Studying the influence of the energy parameters of the plasma dynamic synthesis process on the dispersed products of the W–C system

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Abstract. Tungsten carbide and its different crystalline phases are widely used for production of metalworking tools due to their excellent physical and mechanical characteristics. However, there is still a problem of synthesizing the cubic modification of tungsten carbide. This paper demonstrates the results on studying the influence of the energy parameters of the plasma dynamic synthesis process on the dispersed products of the W–C system. It was revealed that the initial energy parameters directly influence the phase composition of synthesized products. There were found the optimal conditions for synthesizing the dispersed products from the standpoint of the high output of cubic tungsten carbide phase (more than 85 wt.\%). According to transmission electron microscopy data, all the products are characterized by the presence of particles with a core-shell structure embedded into the amorphous carbon matrix.

1. Introduction

Tungsten carbides are widely used in the manufacture of metalworking tools due to their excellent physical and mechanical characteristics [1, 2]. In the W–C system, the most widespread are the hexagonal phases including WC and W\textsubscript{2}C, the formation conditions of which and the existence ranges are well known. However, in the considered system, the existence of a nonstoichiometric cubic tungsten carbide phase (WC\textsubscript{1-x}) is also possible [3]. The conditions for its formation seem to be extremely difficult for most of the known methods, since it is necessary to simultaneously implement several of them, including reaching the synthesis temperature of more than 2700°C and a cooling rate of at least 10\textsuperscript{7} K/s [4]. Thus, obtaining this material in dispersed and bulk form is extremely difficult.

It was previously shown that using the method of direct plasma dynamic synthesis, it is possible to obtain cubic tungsten carbide both in bulk and in dispersed forms, due to the critical conditions achieved in the arc discharge plasma [5-7]. In the plasma dynamic synthesis system, it is possible to control the energy parameters of the process by changing both the total accumulated energy and the pulse power supply current duration. In this regard, the aim of this work was to study the influence of the energy parameters of the plasma dynamic synthesis system on the formation of dispersed materials in the W–C system.
2. Experimental part
The synthesis of dispersed materials in the W–C system was carried out using a unique system of a direct plasma dynamic synthesis [8-10]. The plasma dynamic synthesis system is characterized by the possibility of varying the process energy characteristics in a wide range [11]. This is mainly achieved due to the sectioned capacitive energy storage, which consists of 24 sections of capacitor banks with a capacity of 1.2 mF each. In addition, it is possible to change the value of the charging voltage up to 5.0 kV. This configuration makes it possible to vary the amount of accumulated energy (up to 360 kJ), which, in turn, affects the amount of supplied energy and the power of the plasma dynamic synthesis process. A change in the capacitance of capacitor banks leads to an increase in the arc discharge current duration, since in the first approximation the system can be considered as a sequential RLC process. A change in the capacitance of capacitor banks leads to an increase in the arc discharge which, in turn, affects the amount of supplied energy and the power of the discharge power 

Based on the foregoing, the effect of the initial energy parameters of the capacitive energy storage feeding the coaxial magnetoplasma accelerator on the characteristics of the plasma dynamic synthesis product was studied. Table 1 shows the initial energy parameters (C is the storage capacity, \( U_{cha} \) is the charging voltage, \( W_{ac} \) is the accumulated energy value), the calculated energy parameters (\( W \) is the supplied energy, \( t_{pulse} \) is the pulse duration, \( I_m \) is the maximum arc discharge current value, \( U_\text{av} \) is the voltage at the accelerator electrodes during the arc discharge stage, \( P_m \) is the maximum discharge power, \( P_{av} \) is the average discharge power value, \( \eta \) is the efficiency of the accelerating system (\( \eta = W_{ac}/W \cdot 100\% \)), as well as the precursor mass \( (m_1) \) and the synthesized product mass \( (m_2) \).

| No. | \( C \) (mF) | \( U_{cha} \) (kV) | \( W_{ac} \) (kJ) | \( W_C \) (kJ) | \( t_{pulse} \) (\( \mu \)s) | \( I_m \) (kA) | \( U_\text{av} \) (kV) | \( P_m \) (MW) | \( P_{av} \) (MW) | \( \eta \) (%) | \( m_1 \) (g) | \( m_2 \) (g) |
|-----|-------------|--------------------|-----------------|--------------|----------------|----------------|-----------------|--------------|--------------|-------------|--------------|--------------|
| 1   | 6.0         | 2.5                | 18.7            | 15.1         | 301           | 91.1           | 1.2             | 105.4        | 50.2         | 81.0        | 0.51         | 0.21         |
| 2   | 6.0         | 3.0                | 27.0            | 22.1         | 284           | 110.5          | 1.3             | 143.5        | 78.4         | 82.2        | 0.52         | 0.28         |
| 3   | 6.0         | 3.3                | 32.7            | 20.1         | 280           | 100.0          | 1.4             | 135.0        | 71.8         | 61.6        | 0.52         | 0.47         |
| 4   | 3.6         | 4.0                | 28.8            | 14.3         | 230           | 91.1           | 1.2             | 113.8        | 62.0         | 49.3        | 0.54         | 0.36         |
| 5   | 12.0        | 2.2                | 29.0            | 20.4         | 400           | 89.3           | 1.1             | 95.0         | 51.0         | 70.6        | 0.50         | 0.38         |
| 6   | 18.0        | 1.8                | 29.0            | 8.0          | 273           | 53.6           | 0.9             | 49.5         | 29.1         | 27.6        | 0.52         | 0.23         |

Experiments can be conditionally divided into two categories. The first category was attributed to assessing the effect of the accumulated energy value (maintaining a constant capacity of capacitor batteries when changing the charging voltage - experiments 1–3 in the table), while the second one was aimed at assessing the effect of the power supply pulse duration of the while maintaining a constant value of the accumulated energy (the capacity changed with a corresponding change in the charging voltage, experiments 4–6).

In all the considered experiments, the main energy parameters of the voltage \( U(t) \) and the power supply current \( I(t) \) were recorded using an ohmic voltage divider and a Rogowski coil, respectively, and an Tektronix 2012 oscilloscope. After that, based on the obtained data, the curves of changes in the discharge power \( P(t) \) and the amount of supplied energy \( W(t) \) were built. The data of the mentioned series of experiments are shown in figure 1. When the power switches are closed, a sinusoidal discharge current begins to flow in the accelerator power supply circuit, and at a certain value, an electroexplosive or thermal destruction of the bridge occurs (depending on the type of precursor used and the initiation method) in the plasma formation zone. In this case, an arc discharge with a Z-pinacle structure is formed. The stable state of this plasma structure is ensured by its own magnetic field and the external inductor magnetic field. The formed plasma structure of a high-current arc discharge lengthens and moves along the accelerating channel in the direction of the Z axis, accelerates to supersonic speeds, as well as the electroerosive production of the material from the
barrel-electrode internal surface due to a significant thermal effect. The precursors placed in the plasma formation zone and the material (carbon) eroded from the surface of the accelerating channel pass into the plasma state and are taken out of the accelerator barrel into the free space of the reactor chamber, which was previously evacuated and filled with argon. Sputtering the material from the free boundary of the plasma structure bow shock wave with a subsequent cooling at a rate of $10^8$ K/s leads to the formation of tungsten carbide nanoparticles. The synthesized products were analyzed by means of X-ray diffractometry method (a Shimadzu 7000S diffractometer) and transmission electron microscopy method (a Philips CM12 microscope).

![Figure 1](image-url)

Figure 1. Oscillograms of the voltage at the accelerator electrodes $U(t)$, the discharge current $I(t)$, the discharge power $P(t)$, the curve of the change in the value of the supplied energy $W(t)$. The numbers of the curves in the oscillograms correspond to the numbers in table 1.

3. Results and discussion

An analysis of the results obtained in a series of experiments with a change in the accumulated energy $W_{ac}$ at a constant capacity of the power supply circuit made it possible to establish a number of
features. With an almost constant pulse time \( t_{\text{pulse}} = 280–300 \, \mu s \), a decrease in the \( W_{\text{ac}} \) value (in experiment 1 when compared with experiment 2) leads to a decrease in the maximum value of the electric discharge current \( I_m \), the maximum and average discharge power \( (P_m \, \text{and} \, P_a) \), which should have a positive effect on increasing the dynamic resistance of the main system components and the resource of their further use. At the same time, a relatively high conversion efficiency of accumulated energy into supplied energy is noted at the level of 80%. Judging by these data, such a regime can be considered as optimal one from the standpoint of electrodynamics, but in this case there is a decrease in the mass of the eroded \( m_1 \) and, accordingly, synthesized material \( m_2 \).

It was expected that an increase in the accumulated energy (experiment 3) over 30 kJ would not only increase the system productivity, but also create even more critical synthesis conditions, which would increase the yield of the cubic tungsten carbide phase. However, the implementation of such a regime led to the opposite result. The increase in the maximum and average discharge power led to the fact that at a certain stage in the arc discharge development, the graphite barrel-electrode was partially destroyed due to its limited mechanical resistance. This led to the fact that the discharge current was sharply limited, the voltage at the electrodes increased and large fragments of graphite got into the product, which did not pass into the plasma state and contaminated the resulting dispersed powder and affected its mass increase. That is, the obtained result on the increase in mass \( m_2 \) can not be considered as positive one, since the product contained with unreacted graphite. Thus, the most optimal mode is with a charging voltage of 3.0 kV and a capacity of 6.0 mF, since it does not lead to the electrode system destruction and provides a large production of dispersed synthesis product.

The data comparison on the change in the storage capacity while maintaining an approximately constant value of the accumulated energy due to the corresponding change in the charging voltage (experiments 4–6) also made it possible to establish a number of typical features. With a sequential increase in the capacity \( C \), an increase in \( t_{\text{pulse}} \) occurs from 230 \( \mu s \) at 3.6 mF to 400 \( \mu s \) at 12.0 mF. Comparing the results of 4 and 5 experiments with the data of experiment 2, it can be noted that the main obtained energy parameters of the synthesis process are much lower. However, in case 5, due to a longer power supply pulse, a large electrical discharge operating time occurs, and the final product mass increases, which can be considered as a positive result. The data on experiment 6 stand apart. With an increase in the storage capacity, \( U_{\text{dis}} \) decreased to 1.8 kV that did not allow the effective breakdown of the inter-electrode gap and the stable arc discharge formation because of badly conditions for melting the graphite bridge and sublimating the tungsten precursor. This led to the current and voltage limitation, as well as a significant decrease in the process efficiency. That is, lowering the charging voltage below a certain value is unacceptable due to the occurrence of prequisites for the system failure. However, despite such a distorted result, the obtained powder was also studied by X-ray diffractometry to estimate the phase composition at a very small value of the supplied energy \( (W = 8 \, \text{kJ}) \).

The results of X-ray structural analysis for products synthesized at different energy parameters is shown in figure 2. The main models describing reflections are cubic tungsten carbide \( WC_{1-x} \) (ICDD 00-020-1316), graphite gc (ICDD 00-075-1621), hexagonal tungsten carbides \( W_6C \) (ICDD 00-035-0776) and WC (ICDD 00-051-0939), tungsten W (ICDD 00-04-806). With a change in the accumulated energy due to an increase in the charging voltage (experiments 1-3 in figure 2, table 1), the structure of the resulting synthesis products, judging by the diffraction patterns, remains almost identical. The minimum amount of impurity phases is observed in experiment 2, where the \( WC_{1-x} \) phase percentage reaches up to \( \sim 86\% \) (according to the method of internal standards). The supplied energy level in experiments 4–6 determines the collected powder mass. Its growth leads to enhancement of the final product mass from \( m_2 = 0.26 \, \text{g} \) to \( m_2 = 0.58 \, \text{g} \). Thus, with an increase in the amount of energy supplied to the accelerator due to an increase in the power supply pulse duration, the erosion of the barrel-electrode increases, therefore, the eroded carbon material mass is increased and the yield of the final product naturally also increases. It should be noted when the supplied energy was equal to \( W \approx 8 \, \text{kJ} \), the percentage of the cubic tungsten carbide yield is minimal and amounts to \( \sim 45\% \). In this case, the XRD pattern is characterized by the fact that the most intense reflections
belong to the metallic W phase, the content of which reaches up to 25%. This indicates that during the arc discharge formation due to the low charging voltage value, the effective breakdown of the inter-electrode gap and precursor sublimation does not occur. It is ejected by the bow shock wave front into the reactor chamber space and does not enter into a plasma-chemical reaction with carbon.

The most acceptable result from the point of view of the cubic phase output purity is an experiment with a power supply capacity of 12.0 mF and a voltage of 2.2 kV. In this case, conditions are provided under which the WC$_{1-x}$ phase yield reaches 85%, and only the W$_2$C phase is impurity, since other WC, W, C phases are identified at the trace level. Thus, the noted energy parameters ($C = 12.0$ mF; $U_{ch} = 2.2$ kV) and the parameters of experiment 2 ($C = 6.0$ mF; $U = 3.0$ kV) can be considered as the most optimal for obtaining the necessary cubic tungsten carbide phase.

Figure 2. XRD patterns of plasma dynamic synthesis products obtained at different energy parameters. The numbers in XRD patterns correspond to the numbers in table 1.

Figure 3 represents the results of transmission electron microscopy for the product obtained in the experiment 2 (table 1). This product with a high content of the WC$_{1-x}$ phase of is distinguished by the natural faceting of the particles and includes sphere-like crystallites. The electron microdiffraction pattern was obtained from the area selected in the bright-field TEM image (SAED). This SAED is characterized by a large number of point reflections with close interplanar spacings related to the aggregate of crystalline phases of tungsten carbides with the dominance of the cubic phase. The obtained dark-field TEM images from point reflections in this ring (figure 3) refer to the phase of cubic tungsten carbide WC$_{1-x}$ (111) $d = 2.44$ Å. Other phases of the W–C system, falling into this ring with close interplanar distances, are most likely absent in this reflection, since the total volume of their content in the final product does not exceed 15%. The product also characterized by the presence of carbon C (002) $d = 3.39$ Å in the form of amorphous matrix and crystallites shells.
Figure 3. The results of TEM studies for the product obtained in experiment 2 (table 1).

Figure 4 shows the analysis results of a product obtained with a high carbon content (about 10%). In this case, the carbon ring stands out well against the background of other point reflections. Particular attention should be paid to the form in which carbon is synthesized in this series of experiments. Carbon represents as a shell of typical W–C particles, as well as a large amount of carbon in the material is presented as an amorphous matrix characteristic. Carbon is also determined as wedge-shaped contours in the body of quasi-two-dimensional particles.

Figure 4. The results of TEM studies for the product obtained in experiment 3 (table 1).

In the experiment with a high percentage of "impurity" tungsten-containing phases (figure 5), a ring with a large number of point reflections also stands out, which in this case can be attributed to the phases: $W_2C$ (002) $d = 2.36$ Å and (101) $d = 2.27$ Å, $WC_{1+x}$ (111) $d = 2.44$ Å, WC (100) $d = 2.51$ Å, W (110) $d = 2.24$ Å. Dark-field TEM images for the reflex located in this ring contain a large number of glowing contours in bodies of very small particles. Thus, we can conclude that, regardless of the process energy parameters, the plasma dynamic synthesis products are characterized by the presence of crystalline particles related to tungsten carbide and its various modifications, as well as graphite in the form of crystalline shells and an amorphous matrix.
Figure 5. The results of TEM studies for the product obtained in experiment 6 (table 1).

4. Conclusion
The influence of the energy parameters on the plasma dynamic synthesis products obtained in the W–C system was studied. A series of experiments with varying the value of accumulated energy and pulse duration was carried out. There were found the optimal conditions for synthesizing the dispersed products from the standpoint of the high output of cubic tungsten carbide phase (more than 85 wt.%). The typical particles are characterized by a core-shell structure, where the core is tungsten carbide crystallite, while the core consists of crystalline graphite. Moreover, all of these particles are embedded into the carbon amorphous matrix.

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