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Synthesis of Nano-Sized Titanium Diboride in a Melt of Anhydrous Sodium Tetraborate

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Abstract— X-ray powder diffraction, scanning electron microscopy, infrared spectroscopy, and elemental analysis were used to study the interaction of titanium powder with finely powdered boron of particle size 10–20 μm in $Na_2B_4O_7$ ionic melt, in the temperature range 973–1088 K, at the 5–10 h contact duration. The TiB_2 formation was shown to occur at the temperatures 1018 K or above, that is, at the borax melting temperature. According to the scanning electron microscopy, theTiB_2 powder consists of the 70–75 nm particles, and its coherent scattering region calculated from the XRD data amounts to 55 nm.

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Refractory compounds of the elements of 4th group (oxides, carbides, nitrides, borides) have high hardness, strength and elastic modulus, and are chemically inert, therefore they are widely used in various industries. In the modern material science the interest in these compounds sharply increased owing to the creation on their base of the materials in the nanocrystalline state. The features of nanostructured materials, such as the existence of multiple interfaces, the small size of grains, crystallites, blocks, pores, inclusions, etc., are generated at the stage of the synthesis of these substances and, ultimately, determine their functional properties [1–3].

Typical representatives of refractory compounds are borides, but information on the methods of synthesis of borides of 4th group elements in the nanodispersed state is scarce [4–14]. The Methods of synthesis of nano-sized TiB_2 are not numerous and are mainly related to the thermolysis of titanium borohydride or its derivatives [4, 7, 8], for example, in accordance to scheme (1):

$$Ti(BH_4)_3 \cdot n\,Solv \xrightarrow{\Delta} TiB_2 + 0.5\,B_2H_6 + 4.5H_2 + n\,Solv, \quad (1)$$

where Solv means dimethoxyethane, tetrahydrofuran, diglyme, triglyme, etc. The thermolysis is carried out by heating under isothermal conditions in a vacuum using either conventional methods, or laser irradiation [9].

The TiB_2 prepared along scheme (1) according to X-ray powder diffraction is amorphous, and it crystallizes after annealing in a vacuum at 1123–1273 K.

The reaction (1) is presented in the final form, but actually this is a multistage process and the resultant titanium diboride is contaminated with oxygen, carbon, boron, or their derivatives, which adversely affects its nanostructure.

In [5, 11] a method has been studied for the synthesis of nano-sized TiB_2, based on the interaction of $TiCl_4$ with $NaBH_4$ in the absence of a solvent, at elevated temperature and pressure, in a vacuum or under argon, bypassing the step of isolating titanium borohydride or its derivatives. On the TiB_2 after separation of by-products TiB_2 was isolated with the particle size of 35–50 nm.

Nanodispersed TiB_2 can be obtained by the interaction of sodium vapor with a mixture of $TiCl_4$ and BCl_3, either according to reaction (2) [10] or by the interaction of Ti with BBr_3 in the presence of sodium metal at 673 K [11].

$$TiCl_3 + 2\,LiBH_4 + LiH \xrightarrow{\Delta} TiB_2 + 3\,LiCl + 4.5H_2. \quad (2)$$

We consider in this work an alternative method of the synthesis of nano-sized titanium diboride based on the interaction of titanium and boron in ionic melt of $Na_2B_4O_7$. The table shows the results of studies of the

Conditions and results of reaction of Ti and B powders in the presence of $Na_2B_4O_7$

Temperature T, K	Duration, h	Phase composition of the product
973	10	Ti, B
1018	10	Ti, B, TiB_2
1058	10	TiB_2
1088	10	TiB_2
1088	5	TiB_2

interaction of Ti (1.1 g; 0.023 g.-at.) and B (0.5 g; 0.046 g.-at.) powders in the presence of an excess of $Na_2B_4O_7$ in the temperature range 973–1088 K. It follows from these data that the formation of $TiB_2$is observed at $T \geq 1018$ K, that is, at the melting temperature of borax ($Na_2B_4O_7$). According to IR spectroscopy data, the titanium diboride isolated from the reaction mixture shows no absorption bands characteristic of crystallization water (OH stretching vibrations 3550–3200 cm^{-1} and HOH bending vibrations ~1630 cm^{-1} [15]). The results of cthe chemical analysis of TiB_2 are as follows:were obtained: Found, %: B 31.15, 31.20; Ti 68.85, 68.90. Found, % B 31.15, 31.20; Ti 68.85, 68.90. TiB_2. Calculated, %: B 31.11; Ti 68.89.

According to the results of XRD study (Fig. 1, all data are related to the sample obtained at 1058 K),

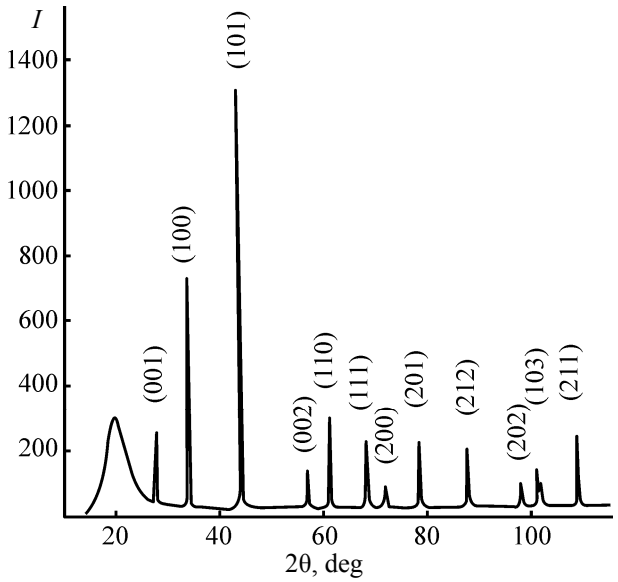

Fig. 1. Diffractogram of the powder particles of TiB_2 obtained at 1058 K.

titanium diboride crystallizes with hexagonal crystal system with the crystal lattice periods a = 0.3030 nm, c = 0.3233 nm, which agrees well with the published values 0.3028 and 0.3228 nm, respectively [16]. Analysis with the Scherrer formula of the reflection lines within the measurement 2θ range 15°–110° showed that the region of coherent scattering D_{hkl} = 55 nm. Amorphous part of the TiB_2 appears as a broad halo in the range of 2θ angles 15°–110° with a peak at 20° (the halo value can partially be associated with the substrate).

The TiB_2 powder particles size measured with scanning electron microscopy is 70–75 nm (Fig. 2).

The observed phenomenon of the boron transfer to titanium in an ionic melt of $Na_2B_4O_7$ according to the concepts developed in [17] can be explained by the formation of ions of lower valence B^{2+} in the reaction (3) followed by their disproportionation in the reaction with titanium proceeding with the energy release due to formation of TiB_2 along reaction (4).

$$B + 2B^{3+} \rightleftarrows 3B^{2+}, \quad (3)$$

$$3B^{2+} + Ti \rightarrow B^{3+} + TiB_2 + Q. \quad (4)$$

EXPERIMENTAL

Initial reagents. Titanium powder with a particle size of 5–10 μm was prepared as follows: the iodide Ti shavings were activated by heating at 773 K in a vacuum of 1.3×10^{-1} Pa, and then subjected to 5 cycles of "hydrogenation–dehydrogenation" technique [18, 19]. The residual content of hydrogen and nitrogen in the powder did not exceed 1.0×10^{-3}%, and of oxygen. 3.0×10^{-3}%. Hydrogen of the purity no less than 99.999% was prepared in an autonomous laboratory hydrogen generator, which contains as a working material the hydride phases based on the intermetallic

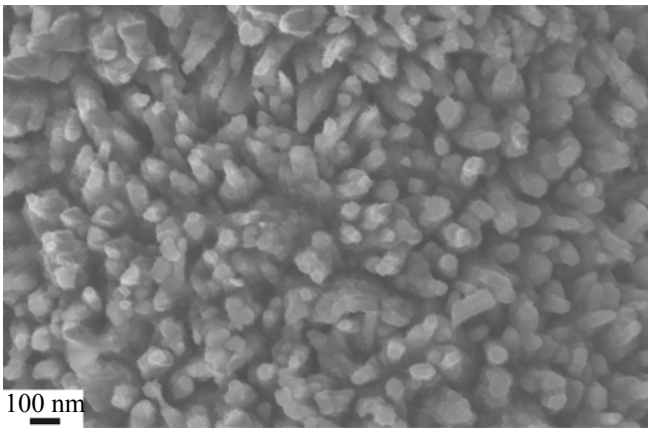

Fig. 2. Electron micrograph of the powder particles of TiB_2 obtained at 1058 K.

TiFe and $LaNi_5$, its operation principle is described in detail in [20, 21]. The commercially available fine crystalline boron of chemically pure grade with particle size 10–20 μm was preliminary evacuated to a residual pressure of 1.3×10^{-1} Pa at 573 K. The anhydrous borax was prepared by evacuation of commercial $Na_2B_4O_7\cdot5H_2O$ of chemically pure grade in a vacuum of 1.3×10^{-1} Pa at 623 K.

Methods of analysis. X-ray studies were performed on an automated complex consisting of ADP-2 diffractometer (monochromatic CuK_α-radiation). The error in determining the TiB_2 crystal lattice periods did not exceed 0.0003 nm. The coherent scattering region (CSR) D_{hkl} of hexagonal titanium diboride in the direction perpendicular to the *hkl* plane was estimated from the powder diffraction pattern with the Scherrer formula $D_{hkl} = k\lambda/\beta_{hkl}\cos\theta_{hkl}$, where k is the anisotropy factor, which in this case was taken equal to 0.9, λ is X-ray wavelength, λ(CuK_α = 1.54178 Å, θ is the diffraction angle, and β is the half-width of the diffraction peak (in radians).

Electron microscopic studies were performed on an autoemission scanning electron microscope Supra 25. The IR spectra were recorded in the range of 4000–675 cm^{-1} on a FT-IR spectrometer Perkin-Elmer Spectrum 100 with an ATR attachment. The content of hydrogen, nitrogen, and oxygen was determined on a CHNSO-analyzer, content of titanium was determined by complexometric titration in the presence of xylenol orange, and boron, by potentiometric titration of mannite-boric acid with alkali after the deposition of titanium from the sample solution using conventional technique.

Experimental procedure. Equimolar amounts of Ti and B powders were mixed with an excess of anhydrous borax ($Na_2B_4O_7$) in a vibratory mill (drum capacity 50 ml, titanium balls, load 1:1, vibration amplitude 10 mm, frequency 28 Hz) under argon at 293 K for 8 h to complete homogenization of the mixture. Then a sample of the mixture in a corundum crucible was placed in a quartz reactor of 50 mm diameter and 500 mm length. The reactor was evacuated to a residual pressure of 1.3×10^{-1} Pa, filled with argon and heated for a desired time in the temperature range 973–1088 K. Then the reactor temperature was brought to room temperature, and the reaction mixture was ground and successively treated with distilled water at 343 K, ethyl alcohol and acetone, and then evacuated to a residual pressure of 1.3×10^{-1} Pa and filled with argon.

All subsequent work with the titanium diboride thus obtained was carried out in an argon atmosphere, including sampling for analysis.

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