

# ELECTROCHEMICAL DISSOLUTION OF PSEUDO ALLOYS OF TUNGSTEN CARBIDE TYPE IN ACID ELECTROLYTES

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The electrochemical behaviour of the WC-Co pseudo alloy in acid solutions of  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  and  $\text{HCl}$  has been studied. For practical use, an aqueous solution of  $4 \text{ mol}\cdot\text{dm}^{-3}$   $\text{H}_2\text{SO}_4$  has been chosen. To prevent the formation of oxides of tungsten, there has been justified the use of a reducing agent - hexamine additive. A method for processing a pseudo alloy in  $4 \text{ mol}\cdot\text{dm}^{-3}$   $\text{H}_2\text{SO}_4$  solution containing  $0.2 - 0.3 \text{ mol}\cdot\text{dm}^{-3}$  reducing agent – hexamine, which allows to obtain a tungsten powder in slime.

## **1. Introduction**

Solid tungsten-cobalt-copper alloys were among the first that were commercially available, and the scope of their use is constantly expanding. This in turn leads to the emergence of tungsten-containing waste, the complex processing of which is topical, since it allows the return of valuable metals (tungsten, cobalt) in the production cycle. The existing methods of extracting the components of tungsten pseudo alloys differ from each other, not only by the processing regime, but also used by the nature of the

reagents.

It is widely known that the use of electrochemical methods is promising, since the existing hydro- and pyro metallurgical processes are multi-stage, complex and contribute to the formation of toxic substances. Electrochemical methods are one of the possible ways to intensify the processing of tungsten-containing raw materials. They deserve special attention, since they provide a high rate of recovery of valuable components, simplify the technological scheme and instrumental design of the process, reduce waste treatment time and improve environmental indicators. The difficulty of dissolving hard alloys of tungsten is in the different ability of its components to oxidize and passivity [1]. Thus, when alkaline electrolytes are used, tungsten (IV) carbide dissolves, and metal bonds (Co) selectively dissolve in acid solutions to form insoluble compounds WC, WO<sub>3</sub>, H<sub>2</sub>WO<sub>4</sub>.

The purpose of this work is to develop conditions for the selective electrochemical dissolution of cobalt (metal-binder), the transfer of tungsten powder to the sludge, excluding the formation of tungstic acid in the slurry.

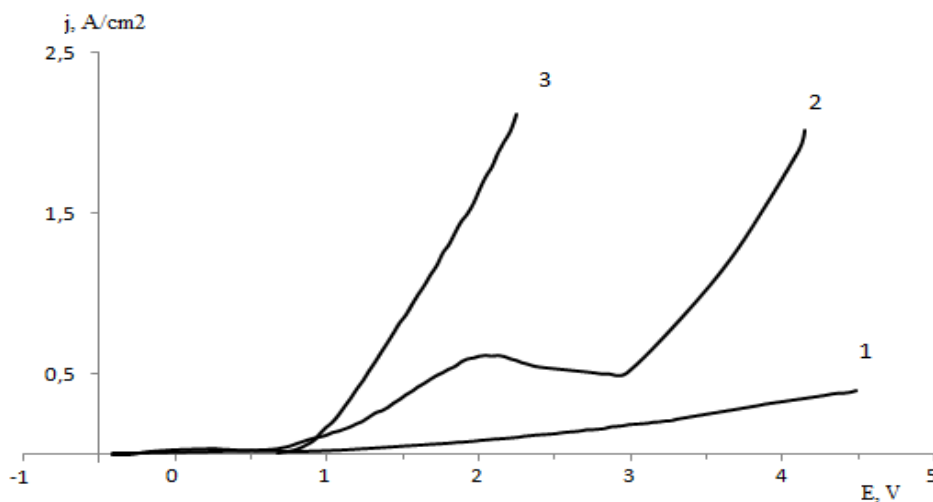
## **2. Methodology**

There have been investigated the samples of the tungsten pseudo alloy carbide type WC-Co-6 (WC - 94%, Co - 6%). The surface of the samples has been degreased and thoroughly washed with distilled water. Anodic dissolution of the pseudo alloy has been carried out in electrolytes with a varying ratio of the concentrations of acids and additives while stirring and a temperature of 20-25 °C. Anode behavior has been studied by voltamperometry. Polarization measurements have been carried out at the potentiostat PI 50-1.1 at a potential sweep rate of  $2 \cdot 10^{-2}$  V/s in the

potentiodynamic mode. The original alloy as the anode, and the cathode-titanium plate have been used. The reference electrode was a saturated silver chloride electrode. The potentials have been given on the normal hydrogen electrode. The output of the current components has been determined by the gravimetric method.

### 3. Results and discussion

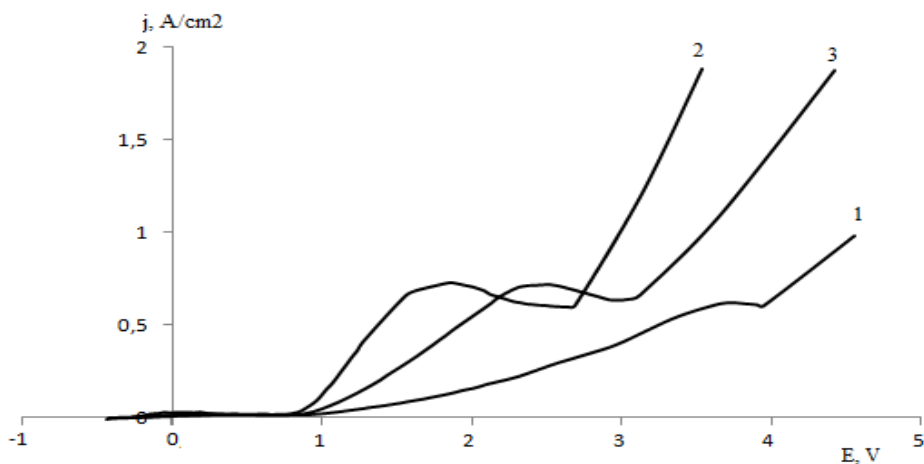
Selective dissolution of metal-bonds has been carried out in solutions of various acids  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ . Fig. 1 shows the anodic polarization dependences in acid solutions with the addition of the HF activator. It is seen that as the concentration of the acid increases, the carbide phase is activated and the reaction rate increases. This effect is observed due to the simultaneous action of the oxidizer - nitrate ion and depassivator agent-fluoride ion, which is also a ligand.



**Fig.1.** Polarization dependence of dissolution of WC-Co-6 alloy in a solution with the addition of  $7 \text{ mol} \cdot \text{dm}^{-3}$  HF in different concentrations of  $\text{HNO}_3$ ,  $\text{mol} \cdot \text{dm}^{-3}$  : 1 – 1  $\text{HNO}_3$ ; 2 – 4  $\text{HNO}_3$ ; 3 – 7  $\text{HNO}_3$ .

However, a significant drawback of this treatment method is the use of high concentrations of nitric acid, reagents to neutralize it, the need for special equipment and the neutralization of nitrogen oxides evolved during electrolysis. In addition, the final product is tungsten compounds, which require additional processing.

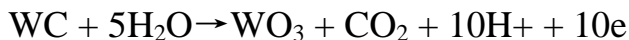
When using chloride acid as an electrolyte for dissolving WC-Co-6 alloy, the process speed decreases with increasing acid concentration (Fig. 2). This phenomenon is connected with a decrease in the electroconductivity of the electrolyte. The final product of oxidation, in this electrolyte, is a mix of oxides of tungsten and tungstic acid.



**Fig. 2.** Polarization dependence of WC-Co-6 alloy dissolution in HCl solutions with different concentrations,  $\text{mol} \cdot \text{dm}^{-3}$ :  
1 - 1 HCl; 2 - 4 HCl; 3 - 6 HCl.

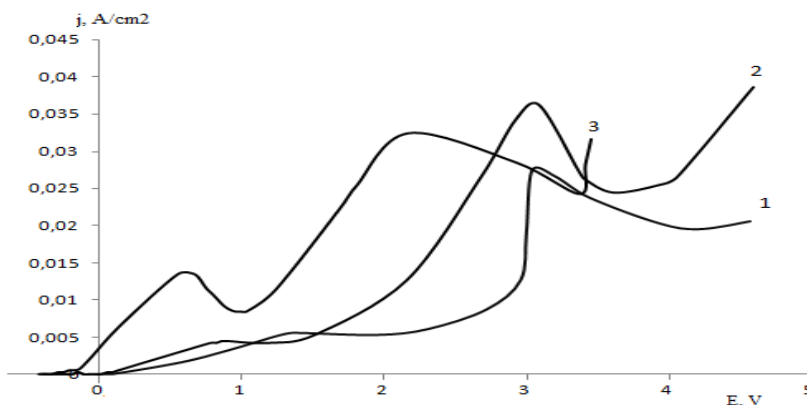
Studies on the use of sulfuric acid as an electrolyte have been carried out by many scientists [2]. Figure 3 shows the polarization dependences of the anodic behavior of the WC-Co-6 alloy in  $\text{H}_2\text{SO}_4$  solutions of various concentrations. The course of the dependences indicates an incomplete

selectivity of the dissolution of the cobalt ligament. The reaction on tungsten (IV) carbide is possible.



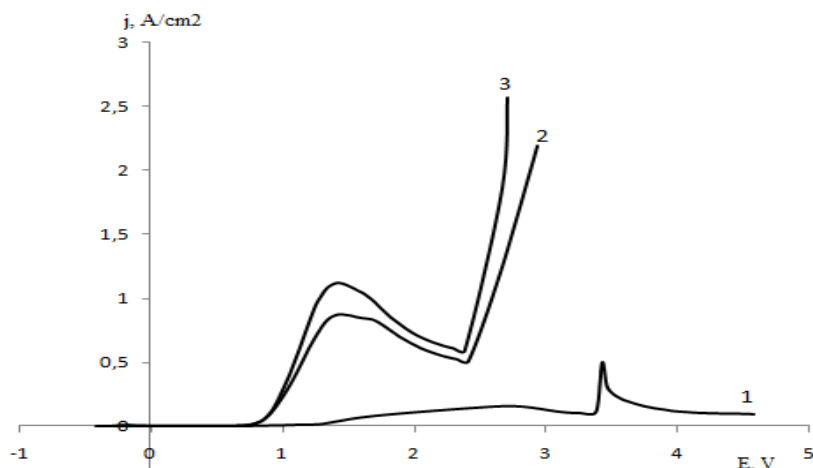
In the range of potentials 0.8 - 2 V in solutions of HCl and H<sub>2</sub>WO<sub>4</sub>, tungsten (IV) carbide oxidizes with the simultaneous dissolution of the metal - binder. The authors of Ref. [3] state that at potentials more positive 0.7 V on the anode surface, the emission of gas - CO<sub>2</sub> is observed. At potentials more than 2 V, oxygen has been also released.

To obtain a tungsten powder without the compounds WO<sub>3</sub> and H<sub>2</sub>WO<sub>4</sub> in the slurry, reducing agent-hexamine, has been introduced into a solution of sulfuric acid. The introduction of the additive results in the disappearance of peaks that correspond to the reaction (Fig. 3).



**Fig.3.** Polarization dependences of dissolution of WC-Co-6 alloy in H<sub>2</sub>SO<sub>4</sub> solution of different concentrations, mol·dm<sup>-3</sup>:  
1 – 1 H<sub>2</sub>SO<sub>4</sub>; 2 - H<sub>2</sub>SO<sub>4</sub>; 3 – 7 H<sub>2</sub>SO<sub>4</sub>.

The polarization dependences indicate the selectivity of the dissolution of the cobalt phase at a hexamine concentration of 0,2 - 0,3 mol·dm<sup>-3</sup> (Fig. 4). Cobalt has been recovered from the solution in the cathode.



**Fig.4.** Polarization dependence of dissolution of WC-Co-6 alloy in  $4 \text{ mol} \cdot \text{dm}^{-3} \text{ H}_2\text{SO}_4$  electrolyte with different hexamine concentration,  $\text{mol} \cdot \text{dm}^{-3}$ : 1 – 0,1; 2 – 0,2; 3 – 0,3.

The conditions for selective dissolution of WC-Co-6 alloy in the acidic electrolyte have been developed. Application of acidic electrolyte allows to obtain pure tungsten through the selective dissolution of WC-Co-6 alloy. The selective dissolution in  $4 \text{ mol} \cdot \text{dm}^{-3}$  sulphuric acid with addition of hexamine ( $0,2 - 0,3 \text{ mol} \cdot \text{dm}^{-3}$ ) has performed the best results.

## References

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