Electrochemical recycling of nickel-cobalt-containing tungsten alloys

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Abstract. The potentiodynamic method of linear scanning voltamperometry and chronopotentiometry have been used to investigate the electrochemical dissolution of VNZhK alloy (wt.%: W 90, Ni 7.2, Fe 1.8, Co 1), VNZh alloy (wt.%: W 90, Ni 7, Fe 3), as well as their components in alkaline-ammonium solutions. The high anode current density of tungsten (~700 mA/cm²), the passivity of iron and the similarity of nickel and cobalt anode behavior in the studied electrolytes were revealed. A higher electrochemical activity of VNZhK alloy has been established as compared with VNZh alloy, it is related with a decrease in the iron content in the alloy. Using the example of VNZh alloy, the possibility of electrochemical processing of tungsten heavy alloys with a degree of tungsten extraction into solution of more than 99% has been shown.

1. Introduction
The expansion of tungsten and its alloys application creates the necessity for the recirculation of this metal from waste, such as tungsten-based alloys [1, 2]. Nickel-cobalt-containing tungsten alloys are widely used in the manufacture of ammunition. Their production is based on the W-Ni-Fe-Co phasing diagram (VNZhK type alloys) and W-Ni-Fe phasing diagram (VNZh type alloys). The preparation of these heavy alloys usually involves the mixing of a tungsten powder with a small amount of metals with a lower melting point. It provides the formation of a liquid phase when heated to appropriate temperatures. Base domestic alloys usually contain 90% W, 7% Ni and 3% Fe. The substitution of 1–2% Fe by Co in the alloy composition has a positive effect on its sintering ability and mechanical properties [3, 4].

A significant amount of older armor-piercing ammunition results in the development of an environmentally safe hydrometallurgical process of valuable components regeneration to obtain pure tungsten compounds (ammonium paratungstate, tungsten acid, tungsten trioxide, etc.), which are the initial products for the production of metallic tungsten powder.

The processing of heavy tungsten alloys, including a binding phase from the metals of the iron subgroup (nickel, cobalt, iron) can be carried out by chemical dissolution methods [5, 6]. However, their effective application requires aggressive reagents and preliminary grinding of the processed material, which has high strength. At the same time, electrochemical oxidation is the most promising method for processing metal tungsten-containing wastes [7], since it provides high extraction of valuable components and quality of commercial products without the using of highly aggressive reagents.
Selective electrochemical dissolution of the iron-nickel binding phase of VNZh alloy was proposed in [2]. For this purpose, the using of acid electrolytes is most appropriate, however, tungsten is passivated in the acid media and the alloy dissolution stops due to the formation of a passivating film. It is also important to note, that according to [3], in case of electrolytic removal of the Ni – Fe – Co binding phase from a tungsten heavy alloy, the bond between the tungsten grains remains strong and causes significant diffusion difficulties with further dissolution of non-ferrous metals. Tungsten at high speed passes into solution when using alkaline electrolytes, but, in this case, nickel and iron are passivated and block the alloy dissolution [8].

A significant intensification of the VNZh and VNZhK alloys processing can be achieved through the dissolution of both the tungsten base and the binding phase. The using of a two-component electrolyte, containing sodium hydroxide and sodium chloride, where the chloride ion promotes the passing of non-ferrous metals into solution, and hydroxide ions - that of tungsten, was proposed in work [9]. The addition of chloride ions improves the electrochemical dissolution of non-ferrous metals, but leads to decrease in the rate of tungsten dissolution.

Currently, the main trends in the processing of tungsten-containing raw materials are aimed at introducing technologies, that provide the most efficient and careful environmental management. This is achieved, first of all, by using alkaline reagents for raw material processing [10]. At the same time, the using of mixed alkaline and ammonium solutions can improve the recirculation process due to the high dissolution rate of tungsten in alkaline electrolytes [9, 11], as well as the ability of nickel and cobalt to form soluble ammonium complexes [12]. In addition, the low electrical conductivity of ammonium solutions significantly increases due to the presence of sodium hydroxide in the electrolyte [13].

The purpose of this work is to study the anode behavior of the components of heavy tungsten-containing alloys (VNZh and VNZhK) in alkaline-ammonium electrolytes and to develop a method for the electrochemical extraction of tungsten from these alloys.

2. Experimental part

Investigations were carried out using linear voltammetry in potentiodynamic conditions in standard chemical cell with universal IPC-Pro potentiostat. Samples of tungsten with purity of 99.9 wt.%, N0 nickel, C0 cobalt, Armco iron, VNZh alloy, wt. %: W - 90, Ni - 7, Fe - 3, and VNZhK alloy, wt. %: W - 90, Ni - 7,2, Fe - 1,8, Co - 1 were analyzed. The electrolyte was a solution of sodium hydroxide with a concentration of 2M and ammonium hydroxide with a concentration of 0 ÷ 6M and a temperature of 20°C. The auxiliary electrode was made of platinum and the reference electrode was a saturated chlorine-silver electrode. The potential sweep speed was 1 mV/s. Investigated samples were preliminarily mechanically cleaned and washed with 4M hydrochloric acid solution and bidistilled water. In addition, anodic dissolution of VNZh alloy was investigated by the using of chronopotentiometry method in a solution, containing sodium hydroxide 2M and ammonium hydroxide 4M. Analytical determination of metals content in solutions was performed by atomic emission spectroscopy.

The study of the anode polarization of tungsten in a solution of NaOH 2M + NH₄OH with a concentration of NH₄OH from 0 to 6M showed that with an increase in the electrode potential from -0,4 to 0,2 V the anodic current density rises significantly. With a further increase in the potential to 1,0 V, the value of the anode current density reaches a plateau for electrolytes, containing NaOH + NH₄OH; however, for the solution of NaOH 2M, this value decreases. It was found that the introduction of ammonium hydroxide in the electrolyte increases the maximum current of tungsten dissolution by more than 30% (up to ~ 700 mA/cm²), that is consistent with [14]. It should be noted that an increase in the concentration of NH₄OH from 4 to 6M does not result in significant intensification of the process, but is accompanied by some decrease in the electrical conductivity of the electrolyte [13].

Figure 1 shows the polarization curves of nickel in the studied electrolytes. It can be seen, that the current is spent mainly on the formation of passivating oxide film in case of nickel anode polarization.
in sodium hydroxide solution (figure 1, curve 2). When a potential reaches the value of ~ 0,5V and above, oxygen is also released.

The addition of ammonium hydroxide to the investigated solution leads to the appearance of a peak on the polarization curves, that apparently corresponds to the active oxidation of nickel. At the same time the potential of the oxygen evolution reaction shifts to the electropositive region to approximately 0,9V. The current at the peak of the anode nickel oxidation reaches a maximum at concentrations of NH₄OH in the electrolyte 4 ÷ 6M. However, deeper passivation of the metal occurs in the potential range of 0,7 ÷ 0,9V at 6M NH₄OH.

The cobalt polarization curves (figure 2), like those of nickel, show the anodic oxidation peak in the potential range of 0,6 ÷ 0,7V, when ammonium hydroxide is added to the sodium hydroxide solution. At the same time, the peak appears at lower concentrations of ammonium hydroxide - 2M. It may be associated with a greater tendency of cobalt to complexation in ammonium solutions, compared with nickel [12].

The polarization curves of iron indicate, that the metal in the studied electrolytes behaves passively and almost all the current, flowing through the electrode, is spent on the release of oxygen at a potential higher, than 0,6V. At the same time, with an increase in the NH₄OH concentration in the solution, a decrease in the polarization of this process is observed.

Thus, the data obtained show, that the using of an alkaline-ammonium electrolyte activates the electrochemical oxidation of tungsten (which constitutes VNZh and VNZhK alloy base), as well as nickel and cobalt. It allows us to recommend a solution of the composition NaOH 2M + NH₄OH 4M for processing heavy tungsten-containing alloys.

Anode polarization curves of VNZh and VNZhK alloys (three uninterrupted cycles in the potential range from -0,5 to 0,6 V) are shown in figures 3 and 4, respectively, in a solution of NaOH 2M + NH₄OH 4M.

Anode polarization curves of VNZh alloy demonstrate the behavior characteristic of passivating materials (figure 3). The initial part of the alloy dissolution curves (in the potential range from -0,4 to 0,1 V) is determined, apparently, by the predominant dissolution of the tungsten base.

In addition, it can be seen, that in each subsequent cycle, the maximum anode current density
Figure 2. Anod polarization curves of cobalt in NaOH 2M + NH₄OH solution. The concentration of NH₄OH, М: 1 – 0, 2 – 4, 3 – 6, 4 – 2.

of the alloys active dissolution decreases significantly. It may indicate a preferential passing of tungsten into solution with simultaneous accumulation of binder components on the anode surface.

It should be noted that the maximum current density of dissolution of fresh alloys of the VNZh and VNZhK is rather high (about 220 mA/cm² for VNZh alloy and 270 mA/cm² for VNZhK alloy). It shows their high electrochemical activity in the selected electrolyte (figures 3, 4). A higher maximum anode current density of VNZhK alloy, as compared with VNZh alloy, is associated with a decrease in the iron content in the alloy (the most passive component).

The electrochemical dissolution of VNZh alloy at the potential of -0.1V was studied. This potential corresponds to the maximum rate of alloy dissolution in the electrolyte of the composition NaOH 2M + NH₄OH 4M. The duration of process was 9 hours. It was established, that the dissolution is carried out at an average rate of 0.57 kg/m²·h with a current efficiency close to 100% (based on tungsten ionization in oxidation level +6) and specific power consumption 1.51 kW·h/kg. The degree of tungsten extraction in solution amounted to 99.3%, and Ni+Fe - 0.7%. Thus, when the alloy is being dissolved in a alkaline-ammonium electrolyte, the tungsten base of the alloy preferentially passes into solution. The weak electrochemical activity of the iron-nickel binder alloy may be related with the prevailing influence of iron, that is deeply passivated in alkaline and ammonium media.

The obtained data suggest that the process of dissolution of the VNZhK alloy will proceed with no less high rates under similar conditions due to the more active electrochemical behavior of VNZhK alloy in comparison with VNZh alloy (figures 3, 4).

3. Conclusions

1. The electrochemical behavior of the individual components of VNZh (W-Ni-Fe) and VNZhK (W-Ni-Fe-Co) alloys has been investigated in solutions of sodium hydroxide with a concentration of 2M and ammonium hydroxide with a concentration of 2 ÷ 6M. It has been shown, that the dissolution rate of tungsten is 10 times higher, than that of other alloy components in these electrolytes.
Figure 3. Anode polarization curves of VNZh alloy (W-Ni-Fe) in solution NaOH 2M + NH₄OH 4M.
1 - the first cycle, 2 - the second cycle, 3 - the third cycle.

Figure 4. Anode polarization curves of VNZhK alloy (W-Ni-Fe-Co) in solution NaOH 2M + NH₄OH 4M. 1 - the first cycle, 2 - the second cycle, 3 - the third cycle.
2. It has been revealed, that the addition of ammonium hydroxide to the sodium hydroxide solution: increases the electrochemical dissolution rate of tungsten by more than 30%, leads to the appearance of the peak on nickel and cobalt polarization curves, responding to their active anode oxidation and does not have a significant effect on the electrochemical behavior of iron. The optimal composition of the electrolyte is NaOH 2M + NH₄OH 4M in terms of the process rate and the specific conductivity of solution.

3. Electrochemical dissolution of VNZh alloy in the solution of NaOH 2M + NH₄OH 4M has been investigated. It has been shown, that a degree of tungsten extraction into solution exceeds 99% at the anode potential of 0.1V with a current efficiency close to 100% and a specific energy consumption ~ 1.5 kW·h/kg.

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