Optimization of the TiB$_2$ plasma dynamic synthesis

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Abstract. Titanium Diboride (TiB$_2$) nanoparticles were obtained by plasma dynamic synthesis in a hypersonic plasma jet. The aim of the work was to optimize synthesis of TiB$_2$ nanoparticles. Firstly, three series of experiments with different ways of a discharge initiation were implemented: 1) using titanium conductors; 2) using carbon fibers; 3) using graphite aerosol (graphitization). Secondly, experiments with different atmosphere gas, which filled the volume of the reactor chamber – Ar and N$_2$ were implemented. Thirdly, there were experiments with different mass ratio of Ti:B precursors using graphitization (26.7:73.3; 45.5:54.5; 61.1:38.9; 86.4:13.6). And finally experiments with 16.9 kJ released energy were implemented. The results showed, that the best of way of initiation an arc discharge is graphitization using Ar with mass ratio Ti:B 26.7:73.3 and input energy – 33.9 kJ. The yield of TiB$_2$ was 93.2% with the smallest particles 56.1 nm.

1. Introduction

The role of nanostructured materials in the modern world is very high, since materials in various industries require high physical and mechanical characteristics. Many research teams assert that titanium diboride (TiB$_2$) is an excellent material for the creation of functional ceramics and for its further application in medicine, engineering, metallurgy, aerospace industry, including crucibles, cutting tool materials, corrosion and wear resistance as well as light weight armors for ballistic protection [1-6]. Also, TiB$_2$ does not react with the aluminum substrate, so it is also used as a coating to improve the properties of tools - increasing hardness, wear resistance, and extending tool life. High elastic modulus (565 GPa), high melting point (3225°C), electrical and thermal conductivity, exceptional hardness (~32 GPa) and good strength at room temperature are often reported for monolithic TiB$_2$ and TiB$_2$-based ceramics [7-15].

There are many different ways to obtain nanoscale TiB$_2$. It includes sol-gel [16, 17], mechanical [18], carbothermic [19, 20], self-propagating high-temperature synthesis (SHS) followed by acid leaching technique [21] methods as well as magnesiothermic reduction of titanium and boron oxides [22]. However, such methods require high time of process, expensive precursors, multistage process and etc. The method that used in this paper is based on the use of a pulsed high-current coaxial magnetoplasma accelerator (CMPA) of the erosion type. The main advantages of this method are that the method is direct, no harmful emissions are produced, no additional preparation of source material is required, the process is implemented with high speed (up to 10$^{-3}$ s) and at normal pressures and temperatures.
2. Experiment

Nanoscale TiB₂ powders are obtained by plasma dynamic method in the hypersonic electro discharge plasma jet. This method used capacitor banks with stored energy 67.5 kJ. The coaxial electrode of the accelerator is made of titanium, while titanium is produced by electroerosion. The coaxial electrode has a length \( l_{ac} = 224 \text{ mm} \) and a diameter \( d_{ac} = 21 \text{ mm} \). A detailed description of the installation and its work has already been shown in previous articles [23].

Using this system a series of experiments were implemented in order to study the phase composition of the ultradispersed powder of the titanium diboride in different conditions. Thus, in order to determine the influence of various factors on the product of plasma dynamic synthesis, the following experiments were implemented:

1) change of the method of initiation of the arc discharge (series I);
2) change in the atmosphere gas, which filled the volume of the reactor chamber (series II);
3) change in the energy released during the experiment (series III);
4) change in the ratio of precursors (series IV).

During the experiments, it was assumed that the method of initiation of the arc discharge, as well as other changes, will affect the phase composition of the synthesis product by changing the time and nature of the transition of boron to the plasma state.

2.1. Change of the method of initiation of the arc discharge (series I)

In all three experiments amorphous boron powder was placed into the plasma formation zone. In the first two series of experiments, to initiate an arc discharge in the dielectric space, thin conductors or carbon fibers were stretched between the central electrode and the coaxial electrode along the surface of the plasma formation zone. In the third experiment graphite in the form of an aerosol was sprayed onto the surface of the plasma formation zone. The electrical and energy parameters of the experiments (series I) are presented in table 1.

| Ways of discharge initiations | Atm. | Ti (mass%) | B (mass%) | \( U_w \) (kV) | \( I_{max} \) (kA) | \( \Delta t \) (mcs) | \( P_{max} \) (MW) | \( W_c \) (kJ) | \( W \) (kJ) |
|-----------------------------|-----|------------|----------|-------------|-------------|-------------|-------------|-------------|-------------|
| Ti-conductors Ar            |    | 45.0       | 55.0     | 1.40        | 140         | 100         | 201         | 67.5        | 38.3        |
| Carbon fibers Ar            |    | 38.9       | 61.1     | 1.34        | 150         | 130         | 174         | 67.5        | 36.8        |
| Graphitization Ar           |    | 26.7       | 73.3     | 1.26        | 144         | 150         | 182         | 67.5        | 33.9        |

2.2. Change in the atmosphere gas, which filled the volume of the reactor chamber (series II)

In addition to changing the method of initiation of an arc discharge, the type of the gas atmosphere of a reactor chamber was varied (series II). Argon (Ar) and nitrogen (N₂) gases were used. The chamber pressure was 2 atm., its purity was provided by double pumping. The electrical and energy parameters of the experiments (series II) are presented in table 2.

| Ways of discharge initiations | Atm. | Ti (mass%) | B (mass%) | \( U_w \) (kV) | \( I_{max} \) (kA) | \( \Delta t \) (mcs) | \( P_{max} \) (MW) | \( W_c \) (kJ) | \( W \) (kJ) |
|-----------------------------|-----|------------|----------|-------------|-------------|-------------|-------------|-------------|-------------|
| Ti-conductors Ar            |    | 45.0       | 55.0     | 1.40        | 140         | 100         | 201         | 67.5        | 38.3        |
| Ti-conductors N₂            |    | 42.1       | 57.9     | 1.22        | 144         | 110         | 180         | 67.5        | 35.8        |

2.3. Change in the energy released during the experiment (series III)

The level of released energy changed in various experiments and reached \( W = 33.9 \div 38.3 \text{ kJ} \) and stored energy \( W_c = 67.5 \text{ kJ} \). Next series of experiments was with the released energy \( W = 16.9 \text{ kJ} \) and stored
energy $W_c = 33.75$ kJ (series III). The electrical and energy parameters of the experiments (series III) are presented in table 3.

**Table 3.** Electrical and energy parameters of the experiments (series III).

| Ways of discharge initiations | Atm. (mass%) Ti | B (mass%) | $U_w$ (kV) | $I_{max}$ (kA) | $\Delta t$ (mcs) | $P_{max}$ (MW) | $W_c$ (kJ) | $W$ (kJ) |
|-------------------------------|----------------|-----------|------------|----------------|----------------|----------------|-----------|-------|
| Graphitization                | Ar 26.7        | 73.3      | 1.26       | 144            | 150            | 182            | 67.5      | 33.9  |
| Graphitization                | Ar 12.0        | 88.0      | 0.87       | 57             | 70             | 47             | 33.75     | 16.9  |

2.4. *Change in the ratio of precursors (series IV)*

To see the dependence of the product’s phase composition on the ratio of precursors, a series of experiments were implemented with a change in the mass of the boron from 13.6% to 73.3% (series IV). The electrical and energy parameters of the experiments (series IV) are presented in table 4.

**Table 4.** Electrical and energy parameters of the experiments (series IV).

| Ways of discharge initiations | Atm. (mass%) Ti | B (mass%) | $U_w$ (kV) | $I_{max}$ (kA) | $\Delta t$ (mcs) | $P_{max}$ (MW) | $W_c$ (kJ) | $W$ (kJ) |
|-------------------------------|----------------|-----------|------------|----------------|----------------|----------------|-----------|-------|
| Graphitization                | Ar 26.7        | 73.3      | 1.26       | 144            | 150            | 182            | 67.5      | 33.9  |
| Graphitization                | Ar 45.5        | 54.5      | 1.30       | 141            | 160            | 184            | 67.5      | 35.3  |
| Graphitization                | Ar 61.1        | 38.9      | 1.22       | 148            | 150            | 186            | 67.5      | 33.1  |
| Graphitization                | Ar 86.4        | 13.6      | 1.06       | 153            | 150            | 163            | 67.5      | 31.3  |

3. *Results and Discussion*

The synthesized powder without any treatment was analyzed by X-ray diffractometry method. As a result of the X-ray diffractometry diffractograms were analyzed using the PowderCell 2.4 software. The program PowderCell 2.4 allows you to estimate the mass content in the product phases using the Rietveld method. The values of goodness $S = R_{wp}/R_{exp}$, which take values >1, indicate the correctness of calculations.

3.1. *Change of the method of initiation of the arc discharge (series II)*

According to the quantitative XRD analysis (series I) in table 5 the highest content of TiB$_2$ 93.2% was reached in experiment using graphitization. It can be explained by the different nature of the transition of precursors to the plasma state: from the abrupt and short process in experiments using Ti-conductors and carbon fibers to a smooth and long process in the experiment using graphitization. Conductors explode very quickly and the powder does not have time to warm up, while during graphitization the powder warms up longer. The phase of Ti-O system was formed due to the fact that technically pure boron was used.

**Table 5.** Quantitative XRD analysis (series I).

| Ways of discharge initiations | Atm. (mass%) Ti | Phase composition (mass%) | CSR (nm) | $R_{wp}/R_{exp}$ |
|-------------------------------|----------------|--------------------------|----------|------------------|
| Ti-conductors                 | Ar 66.20       | TiB, TiB$_2$, Ti$_2$O$_3$ | 6.80     | 17.8/6.6         |
| Carbon fibers                 | Ar 21.20       | 62.10, 16.70, 18.4, 61.1 | 17.4/11.1|
| Graphitization                | Ar 6.80        | 93.20, -16.7, 56.1       | 26.8/11.6|

3.2. *Change in the atmosphere gas, which filled the volume of the reactor chamber (series II)*

If argon was used as a gas, the powder didn’t react with it, while nitrogen reacted with titanium and titanium nitride TiN was formed, so an undesirable phase was formed. Quantitative XRD analysis (series II) is shown in table 6.
Table 6. Quantitative XRD analysis (series II).

| Ways of discharge initiations | Atm. Phase composition (mass%) | CSR (nm) | $R_{wp}/R_{exp}$ |
|------------------------------|---------------------------------|----------|------------------|
|                              | TiB/TiN | TiB₂ | TiB/TiN | TiB₂ | TiB₂ |
| Ti-conductors                | Ar      | 66.20 | 26.80 | 22.5 | 46.7 | 17.8/6.6 |
| Ti-conductors                | N₂      | 22.90 | 77.10 | 25.3 | 77.0 | 24.5/13.1 |

3.3. Change in the energy released during the experiment (series III)
When lower energy is supplied, more titanium monoboride is formed. This tendency is explained by the influence of the supplied energy on the velocity of the plasma jet, which determines the level of the pT-parameters in the head shock of plasma jet, the value of which mainly determines the phase composition. So, it is established that at high energy parameters, it is possible to achieve a larger yield of the titanium diboride phase. Quantitative XRD analysis (series III) is shown in table 7.

Table 7. Quantitative XRD analysis (series III).

| Ways of discharge initiations | Atm. W (kJ) Phase composition (mass%) | CSR (nm) | $R_{wp}/R_{exp}$ |
|------------------------------|--------------------------------------|----------|------------------|
|                              | TiB/TiN | TiB₂ | TiB/TiN | TiB₂ | TiB₂ |
| Graphitization               | Ar      | 33.9 | 6.80 | 93.20 | 16.7 | 56.1 | 26.8/11.6 |
| Graphitization               | Ar      | 16.9 | 13.20 | 86.80 | 31.0 | 61.6 | 25.5/15.9 |

3.4. Change in the ratio of precursors (series IV)
According to the table 8 in all experiments the yield of TiB₂ is high – from 86.8% to 96.2%. The smallest particles of TiB₂ 51.0 nm are obtained in the experiment with the ratio Ti:B 86.4:13.6, but the yield of TiB₂ is the smallest in comparison with the rest experiments – 86.8%. In the state diagram of titanium diboride, the percentage of boron for obtaining titanium diboride is 67%, so the best experiment was the experiment with the ratio Ti:B 26.7:73.3 with 93.2% TiB₂ and 56.1 nm particle size.

Table 8. Quantitative XRD analysis (series IV).

| Ways of discharge initiations | Ti (mass%) | B (mass%) | Atm. | Phase composition (mass%) | CSR (nm) | $R_{wp}/R_{exp}$ |
|------------------------------|-------------|-----------|------|---------------------------|----------|------------------|
|                              | TiB/TiN | TiB₂ | TiB/TiN | TiB₂ | TiB₂ |
| Graphitization               | 26.7      | 73.3    | Ar    | 6.80 | 93.20 | 16.7 | 56.1 | 26.8/11.6 |
| Graphitization               | 45.5      | 54.5    | Ar    | 3.80 | 96.20 | 46.7 | 67.8 | 28.2/12.6 |
| Graphitization               | 61.1      | 38.9    | Ar    | 6.40 | 94.60 | 14.5 | 60.8 | 28.0/20.0 |
| Graphitization               | 86.4      | 13.6    | Ar    | 13.20 | 86.80 | 20.7 | 51.0 | 30.9/16.9 |

4. Conclusion
To sum up, by using coaxial magneto plasma accelerator it’s possible to synthesize nanodispersed powders in the titanium-boron system. By changing the experimental conditions, it is possible to achieve a different phase composition of the product depending on the purpose. Four series of experiments were implemented: 1. change of the method of initiation of the arc discharge (series I); 2. change in the atmosphere gas, which filled the volume of the reactor chamber (series II); 3. change in the energy released during the experiment (series III); 4. change in the ratio of precursors (series IV). The resulting powder was analyzed by XRD method. All in all, the results showed, that the best way of initiation of an arc discharge is graphitization using argon with mass ratio of precursors Ti:B 26.7:73.3 and the released energy $W = 33.9$ kJ. The yield of TiB₂ was 93.2% with the smallest particles 56.1 nm.
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