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# Synthesis of titanium carbide and titanium diboride for metal processing and ceramics production

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## ABSTRACT

**Introduction.** Titanium carbide and diboride are characterized by high values of hardness, chemical inertness and for this reason are widely used in modern technology. This paper provides information on the synthesis of titanium carbide and diboride by carbothermal and carbide-boron methods, respectively, on the use of titanium carbide as an abrasive and in the manufacture of tungsten-free hard alloys, carbide steels, wear-resistant coatings, as well as titanium diboride in the production of cutting tools and ceramics based on boron carbide **The aim of this work** is to study the processes of synthesis of highly dispersed powders of titanium carbide and diboride, which are promising for the manufacture of cutting tools, wear-resistant coatings, abrasives and ceramics. **Research methods.** Titanium oxide $TiO_2$, nanofibrous carbon (NFC), and highly dispersed boron carbide were used as reagents for the synthesis of titanium carbide and diboride. Experiments to obtain titanium carbide were carried out in a resistance furnace, and titanium diboride in an induction furnace. X-ray studies of the phase composition of titanium carbide and diboride samples were carried out on an *ARL X-TRA* diffractometer (*Thermo Electron SA*). The determination of the content of titanium and impurities in the samples of titanium carbide and diboride was carried out by the X-ray spectral fluorescence method on an *ARL-Advant'x* analyzer. The total carbon content in the titanium carbide samples was determined on an *S-144* device from *LECO*. The content of boron and other elements for titanium diboride samples was determined by inductively coupled plasma atomic emission spectrometry (*ICP AES*) on an *IRIS Advantage* spectrometer (*Thermo Jarrell Ash Corporation*). The surface morphology and particle sizes of the samples were studied using a *Carl Zeiss Sigma* scanning electron microscope (*Carl Zeiss*). The determination of the particle/aggregate size distribution was performed on a *MicroSizer 201* laser analyzer (*BA Instruments*). **Results.** The paper proposes technological processes for obtaining highly dispersed powders of titanium carbide and diboride. The optimum synthesis temperature for titanium carbide is 2,000…2,100 °C, and for titanium diboride 1,600…1,700 °C. The content of the basic substance is at the level of 97.5…98.0 wt. %. **Discussion.** A possible mechanism for the formation of titanium carbide and diboride is proposed, which consists in the transfer of vapors of titanium oxides to the surface of solid carbon (synthesis of titanium carbide) and vapors of boron and titanium oxides to the surface of solid carbon (synthesis of titanium diboride). Due to the high purity and dispersion values, the resulting titanium carbide powder can be used as an abrasive material and for the manufacture of tungsten-free hard alloys, carbide steels, wear-resistant coatings, and titanium diboride powder can be used for the preparation of cutting tools and ceramics based on boron carbide.

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## Introduction

Titanium carbide and diboride relate to oxygen-free refractory compounds. They are characterized by high hardness and chemical inertness. Carbothermal reduction [1] is considered to be the most promising technique of titanium carbide preparation. However, carbon-diboride reduction is aimed at obtaining titanium diboride [2, 3].

Since tungsten is not readily available and very expensive, titanium carbide is used to manufacture tungsten-free hard alloys. The native industry has mastered the production of hard alloys based on titanium carbide 15Ni6Co0.1Nb-79TiC (TH20) grade. The developed alloy corresponds in hardness, and in strength is close to tungsten-containing grades of the TiC-Co (*TK*) and WC-Co (ВК) groups and has high wear resistance, reduced tendency to adhesion to the processed materials, resistant to oxidation in air at high temperatures and to aggressive media. This allows its wide application instead of a number of standard grades of hard alloys [4]:

– for metal cutting by turning and milling of low-carbon, tool and rapid steels, non-ferrous metals, and some grades of cast iron in conditions where standard alloys 4Co-66WC-30TiC (Т30К4), 6Co-79WC-15TiC (Т15К6), 8Co-78WC-14TiC (Т14К8), 94WC-6Co (ВК6) and 92WC-8Co (ВК8) are used;

– in production of measuring tools, various wear-resistant parts and industrial equipment (spray nozzles, mud pump valves, mold and draw die blocks and etc.) instead of a standard alloy TiC-Co (ВК) grade;

– to reinforce certain types of boring tools.

It was reported [5] on ceramics production from titanium carbide by hot pressing of titanium/graphite powder mixture alloyed with nickel at 1,200 $^{o}$C and 40 MPa for 30 minutes. Its relative density reached 98 %. The authors consider that the ceramics can be used as a cutting tool. When used as a cutting tool, $TiB_2$-TiC ceramics composite was prepared by hot pressing of diboride/titanium carbide powder mixture in vacuum at 1,650 $^{o}$C and 40 MPa [6]. The resulting ceramic with a mass ratio $TiB_2$ : TiC = 75 : 25, had a bending strength of 920 MPa and a microhardness of 22.6 GPa. Crack resistance was 7.6 $MPa \cdot m^{1/2}$. When used as a cutting tool, $TiB_2$–TiC+$Al_2O_3$ ceramics composite was prepared from $TiB_2$, TiC and $Al_2O_3$ powder mixture by hot pressing at 1,650 $^{o}$C and 30 MPa [7]. The prepared samples had a bending strength of 1,100±62 MPa and hardness of 21.53±0.36 GPa. Crack resistance was 8.5±0.8 $MPa \cdot m^{1/2}$. Moreover, titanium carbide can be applied for wear-resistant coatings with high values of microhardness [8, 9].

Abrasive machining appears to be one of the most important steps of the machine building technology. Up to 60 % of the machinery is operational for its accomplishment in certain branches of industry. However, conventional abrasives (corundum, silicon and boron carbides) do not comply with all the requirements for these materials [10]. Titanium carbide is thought to be an advanced material. It is characterized by a combination of high hardness and certain plasticity along with chemical inertness. That is, it does not interreact with the iron-group metals being a base for most structural materials. Consequently, the usage of titanium carbide ensures highly efficient abrasive machining. The technique of titanium carbide production by self-propagating high-temperature synthesis is presented in [11]. Chemical composition (wt. %) of titanium carbide powders prepared by this method is the following: $C_{combined}$ ranges from 19.3…19.7; $C_{free}$ and O don't exceed 0.3; N – trace level; total impurities determined by spectral analysis can't be more than 0.25. The abrasion resistance test has revealed that the titanium carbide powder prepared by self-propagating high-temperature synthesis is superior to the powder produced by carbothermal reduction of the titanium oxide in this respect. Consequently, it is a high-quality, technological and cost-effective tool material. The greatest technical and economic effect is brought by its use as a component of abrasive pastes for grinding and polishing.

Carbidosteels relate to the materials which are composed of steel and carbides with the mass content ranging from 20 to 70 %. Titanium and tungsten compounds are used as carbides. They take intermediate position between rapid steels and hard alloys with regard to their properties and application area. Carbidosteels combine properties of combines the properties of both components: a refractory solid base and a steel matrix. The refractory component gives hardness, strength, and wear-resistance to the alloy. Steel gives viscosity and plasticity. Carbidosteels are obtained by powder metallurgy methods [12]. Titanium carbide is applied to manufacture carbidosteels: 6W5Mo3V (Р6М5Ф3) – 20 % *TiC* (liquid-phase sintering); 6W5Mo3Co (Р6М5К5) – КТ20, 0.6C6Cr3w1Mo1V1Si (6Х6В3МФС) – КТ20 (hot isostatic pressing); 6W5Mo5Co (Р6М5К5) – КТ20 (hot extrusion); 5W5Mo5Co (Р5М5К5)–20% *TiC* (hot stamping). Hardness of these carbidosteels amounts to 86…90 HRA, resistance to bending reaches 1,300-2,000 MPa [13].

Boron carbide is characterized by a unique combination of low density (2.52 g/cm$^3$), high hardness (up to 40 GPa for hot-pressed items), and chemical inertness combined with a high melting point (2,450 $^o$C). As a result, ceramics based on boron carbide have found wide application in different areas of the state-of-the-art technology [14]. However, there are some difficulties arising for manufacture of $B_4C$-based dense ceramics owing to the low value of the self-diffusion coefficient (because of the strong covalent bonds between boron and carbon atoms), its low plastic deformation, and high sliding resistance between the compound grains [15]. An advanced approach to improving operational characteristics of $B_4C$-based ceramics consists in the use of modifying additives. Their presence tends to activate the sintering process by reducing the activation energy, that leads to a decrease in the grain size, an increase in the density, strength, and fracture strength of the sintered compositions. In this case, diborides of transition metals can be used, for example, zirconium diboride [16–19].

Here the objective is to study the synthesis processes of highly dispersed powders of titanium carbide and diboride as advanced materials used in manufacture of cutting tools, wear-resistant coatings, abrasives and ceramics.

## Research techniques

To carry out the synthesis of titanium carbides and diborides, $TiO_2$ ОСЧ 7-3ТУ 6-09-3811-79 (the content of the base material – 99 wt.%), nanofibrous carbon – *NFC* (specific surface area – 150 m$^2$/g, the content of the base material – 99 wt.% [20]), and highly dispersed boron carbide (an average particle size – 2.1 μm, the content of the base material – 98.5 wt.% [21]) were used as reagents. The experiments on obtaining titanium carbide by carbothermal method were conducted in a resistance furnace fitted with a graphite heater, but titanium diboride was prepared in a ВЧ–25АВ crucible-type induction furnace. X-ray studies of the phase composition for titanium carbide and diboride samples were conducted using an *ARL X-TRA* diffractometer (Thermo Electron SA) with CuKα radiation (wavelength λ = 1.5406 Å). The angular rage (2θ) was from 20$^o$ to 70$^o$. The content of titanium and impurities was determined in the titanium carbide and diboride samples by the X-ray spectral fluorescence method with the use of an *ARL-Advant'x* analyzer fitted with *Rh*-anode of the X-ray tube. The measurement inaccuracy was 1 %. The total content of carbon in the titanium carbide samples was determined using a *LECO S-144* device. The measurement inaccuracy was 1 %. The content of boron and other elements in the titanium diboride samples was determined by inductively coupled plasma – atomic emission spectrometry (*ICP AES*) using an *IRIS Advantage* spectrometer (Thermo Jarrell Ash Corporation). The measurement inaccuracy was 1 %. The surface morphology and particle sizes of the samples were studied using a *Carl Zeiss Sigma* scanning electron microscope. The particle/aggregate size distribution was determined with the use of a *MicroSizer 201* laser analyzer (BA Instruments). The measurement inaccuracy was < 5%.

## Results and Discussion

The charge for obtaining titanium carbide was prepared by stoichiometry for the reaction:

$$TiO_2 + 3C = TiC + 2CO. \quad (1)$$

The experiments on the synthesis of titanium carbide were carried out at the following temperatures, $^o$C: 1,600; 1,800; 2,000; 2,100 (samples 1-1, 1-2, 1-3 and 1-4 respectively). The sample diffractograms are given in Fig. 1.

The samples contain not only titanium carbide but also titanium oxide, which was used as a reagent at the temperature of heat treatment – 1,600 and 1,800 $^o$C. At higher temperatures (2,000 and 2,100 $^o$C), the

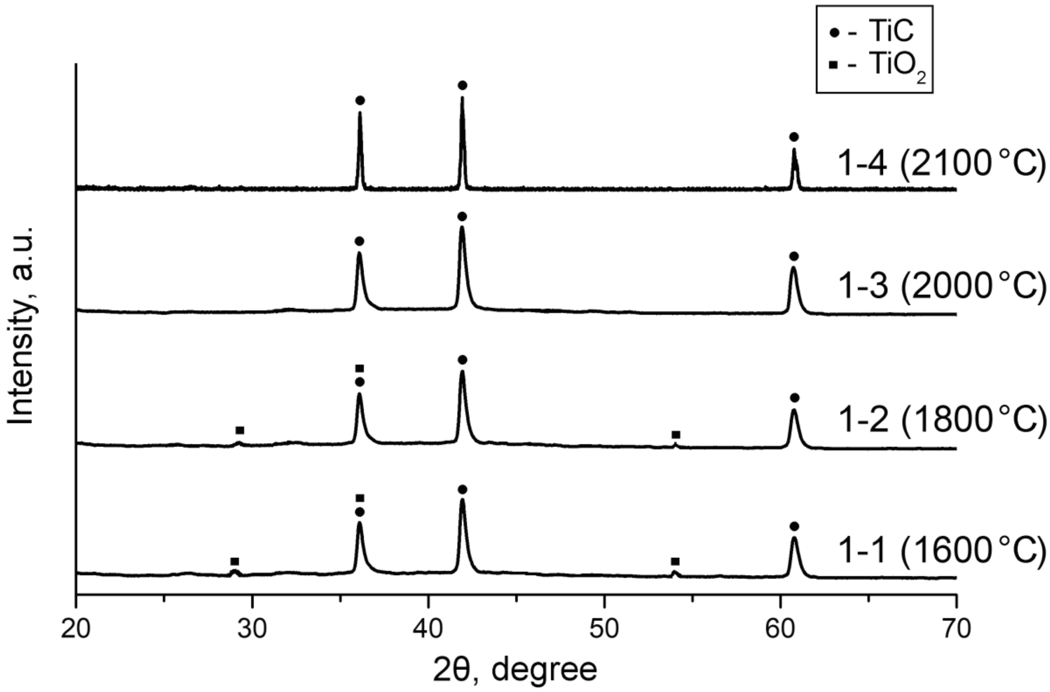



*Fig. 1.* Diffraction patterns of titanium carbide samples

process of carbide formation is completed, as evidenced by the presence of only one phase (TiC) in the samples. The results of the X-ray spectral fluorescence analysis of one-phase samples are presented in Table 1. The content of elements with the atomic weight higher than for fluorine (Al, Ni, Cu, Si, Ca, Fe, Nb, Cr, Zr) is negligible in impurities. As seen from Table 1, the similarity is found between the samples with regard to the content of titanium and total carbon. The calculated content of titanium carbide of the composition *TiC* is: titanium – 80.00 wt.%; carbon – 20.00 wt.%.

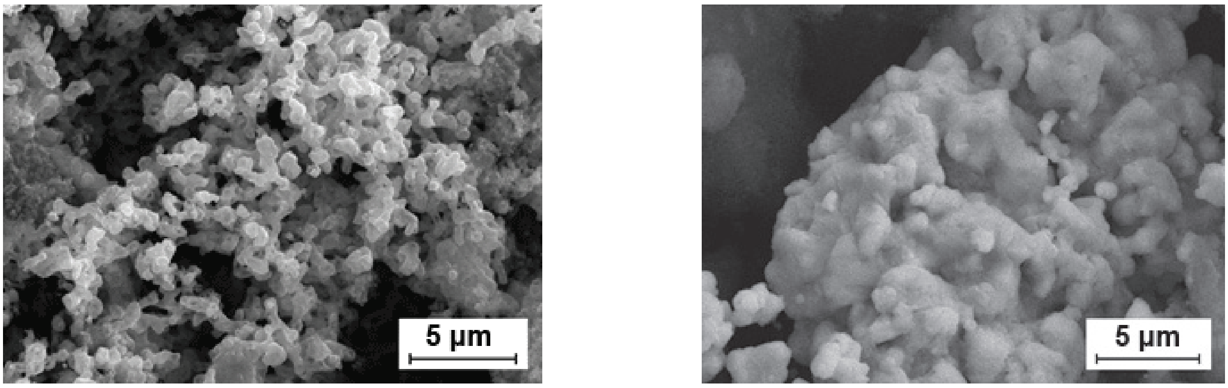
Table 1

**Results of X-ray fluorescence analysis of samples 1-3 and 1-4**

| Sample | Content, wt. % | | |
|---|---|---|---|
| | Ti | $C_{total}$ | Residual elements |
| 1-3 | 79.49 | 19.6 | 1.69 |
| 1-4 | 79.42 | 19.8 | 1.71 |

Calculated impurities content in titanium carbide is equal to 1.92 wt.%, with regard to impurities content (1 wt.%) in titanium oxide and *NFC*. The data given in the table are very close to the calculated ones, and it gives evidence of high purity of the received products despite negligible content of impurities. When taking into account possible content of unreacted titanium dioxide and carbon, the content of impurities in the obtained titanium carbide could be estimated as ~ 2 wt.%. According to cumulative results of X-ray phase and elemental analyses, we can come to conclusion that the process of carbide formation is nearly completed at the temperature of 2,000 °C or more. If *NFC* is used as a reducing agent, optimum conditions of titanium carbide synthesis will be the following: 1) $TiO_2$/C mass ratio by stoichiometry versus TiC, 2) the process should take place in a weak reductive gaseous medium ($N_2$ + *CO* mixture) at 2,000…2,100 °C.

Figure 2 shows *SEM* images of samples obtained by the interaction of titanium dioxide with carbon at different temperatures. Samples 1-3 and 1-4 essentially consist of homogeneous particles. It appears to be an indirect proof of the carbide formation completion. It should be noted that titanium carbide particles are mainly aggregated, their boundaries are even (without shape fragmentation), that is a characteristic feature of compounds obtained by chemical reactions.




*a* *b*

*Fig. 2*. *SEM* images of samples 1-3 (*a*) and 1-4 (*b*)

In accordance with the sedimentation analysis of samples 1-4 performed by the geometrical method of moments [22], an average particles/aggregates size is 9.6 µm and standard deviation is 2.50 µm. When the standard deviation is in the range from 2.0 to 4.0 µm, the particles/aggregates are "poorly sorted" or polydisperse.

To obtain titanium diboride, the charge was prepared by the following stoichiometry for the chemical reaction:

$$2TiO_2 + B_4C + 3C = 2TiB_2 + 4CO. \quad (2)$$

The experiments on the synthesis of titanium diboride were conducted at 1,600 and 1,700 $^{o}$C (samples 2-1, 2-2, 2-3 and 2-4 respectively). Diffraction patterns of the samples are given in Fig. 3. At heat treatment temperatures of 1,600 and 1,700 °C, the obtained samples contain only the target phase ($TiB_2$), regardless of the heat treatment duration. The presence of another possible reaction product, TiB monoboride, was not detected. The results of X-ray fluorescence analysis of samples 2-1 and 2-2 are given in Table 2.

The content of elements with higher atomic weight compared with fluorine (Al, Ni, S, Si, Nb, Zr) is negligible in the impurities. The content of boron and other elements was determined by the method

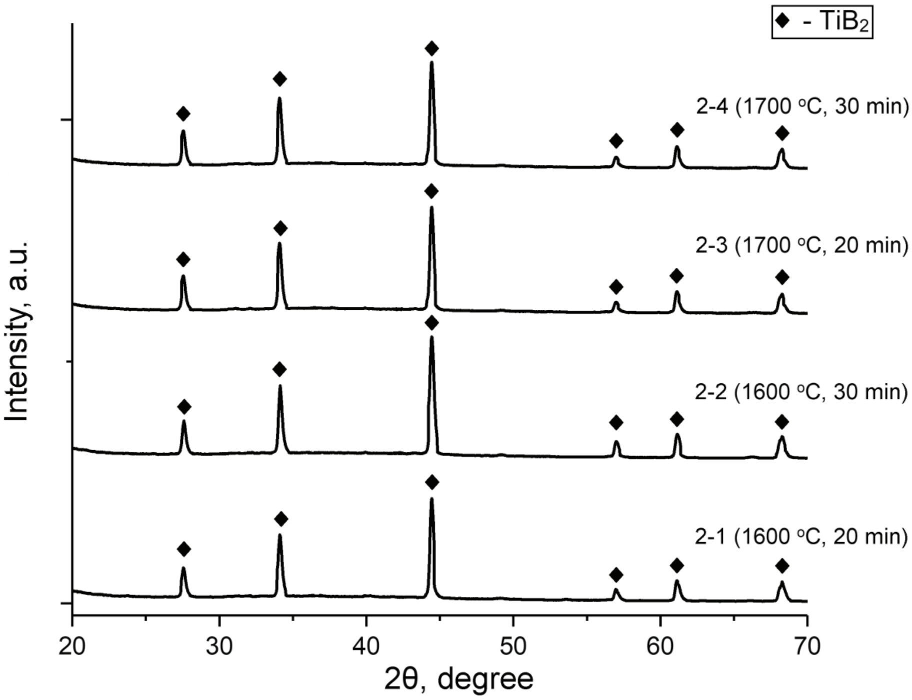



*Fig. 3*. Diffraction patterns of titanium diboride samples

Table 2

**Results of samples 2-1 and 2-2 determined by X-ray fluorescence analysis**

| Sample | Content, wt.% | | |
|---|---|---|---|
| | Ti | Impurities | $\leq F^{*}$ |
| 2-1 | 68.28 | 0.57 | 1.15 |
| 2-2 | 68.36 | 0.48 | 1.16 |

* The total content of elements with atomic mass less than that of fluorine inclusive

of atomic emission spectroscopy-inductively coupled plasma (*AES-ICP*). The results are presented in Table 3.

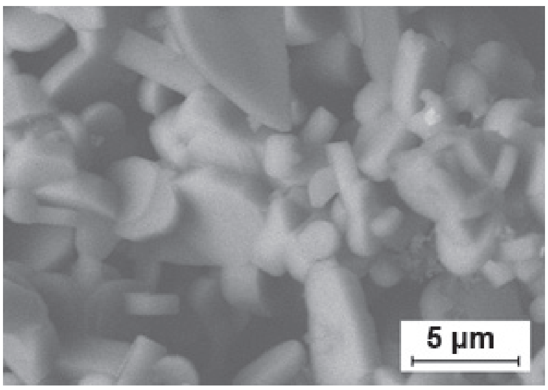
Calculated content of titanium in titanium diboride amounts to 68.57 wt.%, and boron content is 31.43 wt.%. It should be noted that the data obtained on basic elements (Ti and *B*) are comparable and close to the calculated content in spite of the fact that they are received by two absolutely different analysis techniques. It can also be argued that an increase in the duration of heat treatment of the charge from 20 to 30 minutes has practically no effect on the phase and elemental composition of the synthesis products. Taking into account the presence of impurities of reagents in titanium diboride, the content of the basic substance in it can be estimated at 97.5 wt.%. The optimal synthesis conditions in this case are: stoichiometric mass ratio of reagents to titanium diboride and a temperature of 1,600…1,700 °C. *SEM* images of the samples are given in Fig. 4. The images were obtained upon the reaction of titanium dioxide with carbon and boron carbide at 1,700 $^{o}$C, and synthesis time interval – 20 and 30 minutes.

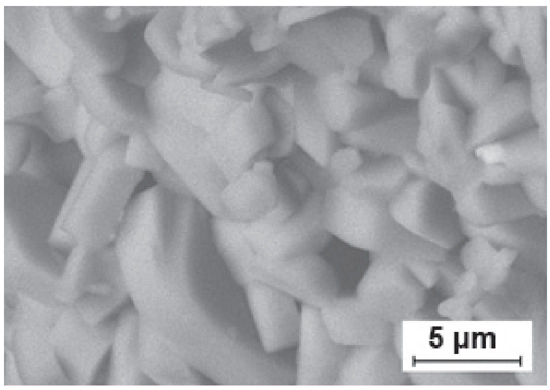
Samples 2-3 and 2-4 are mostly composed of uniform particles. It appears to be an indirect proof of the carbide formation completion. The particles are in the shape of columns, and their boundaries are even.

Table 3

**Results of analysis of titanium diboride samples determined by inductively coupled plasma atomic emission spectrometry**

| Sample | Content, wt.% | | |
|---|---|---|---|
| | Ti | $B_{total}$ | Impurities |
| 2-1 | 67.33 | 31.42 | 0.91 |
| 2-2 | 67.36 | 31.22 | 0.86 |




*a* *b*

*Fig. 4.* SEM images of samples 2-3 (*a*) and 2-4 (*b*)

They are mainly aggregated. The results of sedimentation analysis of titanium diboride samples are given in Table 4. The analysis was conducted according to the technique described in [22].

Table 4

**Results of sedimentation analysis of titanium diboride samples**

| Sample | Average size of particles / aggregates, μm | Standard deviation, μm | Sample | Average size of particles / aggregates, μm | Standard deviation, μm |
|---|---|---|---|---|---|
| 2-1 | 7.4 | 2.41 | 2-3 | 11.1 | 2.22 |
| 2-2 | 8.0 | 2.33 | 2.4 | 11.2 | 2.28 |

As follows from the obtained results, the sizes of aggregated particles tend to increase with the rise in temperature from 1,600 to 1,700 °C. All powder samples are polydispersive.

The analysis of carbide and boron formation process presupposes that the pressure of carbon vapors is significantly lower than the pressure of metal and boron oxide vapors at the synthesis temperatures. Hence, the pressure of carbon vapors reaches $3 \cdot 10^{-6}$; $4 \cdot 10^{-5}$; $2.6 \cdot 10^{-3}$; $8.5 \cdot 10^{-2}$ Pa at 1,630; 1,730; 1,930; 2,130 °C respectively [23]. The vapor pressure above titanium oxide at a temperature of 2,030 °C (almost corresponds to the optimum temperature for the synthesis of titanium carbide) is 1 Pa, and at a temperature of 1,730 °C (almost corresponds to the optimum temperature for the synthesis of titanium diboride) is 0.01 Pa. The vapor contains $Ti^+$ and $TiO^+$ ions, TiO and $TiO_2$ molecules, and *Ti* atoms above this oxide [24]. It is known [25] that pressure of boron vapor above boron-carbon carbide system at 1730° C (that nearly corresponds to optimum temperature of titanium diboride synthesis) is equal to 1 Pa. Furthermore, pressure of other gaseous components is two orders ($BC_2$) and three orders ($B_2C$) lower. Therefore, pressure of oxides/boron vapors significantly (by several orders) exceeds carbon vapor pressure at optimum temperatures under the synthesis of these refractory compounds. Consequently, with a high degree of probability, it can be argued that these processes are carried out by transferring vapors of higher and lower oxides to the surface of solid carbon (synthesis of titanium carbide) and transferring vapors of higher and lower oxides along with boron vapor to the surface of solid carbon (synthesis of titanium diboride). These are conventional adsorption processes. It appears to be an indirect proof of the carbide formation completion. An indirect proof of this is the relatively short synthesis times of the considered refractory compounds. Diffusion processes start on completion of chemical reactions. However, diffusion processes can really take place at the immediate contact between hard reagents. Undoubtedly, a positive role in these relatively fast processes is played by the developed surface of the *NFC*. It clearly reduces the time of diffusion processes, which are completed by the complete conversion of reagents into target compounds. To produce ceramics from boron carbide with the modifying additive from titanium diboride, the charge can be prepared by the reaction (2) with excess boron carbide. Complete transformation of reagents into composite powder $B_4C$-$TiB_2$ occurs in the temperature range 1,560…2,200 °C [26]. Being prepared by the reaction (2), the charge was compacted. *SEM* image of a sintered sample section is given in Fig. 5.

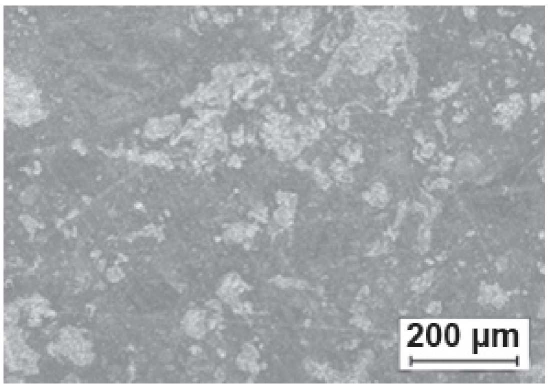



*Fig. 5* SEM image of the surface of a sample of ceramic $B_4C$-$TiB_2$

Light inclusions ($TiB_2$ particles) are evenly distributed in the boron carbide matrix. The inclusions could be the size up to several tens of microns. Pores are absent.

## Conclusion

The analysis of titanium carbide and diboride application area has been presented in connection with metal working. Titanium carbide is used in production of tungsten-free hard alloys, wear-resistant coatings, and carbidosteels. It's an advanced abrasive used for finishing grinding/polishing work. Titanium carbide and diboride find application in manufacture of cutting tools. Titanium diboride can be used as a modifying additive in production of wear-resistant ceramics based on boron carbide.

The synthesis of titanium carbide and diboride is studied. Nanofibrous carbon (*NFC*) is used as a reducing agent and characterized by a high value of the specific surface (about 150 $m^2$/g). Certain characteristics of the obtained powders are examined. The content of the basic substance amounts to 97.5…98.0 wt.% in the powders. The processes of these compounds formation are presumably accomplished through the transfer of high and low oxides vapors onto the surface of hard carbon (synthesis of titanium carbide), and the transfer of high and low oxides vapors together with boron vapors onto the surface of hard carbon (synthesis of titanium diboride). Powders are highly-dispersive (an average particle size is about 10 μm) or polydisperse. For this reason, they are promising for a number of metalworking processes and for producing ceramics based on boron carbide.

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## Conflicts of Interest

The authors declare no conflict of interest.