

Effect of precursor mass on product phase composition in plasma dynamic synthesis of tungsten carbide

K N Shatrova, A A Sivkov, I I Shanenkov and A S Saigash

Institute of Power Engineering, National Research Tomsk Polytechnic University,
Lenin av., 30, Tomsk 634050, Russian Federation

E-mail: Swordi@list.ru

Abstract. An interest in WC_{1-x} cubic tungsten carbide results from its catalytic properties similar to those of platinum group metals and the synergistic effect between WC_{1-x} and Pt in reactions of hydrogen evolution and hydrogen oxidation. However, according to the phase diagram of the W–C system, the cubic phase WC_{1-x} only exists in a narrow range of temperature stability (about 2798–3058 K), which makes it difficult for being obtained. To date, there are different methods for synthesizing tungsten carbide powder with a low content of cubic phase that complicates the study of WC_{1-x} properties. A direct plasma dynamic synthesis is known as one of the promising methods to produce WC_{1-x} . The aim of this work is to find the optimal amount of tungsten precursor to obtain cubic tungsten carbide with a high purity by plasma dynamic method. The synthesized products were examined by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The XRD patterns showed that the main phase was cubic tungsten carbide with negligible content of hexagonal tungsten carbide W_2C and pure tungsten W. According to a quantitative analysis of synthesized products, which were obtained using masses of initial tungsten equal to 1.0, 0.7, 0.6 and 0.5 gram, the yield of WC_{1-x} phase was 84, 89, 95 and 92 wt%, respectively. The results of TEM displayed that the synthesized powders consist of crystallites, having the size less than 100 nm (WC_{1-x}), and a carbon matrix. This carbon was not detected in XRD due to its presence as an amorphous phase.

1. Introduction

Tungsten carbides play an important role in industry because of their high melting point, high Vickers hardness, high Young's modulus, high fracture toughness, low thermal expansion coefficient and good wear resistance [1]. Due to these properties, tungsten carbides are widely used for creating cutting tools, wear resistant materials, drilling tools, etc. [2-5]. Moreover, electrocatalytic properties of tungsten carbides are of utmost interest since this chemical compound may be used as a platinum catalyst substrate. It allows reducing the fuel cell cost and enhancing fuel cell efficiency [1, 2].

It is known that hexagonal tungsten carbide WC is the dominant phase in the W–C system. Nevertheless, there are two more phases in the system: W_2C and WC_{1-x} . According to a recent theoretical analysis [4], cubic WC_{1-x} has the density of states close to the Fermi level twofold greater than that of W_2C and 6 times greater than that of WC. It is the reason to suggest that WC_{1-x} can be the most active catalyst among the three phases of tungsten carbides. Therefore, cubic tungsten carbide WC_{1-x} is now the object of scientific research in the whole world. The problem is yet, that the cubic phase of WC_{1-x} tungsten carbide only exists in a narrow range of temperature stability, which makes it more difficult to obtain as compared to the hexagonal WC and W_2C [3].



To date, in a number of articles [5-9] authors present different approaches to cubic tungsten carbide production while plasma dynamic synthesis shows the best results from the point of cubic phase output [10]. In this paper, investigation was carried out to determine the optimal precursor amount to obtain a greater WC_{1-x} percentage in a product by direct plasma dynamic synthesis.

2. Experimental

The proposed method is based on the use of a high-current pulsed coaxial magnetoplasma accelerator [11] (CMPA) with graphite electrodes [12]. The CMPA-based system includes three main elements such as capacitive energy storage, CMPA and working chamber. The capacitive energy storage consists of 24 sections with 1.2 mF capacitor banks. This allows varying the energy, which is supplied to CMPA during the process. In a set of experiments, capacity of the energy storage was 6 mF and charging voltage of capacitor banks was 3 kV. At chosen energy parameters, the value of energy, which was accumulated in the energy storage, was equal to 27 kJ. This allowed reaching the value of discharge current up to ~130 kA, discharge voltage 1.1 kV and discharged power ~120 MW.

In the set of four experiments, the tungsten powder of 1.0, 0.7, 0.6 and 0.5 gram (average particle size was 1 micron) was used as a precursor, which was placed in the plasma formation zone of the accelerator. Under the influence of a rising discharge current, this precursor was converted to the plasma state and involved into the plasma flow movement. The second precursor was accumulated from the walls of the accelerating channel, made of graphite. Thus, in the moment, when the plasma flow exited the accelerating channel, it included both tungsten and carbon in ionized state. The final powder (tungsten carbide) was synthesized in a super-high-speed tungsten-carbon plasma jet flowing into the working chamber filled with argon atmosphere at normal conditions. The methodology of the experiments was described in detail in our previous works [10, 11]. In order to investigate, how the mass of tungsten precursor influences the yield of cubic tungsten carbide, all synthesized samples were carefully collected and studied without any additional treatment.

The synthesized products were analyzed by X-ray diffraction (XRD) method using a Shimadzu XRD7000 diffractometer ($CuK\alpha$ -radiation, $\lambda = 1.54 \text{ \AA}$) with a graphite monochromator Shimadzu CM-3121 at the pace of 0.02 degrees and exposure time of 1 second. Qualitative analysis was conducted using the standards of the structural data base PDF2+. The size of coherent-scattering regions (CSR) was estimated according to Debye-Scherrer equation. The morphology of the powder was studied by a transmission electron microscope (TEM, Philips CM12) operating at 200 kV and high-resolution TEM (HRTEM, JEOL JEM 2200F).

3. Results and discussion

Figure 1 shows X-ray diffraction patterns of the synthesized products at the initial tungsten fill of 1.0 g (1), 0.7 g (2), 0.6 g (3) and 0.5 g (4). According to the XRD patterns, at the tungsten masses equal to 1.0 g and 0.7 g, the synthesized products consist not only of the main phase (cubic WC_{1-x}), but also include the hexagonal phases of tungsten carbide W_2C and pure tungsten W. Moreover, W_2C and W peaks are quite intense. The appearance of these phases can be explained by the lack of carbon ions in comparison with tungsten ones, which present in the plasma in a large amount due to a larger precursor mass. An electro erosion mechanism, which is used to obtain carbon during the process, has a limited value. It means that at the chosen energy conditions there is a necessity to reduce the mass of tungsten precursor, in order to increase the yield of cubic tungsten carbide. This suggestion is confirmed, when the tungsten mass is reduced to 0.6 g and 0.5 g. W peaks disappear and the intensity of W_2C peaks reduces significantly. The percentage phase content and the size of coherent scattering regions (CSR) for the all synthesized powders were calculated by the XRD patterns and summarized in Table 1.

The changes in the phase composition of the synthesized products can be explained using the phase diagram of the W–C system (Figure 2). Evidently, when the initial tungsten weight is 1.0 g and 0.7 g, it is present in excess. Therefore, in the process of cooling the tungsten-carbon plasma down to about 3,000 K the cubic phase WC_{1-x} forms, after which the atomic carbon amount in the plasma is reduced.

In the conditions of insufficient amount of carbon, W_2C is formed and some amount of pure tungsten remains during further cooling (region 1 in Figure 2). When the mass of tungsten is 0.6 g or 0.5 g, initially WC_{1-x} is formed and then the carbon shortage is not so critical as in the first and the second experiments. Therefore, in these cases, W_2C is formed and the unreacted W disappears (region 2 in Figure 2). Absence of pure W traces indicates that such mass fills are most appropriate from the standpoint of the atomic ratio of W/C, which allows getting rid of the presence of "extra" phases. However, exactly tungsten powder of 0.6 g may be optimal for production of cubic tungsten carbide of high purity in the plasma dynamic system, because in this case WC_{1-x} phase reaches 95 wt%.

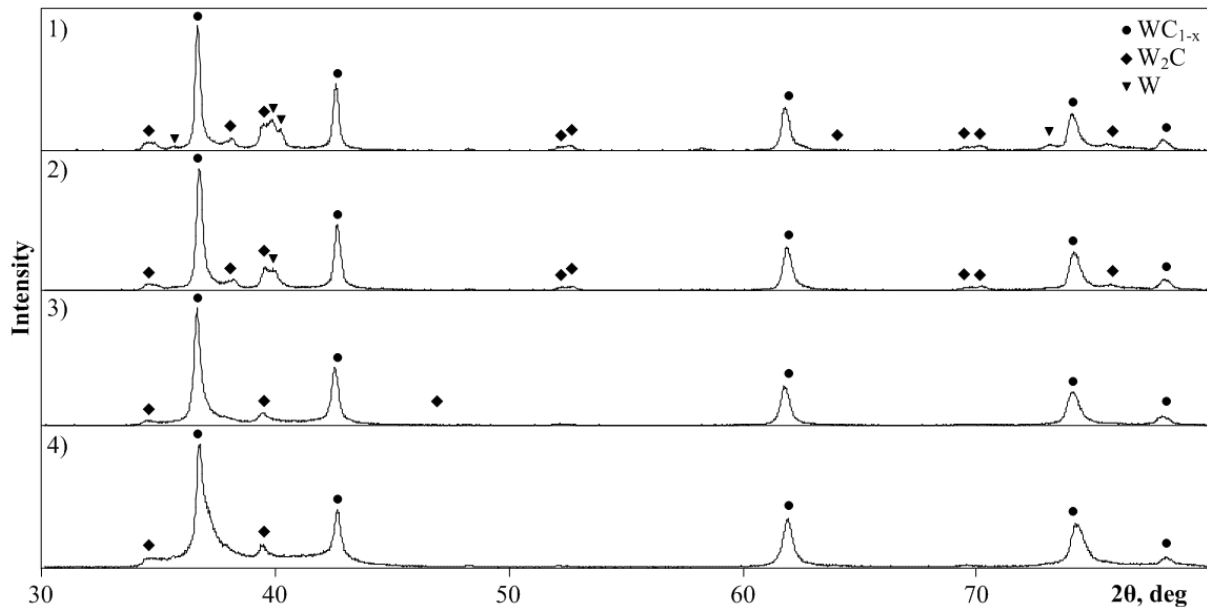


Figure 1. X-ray diffraction patterns of synthesized products.

Table 1. Calculated data of full-profile X-ray diffraction analysis

Number of experiment	WC_{1-x} [%]	W_2C [%]	W [%]	C [%]	CSR [nm]
1	84.0	10.6	4.8	0.6	39.9
2	89.3	7.5	2.5	0.7	32.6
3	95.0	3.7	0.6	0.7	29.6
4	92.2	6.5	0.6	0.7	23.9

Unfortunately, there is a lack of quantitative analysis of materials containing the cubic tungsten carbide phase. Therefore, we estimated the percentage of the phases (wt) by the ratio of the major peak intensities in the XRD patterns to compare our results with the literature data.

In polyporous $C@WC_{1-x}$ composite, intensities of the carbon major peak and the cubic tungsten carbide major peak are practically equal [6]. It means that the cubic tungsten carbide has reached 10–20%. A nanosized tungsten carbide-cobalt composite powder synthesized by thermal plasma contains about 60% WC_{1-x} [7]. After high-intensity pulsed ion beam irradiation of WC-Ni cemented carbides, Zhang et al. have obtained the sample consisting of about 70% WC_{1-x} , 30% WC and Ni traces [8]. In electro-discharge process, nano-structured tungsten carbide powder has been obtained [9]. In this material WC_{1-x} phase has reached about 90%. The powder produced from tungsten powder of 0.6 g, APS 1 micron by the plasma dynamic method proposed in this paper consists of 95% WC_{1-x} . Therefore, this method can be very efficient in obtaining the cubic tungsten carbide phase.

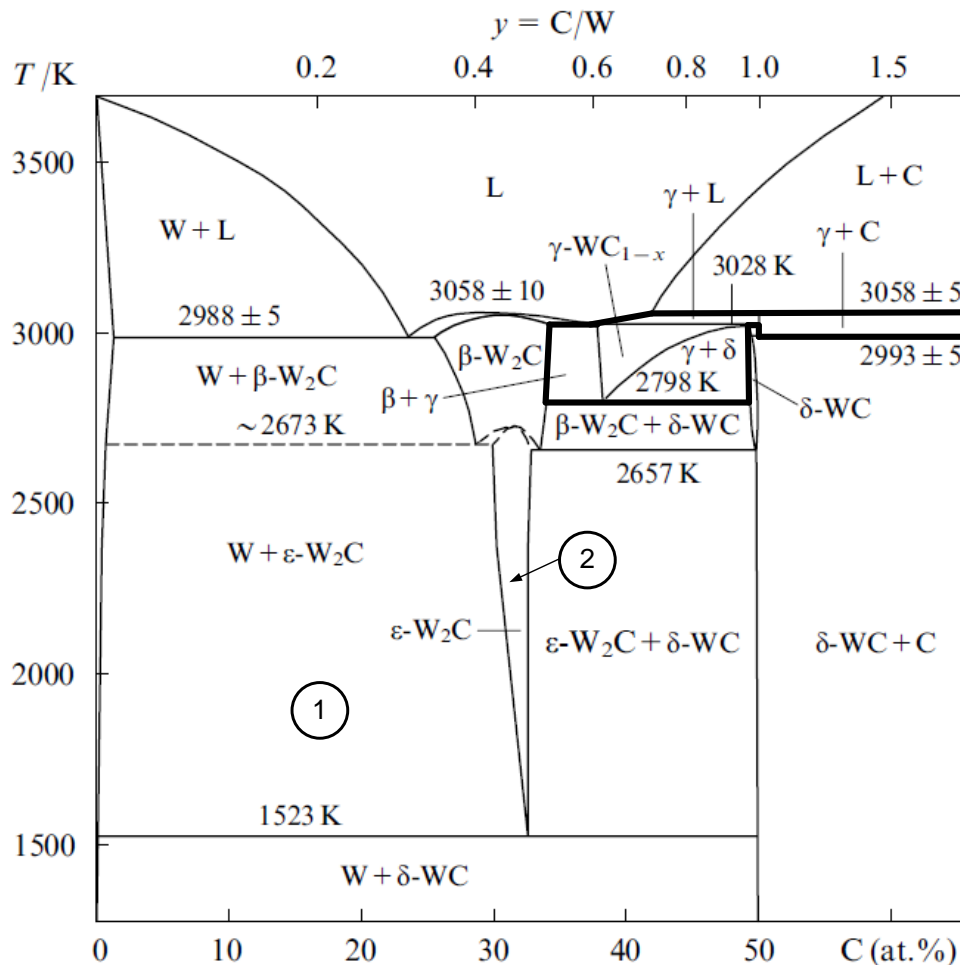


Figure 2. Phase diagram of the W–C system [3].

The results of TEM analysis show that the synthesized powders consist of objects of two types: rounded dark particles with a size of less than 100 nm, corresponding to the cubic phase of tungsten carbide, and graphite matrix (Figure 3a). This carbon is not detected in XRD due to its amorphous state. The particle size obtained from the TEM micrograph is in a good agreement with CSR, calculated from the XRD results. Figure 3b shows the selected-area electron diffraction (SAED) pattern, in which two fuzzy rings of the ultrafine graphite phase and individual point reflexes, belonging WC_{1-x} phase, can be identified. The values of interplanar distances, calculated by HRTEM image (Figure 3c), correspond to one for the phase (ICDD no. 00-020-1316). Crystalline particles of WC_{1-x} phase have a shell with a thickness of about 10.0 nm. It can be argued that the shell consists of crystalline carbon as it shines in the dark-field TEM image in the light of diffracted beam of the carbon structure (Figure 3d).

4. Conclusion

In this paper, the optimal amount of the initial tungsten powder, in order to obtain the cubic phase of high purity by plasma dynamic synthesis, was found. According to the results of X-ray diffraction, cubic tungsten carbide powder with 95 wt% of WC_{1-x} was produced using the tungsten mass of 0.6 g and the charging energy of 27 kJ. The plasma dynamic synthesis, based on using the coaxial magnetoplasma accelerator, may rate as one of the most effective methods for producing the cubic tungsten carbide phase that should outrank the WC and W_2C phases in catalytic activity. This property of the cubic tungsten carbide will be investigated at the next stage of our scientific work.

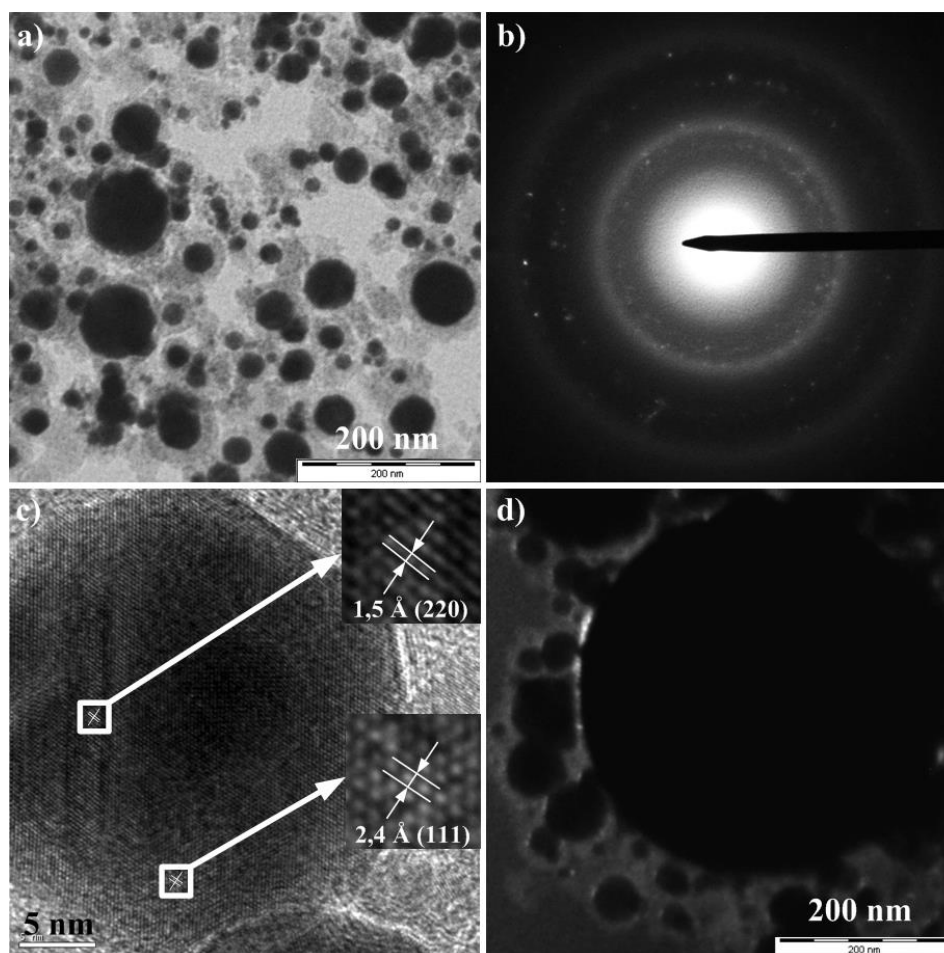


Figure 3. TEM analysis of the plasma dynamic synthesis product: a) bright-field image; b) SAED; c) HRTEM; d) dark-field image.

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