

## Nanosized Vanadium Diboride: Synthesis, Structure, and Properties

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**Abstract**—X-ray diffraction, scanning electron microscopic, and X-ray photoelectron spectroscopic examinations, as well as energy dispersive X-ray and elemental analyses revealed the formation of single-phase VB<sub>2</sub> with the average particle sizes of 20–35 nm from the reaction between vanadium(III) chloride and sodium borohydride at a molar ratio of 1 : 10 in the temperature range of 595–930°C in an argon atmosphere at a contact time of 14–28 h. The reaction between amorphous boron and vanadium powders at 800°C in an argon atmosphere at a contact time of 32 h in Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> and KCl ionic melts gave VB<sub>2</sub> with the average particle size of ~90 nm.

**Keywords:** nanoparticles, vanadium diboride, sodium borohydride, vanadium(III) chloride, ionic melt

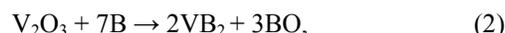
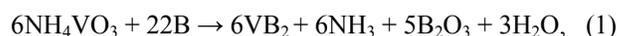
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Vanadium diboride VB<sub>2</sub> is a typical representative of Group V metal diborides. High melting point, as well as high hardness, strength, wear and impact resistance, chemical and corrosion inertness, and some other properties make VB<sub>2</sub> a promising material for applications such as high-temperature technology, vanadium boride air cells, and catalysts of liquid-phase oxidation of various organic compounds containing a double bond, e.g., of cyclooctene, with molecular oxygen [1–9].

Group IV–V metal borides attract today heightened interest from materials scientists due to promise they offer for the development of nanoscale materials whose physicochemical, mechanical, and other properties significantly differ from those of microcrystalline materials [10].

In this context, development of new efficient synthesis routes to nanoscale vanadium diboride is particularly important. Existing routes include direct synthesis from elements (sintering at high temperatures), borothermal reduction of various vanadium oxides and salts, carbothermal reduction of vanadium and boron oxides, mechanochemical synthesis, and plasma-chemical synthesis in a low-temperature nitrogen plasma [11–23].

Sintering provides is a facile route to high-speed synthesis of vanadium boride [11], but the resulting VB<sub>2</sub> appears as a molten sinter admixed with vanadium and boron oxides. A VB<sub>2</sub> powder with sufficiently large with particle sizes of <300 nm can be produced by borothermal reduction of NH<sub>4</sub>VO<sub>3</sub> at 900–1000°C under argon in the presence of a NaCl–KCl ionic melt or without it by reaction (1) [12].



Vanadium diboride powder can be synthesized by reducing vanadium oxide V<sub>2</sub>O<sub>3</sub> with boron in a vacuum at a temperature of >1500°C by reaction (2) [13] or from boron carbide at 1500°C in an argon atmosphere by reaction (3) [14]. Synthesis of vanadium diboride nanopowder by mechanochemical route in a high-energy ball mill by reaction (4) [15] gave a VB<sub>2</sub> powder with particle sizes of 15–60 nm after removal of lithium chloride.

Vanadium borides V<sub>3</sub>B<sub>2</sub>, VB, V<sub>5</sub>B<sub>6</sub>, V<sub>3</sub>B<sub>4</sub>, V<sub>2</sub>B<sub>3</sub>, and VB<sub>2</sub> were prepared by the method of self-propagating high-temperature synthesis from vanadium and

**Table 1.** Data for the reaction between  $VCl_3$  and  $NaBH_4^a$  and between V and B powders<sup>b</sup> in  $Na_2B_4O_7$  and KCl ionic melts

$T, ^\circ C$	Ionic melt	Time, h	Chemical composition of the synthesis products	Phase composition of the synthesis products	Lattice constants, nm		$S_{sp}, m^2/g$
					$a$	$c$	
420	–	48	$V_{0.98}B_{3.8}Cl_{0.3}H_{2.7}O_{0.01}$	X-phase <sup>c</sup>	–	–	–
495	–	40	$V_{1.01}B_{3.9}Cl_{0.4}H_{2.8}O_{0.04}$	X-phase <sup>c</sup>	–	–	–
570	–	32	$V_{1.1}B_{2.9}Cl_{0.2}H_{1.8}O_{0.03}$	$VB_2^d + X\text{-phase}^c$	–	–	–
595	–	28	$VB_{2.02}O_{0.03}$	$VB_2^d$	–	–	73.9
645	–	24	$VB_{2.03}O_{0.03}$	$VB_2^d$	–	–	64.4
725	–	18	$VB_{2.01}O_{0.01}$	$VB_2$	0.3006	0.3046	53.2
850	–	16	$VB_{2.03}O_{0.02}$	$VB_2$	0.3002	0.3038	39.2
930	–	14	$VB_{2.03}O_{0.03}$	$VB_2$	0.2997	0.3057	36.0
800	$Na_2B_4O_7$	32	$VB_{2.01}O_{0.02}$	$VB_2$	0.2998	0.3045	12.5
	KCl	32	$VB_{2.02}O_{0.02}$	$VB_2$	0.3002	0.3039	13.1

<sup>a</sup> Molar ratio 1 : 10, argon pressure 4 MPa. <sup>b</sup> Molar ratio 1 : 2, 800°C, argon pressure 4 MPa, 32 h. <sup>c</sup> Because of insufficient number of reflections the lattice constants of X-phase were not determined. <sup>d</sup> Because of insufficient number (3–4) and diffusivity of reflections the lattice constants of  $VB_2$  were not determined under the conditions indicated.

amorphous boron powders and studied [16]. Nanosized vanadium boride with a particle size of ~36 nm was mechanochemically synthesized from a mixture of Mg,  $V_2O_5$ , and  $B_2O_3$  in a high-energy ball mill [17]. Reaction of  $VCl_4$  with  $NaBH_4$  and Mg at 650°C in a stainless steel autoclave reactor gave 50–100 nm  $VB_2$  nanoparticles [18], and that of  $VCl_3$  with  $NaBH_4$  in a eutectic mixture of anhydrous lithium and sodium chlorides in a quartz reactor at 900°C, ~10 nm  $VB_2$  nanoparticles [19]. Plasma synthesis of vanadium diboride with particle sizes of 46–60 nm at temperatures of 2000–2600 K in a low-temperature nitrogen plasma from a mixture of vanadium oxide and amorphous boron was studied [20]. Dispersed powders of various compounds, including  $VB_2$  [21], were obtained using high-energy disintegration technique. Also, high-temperature synthesis of  $VB_2$  via solid-phase reaction of  $VCl_3$  with  $MgB_2$  was reported [22]. Transition metal chlorides reacted with boron and tin powders in a sealed ampule in a vacuum or under argon in the 700–900°C temperature range to give, depending on the reaction conditions, micro- and nanocrystalline transition metal borides, including  $VB_2$  [23].

As alternatives to the above-described routes we consider herein the synthesis of  $VB_2$  nanoparticles by the solid-phase reaction of  $VCl_3$  with  $NaBH_4$  and

“currentless” transport of vanadium to boron in ionic melts of different chemical compositions and structures.

Table 1 presents the data we obtained for the reaction of  $VCl_3$  with  $NaBH_4$  at a 1 : 10 molar ratio in the 420–930°C temperature range at an argon pressure of 4 MPa and a contact time of 14–48 h. It is seen that a single-phase nanoscale vanadium diboride was formed at  $\geq 595^\circ C$ , i.e., at a temperature of intensive decomposition of sodium borohydride [24]. Chemical and X-ray energy dispersive analyses showed that the black powder obtained in the 595–930°C range had the composition  $VB_{2.01-2.03}O_{0.01-0.03}$ , without chlorine and hydrogen traces detected.

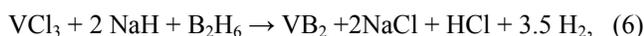
According to the XRD data, the resultant powder is vanadium diboride (hexagonal P6/mmm space group,  $A1B_2$  type structure). No significant amounts of impurity phases were detected. The unit cell parameters (Table 1) of the  $VB_2$  synthesized in the 595–930°C temperature range are consistent with the reference data for  $VB_2$ :  $a = 0.2994\text{--}0.2998$  nm,  $c = 0.3048\text{--}0.3056$  nm [25].

Similarly to the synthesis of zirconium diboride [26],  $NaBH_4$  first decomposes according to reaction (5), whereupon its decomposition products react with vanadium chloride by reaction (6). Diborane

**Table 2.** Average diameter of the VB<sub>2</sub> particle synthesized by reacting VCl<sub>3</sub> with NaBH<sub>4</sub> at a 1 : 10 molar ratio in the 595–930°C temperature range at the initial argon pressure of 4 MPa and contact time of 14–28 h, and average diameter of the particles synthesized by reacting powdered V and B in a 1 : 2 molar ratio at 800°C at an argon pressure of 4 MPa and contact time of 32 h in Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> and KCl ionic melts

<i>T</i> , °C	Ionic melt	Average particle diameter estimated from the electron microscopic data, nm	Coherent scattering region size <i>D</i> <sub>hkl</sub> , nm	Average particle diameter estimated from the <i>S</i> <sub>sp</sub> data, nm
595	–	~20	–	~16
645	–	~20	–	~18
725	–	~25	~10.0	~22
850	–	~32	~9.5	~30
930	–	~35	~10.0	~33
800	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	~90	~80.0	~95
800	KCl	~90	~85.0	~90

formed by reaction (5) decomposes under the actual conditions [27], and its decomposition products also react with VCl<sub>3</sub>. The overall scheme for the preparation of VB<sub>2</sub> is represented by reaction (7).



The reaction of vanadium trichloride with a NaBH<sub>4</sub> excess at 570°C leads to a mixture of vanadium diboride and X-phase. Alongside broadened diffraction lines associated with VB<sub>2</sub>, the diffraction patterns contain two weak diffuse lines which cannot be attributed to possible known phases in the system examined. At temperatures below 570°C the formation of vanadium diboride is not observed, and in the corresponding diffraction patterns there are two diffuse low-intensity reflections from X-phase of the total composition V<sub>0.98–1.01</sub>B<sub>3.8–3.9</sub>Cl<sub>0.3–0.4</sub>H<sub>2.7–2.8</sub>O<sub>0.01–0.04</sub>.

Table 2 lists the average diameters of the VB<sub>2</sub> particles obtained by reacting VCl<sub>3</sub> with NaBH<sub>4</sub> at different temperatures. According to the scanning electron microscopy data, the vanadium diboride particles synthesized in the 595–930°C temperature range were near-spherical, rather than chip-shaped as is typical for compounds formed as a result of a chemical reaction. The VB<sub>2</sub> particle size estimated from the electron microscopy data is consistent with the equivalent diameter of the VB<sub>2</sub> particles, estimated from the measured specific surface area of the powder at the VB<sub>2</sub> density taken as 5.066 g/cm<sup>3</sup> (Table 2). With

increasing synthesis temperature the VB<sub>2</sub> particles tend to grow in size. The VB<sub>2</sub> particles are predominantly aggregated. At the same time, the size of the coherent scattering regions *D*<sub>hkl</sub> for the 595–930°C temperature range was estimated at ~10 nm. At the synthesis temperatures of 595 and 645°C vanadium diboride was poorly crystallized, and at ≥850°C the sample particles were noticeably agglomerated. Thus, the full range of the data presented suggests the optimal synthesis temperature of 725°C.

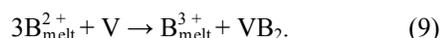
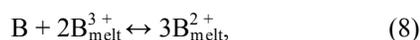
Table 1 also presents the data on the reaction between vanadium and boron powders taken in a 1 : 2 molar ratio at 800°C, argon pressure of 4 MPa, and contact time of 32 h in Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> and KCl ionic melts. This reaction followed the procedure previously developed for the synthesis of nanoscale TiB<sub>2</sub> [28].

Use of ionic melts, with their peculiar structure and properties, as a reaction medium is conducive for the production of metal borides in the form of dispersed powders. Chemical and X-ray energy-dispersive analyses showed that the vanadium diboride obtained under the conditions indicated has the composition VB<sub>2.01–2.02</sub>O<sub>0.02</sub>. According to the XRD data, the resultant powdered vanadium diboride (hexagonal space group *P6/mmm*, A1B<sub>2</sub> type structure) is a single phase; no significant amounts of impurity phases were detected. The lattice constants of the samples (Table 1) agree satisfactorily with the reference data for VB<sub>2</sub>. Analysis of nine reflections in the 2θ = 10°–110° measurement range revealed the coherent scattering region *D*<sub>hkl</sub> sizes of ~80 and ~85 nm for the VB<sub>2</sub> particles obtained in the Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> and KCl ionic melts,

respectively. The amorphous component of  $\text{VB}_2$  gave a halo (partly attributable to the substrate used for the sample deposition) with a maximum at  $20^\circ$ .

According to the scanning electron microscopy data, the powdered vanadium diboride synthesized in the both ionic melts consists of variously shaped particles some of which are close to spherical, with a diameter of  $\sim 90$  nm (Table 2). The same diameters estimated from the measured specific surface areas under assumption of the spherical shape of the  $\text{VB}_2$  particles ( $S_{\text{sp}} = 12.5$  and  $13.1 \text{ m}^2/\text{g}$ ) at their theoretical density of  $5.066 \text{ g/cm}^3$  were  $\sim 95$  and  $\sim 90$  nm for the  $\text{Na}_2\text{B}_4\text{O}_7$  and KCl ionic melts, respectively. Hence, irrespective of the chemical composition and nature of the ionic melt, the average diameter of the powdered  $\text{VB}_2$  particles is close to 90 nm.

Thus, in line with the ideas presented in [29], the observed transport of B to V in the  $\text{Na}_2\text{B}_4\text{O}_7$  or KCl ionic melt can be explained by the formation of lowest-valence ions  $\text{B}^{2+}$  by reaction (8), followed by reaction (9) of these ions with vanadium to give  $\text{VB}_2$ .



When heated in an argon atmosphere to  $1000^\circ\text{C}$ , the vanadium diboride samples synthesized by the both routes developed did not experience phase transitions accompanied by heat evolution or absorption or by a change in mass.

For more precisely determining the qualitative composition of the vanadium diboride surface, the X-ray photoelectron spectra of the samples were recorded. The XPS data show that  $\text{VB}_2$  is the main component of the powders, with the V  $2p_{3/2}$  electron binding energy being  $512.6\text{--}512.8$  eV, and the B1s electron binding energy,  $188.6\text{--}188.9$  eV, which is in agreement with the published data [30, 31]. Alongside the characteristic lines of vanadium diboride, weak lines corresponding to boron oxides or boric acid, vanadium pentoxide  $\text{V}_2\text{O}_5$ , and elemental boron were recorded ( $191.5\text{--}191.6$ ,  $516.8\text{--}517.0$ ,  $532.5\text{--}532.8$ ,  $529.7\text{--}530.3$ , and  $186.9\text{--}187.1$  eV). Therefore, an up to  $\sim 40$  Å deep surface layer of the vanadium diboride powder contains an insignificant amount of vanadium oxides, boron oxide, or boric acid with elemental boron inclusions.

The position of the B1s peak at  $191.5\text{--}191.6$  eV in the XPS patterns corresponds to  $\text{B}_2\text{O}_3$  or  $\text{H}_3\text{BO}_3$  [31].

The IR-spectroscopic data support the first assumption, since the ATR-IR spectrum of the sample was almost identical to that of individual boric anhydride [32] and did not exhibit characteristic vibrations of  $\text{H}_3\text{BO}_3$  ( $3200$ ,  $1450$ , and  $1196 \text{ cm}^{-1}$ ) [33].

Thus, the two synthetic routes to nanoscale vanadium diboride we developed allow preparation of vanadium diboride of a near-stoichiometric composition with low oxygen content and average particle diameters of  $20\text{--}35$  and  $85\text{--}90$  nm.

## EXPERIMENTAL

Sodium borohydride with  $>99.3\%$  purity was obtained by crystallization of technical-grade reagent from 1 N NaOH solution and dried in a  $1.33 \times 10^{-2}$  Pa vacuum at  $100^\circ\text{C}$ . Commercial  $\text{VCl}_3$  with a purity of  $99.5\%$ , high-purity argon [ $99.998\%$ , TU (Technical Specifications) 2114-005-0024760-99], and reagent-grade potassium chloride were used. Grade B-99A amorphous boron (TU 1-92-154-90) with the particle size of  $10\text{--}20$   $\mu\text{m}$  was preliminarily evacuated to a residual pressure of  $1.3 \times 10^{-1}$  Pa at  $300^\circ\text{C}$ . Anhydrous sodium tetraborate was obtained by dehydrating reagent-grade  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$  in a  $1.3 \times 10^{-1}$  Pa vacuum at  $350^\circ\text{C}$ .

Vanadium powder with the particle size of  $10\text{--}15$   $\mu\text{m}$  was obtained by activating commercial vanadium powder ( $99.8\%$ ) via heating at  $900^\circ\text{C}$  in a  $1.3 \times 10^{-1}$  Pa vacuum and then subjected to 5 hydrogenation–dehydrogenation cycles by the procedure described in [34]. The residual amount of hydrogen in the powder did not exceed  $1.0 \times 10^{-3}\%$ , and that of oxygen,  $3.0 \times 10^{-3}\%$ . The source of  $\geq 99.999\%$  pure hydrogen was a self-contained laboratory-scale hydrogen generator in which hydride phases based on  $\text{LaNi}_5$  and  $\text{TiFe}$  intermetallic compounds served as working materials and whose operation principle is described in detail in [35].

X-ray diffraction analysis was performed on an ADP-2 diffractometer (monochromatic  $\text{CuK}_\alpha$  radiation). The error in determining the lattice constants of  $\text{VB}_2$  did not exceed  $0.0003$  nm. Using the powder diffraction patterns, the coherent scattering region size  $D_{hkl}$  was calculated by the Scherrer formula (10) for the direction perpendicular to the  $hkl$  plane.

$$D_{hkl} = k\lambda/\beta_{hkl}\cos\theta_{hkl} \quad (10)$$

Here,  $k$  is the anisotropy coefficient taken to be  $0.9$ ,  $\lambda$ , X-ray radiation wavelength [ $\lambda(\text{CuK}_\alpha)$   $1.54178$  Å],  $\theta$ ,

diffraction angle, and  $\beta$ , full width at half maximum of the diffraction peak (in rad).

The attenuated total reflection infrared (ATR-IR) spectra in the range from 500 to 4000  $\text{cm}^{-1}$  were measured using PerkinElmer Spectrum 100 and Vertex 70V Fourier transform spectrometers equipped with attachments for recording the reflection spectra. Thermal studies were performed using a Netzsch STA 409 PC Luxx simultaneous thermal analyzer coupled to a QMS 403 C Aëolos quadrupole mass spectrometer, with a linear heating rate of 10°C/min in an argon stream over the temperature range from 20 to 1000°C. Electron-microscopic studies and energy-dispersive X-ray analysis (EDX) were performed on a complex consisting of a Zeiss Supra 25 field emission scanning electron microscope and an INCAx-sight X-ray energy-dispersive spectrometer. Electron microscopic images were obtained at low accelerating voltages of electron beam (~4 kV), at which the contribution to the recorded signal from the substrate is minimal or totally lacking. The EDX analysis was carried out at an accelerating voltage of ~8 kV. X-ray photoelectron spectra were recorded on a PHOIBOS 150 MCD electron spectrometer for chemical analysis. A Quadrasorb SI analyzer was used to measure the specific surface area. The boron, vanadium, chlorine, and oxygen contents were determined by standard analytical procedures, as well as by the energy-dispersive X-ray analysis technique. The hydrogen content was determined on a Vario EL cube Elementar CHNS/O elemental analyzer. The pressure in the system was measured using standard pressure gauges of accuracy class 0.4.

## EXPERIMENTAL

*a.* A quartz ampule with weighed portions of vanadium trichloride and sodium borohydride taken in a 1 : 10 molar ratio was placed into a stainless steel autoclave in an atmosphere of ultrapure argon. Next, the autoclave reactor was evacuated at room temperature for 5 min at  $1.33 \times 10^{-2}$  Pa, filled with argon at a pressure of 4 MPa, and heated at the specified temperature for 14–48 h. The pressure in the reactor after the reaction reached 10 MPa due to hydrogen evolution. The reactor was cooled down to ambient, the pressure in the reactor was reduced to atmospheric, and the reactor was evacuated and filled with argon. After opening the reactor in an argon atmosphere the reaction mass was sequentially treated with distilled water cooled to 3°C, acetone, and

ethanol and then evacuated for 5–6 h at 40°C to a residual pressure of  $1.33 \times 10^{-1}$  Pa. The resultant powder was again placed into the reactor, treated with hydrogen under flow conditions at a pressure of 5 MPa at 100°C, then evacuated at room temperature to a residual pressure of  $1.33 \times 10^{-1}$  Pa, and unloaded from the reactor in an argon atmosphere.

*b.* Powdered V and B taken in a 1 : 2 ratio (0.71 g V, 0.3 g B) were stirred with 0.7 g of sodium tetraborate or potassium chloride for 8 h in a vibratory mill (drum capacity 50  $\text{cm}^3$ , vanadium balls, ball load 1 : 1, vibration amplitude 10 mm, vibration frequency 28 Hz) in an argon atmosphere at room temperature until the mixture was completely homogenized. A weighed portion of the resultant mixture in a corundum crucible was placed into a stainless steel autoclave reactor. The reactor was evacuated to a residual pressure of  $1.33 \times 10^{-1}$  Pa, filled with argon at a pressure of 4 MPa, and heated for the specified time at 800°C. Next, the reactor was cooled down to ambient, and the reaction mass was unloaded. The sinter was crushed and sequentially treated with distilled water cooled to 3°C, ethanol, and acetone, and then evacuated to a residual pressure of  $1.33 \times 10^{-1}$  Pa. The resultant powder was again placed into the reactor, treated with hydrogen under flow conditions at a pressure of 5 MPa and temperature of 100°C, evacuated at room temperature to a residual pressure of  $1.33 \times 10^{-1}$  Pa, and unloaded from the reactor in an argon atmosphere.

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## CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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