Production of ultrafine-grained spherical $\beta$-WC-$W_2C$-Co microparticles by electro discharge erosion of WC-15Co alloy in glycerol and their solutions

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Abstract
The present work is devoted to the study of the production of ultrafine-grained (UFG) spherical microparticles by electro discharge erosion (EDE) of the WC-15Co cemented carbide in glycerol, distilled water, and their solutions. Energy costs, productivity, particle size distribution, and morphological and chemical compositions of the obtained powders were studied. It was found that energy cost is reduced by 2.2 times when glycerol was used instead of water. The use of water reduces carbon content from 5.2% to 1.4%. The use of glycerol and its aqueous solutions reduces carbon loss and increases its content in the obtained powders from 3.2% to 6.1%. During SE, cobalt, carbon, and tungsten evaporate from spherical particles and crystallize in the form of ultrafine particles, which subsequently remain in suspension after sedimentation of spherical particles. Mass fractions of sedimented spherical particle fractions ranged from 75% to 82%. Cobalt and carbon content in the spherical particles obtained in glycerol decrease from 15% to 10% and from 5.2% to 3.1% respectively. The particles consist of rounded carbide grains ($\beta$-WC and $W_2C$) with a diameter of up to 500 nm, the space between which is filled with cobalt. Microhardness of the particles increased from 12.1 GPa (initial alloy) to 15.6 (EDE in water)—23.7 GPa (EDE in glycerol).

1. Introduction

The WC-Co alloys and coatings are widely used in the industry, as they are characterized by a combination of high hardness and wear resistance [1]. In recent years, research has been actively conducted in three directions: producing ultrafine-grained (UFG) WC-Co alloys [1–18] and UFG coatings [19–24] with increased hardness and wear resistance and increasing possibilities of manufacturing products using three-dimensional (3D) printing [25–27]. To obtain the highest quality coatings [19–24] and manufacture products using 3D printing [25–27], spherical particles (WC-Co and WC) are used. Currently, the spherical particles are obtained using relatively hazardous chemical methods and expensive physical methods [28–33]. To obtain spherical particles by chemical methods, hazardous reagents are required [28–30]. A high temperature (2780 °C) is required to melt WC and obtain spherical particles by physical methods [31–33]. Spherical WC-Co particles for 3D printing with a loose structure and properties are obtained by sintering prefabricated granules [25–27].

An alternative promising economical method for producing UFG spherical particles is electro discharge erosion (EDE) [34–53], based on the action of a spark discharge between the anode and cathode. Currently, indirect recirculation methods of WC-Co scrap are widely used, which have disadvantages associated with the long reaction time and multi-stage process [54–57]. The EDE is one of the direct recirculation methods that allow the direct production of good-quality powders from waste and control the size and morphology of particles.

The method is based on the erosion of electrodes’ surface and formation of particles due to the passage of a spark discharge in a dielectric fluid. Under the influence of a spark discharge, the surface of the electrodes heats
up to $10^4\,\text{K}$ \cite{58, 59}, leading to melting and boiling of the initial material inside the vapor bubble formed when the dielectric fluid used is boiled. After the passage of the spark discharge, the steam bubble is destroyed, and the boiling material is washed out into the inter-electrode gap. Nanosized \cite{34–44}, nanostructured \cite{45, 46} and amorphous \cite{48–52} particles are formed as a result of quenching of droplets of the molten and boiling material at a rate of $10^6$–$10^9\,\text{K}\cdot\text{s}^{-1}$.

Predominant disadvantages of EDE are the relatively high energy costs, heterogeneity of morphological composition and particle size distribution of the powders (mix of nanoparticles and spherical microparticles), and change in their chemical composition due to an increase in the carbon content during EDE in oil and kerosene \cite{3, 35, 53} or a decrease in the carbon content during EDE in water \cite{34, 45, 46}.

Energy costs can be reduced by increasing the viscosity of the fluid used, leading to an increase in energy concentration in the spark discharge and an increase in the efficiency of removal of molten material from the well \cite{58–66}. Due to the high demands on surface roughness, the kinematic viscosity of the fluids used for EDM (Electrical discharge machining) is usually limited to 1 to 20 mm$^2\,\text{s}^{-1}$ \cite{67}. When the EDE aims to obtain a powder, there are no such restrictions. Glycerol, whose kinematic viscosity is 1118 times higher than that of water, meets all these requirements. It has already been proven that the use of glycerol \cite{63, 66} and its solutions \cite{60, 65, 66} leads to an increase in EDM productivity. The problem of heterogeneity can be solved by fractionation of the obtained powder into fractions containing spherical and ultrafine particles by sedimentation in a liquid. Changing the volume fraction of glycerol in the solution can aid in controlling the carbon content in the resulting powder.

This work aims to study the effect of glycerol and its solution in water on specific energy consumption, process productivity, chemical, phase, particle size, and morphological compositions of the powder obtained by EDE of a WC-Co alloy in them.

2. Materials and methods

A medium-grained tungsten-cobalt hard alloy WC-15Co (85% WC and 15% Co) in the form of standard samples of 6.5 $\times$ 5.25 $\times$ 20 mm (produced in KZTS) was the source material for the EDE. The structure of the material is shown in figure 1(a). The EDE was conducted through a special installation consisting of a pulse generator and a vessel with electrodes with an inner diameter of 60 mm and a volume of 150 ml (figure 1(b)). The pulse energy was 0.9 J at a pulse duration of 300 $\mu\text{s}$, a voltage of 30 V, and a frequency of 100 Hz. The shaker operating at a frequency of 50 Hz and amplitude of 0.4–0.8 mm provided interruption of the contacts formed between the electrodes, protecting them from short circuit. Distilled water, glycerol, and solutions of glycerol in water with a volume fraction of glycerol of 25%, 50%, and 75%, respectively, were used. The EDE in each liquid was conducted thrice for 20 min. Glycerol viscosity was calculated by the proposed formula \cite{68}. Energy consumption was estimated using an energy meter. The temperature of the vessel with a liquid with a volume of 1 liter was kept constant (20°C).
After EDE of 5 batches of powders, they were sedimented for 24 h in an oven at elevated temperatures (from 50 °C for water to 160 °C for glycerol) to reduce the viscosity of the liquids and accelerate sedimentation. In addition, spherical microparticles were separated from solutions by partial precipitation. The sedimentation from solutions containing 25%, 50%, 75%, 100% glycerol, was carried out for 5, 11, 40 min, 4.5 h, and 5 days, respectively. The pastes obtained after draining the liquids were dried in vacuum at a temperature of 600 °C. Then the phase composition and carbon content of each batch were investigated. To study the microstructure, a thin section of particles mixed with epoxy was prepared. The particle size distribution was determined on an Analysette 22 Microtec laser particle size diffraction analyzer (5% error). The carbon content was determined using an Emia-320V2 analyzer. The phase analysis of the powders was conducted on a DRON-7 x-ray diffractometer. The morphology of the powders and particle microstructure were analyzed using Vega Tescan and EVO 40 scanning microscopes. The distribution of the mass concentration of tungsten and cobalt was determined using the X-Max 80 energy-dispersive x-ray analyzer (EDX) and TESCAN VEGA 3 microscope. The microhardness of the obtained particles and the initial alloy was measured using a PMT-3M hardness tester with a load of 30 g.

3. Results and discussion

3.1. Material removal rate

As a result of the EDE of the WC-15Co alloy, 15 batches of powder with a mass of 0.4 to 1.2 g were obtained. Power consumption depended little on the composition of the liquid (figure 2(a)). In all liquids, it was 45–60 W —approximately 1.5–2 times lower than the calculated values of the maximum useful power of the pulse generator used mode (90 W). This difference is explained by the fact that discharges occurred at the moment contacts were formed by the shaker operating at a frequency of 50 Hz—twice lower than that of the pulse generator (100 Hz).

An increase in the volume fraction of glycerol from 0% to 100% led to an increase in the productivity of the process by 2.2 times (from 1.6 to 3.6 g per hour). At the same time, the specific energy consumption decreased on average from 28.9 to 12.3 W h/g. Glycerol differs from water in the presence of carbon and viscosity. Shabgard and Kabirinia found [34, 35] that the carbon released during the pyrolysis of liquids contaminates the inter-electrode gap, leads to short circuits, reduces productivity, and increases energy costs. Consequently, an increase in productivity can only be explained by an increase in the viscosity of the liquid [58–66]. With an increase in the kinematic viscosity of the liquids used, productivity increases (figure 2(b)) and the specific energy consumption (figure 2(c)) decreases, which are satisfactorily described by logarithmic dependences. With an increase in glycerol volume fraction from 0 to 75% and a corresponding increase in kinematic viscosity by 46 times, productivity increases by only 53%, and energy consumption decreases by only 22%. The greatest increase in productivity occurs on switching to pure glycerol when the kinematic viscosity increases 1118 times.

In the graphs (figure 2), a scatter of values is observed, which can be explained by the influence of liquid contamination and inconsistency in the conditions for the occurrence of electric discharges, which depend on the relative position of the electrodes. Such scattering is inevitable during EDE of the bulk pieces in such installations when the relative position of the electrodes and conditions for the occurrence of discharges can vary over a wide range.
Weighing showed that the mass of powders collected after drying is 97%–99% of the mass loss of the initial samples of WC-15Co alloy. An analysis of the particle size distribution showed that powders obtained in water [figure 3(a)] and glycerol [figure 3(b)] have a similar particle size distribution. The average diameters of spherical particles obtained in water and glycerol were 10.2 μm and 10.8 μm, respectively. The resulting powders have wide particle size distributions (from 0.1 to 50 microns). This distribution is caused by the simultaneous presence of spherical microparticles with a diameter of up to 50 μm obtained by the crystallization of the liquid phase and ultrafine particles with a diameter of several nm obtained by the crystallization of the vapor phase. In the powder obtained in water, individual agglomerates of ultrafine particles are clearly visible [figure 4(a)]. In the powder obtained in glycerol, nanosized agglomerates cover almost all spherical particles [figure 4(b)].

During the formation of spherical particles, a part of cobalt boils out of them because its boiling point (2870 °C) is near the melting point of WC (2780 °C). As a result, cobalt content in the ultrafine particles obtained by the crystallization of the vapor phase is higher than in the initial alloy (15%). The EDX analysis showed that cobalt content on the surface of the particles obtained in water increased to 19.0% [figure 5(a)] and on the surface of particles obtained in glycerol to 22.5% [figure 5(b)]. The powder obtained in glycerol has higher cobalt content because ultrafine particles with high cobalt content coat the spherical particles during the sedimentation process in glycerol. In water, part of the ultrafine particles form agglomerates, which precipitate as separate particles. They are clearly visible in figures 4(a), (b). During micro-EDM of WC-Co, the entire powder consists only of agglomerates of ultrafine particles formed by crystallization of the vapor phase [34–39]. However, energy costs for its production are much higher. Furthermore, in such a powder, there are no spherical microparticles of practical interest.

The separation of the fraction (+6 μm) from the obtained suspensions containing mainly spherical particles was carried out by partial sedimentations. Weighing showed that the masses of powders obtained in water and glycerol were approximately 75% and 82%, respectively, of the total erosion of the initial electrodes in the corresponding liquids. In other words, the mass fraction of particles with a diameter less than 6 μm was approximately 20%—much less than the volume fraction of the −6 μm fraction (approximately 50%)—which can be estimated from the particle size distribution of the initial powders (figures 3(a), (b)). This is because, as will be shown below, ultrafine particles largely comprise free carbon and cobalt, whose density is much lower than that of tungsten and its carbides. Accordingly, the mass fraction of these particles is less than their volume fraction.

The average diameter of the sediment fraction in water is 16.2 microns. Some particles with a diameter of less than 6 μm were preserved in this fraction, the volume fraction of which is approximately 5% (figure 3(c)). The morphological analysis confirmed that in the powder fraction obtained in water (figure 4(c)), in addition to spherical particles, there is a small number of agglomerates of ultrafine particles, deposited together with

**Figure 3.** Particle size distributions of powders obtained by EDE in water (a), (c) or glycerol (b), (d) after complete (a), (b) or partial precipitation (c), (d).
spherical particles. The fraction that sedimented from glycerol consists entirely of particles with a diameter of more than 6 μm (figure 3(d)). The average particle diameter of this fraction is 18.5 μm. As shown by the morphological analysis, all particles obtained and sedimented in glycerol have a spherical shape (figure 4(d)).

The boiling of cobalt from the melted drops in the formation of spherical particles during EDE led to a decrease in its content. Its concentration on the surface of the particles of the sedimented fraction (~6 μm) obtained in water (figure 5(c)) turned out to be slightly higher (12.6%) than on the surface of the particles obtained in glycerol (figure 5(d)) (10.2%). This difference can be explained by the different lifetime of the particles in the molten form and by different particle size distributions of the isolated fractions. The short lifetime of the particles in the form of melted droplets made it possible to retain most of the cobalt inside the spherical particles. Assuming that certain values of cobalt concentrations in fully and partially isolated powders
are equal to the cobalt contents in ultrafine and spherical particles, respectively, and knowing the total cobalt content in the initial alloy without carbon (15.8%), we can estimate the mass content of spherical particles. This assessment demonstrated that the content of spherical particles is 90% and 80% in the powders obtained in water and glycerol, respectively. These values are close to the above mass fractions of the precipitated fractions (75% and 82%). In other words, the mass fractions of the selected fractions (+6 µm) correspond to the estimated content of spherical particles.

5. Phase composition and carbon content

Phase analysis showed that during EDE in water, glycerol, and their solutions, α-WC loses carbon and turns into β-WC, W₂C, or W (Figure 6). Cobalt phases were not detected in the XRD patterns like in other studies [34, 45, 46]. This effect can be explained by the presence of many modifications of cobalt, peak broadening related to crystallite shape, defects, and microstrain.

An analysis of the literature data showed that tungsten carbide loses carbon during EDE in any liquids (water, kerosene, and ethanol) and gases [34, 35, 45, 46]. The main reason for the loss of carbon by carbide is its evaporation from the melt together with cobalt. Oxygen, formed as a result of thermal decomposition of water or glycerol, and then interact with carbon on the surfaces of electrodes and particles is an additional factor leading to the loss of carbon by carbide [69].

Analysis of the carbon content showed that carbon content in the obtained powder during EDE in water decreases from 5.2% to 1.4% (figure 7). Phase analysis showed that WC turns into tungsten with a small amount of W₂C (figure 5(a)), consistent with the obtained content of carbon (1.4%).

As a result of pyrolysis, the carbon in glycerol is released in the form of gaseous compounds with oxygen and hydrogen (CO, CO₂, CH₄, and C₂H₄ [69]), reducing the loss of carbon by tungsten carbide. The phase analysis confirmed (figures 5(b)–(d)) that an increase in the volume fraction of glycerol in the solution is accompanied by an increase in the carbides content (W₂C and β-WC). The powder obtained in glycerol contains only these
carbides (W₂C and β-WC) and not a tungsten phase. With an increase in the volume fraction of glycerol in the solution from 25% to 75%, the carbon content in the obtained powders increases linearly from 3.2% to 4.6% (figure 6). The content of bound carbon in these powders comprising mixtures of W, W₂C, β-WC, and cobalt (15%) ranges from 1% to 4%, which is less than in the obtained powders, meaning that a significant portion of the obtained carbon is in free form. Carbon analysis of spherical particles separated by sedimentation from glycerol and its solutions showed (figure 7) that their carbon content (1.8%–3.1%) is about one and a half to 2 times less than in a completely precipitated powder (3.2%–4.6%). This carbon content corresponds to their phase compositions. Accordingly, these powders do not contain free carbon.

In the powder obtained by EDE in glycerol, the carbon content is 6.1%–0.9% higher than in the initial concentration (5.2%). Thus, glycerol not only prevents the loss of carbon but also partially turns into free carbon, increasing its concentration.

The phase analysis did not identify significant differences in the compositions of fully and partially sedimented powders. It means that the phases of cobalt, carbon, tungsten, and its carbides in ultrafine particles are not detected by diffraction analysis due to the presence of many modifications and high dispersity of these phases. The carbon content in the spherical particles obtained in glycerol and its solutions is 1.4%–3.0% lower than in completely precipitated powders (figure 7). This is because free carbon crystallizes in the form of ultrafine particles, on the removal of which its content decreases. The carbon content in the powders obtained in water and precipitated completely and partially differ slightly from each other. In other words, there is no free carbon in these powders.

6. Microstructure and microhardness of obtained particles

The microstructures of the surfaces (figures 8(a), (b), (e), (f)) and cross-sections (figures 8(c), (d), (g), (h)) of the spherical particles obtained by EDE in water and glycerol are very different from that of the initial cemented carbide (figure 1(a)). In the initial alloy, WC grains with an average diameter of 1.8 μm have a prismatic shape. On the surface of particles obtained in water (figures 8(a), (b)) and glycerol (figures 8(e)), (f)), rounded grains of tungsten and its carbides (β-WC, W₂C) are clearly visible, the space between which is filled with cobalt. In photographs of particle cross-sections obtained in water (figures 8(c), (d)) and glycerol (figures 8(g)), the same rounded grains are visible. Such structures are formed as a result of rapid cooling of a melt consisting of tungsten, carbon, and cobalt. The grain size is determined by the cooling rate of particles, which reaches 10⁶ K s⁻¹ on their surface [48]. The average grain diameter of different particles range from 100 nm to 500 nm. Based on the classification of hard alloys, the obtained spherical particles can be classified as UFG. Only in the center of the individual largest particles (figures 8(g), (h)) can one find dendrites comprising branches of several microns long and up to 500 nm wide. The formation of dendrites is due to the relatively low cooling rate of these particles. The average grain diameter in the particles is 320 nm.

The microhardness of the obtained spherical particles (14.6–23.7 GPa) significantly exceeds the microhardness of the initial WC–15Co alloy (12.1 GPa). The main reason for their high microhardness is a decrease in the grain size and cobalt content during EDE. An increase in the glycerol content in the solution leads

![Figure 7. Effect of volume glycerol fraction on carbon content in the obtained powders (♦ and their fractions of spherical particles (■).](image-url)
to an increase in the microhardness of the obtained particles from 14.6 GPa to 23.7 GPa (figure 9) due to an increase in the carbide content (figure 6). The microhardness of particles obtained in glycerol (23.7 GPa) exceeds the hardness of UFG alloys by 16.1–19.3 GPa [5–11] and nanostructured alloys (85 nm 20.1 GPa) [12], (65 nm–20.1 GPa) [13] containing 10% cobalt. According to the hardness model [4], a cemented carbide with an

Figure 8. Microstructures of surfaces (a), (b), (e), (f) and cross-sections (c), (d), (g), (h) of particles obtained by EDE in water (a)–(d) and in glycerol (e)–(h).
average grain diameter WC of 320 nm, containing 10 wt% cobalt should have a hardness of about 18 GPa, which is 30% higher than the hardness of particles obtained in glycerol. Even if, taking into account the size effect of indentation (10%–15%) [70, 71], the hardness of spherical particles turned out to be higher than the hardness of WC-10Co UFG alloys. The only explanation for the high microhardness of spherical particles is the presence of metastable carbide \(eta\)-WC, the microhardness of which (28–31 GPa [4, 72, 73]) is higher than that of sintered UFG \(\alpha\)-WC carbide (25–28 GPa [15]).

The powders obtained by EDE of WC-15Co alloy can be used for manufacturing UFG and sub-micron alloys. At a certain volume fraction of glycerol (about 85%), it is possible to obtain a powder with the required carbon content (5.2%). Moreover, for free carbon to return to the WC, heat treatment in the corresponding gas (\(\text{H}_2\) or \(\text{CO}_2\)) will be required. Spherical particles separated by partial precipitation from the obtained powder are distinguished by high surface cleanliness and composition homogeneity in comparison with analogs [28–33]. The carbon deficiency that appeared in the particles during EDE can be eliminated as a result of heat treatment of the obtained powder in a carbon-containing gas according to existing methods [45, 46]. The obtained hard spherical particles can be used for 3D printing and coating.

7. Conclusions

1. The study showed that EDE of WC-15Co cemented carbide in glycerol allows producing spherical \(\beta\)-WC-W\(_2\)C-Co particles carbides with high hardness (23.7 GPa).

2. An increase in the kinematic viscosity of the used liquid by 1118 times due to an increase in the volume fraction of glycerol in water solution from 0% to 100% leads to a decrease in energy costs by 2.3 times (from 28.9 to 12.3 W*h/g) and an increase in the productivity of the process by 2.2 times.

3. All the resulting powders consist of mixture of spherical microparticles with decreased cobalt content obtained by the crystallization of a molten material and ultrafine particles with increased cobalt content obtained by the crystallization of a vaporous material. The mass fraction of separated spherical particles obtained in water (average diameter 16.2 \(\mu\)m) and glycerol (average diameter 18.5 \(\mu\)m), relative to the original powder, was 75% and 82%.

4. An increase in the volume fraction of glycerol in the solution from 0 to 100% allows to increase the carbon content from 1.3% to 6.1% in obtained powder and to control its concentration, which is unattainable when using water and oils. Spherical particles obtained in glycerol consist of carbides (\(\beta\)-WC, W\(_2\)C) and cobalt. An increase in the tungsten carbides content in the particles with an increase in glycerol fraction led to an increase in microhardness from 14.6 to 23.7 GPa.

5. Rapid crystallization of the melt of tungsten carbides (or tungsten) and cobalt in spherical particles leads to the formation of rounded carbide grains with a diameter of 100 to 500 nm and dendrites, the space between which is filled with a cobalt phase. Due to grain refinement, a decrease in the cobalt concentration and hard \(\beta\)-WC carbide presence, the microhardness of the obtained spherical \(\beta\)-WC-W\(_2\)C-Co particles (23.7 GPa) turned out to be higher than the microhardness of UFG WC-10Co cemented carbides.
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