Composition, structure and properties of hard alloy products from electroerosive powders obtained from T5K10 hard alloy waste in kerosene

E. V. Ageev, *Professor of Department "Technology of Materials and Transport", Head of Scientific Education Center "Powder Metallurgy and Functional Coatings"[1], e-mail: ageev_ev@mail.ru*
E. V. Ageeva, *Professor of Department "Technology of Materials and Transport"[1], e-mail: ageeva-ev@yandex.ru*

[1]South-West State University, Kursk, Russia.

The paper implements scientific and applied principles of coupling the technology of obtaining new powder materials from waste of hard alloys of the T5K10 brand by electroerosive dispersion and the technology of compacting them by SPS synthesis.
The aim of the work was to study the composition, structure and properties of carbide products made from powders obtained by electrodispersing T5K10 alloy waste in kerosene.
Electrodispersion of T5K10 alloy waste was carried out in lighting kerosene on a patented installation. The consolidation of the obtained powder was carried out by the spark plasma sintering (SPS) method using the spark plasma sintering system SPS 25-10. The choice of powders obtained by electroerosive dispersion of the T5K10 hard alloy waste was justified by its cost and properties. The resource of tungsten-titanium-cobalt hard alloys from T5K10 electroerosion powders is determined not only by the properties of the feedstock, but also by the technology of their production (SPS synthesis).
Based on the conducted experimental studies, it can be concluded that the use of the spark plasma sintering method to produce products from powder obtained by electroerosive dispersion of the T5K10 alloy will ensure high performance of products (cutting tools) due to the uniformity of the surface, favorable structure and low porosity of the product. It is noted that hard alloys made of electroerosion dispersed T5K10 alloy particles obtained by spark plasma sintering under conditions of rapid heating and short working cycle duration have higher physico-mechanical properties compared to industrial alloys from which the initial powder particles were obtained by suppressing grain growth and obtaining an equilibrium state with submicron and nanoscale grain.
Key words: hard alloy waste, electroerosion dispersion, powder, spark plasma sintering, tungsten-cobalt hard alloy, properties.
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Introduction

Sintered tungsten-containing hard alloys possess a number of highly valuable properties which have led to their effective use in many technical fields. In the production of metal-ceramic hard alloys, expensive tungsten carbides WC, titanium TiC and tantalum TaC are used, and metallic cobalt powder Co is used as a binder [1–4].

Currently, one of the main problems in using hard alloys is the high cost of tungsten, titanium, and cobalt [5-8]. This problem can be solved by grinding their waste and reusing them. Due to the high melting point of hard alloys there is a problem of their processing for recycling. In addition, existing industrial grinding technologies are characterised by large tonnage, high energy consumption and environmental concerns [9–11].

One of the ways to solve the problem of saving expensive alloying components is the processing of metal waste containing expensive components (such as W, Ti, Co, etc.) into finely dispersed raw material, using the enterprises' own production facilities with minimal energy consumption and environmental friendliness [12, 13].

One of the effective, but insufficiently studied metallurgical methods of obtaining alloy powders by grinding metal waste is electrodispersion [14–17]. At present, this method is practically not used in industry, due to the lack of complex and comprehensive data on the composition, structure and properties of particles dispersed by electric erosion.

In the modern scientific and technical literature, there is no complete information about the use of particles of T5K10 alloy dispersed by electroerosion as a charge to produce tungsten-titanium-cobalt alloys and cutting tools made of them. For these purposes, comprehensive theoretical and experimental investigations are required. Implementing the planned activities will solve the problem of recycling waste tungsten-titanium-cobalt alloys and their reuse in the manufacture of tools.

The aim of this work was to study the composition, structure and properties of hard alloy products from powders obtained by electrodispersion of T5K10 alloy waste in kerosene.

Materials and methods of research

Electrodispersion of T5K10 alloy waste was carried out in illuminating kerosene on a patented unit **(Fig. 1)**.

The process of electrodispersion of T5K10 alloy comprised the following **(Fig. 1)**. At the beginning, electrodes *5* and *6* were assembled from dispersed waste *8*. Next, the dispersed metal waste granules *8* were loaded into the reactor *3* and the working fluid (kerosene) *10* was poured. Using the control panel of the pulse generator *2*, the required parameters for electric dispersion of metal wastes were set: the capacitance of discharge capacitors and pulse repetition rate. Then, by means of voltage regulator *1* such voltage was set, at which there was an electric breakdown of working fluid *10* in interelectrode space. When the discharge channel was formed, pieces of metal waste in the discharge point melted and evaporated. The working fluid *10* in the electric discharge channel also boiled and evaporated, forming a gas bubble *9*. Droplets of molten and evaporating metal waste fell into the liquid working medium with formation of spherical and elliptical particles *7*, as well as agglomerates. Agitator *4* moved one of the electrodes and provided continuous progress of the electrodispersing process.

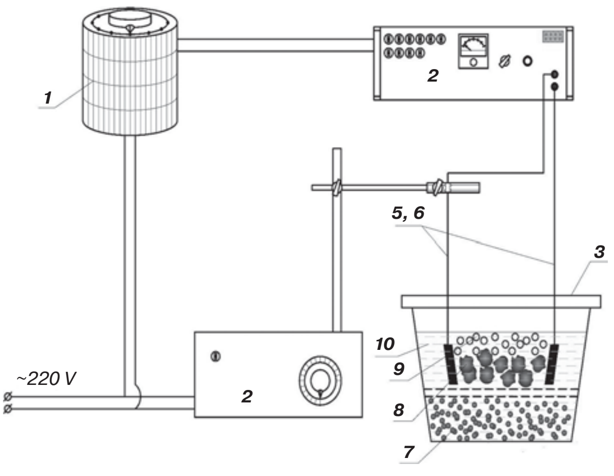

Fig. 1. Schematic diagram of electroerosion dispersion of T5K10 alloy waste:
1 — voltage regulator; *2* — pulse generator; *3* — reactor; *4* — agitator; *5*, *6* — electrodes; *7* — electroerosion particles; *8* — metal waste; *9* — gas bubble; *10* — working fluid

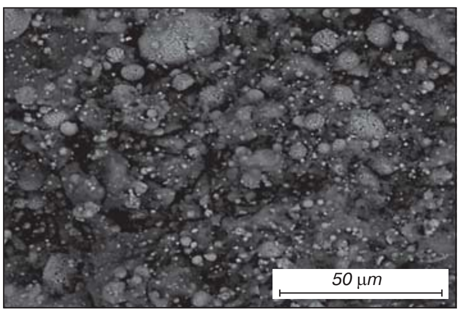

Fig. 2. Scanning electron microscopic image of electroerosive hard alloy powders

Dispersion of hard alloy waste led to its destruction with the formation of powder particles as a result of local influence of short-term electric discharges between electrodes placed in the working fluid. **Fig. 2** shows the shape of the powder particles determined on a QUANTA 600 FEG electron-ion scanning microscope with field emission of electrons (Netherlands).

In the process of electrodispersion, waste metal particles crystallize very quickly, which are ejected from the electric discharge channel in molten form into a reactor filled with a working fluid. The process of rapid crystallization of the molten material in the liquid working medium contributes to giving spherical and elliptical shapes to the particles.

After leaving the discharge zone, the particles of the molten material very often collide with each other. If at the moment of collision crystallization was fully completed, the particles have characteristic traces of impact and a reticulated surface. If the temperature difference between the colliding particles is not significant, then they stick together with the formation of irregularly shaped agglomerates.

Based on earlier studies [18], it was found that the powder materials obtained by electroerosion dispersion of T5K10 hard alloy waste in kerosene have the following characteristics: shape – spherical, elliptical and agglomerates; volume average diameter of particles is 64.1 μm; there is excess carbon on the particle surface, and all other elements W, Ti and Co are distributed relatively evenly; phase composition consists of WC, TiC, and W.

Consolidation of the obtained electroerosion powders was carried out by spark plasma sintering (SPS) using a spark plasma sintering system SPS 25-10 (Thermal Technology, USA) according to the scheme shown in **Fig. 3**. Alloy samples were obtained at temperature $T = 1200$ °C and holding time $t = 10$ min. The initial material was placed in a graphite matrix placed under the

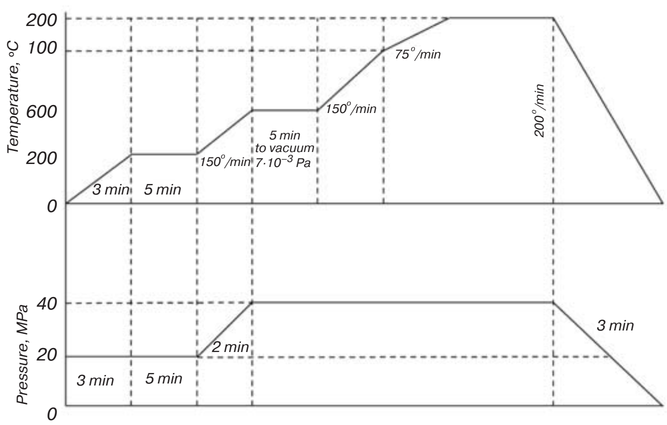

Fig. 3. Scheme of consolidation of powders by SPS method

press in a vacuum chamber. Electrodes integrated into the mechanical part of the press brought electric current to the matrix and created spark discharges between the sintered particles of the material, thereby providing intensive interaction.

The tasks set in this work concerning the study of the composition, structure and properties of hard alloy products were solved using modern equipment and complementary methods of physical materials science, including the following ones. Mechanical processing of the alloy samples was performed on an Accutom-5 automatic high-precision table cutting machine (Denmark) and the LaboPol-5 grinding and polishing machine (Denmark). The microstructure of the alloys was studied on a QUANTA 600 FEG electron-ion scanning microscope with field emission of electrons (Netherlands). X-ray spectral microanalysis of alloys was carried out on an EDAX energy dispersive X-ray analyzer (Netherlands), integrated in a QUANTA 200 3D scanning electron microscope (Netherlands). Alloy phase analysis was performed on a Rigaku Ultima IV *X*-ray diffractometer (Japan). The porosity and grain size of the alloys were studied using an OLYMPUS GX51 optical inverted microscope (Japan) equipped with the SIMAGIS Photolab automated image analysis system. The microhardness of the alloys was determined using the Instron 402 MVD tester (UK). The compressive and flexural strength of the alloy samples were determined using the Instron 300 LX-B1-C3-J1C testing machine (UK). The wear resistance of the alloy specimens was studied according to the standard "ball-disc" test scheme on the CSM Instruments Tribometer automated friction machine (Switzerland).

Research results

Analysis of alloy microstructures showed that the new alloys have a fine-grained structure without inclusions, uniform phase distribution and the absence of significant pores, cracks, and discontinuities **(Fig. 4)**.

Based on the analysis of spectrograms of elemental composition, it was found that the surface of functional alloys contains carbon, and all other elements W, Ti and Co are distributed relatively uniformly **(Fig. 5)**.

The analysis of *X*-ray patterns of the alloys phase composition showed WC and TiC carbide phases, and W pure metal phase **(Fig. 6)**.

The main characteristics of the obtained alloy from electroerosive hard alloy powders are presented in the **Table**.

It has been experimentally established that new hard alloys obtained by spark plasma melting of an electroerosion charge have a grain size of about 1.31 μm.

Fine dispersion of hard alloys is explained by the high dispersion of the initial electroerosion charge and the effect of "grain growth suppression" during spark plasma melting due to the short operating cycle time, high pressure and uniform distribution of heat over the sample subjected to pulsed electric current, and the so-called "plasma effect of the spark discharge".

It was noted that the obtained alloys have a higher microhardness compared with similar industrial alloys. This effect is achieved by spark plasma melting of particles dispersed by electrical erosion due to the practically porosity-free structure and the presence of highly hard phase components. It has been experimentally established that the presence of carbides in the charge produced in kerosene contributes to the microhardness of the alloys.

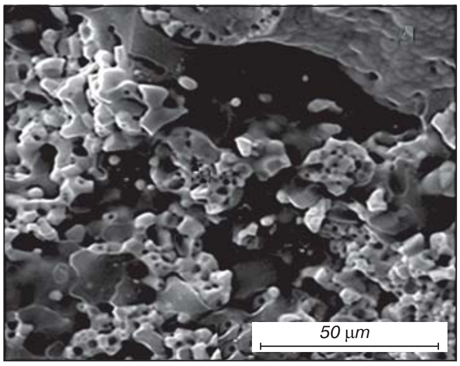

Fig. 4. Alloy microstructure

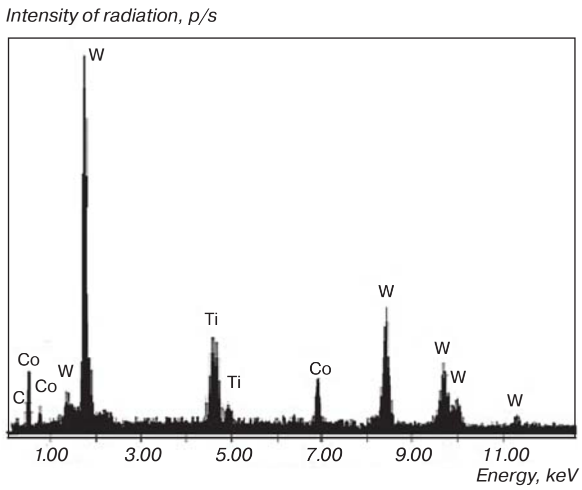

Fig. 5. Spectrogram of elemental composition

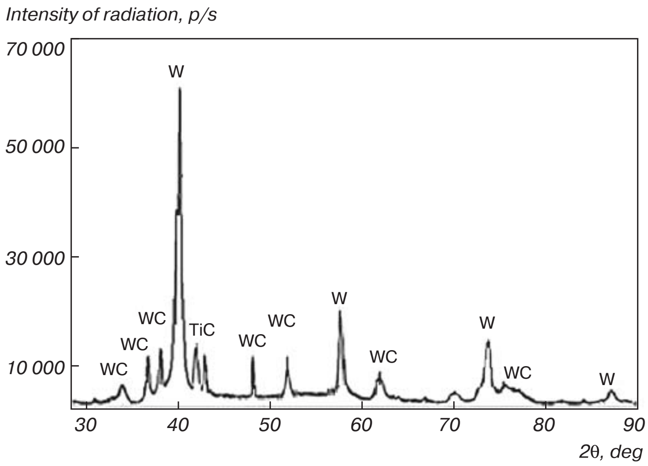

Fig. 6. *X*-ray pattern of the phase composition

Table
Main characteristics of the hard alloy

Parameter under investigation	T5K10 alloy grade
Density, g/cm^3	12.7 / 12.5
Grain size, μm	1.31 / 2.0
Porosity, %	0.64 / 1.0
Microhardness HV, MPa	4729 / 3400
Hardness HRA	90 / 88.5
Flexural strength, MPa	1876 / 1421
Volumetric wear, mm^3·10^{-5}	0.243 / 0.885

Note: The denominator shows the values of parameters for industrial alloys.

It has been established that the new hard alloys have a higher hardness compared to similar industrial ones. This effect is achieved by spark plasma melting of electroerosion charge with fine grain size and is caused by high microhardness, practically porosity-free and defect-free structure and phase composition. It has been experimentally established that the presence of carbides in the charge produced in kerosene contributes to the hardness of the alloys.

It has been experimentally established that the new hard alloys obtained by spark plasma melting of electroerosion charge have a higher ultimate strength in comparison with industrial metals and alloys. The high dispersity and spherical shape of the particles, as well as their relatively small grain size, and porosity-free and defect-free structure contribute to the increase in the strength of the new alloys.

It has been experimentally established that the new hard alloys have less volumetric wear in comparison with industrial metals and alloys. Increased wear resistance of hard alloys produced by spark plasma melting of electroerosion charge is promoted by high microhardness, hardness, as well as relatively fine grain size, and porosity-free and defect-free structure.

As a result of this work, an important scientific and practical problem aimed at creating an advanced, environmentally friendly, low-tonnage and waste-free technology for producing new tungsten-titanium-cobalt particles suitable for industrial application and alloys based on them has been solved.

This work implements the scientific and applied principles of coupling technology of producing new powder materials from T5K10 hard alloys waste by electroerosion dispersion and technology of their compacting by SPS-synthesis method.

The scientific novelty of the conducted investigations consists in a comprehensive study of the effect of initial charge on the structure and properties of hard alloys, in particular, powders obtained by electroerosion dispersion of T5K10 hard alloys waste, and products obtained on their basis by SPS-synthesis.

The above confirms the necessity and relevance of developing scientific principles and technological fundamentals for the production of raw materials for tungsten-titanium-cobalt hard alloys with qualitatively new operating properties and low cost.

The choice of powders obtained by electroerosion dispersion of T5K10 hard alloys waste is justified by its cost and properties. The resource of tungsten-titanium-cobalt hard alloys from T5K10 electroerosion powders is determined not only by the properties of initial charge but also by the technology of their production (SPS-synthesis).

Conclusions

1. Based on the experimental studies, we can conclude that the use of the method of spark plasma sintering to manufacture products from powder obtained by electroerosion dispersion of T5K10 alloy will provide high workability of products (cutting tools) due to the surface homogeneity, favorable structure and low porosity of the product.

2. It is noted that hard alloys made of T5K10 alloy particles dispersed by electro-erosion, obtained by spark plasma sintering under conditions of rapid heating and a short duration of the working cycle have higher physical and mechanical properties compared to industrial alloys, from which the initial powder particles were obtained, due to suppression of grain growth and reaching the equilibrium state with submicron and nanoscale grains.

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