Plasma chemical synthesis of W-C-Co system nano-sized powders

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Abstract. Parameters have been developed and experimental studies carried out for the synthesis of W-C-Co system nanopowders in a limited jet plasma reactor by interaction of tungsten oxide and cobalt with methane in hydrogen-nitrogen plasma flow generated in an electric arc plasma torch. Nanoscale powders with a specific surface area of about 25 m²/g, consisting mainly of tungsten-carbon phases and cobalt, have been produced.

1. Introduction
Metal matrix composites with nano-sized reinforcing particles attract great attention from researchers and developers due to the possibility of a significant increase in the functional and operational characteristics of the resulting materials and products based on them [1-4]. Composite materials have extensive prospects of application in various branches of industrial production, primarily aerospace and defense industries.

Currently, a significant interest in the creation of metal matrix composites is also evident from the new, intensively developing direction of innovative developments - additive technologies [5-9].

Currently number of composites are obtained by the means of SLS/SLM [10-15]. Mixtures of individual components are used as raw materials in the experiments, subjected to homogenization (mixing) by mechanical treatment mainly in planetary mills. The conditions of this treatment are such that in the case of using a nanoscale strengthening phase, only its transfer to the surface of the metal matrix particles is achieved, practically without the introduction of nanoparticles into the metal volume.

Carried out experimental research aimed at developing the foundations for the formation of powder metal-matrix W-C-Co compound nanocomposites for use in additive technologies, as a fundamentally new development in the intensively developing direction of modern research.

2. Experimental setup and methods
Experimental studies on the nanopowders of W-C-Co systems synthesis through the interaction of tungsten oxide and cobalt powders with methane in a nitrogen-hydrogen thermal plasma flow generated in an electric arc plasma torch with a nominal capacity of 25 kW were carried out.

Synthesis was carried out in a limited jet flow plasma reactor. The plasma-forming gas was heated in the plasma torch, the disperse raw materials being transported by the gas into the plasma flow at the plasma torch outlet. After evaporation of the raw material and chemical reactions in the gas phase, the product particles were condensed and then deposited on the reactor water-cooled walls. Smallest fraction of the product was carried out on a filter with the exhaust gases. The experimental plasma setup is shown in Figure 1.
The main parameters of the experiments were changed in the following ranges:

- Plasma gas: nitrogen + hydrogen (15...20 vol. %);
- Plasma jet enthalpy: 6.1–6.5 kW·h/m³;
- Raw material feed rate: 0.3 kg/h;
- Carbidizer excess, [C]/[W]: 7.5–9.5 mole/mole;
- Reducing agent excess [H]/[W]: 2.5–3.0 mole/mole;

The content of cobalt in the initial raw material mixture was 6.8 wt %.

3. Results and Discussion

Thermodynamic calculations of the equilibrium compositions of the W-O-C-H-N-Co system have been performed to evaluate the influence of the concentration of precursors and the temperature of the process on the chemical and phase composition of the resulting tungsten-carbon-cobalt composition:

\[
\text{WO}_3 + K_1 \cdot (\text{H}_2 + 2\text{N}_2) + K_2 \cdot \text{CH}_4 + K_3 \cdot \text{Co},
\]

where \( K_1 \) is the reducing agent excess factor (\( \text{H}_2 \)); \( K_2 \) is the carbidizer excess factor (\( \text{CH}_4 \)); \( K_3 \) is the amount of cobalt added.

It follows from the equilibrium compositions calculations that monocarbide with 100% yield can be obtained in the system considered, but the maximum yield of WC tungsten monocarbide is achieved with significant excesses of the reducing agent over the stoichiometrically necessary.

The full conversion of tungsten into tungsten carbide can be achieved in the temperature range of 800 to 3000 to 3700 K, depending on the excess of the reducing agent and the carbidizer.

Cobalt was found to be present in the system as a condensed phase at temperatures below 2000 K (Figure 2).
Figure 2. Dependence of WC and condensed Co yield on temperature for $K_1 = 5$, $K_2 = 5$, $K_3 = 1$.

Nanopowders with a specific surface area of 20 to 25 m$^2$/g were produced as a result of experimental research (Figure 3).

Based on the results of the X-ray phase analysis, the powders produced consist mainly of tungsten-carbon phases $W_2C$ and $WC_{(1-x)}$ and traces of tungsten (Figure 4). There are no visible peaks of tungsten oxide phases on diffractograms. Cobalt peaks on diffractograms are also not noticeable, due to the low intensity of its peaks in the dominant phases due to the low content of cobalt in ra material. The presence of cobalt in the obtained nanopowders was confirmed by X-ray fluorescence analysis (Figure 5). Powders collected from the filter are characterized by a significant reduction in the amount of pure tungsten.
Figure 4. Characteristic diffractograms of the obtained nanopowder collected from the reactor walls and the filter.

It has been established that when the excess of methane introduced to the process in relation to tungsten increases from 7.5 to 9.5 mole/mole, the total carbon content of the powders produced increases from 5.93 wt % to 6.84 wt %. The specific surface increases slightly: from 20 to 23 m$^2$/g. According to X-ray phase analysis, powders produced with a higher carbidizer content contain more beta tungsten carbide phase $\text{WC}_{(1-x)}$ (Figure 6).
Traditionally, in the development of technological processes for obtaining nanopowders using the plasma method, the powders obtained from the synthesis have a bimodal distribution of particles by size. The first (from 85 wt %) — nanoparticles of the target product, the second fraction — micron-sized, consisting of particles of one or tens of microns in size, the main components of which are non-vaporized raw materials particles and sintered product particles. In the course of further research to find the most efficient and optimized technological and structural process schemes, it is possible to reduce the micron fraction content to values below 1 mass. %.

The method of fraction analysis using sedimentation in the liquid determined the amount of micron fraction contained in the resulting powder. Based on the results of the analysis, the powders obtained contain 9-12 wt. % micron fraction for samples collected from the reactor walls and 1-2 wt. % for powders collected from the filter. The powders of the micron fraction consist of particles up to 40 μm in size, both spherical and irregular shape (Figure 7). According to XRD results, micron fraction powders consist of tungsten semi-carbide W₂C, tungsten oxide phases, and pure tungsten with traces of cobalt.
4. Conclusion
Experimental studies have shown that it is possible to produce W-C-Co system nanoscale composite powders with a specific surface area of 25 m²/g. The possibility of controlling such product properties as specific surface and total carbon content has been demonstrated. Further research will focus on the granulation of the powders produced and subsequent plasma spheronization to obtain powders with spherical particles for additive technologies.

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