

The mechanism of titanium diboride low-temperature synthesis

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To determine the mechanism and conditions for the increased of product yield of titanium diboride TiB₂ low-temperature synthesis, a thermodynamic assessment of the interaction in the TiO₂ – B₂O₃ – C system was performed. A numerical method was used to study a series of consequentially-parallel processes for the reduction of titanium oxide to its non-stoichiometric oxycarbide phase and its subsequent interaction with gaseous boron oxides. The Gibbs energy was estimated for oxycarbide TiC_xO_{1-x} and titanium borate TiBO₃ at 1027 °C, which are related as $\Delta G_{\text{TiC}_x\text{O}_{1-x}}^0 \gg \Delta G_{\text{TiBO}_3}^0$. This energy ratio of intermediate products of the titanium diboride synthesis allowed to make essential corrections in providing conditions and final results of synthesis. At the first stage of the process, it was established that fluorine-doped titanium oxide TiO_{2-x}F_x is reduced to oxycarbide TiC_xO_{1-x} with a deficient carbon content of $x < 0.5$. At the final stage, exposure of isolated system at a fixed temperature requires moderate kinetic stimulation of TiB₂ synthesis by periodic vacuuming. This is due to the need to create conditions for the disproportionation of gaseous boron oxide B₂O_{3(gas)} to its suboxides (B₂O_{2(gas)}, BO_{2(gas)}) in the volume of the reaction mixture TiO₂ – B₂O₃ – C and to suppress the “parasitic” reaction of the titanium borate TiBO₃ formation. The established mechanism assumes observance of balance between temperature and duration of phase transformations during the exposure of the system at the first stage, a balance between the increased $P_{\text{B}_2\text{O}_2}/P_{\text{CO}}$ ratio in the gas phase and the temperature at the final stage of the titanium diboride synthesis. The mechanism and conditions for the TiB₂ synthesis are confirmed by laboratory experiments, the implementation of which allows to obtain titanium diboride powders of technical purity at 1030–1050 °C.

Key words: Anatase-rutile transformation, synthesis mechanism, thermodynamic assessment, phase formation, low-temperature synthesis, titanium oxycarbide, titanium borate, titanium diboride, boron oxide, disproportionation.

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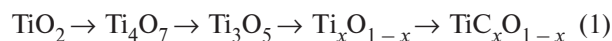
Introduction

The transition to the commercial stage of development of any technology, and in this case, the technology of titanium diboride low-temperature synthesis, requires high reproducibility and a satisfactory output of the target product at the stage of laboratory research. These requirements are provided by understanding the mechanism of sequentially-parallel processes occurring with the reaction mixture TiO₂ – B₂O₃ – C during the entire period of heating and holding the system under synthesis conditions.

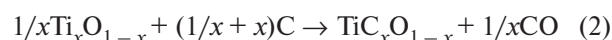
The most favorable conditions for the initiation and completeness of carbothermal reduction of TiO₂ to oxide and oxycarbide phases were determined in [1–2]. It was reported about the principal possibility of titanium diboride synthesis at 1050±1070 °C with an attempt to determine the mechanism of the process at the intermediate and final stages. However, the reproducibility of TiB₂ synthesis results remained low. In this regard, detailed studies of the thermodynamic conditions of TiB₂ low-temperature synthesis and verification of the theoretical data obtained by practical experiments have been undertaken.

Thermodynamical estimation of titanium diboride synthesis

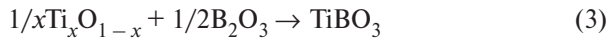
The well-known procedure for doping amorphous titanium oxide with fluoride ions according to the scheme $\text{TiO}_2 \cdot x\text{H}_2\text{O} \rightarrow \text{TiO}(\text{OH})_{2-x}\text{F}_x \rightarrow \text{TiO}_{2-x}\text{F}_x \rightarrow a\text{-TiO}_{2-x}\text{F}_x$ and the anatase-rutile transformation (ART) shift from a temperature range of 600–700 °C to the range of 900–1100 °C extends the period of the crystal lattice rearrangement in the process of $a\text{-TiO}_{2-x} \rightarrow r\text{-TiO}_2$. This ensures the prolongation of the active state of titanium oxide and at 860±980 °C creates the conditions for its sequential recovery according to the scheme [3]:



At the last stage, the carbothermic reduction evolves to the non-stoichiometric phase of oxycarbide TiC_xO_{1-x}



Both non-stoichiometric phases of this process in contact with B₂O₃ initiate the phase formation of another intermediate TiBO₃:



The presence of oxycarbide and titanium borate was confidently reproduced by the XRD results of the synthesis products of the initial $\text{TiO}_2 - \text{B}_2\text{O}_3 - \text{C}$ mixture in preliminary experiments at $1050\div 1070^\circ\text{C}$ [1–2]. This gives basis for estimating the unknown Gibbs free energy values of $\text{TiC}_x\text{O}_{1-x}$ and TiBO_3 at 1300 K. Assume that the reaction product is an oxycarbide of the composition $\text{TiC}_{0.5}\text{O}_{0.5}$ at $x = 0.5$. Calculate the Gibbs energy of reactions ΔG_R^0 excluding $\Delta G_{\text{TiC}_{0.5}\text{O}_{0.5}}^0$ oxycarbide titanium – $\Delta G_{(n)}^0 = (\Delta G_R^0 - \Delta G_{\text{TiC}_{0.5}\text{O}_{0.5}}^0)$.

No.	Reactions at 1300K	$\Delta G_R^0 - \Delta G_{\text{TiC}_{0.5}\text{O}_{0.5}}^0$, kJ/mol
1.	$\text{TiO}_2 + 2\text{C} = \text{TiC}_{0.5}\text{O}_{0.5} + 3/2\text{CO}$	510.82
2.	$1/4\text{Ti}_4\text{O}_7 + 7/4\text{C} = \text{TiC}_{0.5}\text{O}_{0.5} + 5/4\text{CO}$	509.62
3.	$1/3\text{Ti}_3\text{O}_5 + 5/3\text{C} = \text{TiC}_{0.5}\text{O}_{0.5} + 7/6\text{CO}$	505.12
4.	$\text{TiO} + \text{C} = \text{TiC}_{0.5}\text{O}_{0.5} + 1/2\text{CO}$	447.96
Average value $\Delta G_{(1-4)}^0 =$ $= (\Delta G_{\text{CO}}^0 - \Delta G_{\text{Ti}_n\text{O}_{2n-1}}^0 - \Delta G_{\text{C}}^0)$		493.38

The average value of $\Delta G_{(1-4)}^0$ has a positive value. But, since the experiment indicates the course of reactions (1–4) to the formation of $\text{TiC}_x\text{O}_{1-x}$ [1], we can assume:

$$\Delta G_{\text{TiC}_{0.5}\text{O}_{0.5}}^0 \leq -493.38 \text{ kJ/mol} \quad (5)$$

We will make the same reasoning and estimation for the reactions of titanium borate formation TiBO_3 according to reactions (3) and (4). At the same time, we assume that at temperatures above 1000°C , gasification of boron oxide occurs in the system and its participation in gaseous phase formation reactions. The $\text{B}_2\text{O}_3(\text{liquid}) \rightarrow \text{B}_2\text{O}_3(\text{gas})$ process was observed and studied in [4–6] and is a universally recognized effect.

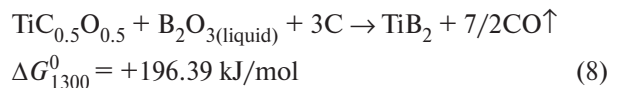
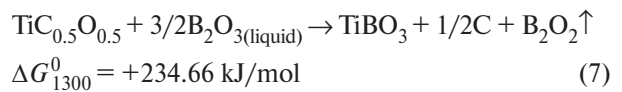
No.	Reactions at 1300K	$\Delta G_R^0 - \Delta G_{\text{TiBO}_3}^0$, kJ/mol
5.	$\text{TiO}_2 + 1/2\text{B}_2\text{O}_3 \rightarrow \text{TiBO}_{3.5}$	1771.86
6.	$1/4\text{Ti}_4\text{O}_7 + 1/2\text{B}_2\text{O}_3 \rightarrow \text{TiBO}_{3.25}$	1411.32
7.	$1/3\text{Ti}_3\text{O}_5 + 1/2\text{B}_2\text{O}_3 \rightarrow \text{TiBO}_{3.17}$	1642.93
8.	$1/2\text{Ti}_2\text{O}_3 + 1/2\text{B}_2\text{O}_3(\text{liquid}) \rightarrow \text{TiBO}_3$	1574.22
9.	$1/2\text{Ti}_2\text{O}_3 + 1/2\text{B}_2\text{O}_3(\text{gas}) \rightarrow \text{TiBO}_3$	1489.65
Average value $\Delta G_{(5-9)}^0 = (-\Delta G_{\text{TiO}_x}^0 - \Delta G_{\text{B}_2\text{O}_3}^0)$		1578.00
10.	$\text{TiC}_{0.5}\text{O}_{0.5} + 3/2\text{B}_2\text{O}_3(\text{gas}) \rightarrow$ $\rightarrow \text{TiBO}_3 + 1/2\text{C} + \text{B}_2\text{O}_2(\text{gas})$	1541.66
11.	$\text{TiC}_{0.25}\text{O}_{0.75} + 3/2\text{B}_2\text{O}_3(\text{gas}) \rightarrow$ $\rightarrow \text{TiBO}_3 + 1/4\text{CO} + \text{B}_2\text{O}_2(\text{gas})$	1454.21
Average value $\Delta G_{(10-11)}^0 =$ $= (\Delta G_{\text{C}(\text{CO})}^0 + \Delta G_{\text{B}_2\text{O}_2}^0 - \Delta G_{\text{TiC}_x\text{O}_{1-x}}^0 - \Delta G_{\text{B}_2\text{O}_3}^0)$		1497.93
Average value $\Delta G_{(5-11)}^0$		1537.97

The average value of $\Delta G_{(5-11)}^0$ has a positive value. But, since the experiment indicates the beginning of the interaction of reactions (5–11) to the formation of TiBO_3 [2], we can assume that

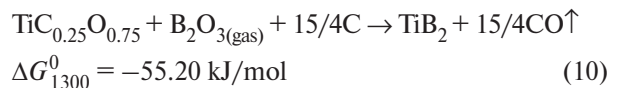
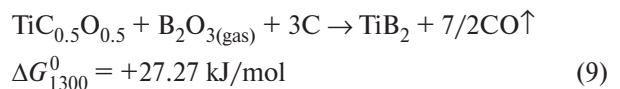
$$G_{\text{TiBO}_3}^0 \leq -1537.97 \text{ kJ/mol} \quad (6)$$

Thus, the Gibbs partial energies for oxycarbide $\text{TiC}_x\text{O}_{1-x}$ and titanium borate TiBO_3 are related as $\Delta G_{\text{TiC}_x\text{O}_{1-x}}^0 \gg \Delta G_{\text{TiBO}_3}^0$. This ratio of the intermediate products energies of the titanium diboride synthesis makes significant adjustments to the conditions and the final results of the synthesis.

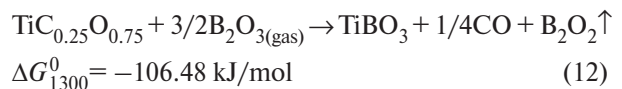
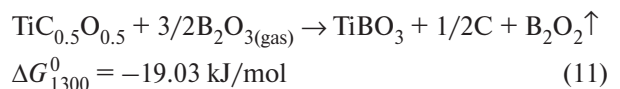
Theoretically and practically, processes involving boron oxide in a condensed state are unlikely:



but develop with the participation of boron oxide in a gaseous state until the formation of titanium diboride:



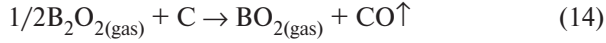
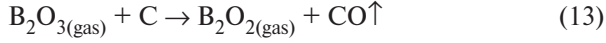
and titanium borate



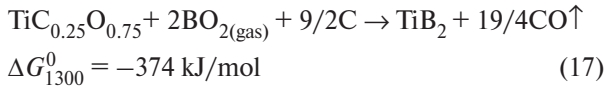
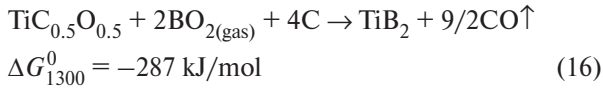
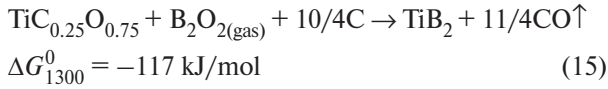
In accordance with eqs. (7)+(12), the formation of titanium borate TiBO_3 , relative to titanium diboride TiB_2 , has an insignificant but greater probability in the presence of the initial $\text{TiC}_x\text{O}_{1-x}$ reagent of the same composition. Titanium diboride is formed only at $x < 0.5$ by reaction (10), i. e., with a lower carbon content in the composition of the intermediate oxycarbide phase. This may mean that carbon depleted $\text{TiC}_x\text{O}_{1-x}$ has the highest reactivity. Freshly formed and active nucleus of these oxycarbides, upon further heating and holding at $1030\div 1060^\circ\text{C}$, are thermodynamically the best starting phases for interaction with boron-containing components in the $\text{TiO}_2 - \text{B}_2\text{O}_3 - \text{C}$ system with the subsequent formation of titanium diboride TiB_2 . On the contrary $\text{TiC}_x\text{O}_{1-x}$ with a composition close to titanium carbide TiC ($0.5 < x \leq 1$) is inactive, or rather, is capable of

interacting with boron oxide only up to titanium borate (reaction (11)).

Thus, the final result of the process depends on the development of two competing processes for the output of TiB_2 boride with $\text{CO}\uparrow$ in the gas phase (10) and TiBO_3 borate with predominant generation of $\text{B}_2\text{O}_2(\text{gas})$ (12). Suppression of the latter reaction development can be ensured by the disproportionation of gaseous boron oxide to its suboxides [7–14]:



Kinetic stimulation of boron oxide carbothermic reduction, i. e., periodic vacuuming of the system, causes increased generation of $\text{B}_2\text{O}_2(\text{gas})$, $\text{BO}_2(\text{gas})$ and $\text{BO}(\text{gas})$ with an increase in the $P_{\text{B}_x\text{O}_y}/P_{\text{CO}}$ ratio in the gas phase. And this creates preferences for the development of reaction (10) with the formation of titanium diboride. In addition, the participation of boron suboxides in phase formation reactions increases the efficiency of the entire process and the yield of the target product:

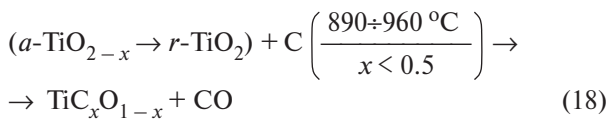


Thus, the essential conditions for the low-temperature synthesis of titanium diboride are:

Condition 1. Pre-doping of amorphous titanium oxide with fluorine $\text{TiO}_{2-x}\text{F}_x$ to stabilize the anatase modification of titanium oxide and transfer of ART from 600–700 °C to a high temperature zone of 900–1000 °C.

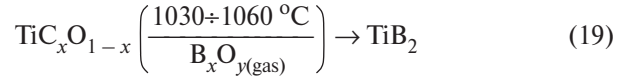
Preliminary studies found that ART of doped with fluorine titanium oxide intensively occurs in the range of 860–980 °C, which is the period of the highest reactive activity of titanium oxide during its carbothermic reduction [3].

Condition 2. The formation of the active intermediate phase of titanium oxycarbide $\text{TiO}_{2-x}\text{F}_x$ with a carbon-deficient composition $x < 0.5$ in an air atmosphere when heated to 960 °C with a maximum development of the process at 890 °C:



Such a condition may be a balance between the temperature and the duration of the phase transformations $\text{Ti}_3\text{O}_5 \rightarrow \text{Ti}_x\text{O}_{1-x} \rightarrow \text{TiC}_x\text{O}_{1-x}$ during the exposure of the system.

Condition 3. Synthesis of titanium diboride TiB_2 at a temperature of 1030–1060 °C for 2–3 hours with the participation of boron oxides in the phase formation reactions in gaseous form $\text{B}_x\text{O}_y(\text{gas})$:



This condition determines the possibility of low-temperature synthesis and the output of the target product, which is higher with an extension of the contact period of $\text{B}_x\text{O}_y(\text{gas})$ with active intermediate products in the volume of the reaction body. The process of gasification and disproportionation of $\text{B}_2\text{O}_3(\text{liquid}) \rightarrow \text{B}_x\text{O}_y(\text{gas})$ is a universally recognized effect and intensifies with an increase in temperature above 1000 °C. Therefore, the reaction contact period depends on the temperature and regulation of the atmospheric pressure in the system.

Experiment and discussion of the results

To verify and confirm the conclusions made based on the results of thermodynamic estimates and formulated conditions for carbothermal synthesis of titanium diboride, two series of experiments were carried out:

Series 1. In an isolated steel retort with a controlled atmosphere for 3 hours according to the method and using the equipment described in [1].

– At 1050 °C, **Conditions 2** and **3** were not fulfilled, namely: at the preliminary stage of heating the system, the exposure time at 960 °C was set to more than 60 minutes (i. e., process output (18) with $0.5 < x \leq 1$) and at the final the synthesis stage did not periodically remove gaseous products from the isolated system (no stimulation of gasification and disproportionation of boron oxides was performed).

– At 1100 °C, **Condition 3** was not fulfilled — an excessively high process temperature with a corresponding increase in the partial pressure of gaseous boron oxides and their rapid evacuation from the volume of the reaction mixture (reduction of the contact time of the reacting components). After the experiments, the samples were removed and sent for X-ray phase analysis. The figures below show the radiographs of the synthesis products.

The synthesis at 1050 °C under the created conditions fixes the phase formation of the entire spectrum of compounds at the final stage of the process — $\text{TiC}_x\text{O}_{1-x}$, TiBO_3 и TiB_2 (Fig. 1, a). At the preliminary heating stage, titanium oxycarbide $\text{TiC}_x\text{O}_{1-x}$ is formed, enriched in carbon and reactive to the formation of TiBO_3 by reaction (12) at the stage of system exposure.

At 1100 °C, the limited contact time of the reacting compounds according to reactions (10), (15)–(17) reduces the yield of the final target product, titanium diboride with a high content of titanium oxycarbide impurities (Fig. 1, b).

Compliance with all conditions of titanium diboride low temperature synthesis allows to obtain technically pure powder TiB_2 (Fig. 2).

Series 2. Reduction of the initial reaction mixture $TiO_2 - B_2O_3 - C$ under a layer of salt melt.

The technique consists in placing compressed samples of the mixture on the bottom of the crucible under a layer of molten salt. The goal is to exclude oxygen access to the sample in the second stage during the synthesis of titanium diboride. In the experiments, the sodium salt NaCl was selected for the melt. After placing the pressed samples of the initial reaction mixture $TiO_2 - B_2O_3 - C$ on the bottom of the crucible and loading the powder and lump material of salt, the furnace was heated in an oxygen-containing atmosphere to $950 \div 960$ °C with a 30-minute exposure, and then after the salt was melted, to a synthesis temperature of 1050 °C with exposure of the system for 3 hours. The exposure time began from the moment of salt melting.

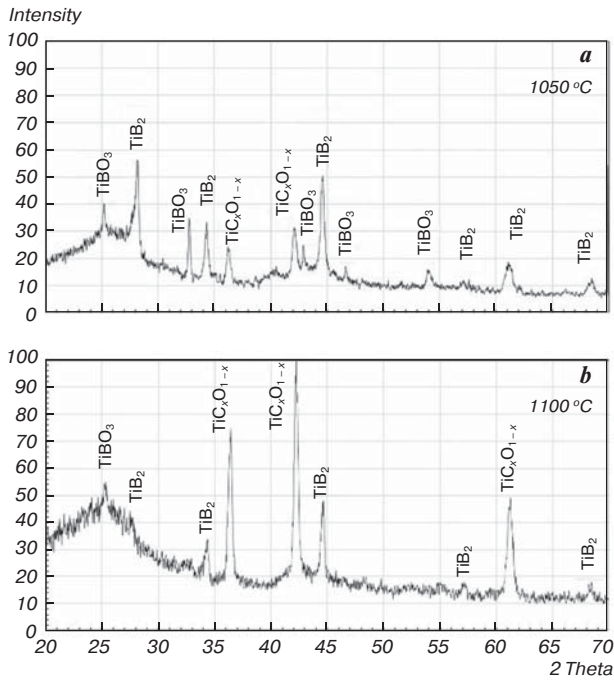


Fig. 1. Phase formation in the $TiO_2 - B_2O_3 - C$ system at: a – 1050 °C; b – 1100 °C

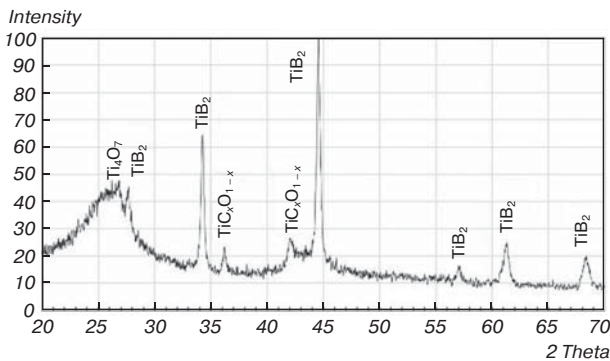


Fig. 2. Low temperature synthesis of titanium diboride at 1030 °C

The type of samples after the experiments under the electrolyte layer is shown in Fig. 3. The Fig. 4 shows a typical result of this series of studies — an X-ray diffraction pattern of products synthesized under a melt during 3-hour exposure. This exposure period is sufficient to obtain compact samples consisting of titanium diboride mixed with titanium borate (without an amorphous phase).

The presence of $TiBO_3$ is associated with the access of oxygen to the samples during crystallization and shrinkage of molten-solid salt after experiments:



The glassy phase of B_2O_3 boron oxide on the surface of the samples protected them from complete oxidation to titanium oxide.

The experimental results under a layer of molten salt mean that the synthesis of titanium diboride can be organized in situ during electrolysis. For this, the reaction mixture is embedded in the cathodes at the stage of their manufacture. After mounting the cathode blocks and starting the cells, the synthesis of titanium diboride will occur in the volume of the cathode, which acquires wetting properties.

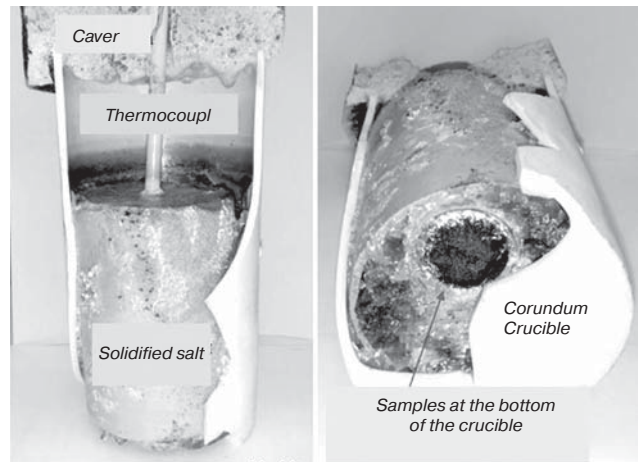


Fig. 3. Cell and samples after experiment

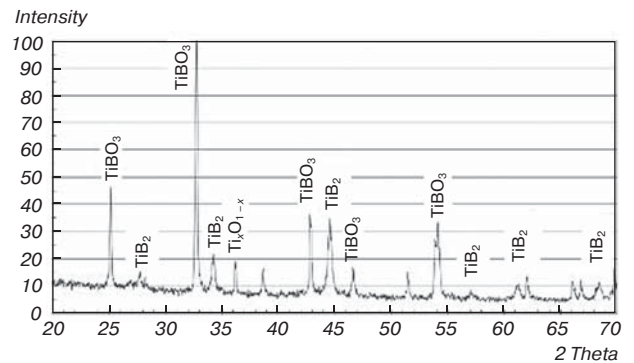
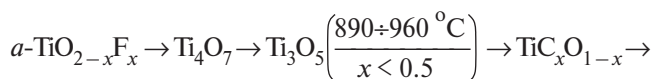


Fig. 4. XRD of samples (Fig. 3) after 3 hours exposure at 1050 °C under the melt

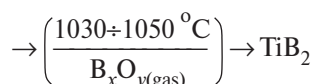
Summary

1. Using thermodynamic evaluation of the interaction conditions in the $\text{TiO}_2 - \text{B}_2\text{O}_3 - \text{C}$ system, the probable mechanism of TiB_2 low-temperature synthesis is determined, which consists in the phased reduction of titanium oxide to its oxycarbide phase with subsequent interaction with gaseous boron oxides:

Stage 1



Stage 2



2. Essential and sufficient conditions for the low-temperature synthesis of TiB_2 are:

2.1. Pre-doping of amorphous titanium oxide with fluorine $\text{TiO}_{2-x}\text{F}_x$ to stabilize the anatase modification of titanium oxide and transfer ART to the high temperature zone $900 \div 1000 \text{ }^\circ\text{C}$;

2.2. The formation of the active intermediate phase of titanium oxycarbide $\text{TiC}_x\text{O}_{1-x}$ in the air at $890 \div 960 \text{ }^\circ\text{C}$ with a deficient carbon composition $x < 0.5$;

2.3. Synthesis of titanium diboride TiB_2 at a temperature of $1030 \div 1050 \text{ }^\circ\text{C}$ for 3 hours with participation in the phase formation reactions of oxide $\text{B}_2\text{O}_{3(\text{gas})}$ and boron suboxides ($\text{B}_2\text{O}_{2(\text{gas})}$, $\text{BO}_{2(\text{gas})}$) in the gaseous state.

3. The mechanism and conditions for the synthesis of titanium diboride TiB_2 are confirmed by laboratory experiments at $1030 \div 1050 \text{ }^\circ\text{C}$, the implementation of which allows to obtain titanium diboride of technical purity by the furnace method and under a layer of molten salt.

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