Electrochemical processing of heavy tungsten alloy wastes for obtaining a microdispersed iron-nickel base powder by using alternating current

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Abstract. Electrochemical processing of heavy tungsten alloy wastes (wt.%: W 78.8, Ni 15.2, Fe 6.0) under the cyclic use of direct and alternating current in ammonia-alkaline solutions has been investigated. High dissolution rate of alloy wastes, as well as degree of tungsten extraction, has been provided. The electrochemical process has been accompanied by production of microdispersed iron-nickel powder, that contains up to 2 wt.% tungsten.

1. Introduction
Tungsten recycling from secondary tungsten-containing raw materials and wastes is extremely important task to meet the demand for this metal. About 8% of the world's tungsten reserves are concentrated in Russia and its consumption is constantly growing in strategically important industries [1]. Tungsten base waste alloys are becoming one of the most important sources of this metal [2, 3]. The processes of obtaining pure tungsten and its compounds are of particular importance when processing tungsten-containing scrap. Moreover, hydrometallurgical methods are very widely used [3-6]. It should also be noted, that the electrochemical dissolution of tungsten base heavy alloys in alkaline and ammonia-alkaline electrolytes is an environmentally safe method for extracting this metal, which is characterized by high current efficiency and the degree of target component extraction in solution [7-9].

It was previously found [7], that the electrochemical dissolution of the VNZh alloy in alkaline-ammonia electrolytes occurs at a rate of about 0.57 kg/m²·h with a current efficiency close to 100% and a low specific energy consumption of 1.51 kW·h/kg. However, the complexity of tungsten base heavy alloys processing lies in the need to renew the surface of the material to be dissolved. This is due to the fact, that in addition to tungsten, nickel and iron are also included in the composition of the VNZh alloy. Metals of the iron group are passivated in alkaline solutions, reducing the efficiency of the electrochemical process. The renewal of the processed alloys surface can be organized using a complicated electrolyzer design, including, for example, vibrating or rotating anode baskets [10, 11]. The most rational way is the using of alternating electric current for this purpose. According to the authors [12, 13], the action of alternating current on metal nickel and iron electrodes in alkaline solutions leads to their destruction with the formation of fine powders of these metals in an oxidized form. Tungsten, as well as a number of its alloys, can dissolve in alkaline solutions under the influence...
of alternating current, but this process is accompanied by a decrease in the current efficiency in comparison with using direct current [14-17].

The using of alternating sinusoidal current in electrochemical heavy tungsten alloy wastes processing in ammonia-alkaline solutions is investigated in this work. The possibility of obtaining a fine iron-nickel base powder in this process is studied.

2. Experimental part

Electrochemical processing of VNZh alloy wastes (wt%: 78.8 W, 15.2 Ni, 6.0 Fe) under the cyclic using of direct (DC) and alternating current (AC) was carried out with the aid of setup, shown in Figure 1. Two VNZh alloy wastes electrodes with a fixed surface area and one glassy carbon electrode were installed in the electrochemical cell. Two VNZh alloy electrodes were used as anodes and a glassy carbon electrode - as a cathode in the electrolysis process under the influence of direct current. Dissolution of VNZh alloy wastes by direct current was carried out according to the method [7] in a galvanostatic mode at a current density of 50 mA/cm². The electrolyte was a solution, containing NaOH 2M + NH₄OH 4M. The studies were carried out in a thermostatically controlled cell at a temperature of 20°C. The oxidation rate of the VNZh alloy was determined by the weight loss of the electrodes. When weight loss of the electrodes was < 0.05 kg/m²·h, the direct current was turned off and the glassy carbon cathode was removed. Then an alternating electric current of industrial frequency (50 Hz) was connected to the VNZh alloy electrodes. The exposure time ratio of alternating and direct current was ~ 1/10. The current efficiency of the alloy was calculated assuming the formation of (WO₄)²⁻ ions in the solution.

The morphology and composition of the electrolysis sludge, resulting from VNZh alloy wastes processing, were investigated, using scanning electron microscopy (SEM) and X-ray microanalysis, a Carl Zeiss NVision 40 microscope, equipped with an Oxford Instruments X-Max analyzer (80 mm²). This research was performed using the equipment of the JRC PMR IGIC RAS.

When the alloy is polarized by direct current, a high extraction of tungsten in electrolyte (more than 99%) is achieved with the current efficiency close to 100% and the alloy dissolution rate - to 0.6 kg/m²·h. At the same time, oxidation of VNZh alloy wastes under the influence of direct current in ammonia-alkaline solutions is characterized by electrode passivation. The oxidation rate of the alloy wastes decreases due to the formation of iron and nickel oxides on the surface of the anode. During the action of alternating current on the processed alloy, the surface of the alloy is depassivated with the concentration of nickel and iron in the electrolysis sludge in the form of a fine powder at a rate of ~ 0.1 kg/m²·h with a current efficiency ~ 20%. Polarity change of the current causes alternate oxidation and reduction of nickel and iron oxides when using alternating current. This leads to the loss of their

![Figure 1. Schematic of the setup for electrochemical processing of VNZh alloy wastes under the influence of direct and alternating current: 1 - VNZh alloy wastes; 2 - glassy carbon electrode; 3 - electrochemical cell housing.](image)
contact with the metal surface and crumble as electrolysis sludge [12, 13].

The microanalysis results of electrolysis sludge powder particles, obtained by electrochemical processing of VNZh alloy wastes by direct and alternating current, are shown in Figure 2. The average content of elements in the electrolysis sludge powder, analyzed at five points, was, wt. %: O - 61.80, Ni - 28.92, Fe - 6.35, W - 1.83, Al - 0.60, Ca - 0.29, C - 0.21. It can be seen, that the main components of the sludge are nickel, iron and tungsten. These components are predominantly in the oxide form, which is consistent with the data of the authors [13, 17]. Such a composition of the sludge suggests the possibility of their use in catalytic processes [18]. Further electrolyte processing in order to obtain tungsten in the form of its compounds (tungstic acid, ammonium paratungstate, calcium tungstate, etc.) can be carried out by known methods.

Thus, as a result of electrochemical processing of heavy tungsten alloy wastes, on the example of VNZh alloy wastes, with the influence of direct and alternating current it is possible to receive not only the main valuable product - pure tungsten salts, but also microdispersed iron-nickel base powder, containing up to 2 wt.% tungsten. Determination of electrolysis conditions, providing the smallest particle size of sludge powder, as well as their subsequent processing (carbon removal, hydrogen reduction, etc. [18]) for the purpose of using in catalytic processes requires further research.

![Figure 2. X-ray spectral microanalysis (a) and micrograph (b) of microdispersed iron-nickel base powder, obtained by electrochemical processing VNZh alloy wastes under the influence of direct and alternating current.](image)

3. Conclusions

It has been established that, the cyclic using of direct and alternating electric current during electrochemical processing of VNZh alloy wastes in ammonia-alkaline solutions leads to dissolution of tungsten with the further obtaining of pure tungsten salts by traditional technologies. The formation of microdispersed electrolytic sludge powder, based on nickel and iron oxides and containing up to 2 wt.% tungsten, that accompanied this process, has been revealed. Microdispersed electrolytic sludge powder can be directed to the extraction of valuable components by methods known or used in catalytic processes.
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