Electrochemical Processing of Tungsten-Cobalt Pseudoalloys, Receiving Tungsten Powder for Modification of Aramid Tissue

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Abstract. Electrochemical research is focused on the tungsten extraction during acid electrochemical treatment of WC-Co pseudoalloy in chloride solutions. The target resulted products of the treatment are: tungsten oxide (VI), tungsten powder with a given particle size distribution (2…3 μm). Based on the analysis of kinetics, the mechanism of dissolution of the WC-Co pseudoalloy in a solution of 2.5 mol·dm^{-3} HCl and with the addition of HF was proposed. It was found that a well-soluble higher tungsten chloride is formed on the surface of the pseudoalloy, which is eventually hydrolyzed in aqueous solution to form tungsten oxides. The dispersion control levers were investigated and the technological parameters of obtaining tungsten metal powder from low-temperature ionic alloys (NaCl-KCl-CsBr-NaF) were determined, which make it possible to obtain tungsten metal powder of a given particle size distribution. It is stated that the use of tungsten powder (W or WO_3) for the modification of aramid fiber can significantly increase the heat resistance of aramid fabric and reduce its wear.

1 Introduction

Tungsten is a strategic metal for Ukraine and is widely used in the metallurgical, machine-building and military-industrial complex. Current demands are satisfied through import, and at the same time there is an accumulation of tungsten-containing scrap. Such scrap metal can contain up to 99 % tungsten, which can be recovered and returned to production. The most widely used in Ukraine is the pseudoalloy of tungsten carbide type WC-Co (soldering, drills, etc.), where the WC content ranges from 90 to 94 %, and the rest is the binding metal of the subgroup iron - cobalt. [1, 2].

Analysis of existing methods of recycling has shown that the use of electrochemical methods is more promising because they allow you to control the composition of the final product and its purity.

There is a widely known technology of fluorination [3] and chlorination [4] of secondary raw materials containing tungsten and molybdenum are known. This method provides oxidation of tungsten or its compounds by halogens and allows the selective separation of tungsten and other components, as the method is based on the volatility of chlorides and fluorides of tungsten. However, this process is energy-intensive, as for the processing process it is necessary to ensure a temperature of at least 500 K, which requires increased safety measures, due to the use of halogens, which are aggressive to the environment. And the use of fluoride also causes complications due to its high cost. The authors of the patent [5] propose treatment of materials with low content of

tungsten and molybdenum by chlorination with chlorine gas at room temperature in the presence of dimethylformamide, with a mass ratio of dimethylformamide and chlorine equal to 1: (20...25): (25...30). The basis of the method is the extremely high solubility of chlorine in dimethylformamide, which allows to create a liquid medium saturated with it and to ensure the course of the hydrochlorination process [6, 7]. The proposed technology allows the process to be carried out in one stage and does not require external heat supply but reaches only up to 70% of the degree of extraction of tungsten. More efficient is the multistage technology, which is designed for processing the grinding sludge of the following composition, %: 78.67 WC; 10.13 Co; 1.68 SiC was proposed by the authors [8, 9, 10] and it allows to obtain a 88 % yield of tungsten trioxide. Also, these authors have developed a technology for processing low-grade sludge containing, %: 12…28 WO_3; 4.0 Mn; 3.2…4.2 Ca; 2.2…3.5 As; 1.3 Fe; 0.28…0.40 Mo, and proved the possibility of obtaining high-purity ammonium paravulfrate (PVA) by hydrometallurgical method. The method includes two-stage treatment in an alkaline environment. In the first stage, about 70 % of the tungsten converts into solution. After removal of Sn, Si, As, P from the solution, molybdenum is extracted from it by liquid extraction or sorption. The yield of tungsten is 90 %. Therefore, due to the two-stage process, selective separation of the alloy components is achieved, but to obtain tungsten metal, it is necessary to conduct additional chemical reactions (precipitation, hydrogen reduction), which leads to a significant increase in the cost of the process. The authors of the patent [5] proposed a method of extracting refractory metals, including tungsten, from superalloy scrap by decomposing the scrap in saline mixture containing 60 to 95 wt.% NaOH and 5 to 40 wt.% Na_2SO_4. When the solution is cooled down to room temperature, the decomposition product of the scrap converts into a solid phase. The solid is ground, and treated with water at a temperature of ~ 80 °C to get an aqueous suspension, which is subjected to filtration. Tungsten, tantalum and rhenium are extracted from the aqueous phase by known methods. However, chemical processing methods are multi-stage and require high costs of both reagents and resources. The alternative is to use electrochemical methods, which provide a high yield of the substance at much lower cost. Among the known methods of dissolving tungsten-based alloys is the method of anodic treatment in alkaline electrolytes.

The following types of alkaline electrolytes are used: electrolytes based on alkalis (NaOH, KOH) [11, 12, 13], ammonia electrolytes [14, 15, 16], polyligand alkaline electrolytes. In alkaline and alkaline-ammonia electrolytes, tungsten is electrochemically oxidized to tungstate ion WO_4^{2-}. The yield of oxidation reactions is about 100 %. The electrolyte is saturated to a concentration of tungsten (VI) oxide of 280...290 $g \cdot dm^{-3}$, which corresponds to 343...355 $g \cdot dm^{-3}$ ammonium tungstate. Due to the low electrical conductivity of pure concentrated ammonia solution, salts are added to the initial solution in order to improve its electrical conductivity, which increase the electrical conductivity of the electrolyte and which are easily removed by hydroelectrometallurgical methods during its processing. Higher tungsten oxide is reduced to tungsten metal in a hydrogen atmosphere or electrochemically from ionic melts. And although the proposed method allows the selective release of tungsten, it requires the use of aggressive reagents, as well as energy-intensive reduction process. The disadvantage of this method is the need to use special corrosion and temperature resistant equipment, which significantly increases the cost of the process. Despite the information available in the literature on technologies for processing tungsten waste, they all have drawbacks. The proposed method of electrochemical dissolution of tungsten carbide - cobalt pseudoalloys in acid chloride solutions, as well as the above mechanism of reactions determines the relevance of the studies presented in this paper. Review of the sources [2, 8, 9] indicates that the electrochemical processing of alloys can be carried out in several ways:

1. In solutions of mineral acids, in particular, 200…250 $g \cdot dm^{-3}$ HNO_3 + 80...120 $g \cdot dm^{-3}$ HF; 300...400 $g \cdot dm^{-3}$ H_2SO_4 + 80...120 $g \cdot dm^{-3}$ HF. This method is designed for the selective separation of alloys, in particular W-Nb. At the same time niobium transfers into solution, tungsten does not dissolve. Electrolysis is carried out at a potential of 0.3...0.45 V relative to the silver chloride reference electrode [17, 18]. Before electrolysis, the raw material is being ground. However, the use

of high concentrations of acids, the toxicity of fluorine compounds, the need for grinding of secondary raw materials limit the use of this method.

2. In solutions of mineral acids of low concentration (1...2 mol·dm^{-3}) [19]. This technology is the most applicable for electrochemical processing of pseudo-alloys of tungsten carbides containing cementing metals of the iron subgroup. Depending on the value of the electrode potential, it is possible to selectively electrochemically dissolve metals - impurities (iron, nickel, cobalt, copper) or to oxidize tungsten carbide to tungsten oxides with simultaneous dissolution of the binder metal [19].

In [11], the high-speed dissolution of heat-resistant chromium-nickel alloys containing tungsten and rhenium in chloride solutions was investigated. It was found that the process can be carried out by dissolving in the active (anode-activated) region of potentials (at a current density less than the limiting current density of salt passivation, due to the concentration of dissolution products on the main component (Nickel), saturation concentrations and salt film formation): a) the difference in the dissolution rates of alloys with different tungsten content; b) the increasing dependence of the current output on the density. The disadvantages of these methods are the insufficient efficiency of the process, because the yield of the target substance (tungsten) does not exceed 90 %.

The distribution of cobalt and tungsten carbide by anodic dissolution of hard alloys of the VK-6 type in solutions of 1.25 mol·dm^{-3} of phosphoric acid was performed in [12]. The advantage of this technology is the minimum energy consumption, the disadvantage is the difficulty of selective separation of alloy components. In [13] it was shown that when processing waste of hard alloys of VK and TTK brands in nitric acid solutions under the influence of alternating sinusoidal current, the current yield per WO_3 does not exceed 19…22 %, which is lower than the corresponding figure (67 %). in comparison with electrolysis in a normal mode at a constant electric current. According to the authors of this paper, this may be due to the mechanism of electrochemical transformations of these wastes, studied in detail in the other researches. According to the results of these researches, the electrolysis of tungsten carbide in a solution of nitric acid in sinusoidal mode occurs through its anodic oxidation:

$$WC + 5H_2O \rightarrow WO_3 + CO_2\uparrow + 10H^+ + 10e \tag{1}$$

and cathodic hydrogen evolution according to the reaction:

$$2H^+ + 2e^- \rightarrow H_2\uparrow. \tag{2}$$

Processing of tungsten-containing waste in acid solutions can greatly simplify the process due to the selectivity of the separation of alloy components, as well as the ability to obtain precipitates of tungsten compounds (WO_3) without its transfer to solution.

The aim of research is an exposure of features of electrochemical anodic behavior of pseudoalloy of WC-Co for development of effective method of his dissolution, receipt of tungsten oxides, and also electrosynthesis of tungsten powder with certain grain-size distribution. It has been offered to apply the tungsten powder for the receipt of heat-resistant aramid fiber.

2 Experimental

Tungsten secondary raw materials were used for the experiments, in particular WC-Co pseudoalloy bars with dimensions of 15 cm × 0.7 cm. The solutions used in the anode process had a variable concentration of hydrochloric acid of 1…5 mol·dm^{-3} without and with the addition of HF. The following equipment was used for the experiment: potentiostat – P-45X; anode – WC-Co alloy, cathode – tantalum plate; reference electrode – saturated silver chloride electrode EVL-1M3; magnetic stirrer MM-M3; pH-meters pH-150M; X-ray diffractometer type DRON-2; Study of electroreduction of fluor-oxide complexes of tungsten is based on triple eutecticum of chlorides of

sodium, potassium, cesium of next composition: 18.3 wt.% of KCl, 13.5 wt.% of NaCl; 72.0 wt.% of CsBr and NaCl–KCl–CsBr–Na$_3$WO$_3$F$_3$ at content of sodium fluoride up to 10 wt.% and the temperature of 500…600 °C; analytical scales VLR-200, 2 class, GOST 19491-74; electric drying cabinet 2B-151; muffle furnace; rheostat type PHO 250-2; DC and reverse current source series B5-43; electronic microscope OptikaXDS-3MET; desktop energy dispersive X-ray fluorescence spectrometer "ElvaX".

3 Results and discussion

Analysis of the anodic dissolution of the pseudoalloy VK-6 in hydrochloric acid was performed by varying its concentration and with the addition of HF to the electrolyte composition. During the experiment, using the X-ray diffraction analysis, it was also established the quantitative process characteristics and determined the composition of the obtained reaction products.

The anodic behavior of the sample in HCl solutions of different concentrations is shown in Fig. 1.
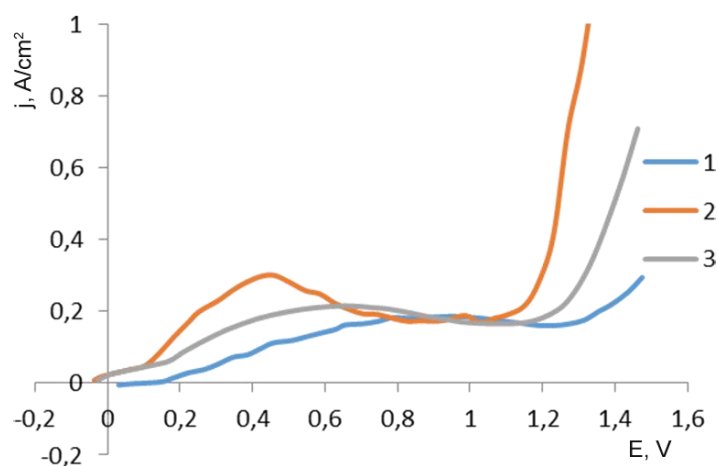

Fig. 1. Polarization dependence of dissolution of pseudoalloy WC-Co in HCl solutions of different concentration, mol·dm^{-3}: 1 – 1; 2 – 2.5; 3 – 5

It was found that the best dissolution rates are observed in a solution of 2.5 mol·dm^{-3} HCl (Fig.1, 2). At a concentration of 1 mol·dm^{-3} HCl, the process kinetics is too slow, because the electrode surface is covered with a layer of tungsten chloride, which blocks further oxidation. Increasing the concentration to 5 mol·dm^{-3} HCl also does not show a positive effect on the value of the limiting current density.

The polarization lines of the dissolution of the alloy in hydrochloric acid (Fig. 1) show several areas: the first in the range of potentials from 0.1 to 0.8 is the dissolution of the metal–bonds (cobalt), oxidation of carbon to CO$_2$, and the conversion of tungsten oxides from lower to a higher degree of oxidation. Second, when the current limit density is reached, the electrode is passivated by tungsten semiconductor oxide. At potentials more positive than 1V, the electrode surface is re-passivated with the release of gaseous products. Thus, the dissolution of tungsten pseudoalloys of the carbide type WC-Co occurs according to the solid-phase multi-surface mechanism.

One of the main features of the electrochemical behavior of a pseudoalloy is its anodic ionization through a nonmetallic solid phase, i.e. during anodic polarization tungsten does not convert into solution in the form of simple ions, but forms surface films. The study of the anodic polarization of the WC-Co system, which consists of 92 % of tungsten coated with a natural oxide film in HCl-based electrolytes, allows us to offer a fundamentally new explanation of the mechanism of the reactions. In electrolytes that do not contain halogen ion, the anodic reactions on tungsten are accompanied by

the formation of a phase oxide having semiconductor properties. The formation of oxide occurs as a result of the transfer of matter and charge through it. Tungsten behaves differently in an electrolyte solution that chemically interacts with it. Films obtained in halogen-containing electrolytes serve as sources of hole conductivity. By interacting with the surface oxide, activating ions significantly increase the concentration of non-basic carriers, which increase the rate of dissolution of the metal due to the formation of oxyhalides, which are hydrolyzed to form WO_3. The results of radiographic analysis of the samples are shown in Fig. 2.
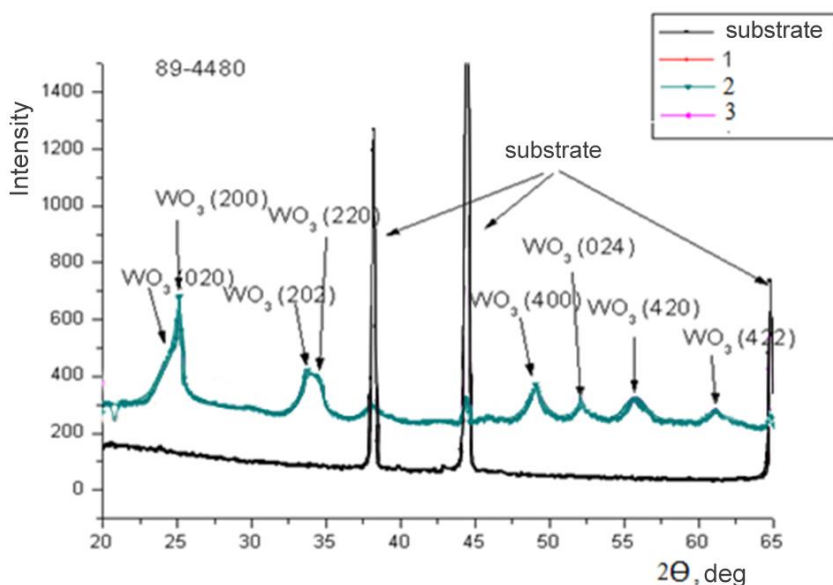

Fig. 2. X-ray analysis of samples obtained in a mixture of HCl-HF

Therefore, when dissolving the WC-Co pseudoalloy in hydrochloric acid, higher tungsten chloride is formed on the surface of the anode, which is well soluble in aqueous solution and has poor adhesion to the surface. However, using research methods, it was found that the oxidation of the main component of the pseudoalloy WC-Co, namely – tungsten, occurs with the formation of oxyhalides.

At a current density of 0.351 A·cm^{-2}, a dark purple (Fig. 3) film of tungsten chloride is formed, which is eventually hydrolyzed in water to form tungsten oxides (Fig. 4).

Inhomogeneous color of the precipitate indicates the presence of underoxidized tungsten compounds. Introduction of additives with oxidizing properties into the hydrochloric acid solution can help the process of oxidation of tungsten to higher oxide to take place in full. For further experiments, it was chosen to add fluoric acid to the hydrochloric acid solution.
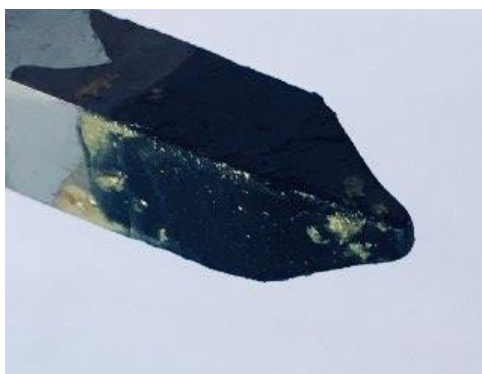

Fig. 3. Anode material after treatment with 2.5 mol·dm^{-3} HCl, treatment time 15 min
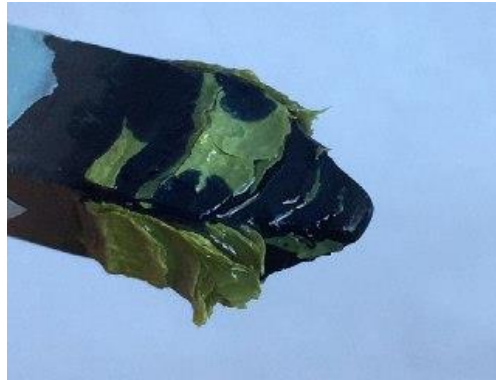
Fig. 4. Anode material after treatment with 2.5 mol·dm-3 HCl, treatment time 45 min

To determine the effect and optimal concentration of fluoric acid on the process of dissolving WC-Co alloy in a solution of 2.5 mol·dm^{-3} HCl investigated the anodic behavior of the system at different concentrations of HF.

Fig. 5 suggests that when 2.5 mol·dm^{-3} hydrochloric acid is mixed with HF additive at a concentration of 0.4 to 1 mol·dm^{-3}, the most noticeable effect has the addition of 1 mol·dm^{-3}. In this case, there is a significant potential shift towards more electropositive values, which may be associated with the formation of tungsten chlorides on the anode surface, and at potentials more positive than 1 V there is a significant increase in the rate of anodic dissolution of WC-Co.

Since the addition of HF when dissolving the pseudoalloy in hydrochloric acid significantly intensifies the process, quantitative indicators of the process were determined (Table 1).
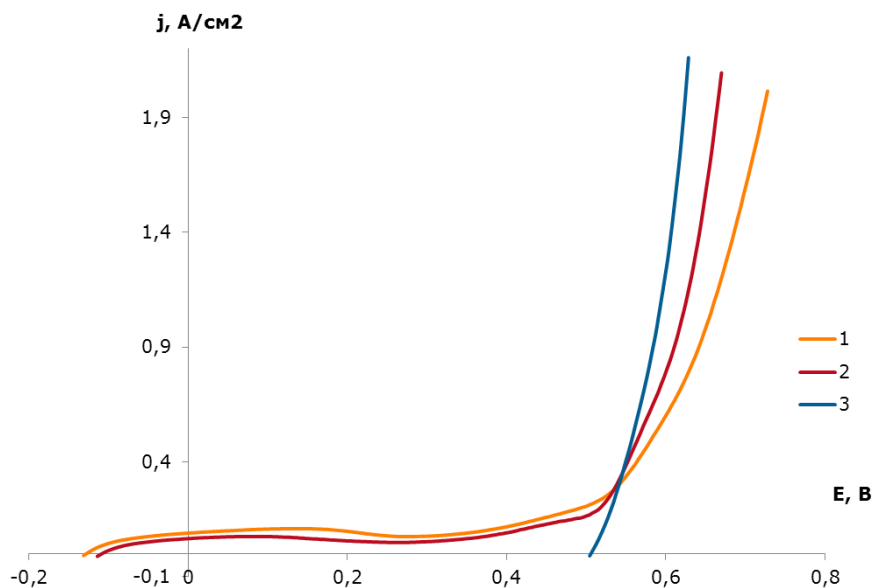

Fig. 5. Polarization dependence of dissolution of WC-Co alloy in 2.5 mol·dm^{-3} HCl with addition of HF, mol·dm^{-3}: 1 – 0.4; 2 – 0.6; 3 – 1

Analysis of surface samples, according to different modes of anode treatment allow to determine possible mechanism of the occurring processes. It turns out that chlorine gas (Cl_2) and oxygen formed as a result of anodic dissolution of the alloy WC-Co, are actively involved in the formation of the product. Thus, at a current density of 0.351 A·cm^{-2} a dark purple film of tungsten chloride is

being formed, which is hydrolyzed in water with the formation of oxychlorides $WOCl_4$ according to the equation:

$$W^{4+} \rightarrow [WO_2Cl_2]^- \rightarrow W^{6+}; \quad (3)$$

$$W^{4+} \rightarrow [WO_2F_4]^{2-} \rightarrow W^{6+}. \quad (4)$$

As a result of electrochemical processing of the pseudoalloy WC-Co in acid solutions, insoluble precipitates of tungsten oxides of various oxidation states were obtained. They can be used as a raw material for the production of tungsten metal powder. Therefore, the aim of the research was also to electrochemically reduce tungsten in the form of powder from chloride and chloride–fluoride mixtures and to determine the factors influencing its dispersion [14].

Table 1. Influence of composition of electrolyte on the efficiency of anodic dissolving of pseudoalloy

Electrolyte composition, [mol·dm^{-3}]	Current density, [A·cm^{-2}]	Materials yield, [%]
2.5 HCl	0.4	65
2.5 HCl + 1 HF	0.4	99

The electrical reduction of tungsten fluorine oxide complexes was analyzed against the background of the triple eutectic of sodium, potassium, and cesium chlorides of the following composition: 18.3 wt.% KCl, 13.5 wt.% NaCl; 72.0 wt.% CsBr and NaCl–KCl–CsBr–Na$_3$WO$_3$F$_3$ at a sodium fluoride content of up to 10 wt.%, The operating temperature was 500…600 ºC.

The process of electron reduction of fluorooxide tungstate ions in the NaCl–KCl–CsBr mixture can be represented as follows:

$$WO_2F_4{}^{2-} + 6e \rightarrow W + 2O^{2-} + 4F^-; \quad (5)$$

$$WOF_6{}^{2-} + 6e \rightarrow W + O^{2-} + 6F^-. \quad (6)$$
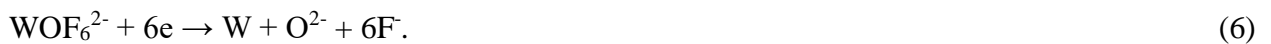
The ratio of concentrations of electroactive particles $WO_2F_4{}^{2-}$ and $WOF_6{}^{2-}$ should depend on the concentration of fluoride ions in the mixture.

The morphological analysis of the sediments structure [15] during electrolysis of a melt with a high content of $WO_2F_4{}^{2-}$ has shown that tungsten is released as a fine powder.

In addition to the target processes (5) and (6), the electroreduction of fluoroxide tungstate ions is accompanied by rapid irreversible chemical reactions in the electrolyte.

In addition, rapid irreversible chemical reactions can occur in the electrolyte.

$$WO_2F_4{}^{2-} + 2O^{2-} \rightarrow WO_4{}^{2-} + 4F^-; \quad (7)$$

$$WOF_6{}^{2-} + O_2 \rightarrow WO_2F_4{}^{2-} + 2F^-; \quad (8)$$

$$WOF_6{}^{2-} + 3O^{2-} \rightarrow WO_4{}^{2-} + 6F^-. \quad (9)$$

Increase of the concentration of F-ions leads to an increase of $WOF_6{}^{2-}$ concentration:

$$WO_2F_4{}^{2-} + 2F^- \leftrightarrow WOF_6{}^{2-} + O^{2-}. \quad (10)$$

It was found that during the electrolysis of a mixture with a high content of $WO_2F_4^{2-}$ tungsten is released in the form of a fine powder. Reduction of tungsten from the electrolyte with high content of WOF_6^{2-} is accompanied by deposition of coarse solid layers. Thus, by changing the concentration of F^--ions in the melt, it is possible to control the dispersion of the tungsten precipitate.

The following factors contribute to the production of fine tungsten powders: temperature increase, use of pulse modes and high current density, especially in the initial period.

The study of the morphology of tungsten powder samples allowed to determine the numerical grain sizes. It was found that the main grain size is up to 20…30 μm (Fig. 6).

To increase the number of nuclei on a cathode surface followed by the formation of fine powders, the current density must be increased from 1.0 to 12.0 A·cm^{-2}.

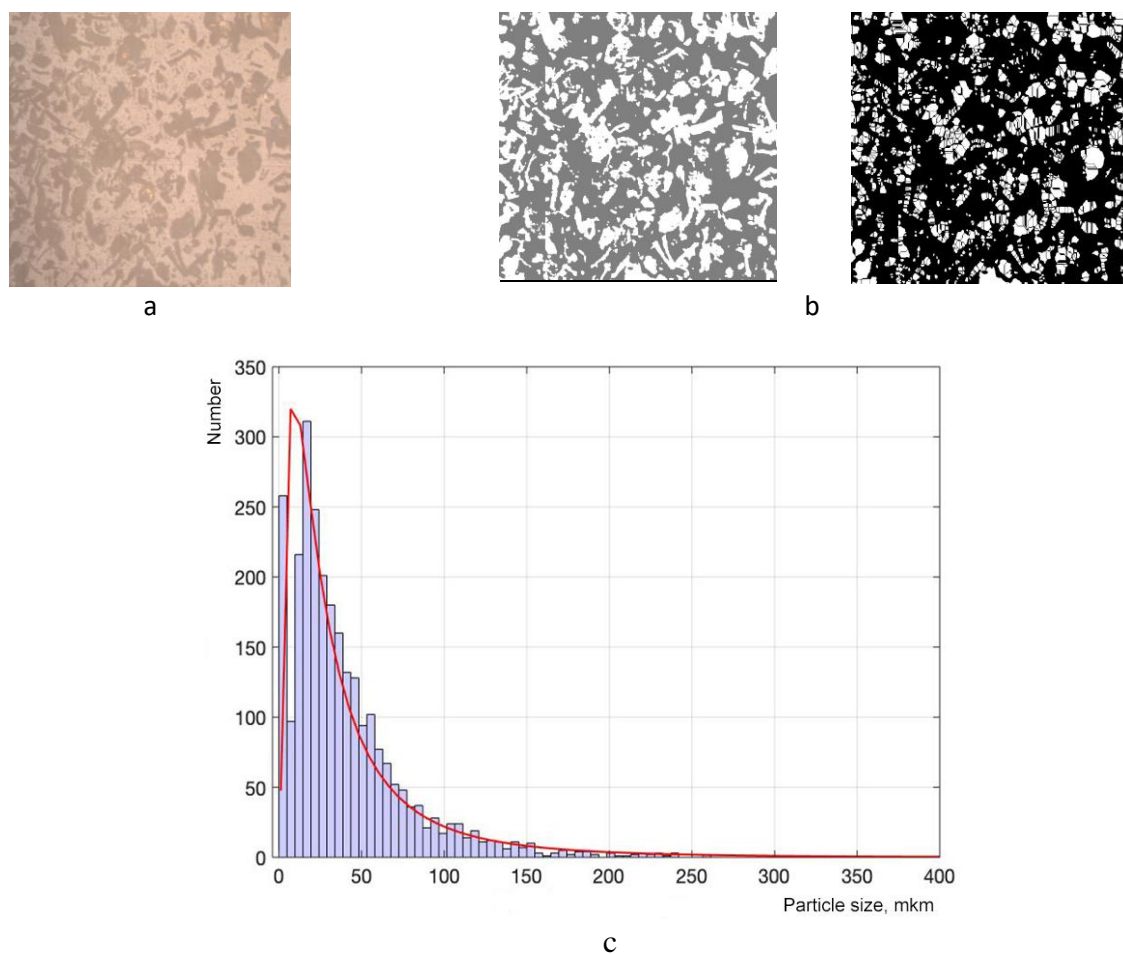a   b

c

Fig 6. The Morphological analysis of tungsten: a – an initial image (×200); b – a sequence of image processing; c – histogram of distribution of tungsten powder particles according to their size

The 99.99 % purity of the obtained tungsten powder was confirmed by X-ray fluorescence analysis. Thus, it was proposed a relatively inexpensive and effective method of producing tungsten powders from various industrial waste, military bases and metallurgy. With sufficient simplicity and efficiency, the method allows to produce high-purity powder metals to create high-tech materials.

Based on the research, a method of modifying aramid fabric with tungsten powder or higher tungsten oxide is proposed. It was found that the application of aramid fiber in the amount of 10 wt.% W or WO_3 allows to increase 3 times the heat resistance of aramid fabric and 6 times to reduce the total processing time, relative to the method of magnetic sputtering [16]. In addition, the

introduction of tungsten powder or higher tungsten oxide in the fiber of the aramid fabric can significantly reduce the wear of such material.

4 Conclusions

Based on the analysis of kinetic and other methods, the mechanism of dissolution of WC-Co pseudoalloy in a solution of 2.5 mol·dm^{-3} HCl and with the addition of HF is proposed. It was found that a well-soluble higher tungsten chloride is formed on the surface of the pseudoalloy, which is eventually hydrolyzed in aqueous solution to form tungsten oxides. It was found that when adding up to 2.5 mol·dm^{-3} HCl to the HF depositor (1 mol·dm^{-3}) the dissolution efficiency of the pseudoalloy is 99 %. The final product of the pseudoalloy processing is WO$_3$.

Indicators of electrochemical synthesis of tungsten powder of a given particle size distribution are determined. It was found that during the electrolysis of a molten electrolyte with high content of WO$_2$F$_4^{2-}$ tungsten is released as a fine powder, and during electrolysis of a molten electrolyte with a high content of WOF$_6^{2-}$ – it's released as a coarse powder. To produce fine powders with the size of 2-3 μm the current density must be increased from 1.0 to 12.0 A·cm^{-2}.

The method of using the obtained tungsten powder (W or WO$_3$) for modification of aramid fabric is indicated, which allows when applied to aramid fiber tungsten powder or higher tungsten oxide to increase significantly the heat resistance of such material and reduce its wear.

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