Changes in electrochemical properties of a heavy tungsten alloy during its processing under the influence of DC current in ammonia-alkali solutions

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Abstract. The method of linear voltammetry in the potentiodynamic mode was used to study the change in the anode behavior of a heavy tungsten VNZh alloy (in wt.%: 78.8 W; 15.2 Ni; 6.0 Fe), as well as the phase composition and morphology of its surface during its electrochemical dissolution under the influence of DC current. It was determined, that the phase composition of VNZh alloy surface is a solid solution of iron-nickel after tungsten dissolution from the surface of the alloy. It has been established, that in ammonia-alkali electrolytes the process of tungsten passing into solution does not stop after dissolution of the metal from the alloy surface, but continues both due to diffusion of the metal from the depth of the sample and the pits formation in the processed alloy.

1. Introduction

Nowadays, a lot of research is being carried out, related to the use of various electrochemical ways for the tungsten alloys processing [1-6]. Electrolysis of fused salts is effective method, but extremely energy-consuming and quite complicated in implementation of a process [7, 8]. It is worth noting the hydrometallurgical method for processing heavy alloys, which does not require preliminary grinding of the alloys and consists in electrolysis in alkaline-chlorine solutions [9], however, the presence of chloride ions in the electrolyte will significantly complicate the further preparation of pure tungsten salts. The using of alkaline electrolyte is most optimal in ecological terms, however, it is accompanied by passivation of the soluble alloy during the process and a significant inhibition of its dissolution [10]. It is known, that the using of ammonia-alkali electrolytes can increase the oxidability of heavy tungsten alloys components [11, 12]. This work is devoted to the study of changes in the surface properties of heavy tungsten alloys, processed under the influence of DC current in alkali-ammonia electrolytes in order to increase their oxidation rate.

2. Experimental part

The studies were carried out by linear voltammetry in the potentiodynamic mode, using the universal IPC-Pro potentiostat. A heavy tungsten alloy of VNZh type (wt.%: 78.8 W; 15.2 Ni; 6.0 Fe) was applied as a working electrode. The measurements were carried out relative to a saturated chlorine-silver reference electrode with a platinum auxiliary electrode. A mixed solution of sodium hydroxide (2 M) and ammonium hydroxide (0÷6 M) was used as the electrolyte. The potential sweep speed was 3 mV/s and a temperature was 20°C. The samples were preliminarily cleaned and washed with a solution of hydrochloric acid (4 M) and distilled water.

The change in the surface composition of the VNZh alloy during hydro electrochemical processing was determined using X-ray spectral analysis (ISM-6380LV equipped with an Energy 250 analyser...
and X-ray diffractometry (ARL XTRA). The morphology of alloy surfaces were examined with TESCAN VEGA II SBU scanning electron microscope (SEM).

Figure 1 shows the anode polarization curves of the fresh VNZh alloy in alkaline-ammonium-electrolytes. It is seen, that the dissolution rate of the alloy in the studied solutions is high due to the predominant tungsten passing into solution. The introduction of ammonium hydroxide into a solution of sodium hydroxide (2 M) to a concentration of 6 M does not significantly affect the value of the maximum current density of the alloy and only shifts this value to the region of more electropositive potentials.

Figure 2 shows the anodic polarization curves of the partially processed VNZh alloy, where tungsten was partially dissolved from its surface in ammonia-alkali electrolytes. Tungsten dissolution from the surface of the VNZh alloy was carried out according to [11], under the influence of DC current in the galvanostatic mode at a current density of 50 mA/cm² and the composition of the electrolyte NaOH 2M and NH₄OH 4M for 1 and 9 hours for partial and complete dissolution of tungsten from the alloy surface, respectively. It is seen, that with partially processed VNZh alloy for 1 hour, the dissolution rate of the alloy decreases. In this case, the introduction of ammonium hydroxide into the electrolyte still does not have a positive effect on the process.

Figure 3 shows the polarization curves of the completely processed VNZh alloy, where tungsten was completely dissolved from its surface for 9 hours, in a solution of sodium hydroxide (2 M) with the addition of ammonium hydroxide (2 ÷ 6 M). The polarization curves have two maxima: the first in the potential region - 0.3 ÷ - 0.2 V, the second - in the range of 0.1 ÷ 0.2 V. It can be seen, that in this case the introduction of ammonium hydroxide in the electrolyte leads to almost double increase the oxidation rate of the alloy. It is important to note, that neither for the fresh VNZh alloy, nor for its individual components (tungsten, nickel, iron), such phenomena were observed [11]. Nickel is the only alloy component, whose anodic oxidation is activated, when ammonium hydroxide is introduced into the electrolyte.

Figure 1. Anodic polarization curves of fresh VNZh alloy in a solution of 2M NaOH + NH₄OH. The concentration of NH₄OH, M: 1 - 6, 2 - 0, 3 - 2.
Figure 2. Anodic polarization curves of a partially processed VNZh alloy in a solution of NaOH + \( \text{NH}_4\text{OH} \). The concentration of \( \text{NH}_4\text{OH} \), M: 1 - 6, 2 - 2, 3 - 0.

Figure 3. Anodic polarization curves of a completely processed VNZh alloy in a solution of 2M NaOH + \( \text{NH}_4\text{OH} \). The concentration of \( \text{NH}_4\text{OH} \), M: 1 - 6, 2 - 2, 3 - 0.

Thus, the complete dissolution of tungsten from the surface of the VNZh alloy significantly changes its electrochemical properties due to a change in the composition of the alloy surface, which is related with a change in the chemical and phase composition of the dissolved sample. The results of X-ray diffractometry of the fresh and completely processed VNZh alloys are shown in Figure 4.
According to X-ray diffraclometry (Figure 4), the fresh VNZh alloy is two-phase and consists of tungsten and iron-nickel solid solution and it is observed the predominance of tungsten with iron-nickel solid solution. It should be noted, that neither solid solutions of tungsten in ferronickel, nor ferronickel in tungsten were found in the fresh VNZh alloy (Figure 4a). However, after the electrochemical dissolution of tungsten by the influence of DC current in ammonia-alkali solution, the surface of the completely processed VNZh alloy has become single-phase and consists of a iron-nickel solid solution with no tungsten in the composition (Figure 4b).

In order to identify the processes occurring on the iron-nickel surface of VNZh alloy after complete dissolution of tungsten, we studied the anodic behavior of the ferronickel alloy (which is similar in the ratio of iron and nickel in the investigated VNZh alloy) in ammonia-alkaline solutions. It was found, that the ferronickel alloy behaves passively in the sodium hydroxide solution until the oxygen evolution potential is reached at a potential of ~0.55 V. When ammonium hydroxide is introduced into the electrolyte (up to a concentration of 6 M), the region of alloy oxidation appears on the polarization curves in the potential range 0.6~0.8 V.

To understand the reasons for the difference in the anode behavior of completely processed VNZh alloy with the iron-nickel surface (Figure 3) and the ferronickel alloy, the morphology of the surface of the fresh and completely processed VNZh alloy surfaces was studied (Figure 5). It raises questions the reason for the presence of anode peaks on the polarization curves of the completely processed VNZh alloy in the potential range of -0.3 ~ -0.2 , corresponding to tungsten oxidation. It can be seen, that as a result of the electrochemical processing of the VNZh alloy under the influence of DC current, pits are formed on the alloy surface (Figure 5b), in the depth of which the processes of tungsten oxidation can continue. This is reflected in the electrochemical properties of the processed heavy alloy.
3. Conclusions

Using the method of linear voltammetry in the potentiodynamic mode, we studied the anode behavior of a heavy tungsten-containing alloy, such as VNZh alloy, in sodium hydroxide solutions (2 M) with ammonium hydroxide (0 \( \div \) 6 M). It has been established, that the VNZh alloy is intensively soluble in ammonia-alkali solutions and its electrochemical properties are determined by the behavior of the tungsten, which is the main alloy component.

It was determined, that the electrochemical properties of the VNZh alloy substantially change during its electrochemical dissolution in ammonia-alkali electrolytes, which is due to a decrease in the tungsten content in its composition and enrichment with a solid solution of iron-nickel.

It was found, that the introduction of ammonium hydroxide in the composition of an alkaline electrolyte has a positive effect on the oxidation of the VNZh alloy after the main amount of tungsten is passed into the solution during alloy processing.

It was revealed, that during the VNZh alloy processing under the influence of DC current in ammonia-alkali electrolyte, tungsten dissolution continues even after it is completely dissolved from the alloy surface due to the diffusion of metal from the depth of the sample and the formation of pits in the processed alloy.

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