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Preparation of Titanium Diboride Nanopowder

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Abstract—We have studied the reaction between $NaBH_4$ and $TiCl_4$ at elevated temperatures in the range 570–1020 K and pressures of up to 10 MPa, with no solvent. The results indicate that nanoparticulate titanium diboride forms at temperatures above 820 K. According to electron microscopy data, the titanium diboride powder obtained at 1020 K consists of spherical particles 35–50 nm in diameter, in reasonable agreement with the equivalent particle diameter of ≃45 nm evaluated from the specific surface area of the TiB_2 and with the crystallite size $D_{hkl} \simeq 30$ nm evaluated from X-ray diffraction data.

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INTRODUCTION

Modern materials research is paying a great deal of attention to the synthesis and characterization of refractory compounds in an amorphous nanoparticulate or nanocrystalline state. The unique functional properties of such materials are due to the specific features of their nanostructure: the small size of crystallites and pores, the structure and composition of interfaces, the presence of residual stress and defects, and others [1–4].

Nanoparticulate titanium diboride is of particular interest among refractory compounds. Only a few processes for the synthesis of nanoparticulate TiB_2 have been proposed to date. Most of them involve the thermolysis of titanium borohydride or its derivatives [5–9] according to the scheme

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

where Solv stands for dimethoxyethane, tetrahydrofuran, diglyme, triglyme, or another solvent. The thermolysis process is run at a constant temperature in vacuum using conventional techniques or laser irradiation [9]. The TiB_2 prepared according to scheme (1) is X-ray amorphous and can be crystallized by vacuum annealing between 1120 and 1270 K.

Scheme (1) represents an overall reaction, which involves many steps, and the resultant titanium diboride is contaminated with oxygen, carbon, and boron or its hydrides, which has an adverse effect on the nanostructure of the TiB_2. Nanoparticulate TiB_2 can also be prepared by reacting sodium vapor with a mixture of $TiCl_4$ and BCl_3 or by the reaction [10]

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

and also by reacting Ti with BBr_3 in the presence of sodium metal at 670 K [11].

In this paper, we describe a different process for the synthesis of nanoparticulate TiB_2, which utilizes the reaction between $TiCl_4$ and $NaBH_4$ at elevated temperatures and pressures, with no solvent. As distinct from the procedure reported by Chen et al. [11], the reaction mixture was heated not in an argon atmosphere but in vacuum (initial pressure of 1.33×10^{-1} Pa), so that the pressure of the hydrogen released in the reactor was within 10 MPa.

EXPERIMENTAL

Starting chemicals. Sodium borohydride of 99.5% purity was prepared by crystallizing a commercial reagent from a 1 N NaOH solution, followed by drying in a vacuum of 1.33×10^{-1} Pa at 370 K. Off-the shelf titanium tetrachloride was vacuum-distilled over copper turnings just before the synthesis.

Characterization techniques. X-ray diffraction measurements were made on an ADP-1 automatic diffractometer (CuK_α radiation). The lattice parameters of TiB_2 were determined with an accuracy of 0.0003 nm or better. From the width of powder diffraction peaks, we evaluated the crystallite size using the Scherrer formula: $D_{hkl} = k\lambda/\beta_{hkl}\cos\theta_{hkl}$ (along the normal to the *hkl* plane). Here, k is a constant (taken to be unity), $\lambda_{CuK_\alpha} = 1.54178$ Å, and β is the half width at half height for the diffraction peak in radians. Electron-microscopic examination was performed on an EMV-100 BR transmission electron microscope. X-ray photoelectron spectra were obtained on a Varian IEE-15 spectrometer (Mg-anode tube, $h\nu = 1253$ eV). As the binding-energy-scale reference, we used the C1*s* level (285.0 eV).

Thermogravimetric scans were combined with mass spectrometric analyses of the decomposition products on an STA 409PC Luxx simultaneous thermal analyzer in an argon atmosphere at a heating rate of 10 K/min. The spe-

$NaBH_4 + TiCl_4$ reaction conditions and products (5 g (0.13 mol) of $NaBH_4$ and 3.45 g (0.019 mol) of $TiCl_4$)

T, K	τ, h	Composition	a, nm	c, nm
570	20	No TiB_2	–	–
670	20	No TiB_2	–	–
820	15	$TiB_{2.03}$	0.3024	0.3214
870	10	$TiB_{2.01}$	0.3025	0.3212
1020	10	$TiB_{2.0}$	0.3027	0.3213

cific surface area S of our samples was determined by BET analysis of low-temperature krypton adsorption isotherms obtained after removing volatile impurities from the solid phase in a vacuum of 1.33×10^{-3} Pa at 570 K. The molecular area of adsorbed krypton was taken to be 19×10^{-20} m^2. The error of determination was within 10%. Hydrogen was determined on an LKhM-8MD chromatograph equipped with a katharometer detector, using a 1-m-long, 3-mm-diameter column packed with tricresyl phosphate (30 wt %) on zeolite 545. The flow rate of argon carrier gas was 30 ml/min.

Boron was determined by potentiometric titration of the mannitol–boric acid complex with an alkali after titanium precipitation from the solution, and Ti was determined by chelatometric titration in the presence of Xylenol Orange, using standard procedures. The pressure in the system was measured with certified reference manometers of accuracy class 0.4.

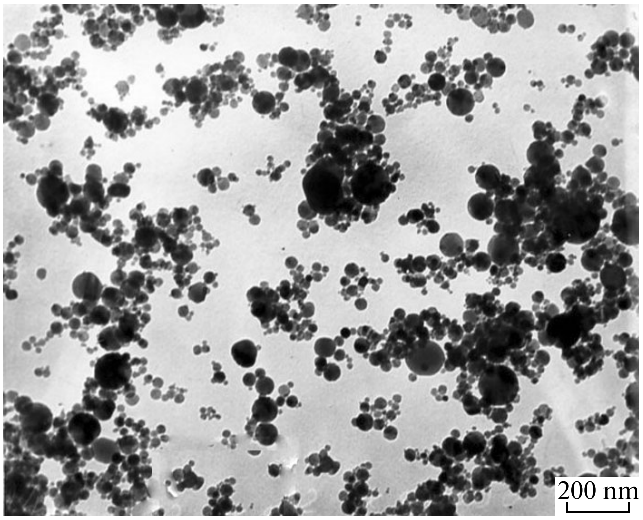
All manipulations with the titanium diboride, including sampling, were carried out under an argon atmosphere or vacuum.

Experimental procedure. $TiCl_4$ and $NaBH_4$ were reacted as follows: A silica ampule containing titanium tetrachloride and an excess of sodium borohydride was placed in a stainless-steel autoclave under an extrapure argon atmosphere. The autoclave was then cooled to 200 K, evacuated for 1 min, and heated at constant temperature for 10–20 h. Next, the reactor was cooled to room temperature, and the reaction products were evacuated for 0.5 h. After opening the reactor, the products were sequentially washed with distilled water cooled to 270 K, acetone, and ethanol and then evacuated at 310 K for 5–6 h to a residual pressure of 1.33×10^{-1} Pa. According to chemical analysis data, the resultant black powder had the composition $TiB_{2.0-2.03}$ and a hexagonal structure. Its lattice parameters (table) agree well with those reported in the literature for TiB_2: a = 0.3026 nm and c = 0.3213 nm [12].

RESULTS AND DISCUSSION

The table presents our results on the reaction between $NaBH_4$ (5 g, 0.13 mol) and $TiCl_4$ (3.45 g, 0.019 mol) at temperatures from 570 to 1020 K. These data demonstrate that the formation of nanoparticulate titanium diboride occurs for $T \geq 820$ K, that is, at temperatures where $NaBH_4$ decomposes [13]. According to electron microscopy results, the titanium diboride powder obtained at 1020 K consists of spherical particles 35–50 nm in diameter (figure), in reasonable agreement with its measured specific surface area, $S = 29.6$ m^2/g, which corresponds to an equivalent particle diameter of ≈45 nm at a TiB_2 theoretical density of 4.5 g/cm^3 [12]. The crystallite size evaluated from X-ray diffraction data is $D_{hkl} \simeq$ 30 nm.

To more accurately determine the surface composition of the titanium diboride powders, we measured their X-ray photoelectron spectra. The results showed that the major component of the powders was TiB_2, with Ti2$p_{3/2}$ and B1s binding energies of 454.4 and 187.5 eV, respectively, which is consistent with typical binding energies in metal borides [5, 14]. In addition to the lines due to titanium diboride, the spectra showed weak features arising from boron and titanium oxides and elemental boron, suggesting that the surface of the $TiB_{2.0-2.03}$ particles was covered with slight amounts of boron and titanium oxides, with elemental boron inclusions. According to X-ray diffraction results, the titanium diboride had a hexagonal structure. Its lattice parameters (table) agree well with those reported in the literature for TiB_2 [12]: a = 0.3026 nm and c = 0.3213 nm. When heated from 290 to



Electron micrograph of the titanium diboride.

1270 K in an argon atmosphere, the material showed no exothermic or endothermic transformations and no weight loss.

Thus, nanoparticulate TiB_2 can be prepared by reacting $NaBH_4$ and $TiCl_4$ in a steel reactor at $T \geq 820$ K.

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