# INNOVATIONS AND PROSPECTS IN MODERN SCIENCE

Proceedings of IV International Scientific and Practical Conference

Stockholm, Sweden

10-12 April 2023

**Stockholm, Sweden**

**2023**

# ENVIRONMENTALLY CLEAN WAY OF OBTAINING VALUABLE RAW MATERIALS FROM PRODUCTION WASTE, OCCURRING IN ORTHOPHOSPHORIC ACID SOLUTIONS AND AT HIGH TEMPERATURE SELECTIVE EXTRACTION OF TUNGSTEN

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**Introduction.** Tungsten carbide is one of the most important carbide and catalytically active compounds. Currently, more than 60% of the processing of these metals is used to obtain carbides. In industry, tungsten carbide is obtained in two ways: metal carbidization and aluminometric reduction of ores and concentrates [1]. Both methods involve a significant number of time-consuming and complex steps. The production of tungsten carbides by high-temperature electrochemical synthesis from melts is at the level of semi-industrial tests [2].

Hard alloys tungsten carbide - cobalt were the first metal-ceramic hard alloys that received industrial application. In order to return valuable components of hard alloys to production, it is necessary to find the possibility of processing secondary waste containing these components. For the production of hard alloys, matrices of used drilling and cutting tools can be used. Due to the shortage of tungsten and cobalt in recent years, the development of new methods for processing lumpy hard alloy waste is very relevant.

The existing methods for isolating the components of hard alloys differ from each other not only in the mode of processing, but also in the nature of the chemical reagents used. Therefore, it is relevant to develop methods that will allow the processing of waste hard alloys tungsten carbide-cobaltate to obtain a high percentage of output $WO_3$.

**Aim.** Studying the separation process of cobalt and tungsten carbide by anodic dissolution in orthophosphoric acid solutions and studying the selective high-temperature extraction of tungsten from the corresponding concentrates and in order to determine the most technological parameters of the conditions (temperature, melt composition, extraction duration) of the process.

**Materials and methods.** To isolate tungsten compounds from ores and concentrates, also in the processing of waste hard alloys, the decomposition method in various acids is usually used, which is environmentally hazardous due to the toxicity of the reagents used. Selective high-temperature extraction in nonaggressive salty melts can be proposed as an alternative method [2, 3].

**Results and discussion.** Due to the shortage of tungsten and cobalt in Ukraine, the issues of developing new methods for processing lumpy hard alloy waste are very relevant [2-4]. For the practical implementation and control of complex processes of interaction between the structural parts of the melt, which occur during the precipitation of tungsten carbide, for example, by the method of high-temperature selective extraction, it is important to purposefully choose the composition of the electrolyte, without conducting preliminary electrochemical studies. This, in turn, requires knowledge of the nature and mechanism of formation of electrochemically active melt particles directly involved in multielectron electroreduction processes.

Therefore, to determine the nature of electrochemically active particles and the conditions for the implementation of multielectron processes at the electrode electrolyte interface, it is advisable to use modern quantum chemical methods that allow one to simulate the process of formation and electrochemical reduction of electrochemically active particles at the electronic level.

The great propensity of tungsten and its carbide to passivation in aqueous solutions determines the specifics of its electrochemical behavior. Electric potentials, cathodic processes in the course of electrical gas evolution and oxidation processes with their participation were studied mainly in solutions of hydrochloric and sulfuric acids. The electrochemical evolution of hydrogen on tungsten carbide was studied in [6]. The authors believe that the release of hydrogen on WC is limited by the recombination of adsorbed hydrogen atoms. According to [7, 8], the shape of the anodic polarization curves of tungsten in sulfuric acid solutions corresponds to the transition of active dissolution to the passive state of the metal.

To confirm the proposed mechanism of dissolution, VK-6 rods were anodically dissolved at different potential values corresponding to segments I and II of the polarization curves and the duration of dissolution. The results of the analysis of the obtained solutions are summarized in table. 1[6].

**Table 1.**

**The rate of dissolution of cobalt and tungsten depending on the potential of the electrode from VK-6. $H_3PO_4$ concentration = 1.25M, T=18°C**

| Electrode potential, *V* | Test duration, *h* | Cobalt dissolution rate, *g/m²h* | Tungsten dissolution rate, *g/m²h* | Mass fraction of tungsten, *% mass* |
|---|---|---|---|---|
| *1* | *2* | *3* | *4* | *5* |
| 0,33 | 30 | 0,095 | *) | - |
| 0,25 | 20 | 3,419 | *) | - |
| 0,20 | 20 | 10,652 | 1,391 | 11,3 |
| *1* | *2* | *3* | *4* | *5* |
| 0,15 | 20 | 18,006 | 2,876 | 12,6 |
| 0,10 | 10 | 25,556 | 4,571 | 14,1 |
| 0.05 | 10 | 28,373 | 5,319 | 14,2 |
| 0,80 | 5 | 16,625 | 48,315 | 87,9 |

*) - below the sensitivity limit of atomic absorption spectroscopy for tungsten analysis.

A three-electrode system was used to study the anodic dissolution of electrodes made of WC-Co alloy, cobalt metal, and tungsten carbide WC. A 1.25 M solution of orthophosphoric acid H, PO served as the working electrolyte; hard alloy electrodes were WC-6% Co(BK-6) rods obtained by conventional powder metallurgy technology [4].

The high manufacturability of high-temperature selective extraction is due to two circumstances:

– the ability of sodium tungstate to mix with sodium chloride in any ratio [7, 8];

- miscibility of the silicate phase, having a melting point below 1000°C, with halide-tungstate.

The most efficient way of processing shelite concentrates is the selective high-temperature extraction of its mixture with wolframite in ratios from 1:4 to 2:1. The use of these mixtures makes it possible to carry out the process of selective high temperature extraction without the introduction of fluxes (usually in the form of alkaline earth metal fluorides and aluminum oxide, which is necessary in the processing of scheelite [7, 8].

**Conclusions.** The use of phosphoric acid solutions as an electrolyte, in contrast to molten media, makes it possible to selectively separate the hard alloy components and isolate tungsten carbide suitable for return to production. It is shown that tungsten ores and concentrates at a temperature of 1050-1100°C decompose in sodium chloride-sodium metasilicate melts, forming two immiscible phases: halide tungstate and silicate. The first contains 96-99% tungsten, the second - more than 90% of various components.

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