25 °C and at small excess of $LiBH_4$: a yield of 86 % was achieved within $\tau = 15$ min. Maximal yields achieved in this process were 93–95 %. In the case of $NaBH_4$ at rather large excess ($n = 5–8$), yield of 73–83 % is achieved after MA for 6–8 h. A possible reason explaining this difference is considered in [21].

A similar way was followed to obtain $Ti(BH_4)_3$ [58]:

$$TiCl_3(s) + 3LiBH_4(s) = Ti(BH_4)_3 + 3LiCl \quad (8)$$

The synthesis was carried out in vibratory mill (see Fig. 1) with $V_m = 100$ cm^3, $f = 23$ Hz, $A = 12$ mm, $\tau = 2$ h. $Ti(BH_4)_3$ (0.522 g) was obtained from 0.615 g $LiBH_4$ and 1.78 g $TiCl_4$; the yield was 74.7 %, calculated per $TiCl_3$. These results demonstrated the possibility to synthesize $M(BH_4)_n$ using mechanochemical methods which can be principal basis for technological processes.

TABLE 2

Mechanochemical synthesis of $Zr(BH_4)_4$ and $Hf(BH_4)_4$ using the reaction (4)

Experiment No.	Reactor type	Starting reactants		Reactant mass, g		n	t, °C at MA	t, min	Yield of $M(BH_4)_n$	
		MCl_4	M^*BH_4	MCl_4	M^*BH_4				g	%
1	Rotary ball mill, V_m = 320 cm^3, d_b = 15 mm, m_b = 210 g, mill rotation frequency: 80 rpm	$ZrCl_4$	$LiBH_4$	5.00	1.97	4.2	25	15	2.77	86.0
2	The same	»	»	5.00	1.97	4.2	25	120	3.02	93.7
3	»	»	»	5.00	1.97	4.2	45	15	3.08	95.3
4	»	»	»	5.00	1.97	4.2	45	60	3.06	95.0
5	Rotary ball mill, V_m = 2.50 l, d_b = 15 mm, m_b = 2.50 kg, mill rotation frequency: 80 rpm	»	$NaBH_4$	130.0	89.1	4.0	45	480	47.0	56.0
6	The same	»	»	130.1	111.1	5.0	45	480	53.0	63.1
7	»	»	»	149.3	150.8	6.0	45	480	56.1	73.7
8	»	»	»	128.0	174.2	8.0	45	480	63.6	77.1
9	Rotary ball mill, V_m = 135 cm^3, d_b = 15 mm, m_b = 100 g	$HfCl_4$	»	12.0	5.9	4.0	40	360	4.33	48.6
10	The same	»	»	8.0	8.1	8.0	40	360	4.97	83.8
11	»	»	»	12.1	9.2	6.0	40	360	4.76	53.5

Note. n is $[M^*BH_4]:[MCl_4]$ molar ratio.

TECHNOLOGICAL ASPECTS OF THE USE OF BORANE COMPOUNDS

The above-considered mechanochemical methods of the synthesis of B_2H_6 and borane derivatives make it possible to use these substances in technological operations due to the simplicity of the synthesis methods. Let us demonstrate such a possibility using the results obtained by us.

The application of $L \times BH_3$ in the processes of strengthening of the technical-grade titanium surface

Titanium and its technical alloys are important construction materials of modern mechanical engineering (aircraft construction, special ship building, *etc.*) [59]. They possess valuable properties, namely, relatively low density (4.505 g/cm^3), high specific strength, corrosion stability, high melting point. However, titanium materials do no exhibit sufficiently good surface strength, so they are poor operating in friction couples (shafts, screw thread, connections of the ball-cone type, *etc.*). A problem of surface strengthening exists for parts made of titanium. A technological principle of strengthening titanium surface by saturating it with boron, carbon, some metals is known. This is accompanied by the formation of boride and carbide phases exhibiting high hardness. For example, microhardness of TiB_2 is as high as 3200 kg/mm^2.

We investigated the chemical principle of strengthening the surface of technical titanium by treating it with $L \times BH_3$ vapour at high temperature. The pyrolysis of $L \times BH_3$ occurs under these conditions. The released B, C, N interact with Ti, diffuse into metal depth and form solid phases based on borides, carbides, nitrides and their combinations. Thus obtained diffuse layers provide substantial increase of the surface hardness and possess high adhesion to the metal. Among known $L \times BH_3$, the most suitable ones were $(CH_3)_3N \times BH_3$ and $(C_2H_5)_3N \times BH_3$. Trimethylamine borane is a white crystalline substance sublimed in vacuum; its melting point is 93 °C, saturated vapour pressure is 5.3 mm Hg at 50 °C, starting point of its thermal decomposition is 160 °C. Triethylamine borane is a colourless liquid, its melting point is −2 °C, saturated vapour pressure is 5.3 mm Hg at 80 °C, starting decomposition point is 200 °C.

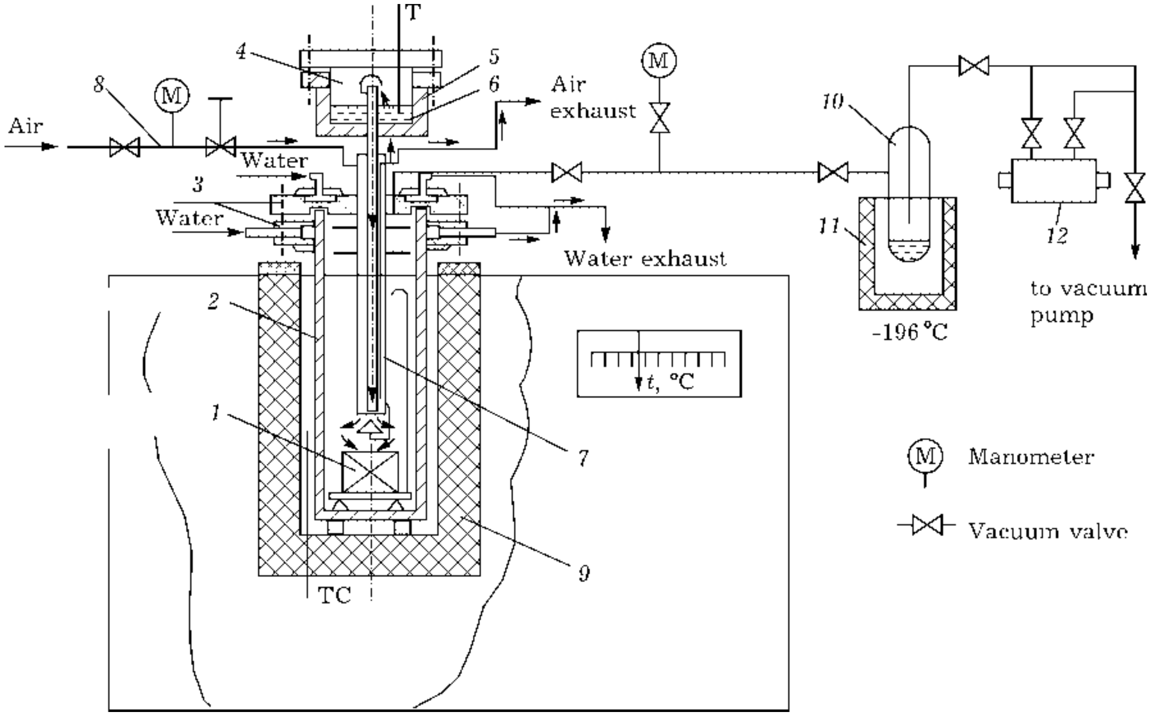


Fig. 5. A schematic of the set-up for the vapour deposition of boron-containing coatings on titanium using $L \times BH_3$ vapour. For designations, see text.

Hence, these compounds can be transferred into gas phase in vacuum and used for thermochemical treatment of the titanium surface.

It was stated in the preliminary experiments on treating the samples of VT-4 alloy, used in aircraft building, with $(C_2H_5)_3N \times BH_3$ vapour that quite satisfactory coatings are formed at 700–950 °C. The treatment was carried out in a vacuum tube reactor with electric furnace. A shortcoming of such a scheme is large losses of the initial $L \times BH_3$ due to the decomposition of its vapour on walls and inside the tube. This difficulty was eliminated by using an apparatus in which the $L \times BH_3$ vapour was admitted from the evaporator to the heated working region (700–800 °C) through a tube cooled from outside with a flow of compressed air.

A schematic of the set-up is shown in Fig. 5. The samples or parts *1* to be treated were placed in a tight reaction chamber *2* made of heat-proof steel and sealed with a flange cap *3*. The gasket of the flange was made of heat-proof rubber; it was cooled with water. An evaporator *4* with controllable electric heater *5* was connected to the flange cap. The $L \times BH_3$ *6* was placed on bottom of evaporator. From the evaporator, $L \times BH_3$ vapour passed through a tube *7* cooled with compressed air into the working space of the chamber above the samples *1*. The chamber and samples were heated with electric furnace *9* of the SShOL-1.16/11-M1 type, equipped with temperature-control device and with temperature measurement unit. Air and gases formed in the chamber were evacuated with a vacuum pump through a trap *10* cooled with liquid nitrogen. The necessary $L \times BH_3$ evaporation rate was maintained according to preliminary calibration of its dependence on temperature in evaporator (within the range 50–70 °C). The samples to be treated thermochemically were the plates 5 mm thick, made of VT-4 alloy.

Conditions and generalized results of experiments are shown in Table 3. These data suggest that thermochemical treatment of the VT-4 with $(CH_3)_3N \times BH_3$ and $(C_2H_5)_3N \times BH_3$ vapour at 800 °C resulted in an increase of the surface microhardness from 300–310 to 1114–1310 kg/mm^2. The thickness of the coatings was 30–40 mm. The B, C, N content in the subsurface layers was determined using the analytical MS-702 mass spectrometer (AEI Company) with spark ion source. Variations of these elements with depth confirm the diffusion nature of this layer, providing a good adhesion of the coating with metal. Investigations of microsections of the samples by means of microphotographs showed that the structure of metal remains unchanged under the coating layer. The set-up (see Fig. 5) was used to carry out thermochemical treatment of M6 and M12 bolts and nuts. The test according to a standard procedure showed that bolts and nuts survived not less than 50 screwing-unscrewing cycles and did

TABLE 3

Results of measurements of surface microhardness (*H*) and the distribution of elements in layer on the titanium alloy VT-4

Alloy	*H*, kg/mm^2	*h**, mm	Distribution of elements over the layer depth, %**		
			B	C	N
Initial	300–310	0.0	1.5×10^{-4}	1.1×10^{-2}	0.1
Treated with $(C_2H_5)_3N \times BH_3$	1114–1226	0.0	30	56	10
vapour at 800 °C (t = 5 h,		2.7	34	52	14
evaporator temperature: 70 °C)		8.1	55	30	15
		12.2	62	25	14
Treated with $(CH_3)_3N \times BH_3$		0.0	62	32	6
vapour at 800 °C (t = 5 h,	1200–1310	3.0	44	40	14
evaporator temperature: 50 °C)		5.2	28	51	21

*Sampling depth.

**Ratio of the number of atoms of an element to the sum of number of atoms B + C + N (according to mass spectrometric data).

not get sticky when screwed up for a long time, which was quite satisfactory for using them.

Application of $H_3B_3N_3H_3$ and L ×BH_3 in obtaining boron-nitrogen films from gas phase

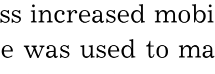
As we have already mentioned, thermal or plasmachemical decomposition of borazine vapour was used to obtain insulating BN films according to the reaction

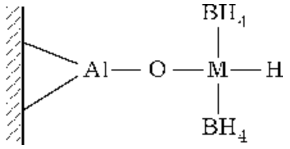
$$B_3N_3H_6\ (g) = 3BN + 3H_2,\ t = 600-800\ ℃$$

By deposition on aluminium or copper substrates at a pressure of 5 10^{-1} mm Hg and vapour flow 3 10^{-5} g/(cm^2 min), film growth rate of 2–10 mm/h was achieved. The films 5–10 mm thick have specific resistance ~10^{14} Ohm cm, their dielectric constant e ~ 4.5–5.0, and breakdown voltage is 4 10^6–6 10^6 V/cm. Plasmachemical decomposition of borazine vapour above heated metal substrates was applied to the technology of thin film capacitors with BN insulation.

Preliminary results on obtaining boron carbonitride thin films (500–9000 Å thick) by thermal or plasmachemical decomposition of $(C_2H_5)_3N$ ×BH_3 vapour were published [60, 61]. Film growth conditions, their structure and composition depending on deposition conditions are reported. Films were deposited on Si, GaAs; they possess high light transmittance coefficients.

The application of transition metal tetrahydroborates as supported catalysts for ethylene polymerization

Tetrahydroborates of the transition metals $Zr(BH_4)_4$ and $Ti(BH_4)_3$ contain bridging structures with fragments  $Zr\overset{H}{\underset{H}{—H—}}B—H$ in which hydrogen atoms possess increased mobility and reactivity. This feature was used to make supported catalysts for ethylene polymerization [62, 63]. Tetrahydroborates of Zr(IV), Hf(IV), Ti(III) obtained mechanochemically were used for this purpose. Anhydrous silica gel and alumogel served as supports; they were treated with $M(BH_4)_n$ solution in pentane. After removal the excess solution, the resulting solid phases were activated by heating in vacuum to 80–290 ℃. This resulted in the formation of active centres on the surface of supports:



The systems of this kind were found to be efficient catalysts for liquid-phase polymerization of ethylene.

CONCLUSIONS

The above-considered results of mechanochemical synthesis of borane compounds and the equipment used for this purpose demonstrate the possibility of wider technological application of the processes of this kind.

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