

ACTUALITY. Tungsten carbide-cobalt hard alloys were first cermets that found an industrial application. The high importance of these materials has not become lower until now. To return the valuable components of hard alloys to the production industry, it is necessary to find a way of recycling the waste materials containing these components. These waste materials can be represented by matrices of drilling and cutting tools and by scrap. Because of the high cost and, sometimes, deficiency of tungsten and cobalt, the problems of developing new methods of recycling lumps of waste hard alloys have become of high concern recently. The existing methods of extracting the components of hard alloys differ from each other by not only the treatment mode but also the nature of the applied chemical reactants. The essential disadvantage of the methods of dissolving components of hard alloys with various acids and their mixtures is the toxicity of the applied reactants. This disadvantage is partially eliminated by treating waste diamond and hard alloy tools with anodic dissolution in hydroxide-chloride melts. In this case, the tungsten and carbon transfer into the melt in the form of tungstate and carbonate, respectively, and the impregnating materials for the hard-alloy matrix accumulate at the cathode in the form of finely dispersed metal powders. The end product of the proposed method is tungsten oxide WO_3 , which requires further treatment to be returned into the process of manufacturing hard-alloy tools. The results of using the method of high-temperature selective extraction of tungsten from the concentrates and materials in halide-silicate melts are reported by Malyshev et al. In the present paper, we study the separation of cobalt and tungsten carbide by anodic dissolution in phosphoric acid solutions. In contrast to molten media, the application of phosphoric acid solutions as the electrolyte makes it possible to selectively separate the components of hard alloys and directly extract the tungsten carbide suitable for being returned to the production process. The high susceptibility of tungsten and its carbide to passivation in aqueous solutions determines the specific features in their electrochemical behavior. The electrode potentials, cathode processes with electric evolution of gas, and oxidation processes using tungsten and its carbide were studied mostly in hydrochloric and sulfuric acid solutions. The electrochemical evolution of hydrogen on tungsten carbide was studied by Baibaturov et al. It was shown that the evolution of hydrogen on WC is limited by the recombination of the adsorbed hydrogen atoms. The shape of the curves of anode polarization in sulfuric acid solutions corresponds to the transition of the active dissolution of the metal to its passive state. Tungsten compounds are usually extracted from ores and concentrates by dissolution in different acids, the environmental danger and technological ineffectiveness of which are obvious. High-temperature selective extraction in nonaggressive salt melts can be suggested as an alternative method. The method of producing tungsten carbide by treating tungsten-containing melts by reducing gases, carbon or calcium carbide has recently been developed. Its first step is usually the decomposition of the ore or concentrates by the method of high-temperature selective extraction. Sodium chloride and sodium silicate melts can be recommended as extracting components. When they are melted together with tungsten (wolframite or scheelite) concentrates, the tungsten compounds are transferred into the chloride phase while the oxides of iron, manganese, and calcium are transferred into the silicate phase. The phases are separated by selective decantation. The degree of extraction of tungsten into the chloride phase largely determines the further profitability of the method of producing tungsten carbide by treating the melts with gases. In the present paper, we will study the method of high-temperature selective extraction of tungsten from its concentrates and determine the most effective conditions (temperature, melt composition, extraction duration) for operating the process.

EXPERIMENTAL. The anodic dissolution of electrodes made of the WC-Co alloy, metallic cobalt, and tungsten carbide WC was studied using a three-electrode system. The working electrolyte was a 1.25 M solution of phosphoric acid H_3PO_4 . Small-bar electrodes were made of the WC-Co (6%) hard alloy by the Svetlovodsk Factory of Hard Alloys and Refractory Metals using the regular process of powder metallurgy. The tungsten carbide electrodes were manufactured by the pressure sintering of tungsten and carbide powders at a temperature of 2200°C and a pressure of 1000 kg/mm² in a laboratory of the Institute of Materials Problems, National Academy of Science of Ukraine.

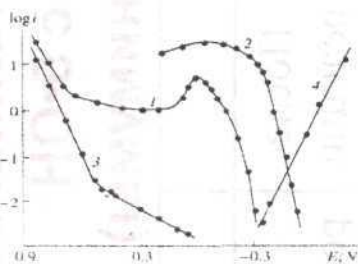


Figure 1 – Steady-state potentiostatic polarization curves for the anodic dissolution of (1) the WC-Co (6%) hard alloy, (2) cobalt, and (3) tungsten carbide and (4) the reduction of hydrogen ions on the tungsten carbide electrode in the 1.25 M H_3PO_4 solution at a temperature of 18°C

RESULTS AND DISCUSSION. Figure 1 illustrates the typical steady-state potentiostatic polarization curves for the anodic dissolution of the WC-Co (6%) hard alloy, cobalt, and tungsten carbide and the reduction of hydrogen ions on the tungsten carbide electrode. The polarization curves are reproduced in the cycling of the potential almost without any hysteresis. The stirring does not affect the behavior of the curves. The value of the steady-state potential of the WC-Co (6%) electrode is $-0.32-0.34V$ and is located between the values of the potentials of its components: $(0.55-0.57 V)$ for cobalt and $(0.09-0.11V)$ for tungsten carbide. The polarization curves for the WC-Co (6%) electrode (curve 1) show three clearly cut zones. In the first zone, -0.30 to $-0.05 V$, the value of the logarithm of the electric current density increases linearly with increasing potential. At a potential value of $-0.02V$, the current density sharply decreases and remains almost constant until the potential increases to $0.70 V$ (second zone). As the potential increases further, the electric current density again exponentially increases (third zone). The anodic dissolution of the WC-Co (6%) bars was accomplished under potentiostatic conditions at potential values of -0.25 to $-0.05V$, which correspond to the first section of the potentiostatic curve. In this case, the electric current density slowly decreases with time (usually, during 10 to 12 h) and then remains almost constant.