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RESOURCE PROCESSING TECHNOLOGY WASTE TUNGSTEN CARBIDE-COBALT PHOSPHORIC ACID SOLUTION TO MAINTAIN THE PURITY NATURE PREVENTION AND CORRECTION OF ENVIRONMENTAL PATHOLOGIES

N.V. Solovieva[a], L.A. Chernenko[b]

[a] Higher medical educational institution of Ukraine "Ukrainian medical stomatological academy", Poltava;

[b] Poltava National Technical Yuri Kondratyuk University, Poltava
Schernenko@mail.ru

Increased interest in the development of new and effective methods for obtaining refractory compounds – carbides, borides, silicides, alloys and intermetallic compounds of metals of IV-VI B groups is dictated by their use for the needs of modern technology. 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 [1]. These waste materials can be represented by matrices of drilling and cutting tools and by scrap.
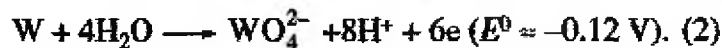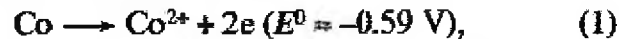
In the present paper, we study the separation of cobalt and tungsten carbide by anodic dissolution in phosphoric acid solutions. In contrast to molten media, the application of phosphoric acid solutions as the electrolyte makes it possible to selectively separate the components of hard alloys and directly 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 [2, 3]. The electrochemical evolution of hydrogen on tungsten carbide was studied by Baibatyrov et al. [4]. 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 [2, 3]. Tungsten compounds are usually extracted from ores and concentrates by dissolution in different acids, the environmental danger and technological ineffectiveness of which are obvious.

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 H3 PO4. 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 [5]. 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/mm^2 in a laboratory of the Institute of Materials Problems, National Academy of Sciences of Ukraine. The cobalt electrodes were plates made of an ultrapure metallic foil. The surface area of the electrodes to be studied was 1 to 2 cm^2.

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 –(0.32–0.34) V and is located between the values of the potentials of its components: –(0.55–0.57) V for cobalt and –(0.09–0.11) V 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 –0.02 V, the current density sharply decreses 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 –0.05 V, 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 (Fig. 2). Two zones on the surface of the cross-sectional microsection of the WC–Co (6%) bar treated by anodic dissolution can be visually observed (Fig. 3). The observed boundary separates the base, which was not dissolved, from the partially dissolved layer. According to the results of the X-ray phase analysis, the partially dissolve layer consists of the WC phase. Neither cobalt nor tungsten is detected in it. These data are supported by the results of the X-ray spectral microanalysis. The weight fraction of tungsten in the partially dissolved layer is lower than that in the reference tungsten specimen and is equal to 91.3 to 93.8%, which corresponds to its weight fraction in the carbide.

To validate the suggested dissolution mechanism, the WC–Co (6%) bars were anodically dissolved at the different values of potential corresponding to the zones I and II in the polarization curve and the dissolution duration. Table 1 summarizes the results of analyzing the produced solutions. As the potential rises, the dissolution rate of the cobalt and tungsten and the weight proportion of Co and W in the total weight fraction of the dissolved metals increase. At potentials more positive than 0.70 V, the evolution of gas at the anode surface is observed. The results of its chromatographic analysis identified it as carbon dioxide. Analysis of the solutions resulting from the anodic dissolution of the alloys (Table 1) and the results of the metallographic, X-ray phase, and micro-X-ray spectral analyses enable us to state that zone I of the polarization curve corresponds to the selective dissolution of the Co–W phase, which leaves W–C grains in the bar. In this case, the dissolution process can be described by the expressions:

$$Co \longrightarrow Co^{2+} + 2e \ (E^0 \approx -0.59 \ V), \qquad (1)$$

$$W + 4H_2O \longrightarrow WO_4^{2-} + 8H^+ + 6e \ (E^0 \approx -0.12 \ V). \quad (2)$$

According to the data listed in Table 1, the weight fraction of tungsten in the total weight of the dissolved metals is 11.3 to 14.2%, which corresponds to the data on its dissolution in cobalt [6]. It should also be noted that the main part of the anode current is spent for the cobalt dissolution. That is why the polarization curves for the WC–Co (6%) and cobalt electrodes are much alike in shape and close in value (Fig. 1; curves 1, 3).

The simultaneous dissolution of the cobalt and tungsten is noticeably accelerated as the potential increases. When the potential reaches a value of –0.02 V, the electric current density sharply decreases to a value equal to 15 to 20% of its maximum value. According to the data of X-ray phase analysis, the passivated film consists mainly of tungsten oxide WO3 and cobalt phosphate.

As the potential rises further, the electric current density begins to slowly increase and then sharply jumps as soon as the potential reaches 0.7 V. This is attributed to a considerably increased contribution of the reaction into the process

$$WC + 6H_2O \longrightarrow WO_4^{2-} + CO_2$$
$$+ 12H^+ + 10e \ (E^0 \approx 0.02 \ V) \qquad (3)$$
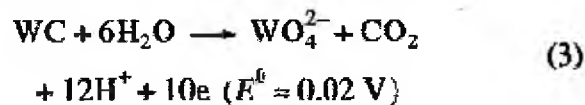
at the anode at potentials that are more positive than the reaction reversible potential. In this case, almost all dissolved tungsten except for the small amount that resulted from reaction (2) and was calculated using the cobalt dissolution data is formed as a result of reaction (3). This is supported by the data on the contributions of separate simultaneous anode reactions into the total process at the anode. When oxygen is absent in the solution, the cathode current corresponds to

the reduction of hydrogen ions (Fig. 1, curve 4). The extrapolation of the corresponding polarization curve to the potential axis (Ecor) corresponds to electric currents of the same order as those measured for cobalt dissolution without polarization. It can also be assumed that the rate of dissolution of the Co–W phase from the hard alloys depends on the thickness of the sample, the cobalt weight fraction in the alloy, and the sizes of cobalt and tungsten carbide grains. Indeed, the replacement of WC–Co (6%) alloy particles of size 1.0 to 2.0 μm by WC–Co (5%) particles of size 0.5 to 1.0 μm leads to 1.1 to 1.3 times higher dissolution rates.

The selective dissolution of the WC–Co phase can be used for the recycling of hard alloy scrap. In this case, it is desirable that the separation of cobalt from carbide be accomplished at as low power consumption as possible. After the WC–Co phase is dissolved, the residual tungsten carbide after grinding can be again suitable for the production of hard-alloy tools.

Conclusions

The potentiostatic mode of anodic dissolution of tungsten carbide–cobalt alloys in phosphoric acid solutions, which makes it possible to selectively dissolve tungsten and cobalt and separate the solid tungsten carbide phase, is experimentally validated and practically implemented.

The curves of the rate of dissolution of cobalt and tungsten in the WC–Co (6%) alloy versus the electrode potential and dissolution duration are determined.

It is shown that tungsten is extracted from tungsten ores and concentrates in sodium chloride–sodium metasilicate melts into the halide phase at a temperature of 1050 to 1050–1100°C. The compositions of the melts that provide the extraction efficiency as high as 99% and maximal ratios of separation of the components between the phases are chosen.

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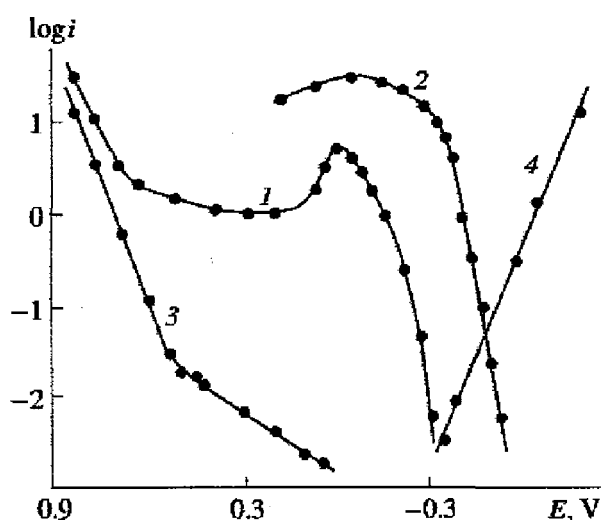
Fig. 1. Steady-state potentiostatic polarization curves for the anodic dissolution of (1) the WC–Co (6%) hard alloy, (2) cobalt, and (3) tungsten carbide and (4) the reduction of hydrogen ions on the tungsten carbide electrode in the 1.25 M H_3PO_4 solution at a temperature of 18°C

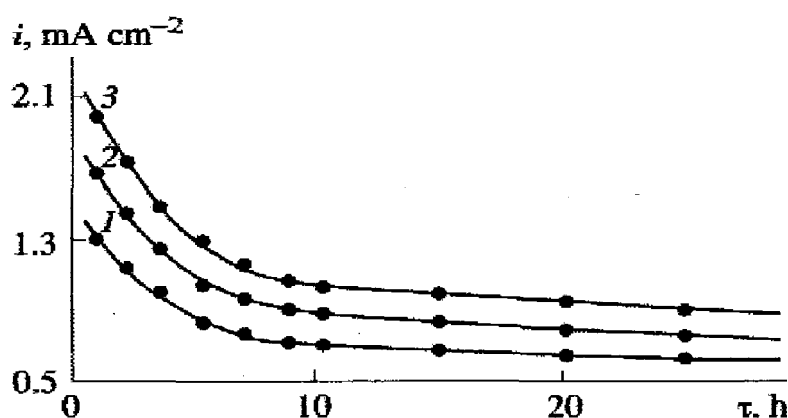*Fig. 2. Time dependence of the rate of dissolution of the CO–W phase from the WC–Co (6%) hard alloy at electrode potentials of (1) −0.15, (2) −0.20, (3) −0.25 V and a temperature of 18°C*
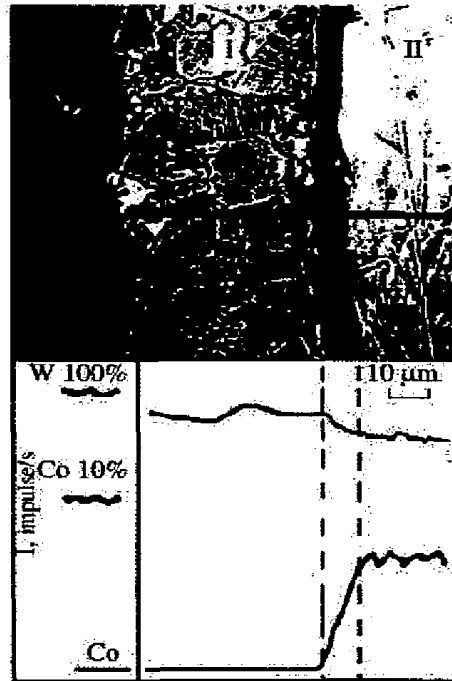
Fig. 3. Micrograph of the cross-sectional microsection of a WC–Co (6%) alloy specimen after anodic dissolution in the 1.25 M H₃PO₄ solution and concentration profiles for the distribution of cobalt and tungsten between zone I, subjected to dissolution, and base zone II at an electrode potential of –0.10 V and experiment duration of 10 h (magnification x600)