AC electrochemical oxidation of nickel and VNZh alloy in alkaline-ammonium solutions

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Abstract. It was studied the electrochemical oxidation of nickel in an electrolyte of the composition NaOH 2M + NH₄OH 4M by using linear and cyclic voltammetry. A significant increase in the process rate has been revealed due to the cathodic polarization of the electrode under study. It was shown the possibility of heavy tungsten alloy processing, such as VNZh-type alloy (in wt%: 78.8 W, 15.2 Ni, 6.0 Fe), under the influence of alternating electric current of industrial frequency in alkaline-ammonium solutions.

1. Introduction
Alkaline solutions are often used for electrochemical processing tungsten alloy waste [1-4] and, in particular, for nickel-containing heavy alloys, based on tungsten [5-9]. The anodic polarization of nickel in these electrolytes is accompanied by the formation of a passivating oxide film with various oxidation levels, as well as oxygen evolution [10-12]. The formation of nickel oxides during the electrochemical dissolution of nickel-containing heavy tungsten alloys under the influence of direct current prevents the passing of tungsten into solution and significantly reduces the rate of alloys oxidation [5, 8]. According to the data of [8, 9], the introduction of ammonium hydroxide (4M) into the composition of the alkaline electrolyte significantly accelerates the oxidation of nickel and cobalt without significantly affecting the behavior of iron. It is known [10-16], that oxides of the iron group metals can be removed from the electrode surface due to their cathodic reduction and mechanical detachment by hydrogen, released during cathodic polarization. In this regard, the aim of this work is to:
- investigate the effect of cathodic polarization of nickel in the hydrogen evolution region on the process of its subsequent electrochemical oxidation in alkaline ammonia solutions;
- study the possibility of using alternating electric current for nickel-containing heavy tungsten alloys processing in alkaline-ammonium electrolytes on the example of VNZh alloy (tungsten-nickel-iron).

2. Experimental part
Using the methods of cyclic voltammetry (CVA) and linear voltammetry in the potentiodynamic mode, the anodic behavior of nickel in a solution, containing 2M sodium hydroxide and 4M ammonium hydroxide, was studied [8]. The studies were carried out with the IPC-Pro universal potentiostat with the use of grade N0 nickel, an auxiliary glassy-carbon electrode, and a saturated chlorine-silver reference electrode.

Preliminarily, the samples were stripped and washed with distilled water. The polarization of the electrode was carried out from the steady state potential of the nickel electrode (E⾊) to the oxygen evolution potential (+0.9 V) and in the opposite direction to the potential of -1.5 V. In this case, the
potential sweep speed in the range of \(-1.0 \div +0.9\) V was 25 mV/s, while in the range of potentials \(-1.5 \div -1.0\) V (in the hydrogen evolution region) the polarization rate was set in the range from 1 to 25 mV/s. Immediately, after the end of the CVA cycle, the nickel electrode was polarized from \(E_{st}\) up to a potential value of +0.9 V with a potential sweep speed of 25 mV/s. Studies were carried out at the temperature of 20°C. The amount of electricity, that passed during the cathode period of CVA \((Q_{cat})\), was calculated as the area under the corresponding dependence \(I_{cat} = f(\tau_{cat})\). Where \(I_{cat}\) is the cathode current strength (A), \(\tau_{cat}\) - cathodic polarization time (h).

Electrochemical oxidation of a heavy nickel-containing tungsten alloy (VNZh alloy, wt.\%: 78.8 W, 15.2 Ni, 6.0 Fe) under the influence of alternating current (ac) of industrial frequency (50 Hz) was carried out in a solution, containing 2M sodium hydroxide and 4M ammonium hydroxide, in a thermostatic cell at a temperature of 25°C by using two electrodes from the investigated alloy with a fixed surface area. The oxidation rate of VNZh alloy was determined based on the decrease in the electrodes mass during the experiment. The current efficiency for the alloy was determined in terms of tungsten for the ionization of tungsten at an oxidation level of +6. Distilled water and reagent grade reagents were used for the preparation of solutions.

Figure 1 shows the anodic polarization curves of nickel in the solution of NaOH 2M + NH\(_2\)OH 4M
(curves 1–3), each curve was taken after a CVA cycle (curve 4) with a different potential sweep speed (from 1 to 25 mV/s) in the hydrogen evolution region (-1.5 ÷ -1.0 V).

It can be seen, that a decrease in the potential sweep speed in the cathode region of CVA (-1.5 ÷ -1.0 V) from 25 to 1 mV/s leads to a four-fold increase in the maximum anode current density ($i_{max}$) from 26 to 106 mA/cm$^2$. It is important to note, that similar studies in a NaOH 2M solution, without ammonium hydroxide, showed the absence of anode effects of nickel, regardless of the potential sweep speed in the cathode region of CVA.

The effect of the amount of electricity, transmitted during the CVA cathode cycle, on the value of the maximum anode current density of nickel in the solution of NaOH 2M + NH$_4$OH 4M is presented in the table.

| $Q_{cat}$, mA·h | 0   | 0.06 | 0.12 | 0.38 | 1.12 | 10  |
|-----------------|-----|------|------|------|------|-----|
| $i_{max}$, mA/cm$^2$ | 12  | 26   | 34   | 47   | 106  | 200 |

It can be seen, that the maximum anode current density of nickel is only 12 mA/cm$^2$ in the absence of cathodic polarization. Cathodic polarization of the nickel electrode at $Q_{cat}$ equal to 1.12mA·h leads to a tenfold acceleration of the nickel electrode oxidation to $i_{max}$= 106 mA/cm$^2$. Further increase in $Q_{cat}$ is impractical, since at $Q_{cat}$ = 10 mA·h the $i_{max}$ only doubles (up to 200 mA/cm$^2$).

Thus, the obtained data show, that the introduction of ammonium ions into the alkaline electrolyte significantly activates the oxidation processes on the nickel electrode, when using the current mode, which includes both the anode and cathode components. In this case, the most technologically simple current mode with different polarity is a sinusoidal alternating electric current of industrial frequency. This can be used to intensify the oxidation processes of VNZh-type alloys during their electrochemical processing in alkaline electrolytes.

Figure 2 shows the dependences of the oxidation rate of VNZh alloy and its current efficiency on the ac current density in the solution of NaOH 2M + NH$_4$OH 4M. It is seen, that an increase in current density leads to a substantial growth in the rate of the alloy with a simultaneous increase in current efficiency. Studies have established, that at a current density of 7 A/cm$^2$, the alloy oxidation rate is $\sim$1250 mg/cm$^2$·h, and the current efficiency reaches 30%.

![Figure 2](image_url)
3. Conclusions
The positive effect of the cathodic component of the current on the process of nickel anodic oxidation in an alkaline-ammonium electrolyte has been established. It consists in the increasing the oxidation rate of nickel. It has been shown, that the electrochemical oxidation of a nickel-containing tungsten heavy alloy of the VNZh-type under the influence of alternating current of industrial frequency reaches ~1250 mg/cm²·h for current efficiency of ~ 30% in a solution of NaOH 2M + NH₄OH 4M.

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