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 TiB_2 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 mm and a diameter d_{ac} =21 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.

Table 1. Electrical and energy parameters of the experiments (series I).

Ways of discharge initiations	Atm.	Ti (mass%)	B (mass%)	U_w (kV)	I_{max} (kA)	Δt (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 (N_2) 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.

Table 2. Electrical and energy parameters of the experiments (series II).

Ways of discharge initiations	Atm.	Ti (mass%)	B (mass%)	U_w (kV)	I_{max} (kA)	Δt (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	N_2	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÷38.3 kJ and stored energy W_c = 67.5 kJ. Next series of experiments was with the released energy W = 16.9 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.	Ti (mass%)	B (mass%)	U_w (kV)	I_{max} (kA)	Δt (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.	Ti (mass%)	B (mass%)	U_w (kV)	I_{max} (kA)	Δt (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.	Phase composition (mass%)			CSR (nm)			R_{wp}/R_{exp}
		TiB	TiB_2	Ti_2O_3	TiB	TiB_2	Ti_2O_3	
Ti-conductors	Ar	66.20	26.80	7.00	22.5	46.7	20.5	17.8/6.6
Carbon fibers	Ar	21.20	62.10	16.70	18.4	61.1	35.5	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	TiB_2	TiB/TiN	TiB_2	
Ti-conductors	Ar	66.20	26.80	22.5	46.7	17.8/6.6
Ti-conductors	N_2	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	TiB_2	TiB	TiB_2	
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 TiB_2 is high – from 86.8% to 96.2%. The smallest particles of TiB_2 51.0 nm are obtained in the experiment with the ratio Ti:B 86.4:13.6, but the yield of TiB_2 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% TiB_2 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	TiB_2	TiB	TiB_2	
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 TiB_2 was 93.2% with the smallest particles 56.1 nm.

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References

[1] Chlup Z, Bača Ľ, Halasová M, Neubauer E, Hadraba H, Stelzer N and Roupcová P 2015 *Journal of the European Ceramic Society* **35** 2745
[2] Ahmadi Z, Nayebi B, Asl M, Farahbakhsh I and Balak Z 2018 *Ceramics International* **44** 11431
[3] Mahaseni Z, Germi M, Ahmadi Z and Asl M 2018 *Ceramics International* **44** 13367
[4] Wu J, Niu B, Zhang F, Lei L, Zhang J, Ren L, Wang W and Fu Z 2018 *Ceramics International*
[5] Dong L, Li D, Zhang S, Yan J, Liu M, Gao C, Wang W, Liu G, Gu H and Wan R 2012 *Thin Solid Films* **520** 5328
[6] Ping L, Shijie D, Anzhuo Y, Shixuan S, Zhixiong X, Zhong Z and Wei Y 2016 ZrB_2-TiB_2 *Rare Metal Materials and Engineering* **45** 1381
[7] Malik I, Banerjee S, Gayner C, Chowdhuri A and Kar K 2018 *Ceramics International* **44** 10685
[8] Chao S, Goldsmith J, and Banerjee D 2015 *International Journal of Refractory Metals and Hard Materials* **4** 314
[9] Torres A, Luis C and Puertas I 2017 *J. of Alloys and Compounds* **690** 337
[10] Asl M, Ahmadi Z, Parvizi S, Balak Z and Farahbakhsh I 2017 *Ceramics International* **43** 13924
[11] Torres A. Luis C and Puertas I 2017 *Procedia Manufacturing* **13** 579
[12] Meng X, Yi F, Pei T, Zhaokun S, Lan Z and Chengyu C 2017 *Rare Metal Materials and Engineering* **46** 3260
[13] Meng J and Ji Z 2013 *Physics Procedia* **50** 253
[14] Namini A , Azadbeh M and Asl M. 2017 *Adv. Powder Technol.* **28** 1564
[15] Heydari M, Baharvandi H and Allahkaram S 2018 *International Journal of Refractory Metals and Hard Materials*
[16] Rabiezadeh A, Hadian A and Ataie A 2014 *Ceramics International* **40** 15775
[17] Masanta M, Ganesh P, Kaul R and Choudhury A 2010 *Surface and Coatings Technology* **204** 3471
[18] Luo P, Xiong C, Xiao Y, Li Z, Qin F, Wang C, Liu K, Guan X and Dong S 2017 *Journal of Asian Ceramic Societies* **5** 397
[19] Kang S and Kim D 2007 *Journal of the european ceramic society* **27** 71
[20] Derin B, Kurtoglu K, Sahin F and Yucel O 2017 *Ceramics International* **43** 10975
[21] Lok J, Logan K and Payyapilly J 2009 *Journal of the American Ceramic Society* **92** 26
[22] Nozari A, Ataie A and Heshmati-Manesh S 2012 *Materials Characterization* **73** 96
[23] Nikitin D, Sivkov A, Gerasimov D and Evdokimov A 2017 *Journal of Physics: Conference Series* **830** 012121