Properties of WC-6Co Hard Alloy Powders Obtained by the Method of Spark Plasma Dispersion

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Abstract. Powders of WC-6Co hard alloy were produced using spark erosion in distilled water. The properties of powders, such as specific surface area, morphology, structure and size distribution, were studied. Investigation of the powder properties was made using the methods of scanning electron microscopy, X-ray phase analysis and disk centrifuge.

Introduction

Tungsten-containing wastes of instrument manufacture are of high practical value. The problem of wastes recycling is solved by two conceptual approaches: the manufacturing operations to produce technical pure tungsten (for example, for use as a dopant material) and reprocessing with subsequent modification of carbide material to use it for its direct purpose (tools and surface hardening coating). A technological processing scheme for recycling of tungsten-containing wastes of hard alloys is determined by the degree of integration of their valuable components, ecological requirements and market demand for a particular use of tungsten products [1]. In turn, the processing methods by applied sources of energy can be divided into chemical-metallurgical, chemical, electro-mechanical and electric pulse (or spark plasma) \([2-6]\).

The results of mechanical recycling of WC-Co wastes with the drum mills and with an attritor are shown in \([4]\). It has been determined that the use of this process for grinding metal wastes has limitations related to the dispersion of powders, as after grinding to particle sizes of 10-30 µm, further material destruction practically stops and is followed by the self-sheathing and the formation of conglomerates from grinding.

At the same time, it is known that particles with smaller sizes, in particular nanoparticles, become more active through the accumulation of free surface energy. The products, created with the use of those mixtures of particles, show high strength properties.

Efficient methods of producing of the nano-sized metal powders are electric pulse methods: electric explosion of conductor in gas atmosphere and electric pulse spark plasma erosion (SPE) of metal granules in water or other liquid \([9]\). Both of these methods are energy efficient and energy-saving. However, only SPE allows processing metal waste into fine powders with voltages of up to 1000 volts and in liquid environment that greatly simplifies the manufacturing process \([10]\).

The goals of this work are to study the physical and chemical processes occurring during spark plasma erosion in water environment and to obtain initial data for development of technology for the production of fine powders with the desired properties.

Materials and methods

To obtain powders of hard alloy WC-6Co, the plant for electric pulse spark plasma erosion dispergation of metals was used \([9]\). Distilled water was applied as an insulating liquid. Experimental setup consisted of a pulsed power supply IP-1-3 and reactor was made of dielectric material, in which the metal tungsten electrodes with a form of a rod with a diameter of 3 mm, were placed. The volume of reactor was 0.5 dm\(^3\). The space between electrodes was filled with chip scrap - cutting wastes of the WC-6Co alloy. The thickness of the load was 15 mm and the distance between the electrodes – 58 mm. The power source generated voltage pulses with length of 15 µs.
with an amplitude of 1000 V and pulse frequency of 1000 pulse/s. Maximum discharge current was 250 A. Power supply was built on the principle of discharge of capacitive drive on the load via the fast thyristor and pulse transformer.

Duration of one stage of dispersing was approximately 10 min. After the completion of each stage of dispersing the installation was turned off. The layer of produced suspension, formed over chip scrap, was decanted. Solid products of SPE were divided into fractions by sedimentation or defecated for dewatering. Then the level of insulating liquid was restored and the process of dispersing was repeated.

After that the wet precipitations were combined and dried in vacuum drying cupboard WСV at the temperature not exceeding 40°C, and then brought up to constant weight at 100°C. Next, the specific surface, particle size distribution, phase composition and morphology of the dried sediments were investigated.

The value of the specific surface of obtained powder was determined by the thermal desorption of nitrogen by analyzer of specific surface area and porosity «Sorbometr M» (CJSC «Catacon»). Based on the obtained experimental data the software automatically calculated the value of specific surface area of the sample by BET method.

Particle size distribution was determined using CPS Disk Centrifuge DC24000 (CPS Instruments, United States) in working fluid of ethanol. CPS centrifuge is a fast and sensitive method for analysis of particle size of colloidal solutions. The device can work with particles with sizes from 10 nm up to 40 µm. The CPS Disc Centrifuge separates particles by size using centrifugal sedimentation in a liquid medium. The sedimentation is stabilized by a slight density gradient within the liquid. The particles sediment within an optically clear, rotating disc. When particles approach the outside edge of the rotating disc, they block/scatter a portion of a light beam that passes through the disc. The change in light intensity is continuously recorded, and converted by the operating software into a particle size distribution using Stokes law and assuming spherical particles. Mie Scattering Theory is used to determine the quantity of particles of that diameter which will produce the measured reduction in beam intensity. Particles that are very small scatter much less light per unit weight than particles comparable in size to the wavelength of light.

X-Ray Diffraction study of the phase composition and structural parameters of the sample was carried out by diffractometer Shimadzu XRD-7000 at CuKα radiation. Analysis of the phase composition was performed using the database PCPDFWIN.

The morphology of the WC-6 based powders was investigated by scanning electron microscopy (SEM) using a bitmap electron microscopy LEO1455VP by “Carl Zeiss” and JEOL 6000 by “Nikon Metrology NV”.

Results and Discussion

Under the influence of the pulses of electrical energy between particles of chip scrap (fig. 1A) located in the interelectrode gap, numerous microdischarges were generated, causing erosion of the granules. Due to small gaps between the particles in the discharge channel the most energy was found to be spent on heating of metal at the anode and cathode zones on the surface of these particles [11], causing local heating of metal to temperatures of melting and boiling points. This resulted in melting, evaporation and spraying (dispersion) of melted metal. On the surface of a particle, met with the erosion, a hole was formed.

Fractional composition of chip scrap is presented in table 1, and morphology of the source material is presented in Figure 1a.

The first experiments for the SPE of WC-6Co wastes showed that after drying, dispersion products have formed brittle conglomerates (Figure 1b), destructible after low-energy influence (pressure application). The formation of conglomerates was probably caused by the presence of fine particles with high free energy due to the high specific surface area and aspiration of the system to decrease its free energy. This fact was taken into account in future development of the technological process of wastes desperation. Water suspension products were evaporated and then mixed with the ethyl
alcohol, and stored in the form of paste. The products in this condition can be stored until the next technological operation.

Table 1. Distribution of source material by size

| Fractional composition, [mm] | Content, [% by weight] |
|-----------------------------|-----------------------|
| +1                          | 54                    |
| -1 +0.5                     | 26.4                  |
| -0.5                        | 19.1                  |

Figure 2 shows morphology of nanosized and submicron sized particles, obtained by SPE of WC-6Co wastes, SEM bitmap by LEO1455VP (a) and by JEOL 6000 (b).

According to images shown in Figure 2, particle shape is predominantly spherical, there are large (up to 20 µm) particles with melting and spraying nature and small (50-100 nm), the origin of which is probably related to the evaporation of metal in micro discharges zones and subsequent
condensation of vapors. On the surface of the large particles very small particles and agglomerates are well seen. In addition, around the spherical particles there are shapeless three-dimensional fibered structures, which are likely to consist of products of metal interactions with each other and with working fluid.

Experimental data of particle size distribution in ethanol suspensions correspond with the microscopy data. Fig. 3a shows the particle size distribution curves, while Fig. 3b illustrates relationship between mass fraction of particles and their diameter.

![Fig 3a Distribution curve of particle size](image1)
![Fig 3b Distribution curve of particle masses](image2)

According to the data provided in Figure 3a, the size of the particles of the powder is mostly in the range from 50 to 200 nm, the maximum number of particles in the suspension have a diameter of about 70 nm.

Distribution curve of particle masses (fig. 3b) has two defined peaks - first for particles (or agglomerates) diameter in the range of 270-280 nm, and the second for particles (or agglomerates) diameter in the range of 820-830 nm.

Table 2 shows the data of specific surface of SPE products in different conditions of dispersion in compartment with the value of specific surface of WC-6Co chip scrap after mechanical grinding sifted to the fractions less than 63 µm.

| Nos. | Sample       | Conditions of dispersion                               | Specific surface d, [m²/g] |
|------|--------------|-------------------------------------------------------|---------------------------|
| 1    | WC-6Co M    | 63 µm fraction of original mechanical grinding         | 0.13                      |
| 2    | WC-6Co SPE 1| 400 pulse/s, light fraction of the sedimentation separation of powder | 36.99                     |
| 3    | WC-6Co SPE 2| 400 pulse/s, mass fraction of the sedimentation separation of powder | 10.8                      |
| 4    | WC-6Co SPE 3| 600 pulse/s, gross sample                             | 12.9                      |
| 5    | WC-6Co SPE 4| 800 pulse/s, gross sample                             | 13.8                      |

Thus, the specific surface of powder, prepared by spark plasma erosion of WC-6Co alloy more than a hundred times exceeds this value for a fraction of >63 micron size, obtained by mechanical grinding.

According to the XRD shown in table 3, the dispersion products include at least five components, reflecting the non-uniform distribution of elements and their compounds in the alloy.
Table 3 XRD data of powder produced from alloy WC-6Co

| The phase  | Content, [% of the mass.] | Lattice spacing |
|------------|---------------------------|-----------------|
| W<sub>2</sub>C<sub>0.84</sub> | 10.31                     | a: 5.1579       |
| Co         | 2.5                       | a: 3.52         |
| WC         | 0.62                      | a: 2.9181       |
| Co<sub>2</sub>W<sub>3</sub>C | 86.06                     | a: 11.1047      |
| W          | 0.51                      | a: 3.1337       |

Conclusions

1. It was found that the spark plasma erosion method provides the dispersion of carbide powders with particle sizes in the range from 50 to 200 nm.
2. The results of XRD show that the hard alloy dispersion products correspond to the composition of the source material.

References

[1] Kurkchi E.U., Yakubov F.Ya., Kurkchi U.M., Valiyev E.V. The current state and prospects of development of electrochemical recycling of the tungsten containing waste of hard alloys. Uchenye zapiski Krymskogo inzhenerno-pedagogicheskogo universiteta, 6 (2006) 50-56.
[2] M.I. Dvornik, T.B. Yershova, Patent RF 2,443,507 (2012).
[3] Afanasyev L. N., Vereshchagin M. N., Goransky G.G. Technological bases of preparation of hard-alloy powders from wastes of metallurgical production. Materials of the international scientific and technical conference “Materials, equipment and resource-saving technologies”, Mogilev, 1 (2010) 161 [In Russian].
[4] Vereshchagin M. N. Goransky G. G., Kirilyuk S. I., Agunovich I. V. Research of processes of formation of structures and phases of powder mixes on the basis of wastes of the hard alloys containing tungsten at their mechanosynthesis and high-speed mechanical dispersgating for receiving powder compositions. Lit'e i metallurgija, 1 (2012) 110-114.
[5] Ageev E.V., Gadalov V.N., Romanenko D.N., Trigub V.B., Samojlov V.V., Ageeva E.V. Research of physical-technological properties of the powders received by electroerosive dispersgating of a hardalloy. Fundamental researches, 12, 2 (2011) 336-340.
[6] Malyshnev V. V., Gab A. I. Resource-saving ways of processing of waste of hard alloys, based on tungsten carbide-cobalt and extraction of tungsten from tungsten concentrates, Teoreticheskie osnovy himicheskoi tehnologii, 41, 4 (2007) 461-466.
[7] Ageev E.V., Semenikhin B. A. Producing of powder materials from waste of the sintered hard alloys method selection, Izvestija Samarskogo nauchnogo centra RAN, Samara, Special issue.: Actual problems of mechanical engineering. (2009) 12-15.
[8] Zhuravkov S.P., Lobanova G. L., Pustovalov A.V. The defining role of electropulse methods of receiving nanopowders of aluminum on special aspects of their interaction with water and phase structure of products, Russian Physics Journal, 57 9/3 (2014) 38-42.
[9] Goloveyko, A. G. Kinetics of emission of a liquid phase of material of electrodes at an electric discharge, Russian Physics Journal, 6 (1966) 83-88.