The influence of the method of an arc discharge initiation on the product of plasma dynamic synthesis in the W-C system

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Abstract. Cubic tungsten carbide WC_{1-x} is distinguished by the difficulty of obtaining in a dispersed and bulk form. The article attempts to plasma dynamic synthesis of cubic tungsten carbide in powder form. The method is based on the use of a coaxial magnetoplasma accelerator for the generating a supersonic plasma jet, which is then rapidly cooled. The possibility of obtaining a powder with a predominant content of WC_{1-x} (up to 95%) is shown. Studying the influence of the method of an arc discharge initiation allowed to reveal the efficiency of using graphitization in comparison with carbon fibers.

1. Introduction

Currently, a particularly pressing problem in the industry is the production of superhard and refractory materials. Carbides of transition d-metals of groups IV-VI have the such properties [1, 2]. Carbides are widely used in the production of materials for work under high loads and temperatures in corrosive environments. One of the notable carbides is tungsten carbide. Tungsten carbide has a high melting point, hardness, wear resistance, chemical resistance [3]. Along with high hardness and melting point, tungsten carbide has a high modulus of elasticity and a low coefficient of thermal expansion than carbides of other metals of the group. The combination of WC properties allows it to be used in the processing of various materials, including as an abrasive material [4].

The dominant phase in the tungsten-carbon system is the hexagonal stoichiometric phase WC. However, according to the state diagram, there are also phases W_2C and WC_{1-x} [5]. The last crystalline modification is characterized by increased electro- and photocatalytic activity [6–9]. The WC_{1-x} cubic phase is known for its narrow range of temperature stability, which makes its production laborious compared to hexagonal phases [10]. The attempts to obtain cubic tungsten carbide in a dispersed and bulk form are known [11–17], however, until now, methods of synthesis of WC_{1-x} are not effective enough. Therefore cubic tungsten carbide WC_{1-x} is the object of active research now. It is known that the cubic phase WC_{1-x} can be synthesized by ultrafast cooling of tungsten carbide melt at a speed of 10^8-10^{11} K/s [18].

Plasma dynamic synthesis of various powder materials and coatings is one of the promising synthesis methods. This method has already been used to obtain carbide compounds in ultrafine form, in particular, silicon carbide [19] and boron carbide [20]. In the present work, plasma dynamic synthesis is used to synthesize cubic tungsten carbide, since it provides the heating to a high temperature required for the formation of this phase and rapid cooling. An important task of the study is to determine the most effective way of initiating an arc discharge, which may influence the precursors sublimation process in the zone of plasma structure formation due to preionization [21].

2. Experimental

The synthesis of ultrafine cubic tungsten carbide was carried out using a high-current pulsed coaxial magnetoplasma accelerator with graphite electrodes (CMPA). The CMPA was powered from a capacitive energy storage device with a capacitor bank capacity of C = 6 mF and a charging voltage of U = 3 kV. Two series of experiments were carried out with different methods for initiating an arc discharge a plasma flow in order to determine the most effective way. Carbon fibers and graphitization were used as an initiating way. Figure 1 shows the assembly of a central electrode using different methods of plasma jet initiation. In the case (*a*) the carbon fibers were stretched from the bottom of the zone of plasma structure formation to the outer cone-shaped surface of the insulator which is the place of contact with the graphite electrode. In case (*b*) a thin layer of graphite aerosol was placed on the inner surface of the zone of plasma structure formation, as well as the surface of the precursor embedded into the zone of plasma structure formation.

A micron tungsten powder with a mass of 0.5 g was used as a precursor, which was placed into the zone of plasma structure formation at the beginning of the accelerator channel. Obtaining carbon was carried out by means of electric erosion when the plasma structure of an arc discharge was moving through a graphite electrode.

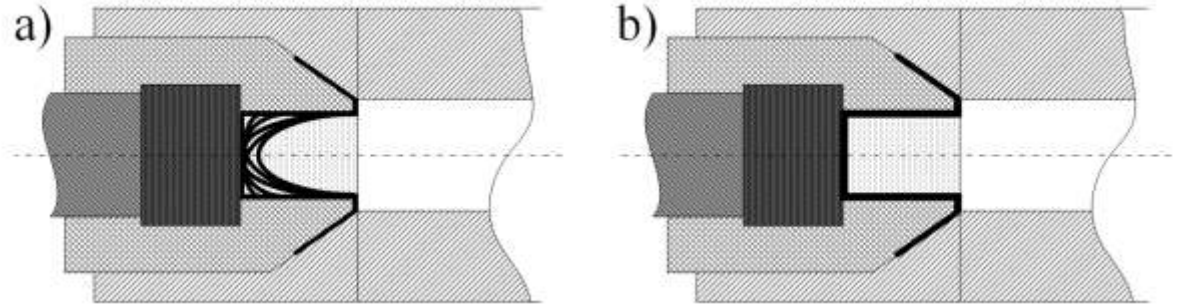

Figure 1. The assembly of a central electrode using different methods of plasma jet initiation by carbon fibers (a) and graphitization (b).

After the power switch was closed, the discharge current of the capacitor battery began to flow through the zone of plasma structure formation, the arc discharge was initiated, and the plasma structure containing the precursors was formed. An electrical erosion of material occurred from walls of a graphite acceleration channel when a plasma flow moved. The plasma flew into the space of the reactor chamber, the synthesized material cooled down and deposited on the walls.

The obtained powder products were analyzed without prior preparation by X-ray diffractometry (XRD) on a Shimadzu XRD7000 diffractometer (Cu-Kα radiation). The quantitative X-ray analysis was carried out by the Rietveld method using the PDF2+ structural data base and the PCW software package. The study of the morphology of the particles and the particle size distribution of the obtained powder was carried out by a transmission electron microscopy (TEM) using a Philips CM 12 microscope with functions of a microdiffraction on a selected area (SAED) and obtaining dark-field images.

3. Results and discussion

During the experiments, it was assumed that the way for initiating an arc discharge affects the phase composition of the synthesis product by changing the nature of the precursor transition to the plasma state. The phase composition of the product is determined by X-ray diffraction. Figure 2 shows the typical XRD patterns of powders obtained by different ways for initiating an arc discharge. The most obvious difference in the XRD patterns is the high intensity peaks of the side phases such as hexagonal carbides and carbon in the case of the product obtained using carbon fibers. The results of the quantitative X-ray diffraction analysis are shown in table 1. The data show that the content of the cubic tungsten carbide is maximum and is about 95% in the product obtained using graphitization. The presence of tungsten carbide W_2C is observed in the product obtained using carbon fiber. In addition to

the phase content, the values of coherent scattering areas (CSA) were found, which showed a significant difference in the values of the cubic WC_{1-x} phase from the values of the hexagonal W_2C phase.

Table 1. The results of the quantitative X-ray diffraction analysis.

No.	Phase content, %					CSA	
	WC_{1-x}	WC	W_2C	W	C	WC_{1-x}	W_2C
1	78.4	1.8	18.4	0.8	0.6	35	15
2	94.9	0.4	3.8	0.2	0.7	32	14

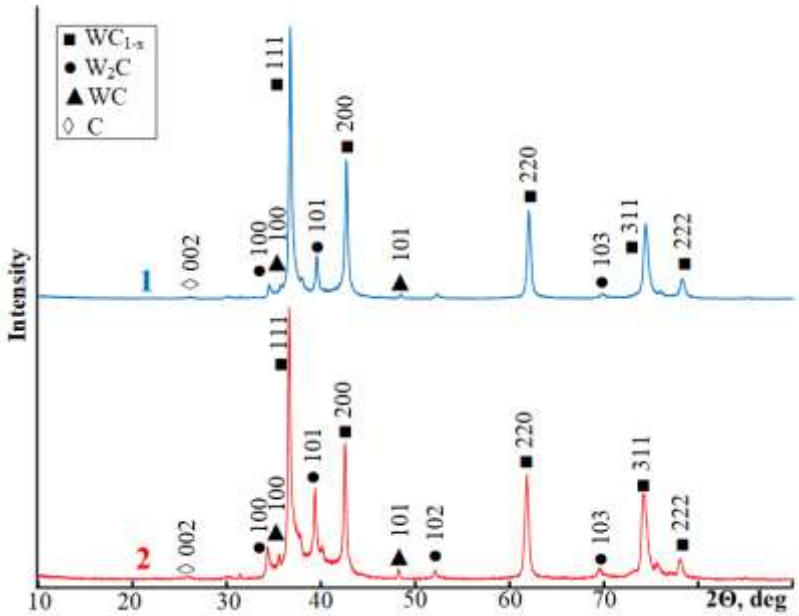

Figure 2. The typical XRD patterns of powders obtained by different ways for initiating an arc discharge: carbon fibers (1) and graphitization (2).

Figure 3*a* shows a bright field TEM image of the product obtained using carbon fibers. The material contains several types of objects. Objects 1 are the largest particles with sizes up to 150 nm. One of such particles in an enlarged form is presented in Figure 3*b*. Analysis of a large number of such objects allowed them to be identified. Figure 4*a* shows a bright-field TEM image of a particle with the corresponding SAED (Figure 4*b*), which is a set of phase reflections of cubic and hexagonal tungsten carbide in the form of Debye rings. The reflexes of the cubic phase have the greatest intensity. When the aperture diaphragm is shifted to the region of tungsten carbide reflexes WC_{1-x}, the reflecting planes of a relative large particle 1 are observed (Figure 4*c*). In addition, there are particles of medium size up to 40 nm in the product (objects 2, Figure 3*b*). In contrast to the sphere-like shape of the particle 1, objects 2 are more pronounced in morphological type and close to hexagons in the plan. It shows the possible belonging of these particles to the hexagonal W_2C phase contained in the product in an amount of ~ 18%. In addition, it is obvious that the large objects 1 and medium particles 2 are in the matrix, which is identified as carbon. The carbon of the synthesized product can also be formed in the form of other forms, including 4 in Figure 3*c*. These are the so-called pineapple-like particles, which are highly deformed particles of graphite [22].

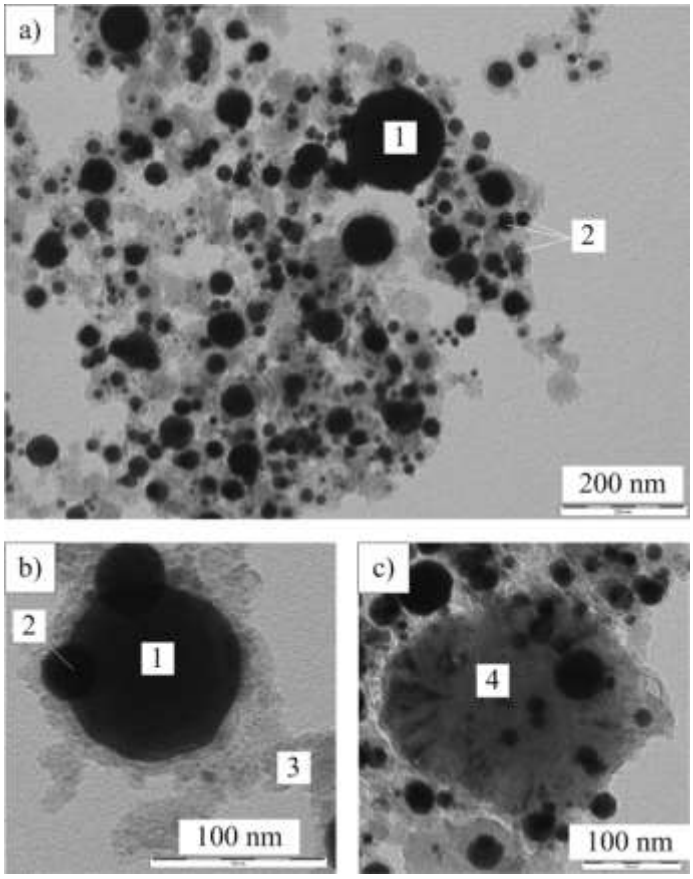

Figure 3. TEM-images of the plasma dynamic synthesis product obtained using carbon fibers: a particle accumulation (a), typical particles (b), carbon structures (c).

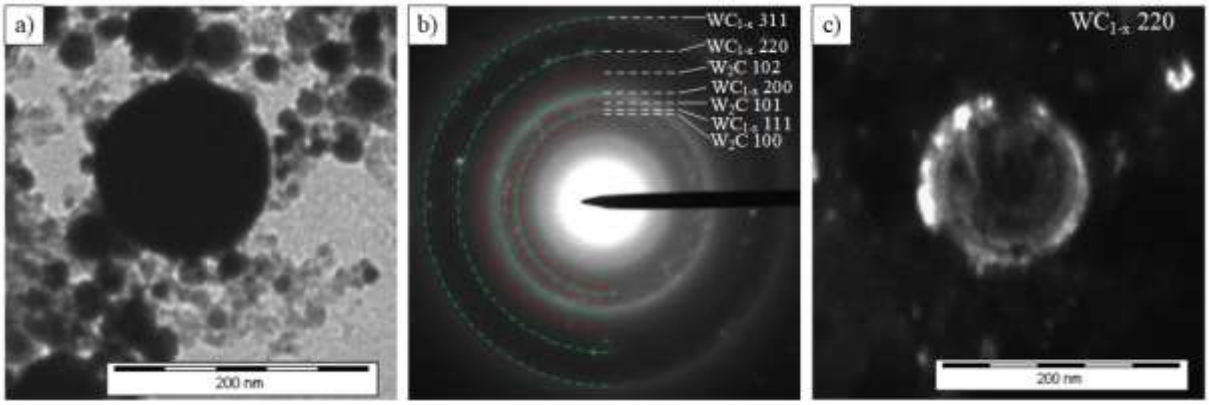

Figure 4. TEM-images of the plasma dynamic synthesis product: bright-field image (a), SAED (b), dark-field image (c).

According to the micrograph of Figure 5, the product obtained using graphitization consists of particles 1 overwhelmingly. A small amount of particles 2 is also contained in the product in the form of smaller particles. An important distinguishing feature is the absence of a carbon matrix, as well as carbon in other morphological forms.

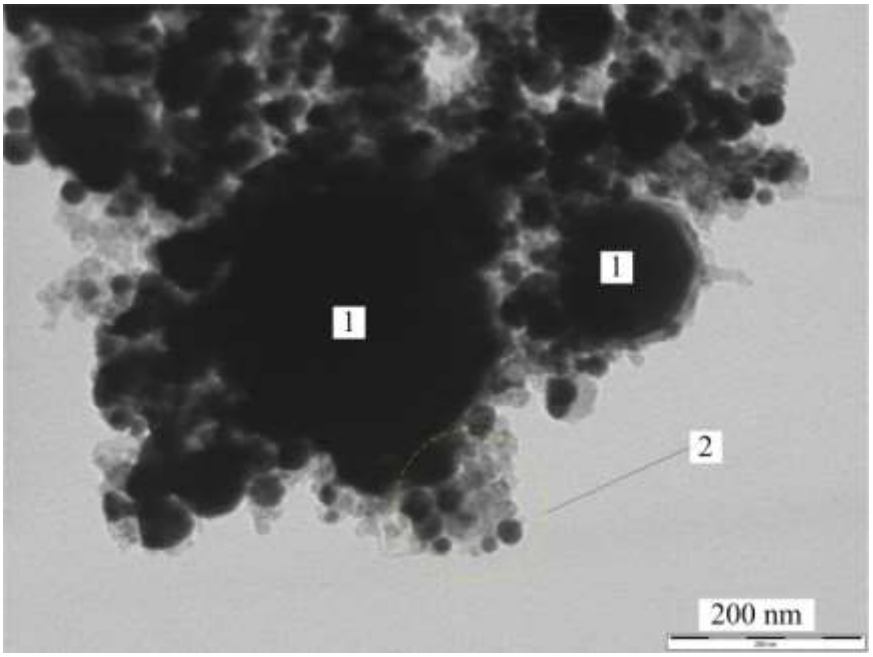

Figure 5. TEM-images of the plasma dynamic synthesis product obtained using graphitization.

According to the combination of X-ray diffractometry and transmission electron microscopy, graphitization is the most effective initiating way of an arc discharge. It can apparently be explained by the physical processes occurring at the initial moment of time. In the case of graphitization of the insulator surface, preionization of the precursor occurs in the zone of plasma structure formation. The activation of the precursor at the preionization stage leads to a smoother entry of precursors into the chemical reaction zone and causes the effectiveness of the chemical reaction and the preferential formation of particles of the cubic phase WC_{1-x}. In the case of using carbon fibers, an electrical explosion of carbon fibers as conductors occurs. It leads to incomplete sublimation of the precursor to the plasma state and the amount of unreacted precursor phases increases in the final product of the synthesis. Also the hexagonal phases of higher and lower carbides (WC and W_2C) are formed. The described process of precursor sublimation in various cases of initiating way of an arc discharge is close to the results of work describing processes in the SiC carbide system [15].

4. Conclusion

The paper discusses the plasma dynamic synthesis in the W-C system. The ways of initiating an arc discharge through the use of carbon fibers and graphitization are considered. The results of analytical studies show that unique phase of cubic tungsten carbide WC_{1-x} is formed as nanoscale particles with sizes up to 150 nm. The most effective way of initiating an arc discharge is the use of graphitization. In this case, the maximum yield of the cubic tungsten carbide WC_{1-x} is up to 95%.

Acknowledgments

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References

[1] Pierson H 1996 *Handbook of Refractory Carbides & Nitrides: Properties, Characteristics, Processing and Apps* (New Jersey: Noyes Publications) p 339
[2] Naboychenko S, Murashova I, Neikov O 2009 *Handbook of Non-Ferrous Metal Powders* (Amsterdam: Elsevier) p 995

[3] Kurlov A, Gusev A 2006 *Inorg. Mater* **42** (2) 121–127
[4] Bondarenko V, Andreyev I, Savchuk I. 2013 *Int. J. Refract. Met. Hard Mater* **39** 18–31
[5] Kurlov A, Gusev A 2006 *Russ. Chem. Rev*. **75** (7) 617–636
[6] Kim J, Jang J-H, Lee Y-H 2009 *J. Power Sources* **193** (2) 441–446
[7] Zheng H, Yu A, Ma C 2011 *Chinese Chem. Lett.* **22** (4) 497–500
[8] Bott-Neto J, Beck W, Varanda L 2017 *Int. J. Hydrogen Energy* **42** (32) 20677–20688
[9] Wei X and Li N 2019 *Appl. Surf. Sci.* **463** 1154–1160
[10] Abad M, Muñoz-Márquez M, Mrabet S 2010 *Surf. Coatings Technol.* **204** (21-22) 3490–3500
[11] Gao Y, Song X, Liu X 2013 *Scr. Mater.* **68** (2) 108–110
[12] Carim A, De Jong A, Houdy P 1989 *Thin Solid Films* **176** (2) 177–182
[13] Raekelboom E, Abdelouahdi K, Legrand-Buscema C 2009 *Thin Solid Films* **517** (5) 1555–1558
[14] Reddy K, Rao T, Joardar J 2011 *Mater. Chem. Phys.* **128**(1-2) 121–126
[15] Fenggang Z 2019 *Vacuum* **159** 254–60
[16] Du S, Wen M, Ren P 2017 *Mater. Sci. Forum* **898** 1505–1511
[17] Pawlak W, Kubiak K, Wendler B 2015 *Tribol. Int.* **82** 400–406
[18] Zhang F, Zhu X, Lei M 2017 *Vacuum* **137** 119–124
[19] Sivkov A, Nikitin D, Shanenkov I 2019 *Int. J. Refract. Met. Hard Mater.* **79** 123–130
[20] Sivkov A, Rakhmatullin I, Shanenkov I 2019 *Int. J. Refract. Met. Hard Mater.* **78** 85–91
[21] Kuzenov V, Polozova T, Ryzhkov S 2015 *Probl. At. Sci. Technol.* **98** (4) 49–52
[22] Sivkov A, Pak A, Nikitin D 2013 *Nanotechnologies Russ*. **8** (7-8) 489–494