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ELECTROCHEMICAL ACTION OF COBALT AND OXIDE FORMS OF MOLYBDENUM (TUNGSTEN) (VI) IN BASIS OF ELECTRODEPOSITION OF COBALT-MOLYBDENUM (TUNGSTEN) ALLOYS IN OXIDE FUSIONS

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Electrochemical behavior of cobalt in tungstate melt and the influence of electrolysis conditions on the composition and structure of precipitates of cobalt-molybdenum (tungsten) alloys in tungstate-molybdate melts were studied. It is shown that, with decrease of the cobalt concentration and increase of the molybdenum (tungsten) concentration in the melt, phase composition of the cathode depositions varies from cobalt through cobalt-molybdenum (tungsten) alloys of different composition to pure molybdenum (tungsten).

Key words: cobalt, molybdenum, tungsten, electrochemical behavior, tungstate-molybdate melts, phase composition of cathodic depositions

Before by the authors of works [1-3] were found out general mechanism to law at the electrodeposition of metals alloys for iron triad with titan in halogenide fusions. In this connection both practical and theoretical interest presents the presence of general mechanism to law at the electrodeposition of nickel and cobalt with a molybdenum (a tungsten).

A molybdenum (tungsten) and cobalt have polytypic crystalline grates [4]. Standard electrode potentials of these metals differentiate on 0.070 V halogenide-chloride fusion on the basis of $NaCl\text{-}KCl$ at a temperature 1073 K and on 0.080-0.280 V halogenide-oxide fusion of $NaCl\text{-}KCl\text{-}Na_2MoO_4(Na_2WO_4)\text{-}CoCl_2$ at a temperature 1023 К. In both fusions value of potentials for selection of molybdenum (tungsten) is more possitive values of potentials for selection of cobalt and possibility of receipt is marked continuous molybdenum (tungsten)-cobalt and molybdenum (tungsten)-cobalt sediments of different composition depending on composition of electrolyte and conditions of electrolysis.

Chronovoltage-amperometry with the derivatives of potential at times from $5 \cdot 10^{-3}$ to 10.0 V/s to the regimes of polarization was the basic methods of researches. Experiments executed at an air atmosphere in a quartz reactor. The electrode of comparison is served a platinum-oxygenic electrode - 0,8 Na_2WO_4 – 0.2 WO_3/Pt, air with an alundum diaphragm.

At current-voltage dependences in tungstate fusion, containing the oxide of cobalt (II), looked the wave of renewal at potentials -(0.8-0.9) V. Increase of concentration of depolarizator is accompanied by the encrease of wave height and it displacement to positive direction. Increase of change speed of polarization to 5.0 V/s does not allow to find out phasicness of process. Controlled potential electrolysis at potentials of the looked after wave finds out an only product - cobalt. Dependence of current from the concentration of oxide of cobalt at varying of derivative polarization at times has exactly proportional character. Correlation $i_p/V^{1/2}$ was practically constant in the interval of derivative from 0.05 to 2.0 V/s. The constant of mass transfer of $i_p/n{\cdot}F{\cdot}C$ makes $(2{,}1\text{-}2{,}7){\cdot}10^{-4}$ sm/s, that comports with diffusive delivery.

The mechanism of formation of electro-active particles becomes clear, if to come from the presentation of existence in tungstate fusions of acid-basic balance with participation tungstate- and ditungstate-ions. At addition of cobalt oxide (II) activity of oxygen ions increases, potential of oxygen electrode falls down, that explained by flowing of reaction:

$$CoO \Leftrightarrow Co^{2+} + O^{2-}\ , \tag{1}$$

and electrode process at such conditions it is possible to present as:

$$Co^{2+} + 2e \Leftrightarrow Co^{0}. \tag{2}$$

In obedience to dependence of balanced potential of cobalt electrode on the concentration of cobalt oxide (II) in fusion of tungstate of sodium the number of electrons, being on one electro-active particle, is made 1.9-2.2. An electrode reaction (2) answers to this value.

Quantity of electrons, participating in an electrode process, is determined the on the difference of potentials of peak and semipeak of non-stationary current-voltage dependences $E_{p/2}$ - E_p = 2.2 $R{\cdot}T/n{\cdot}F$. For the different concentrations CoO and speeds of change of polarization from 0.05 to 0.2 V/s value n = 1.7-2.0.

The wave of renewal for ditungstate-ion appears with addition of oxide tungsten (VI) to nickelcontaining tungstate fusion:

$$W_2O_7^{2-} + 6e \Leftrightarrow W^{0} + WO_4^{2-} + 3O^{2-}\ , \tag{3}$$

As a base electrolyte for deposition of alloys of wide composition used fusion of Na_2WO_4 - 1.5 mol. % WO_3. In this electrolyte after it cleaning by electrolysis was execute the electrodeposition of tungsten coverages with a tungsten anode at a temperature interval 1123-1173 K and the cathode closeness of current from 0.04 to 0.14 A/sm^2 with the purpose of determination of structure of fallouts of tungsten. It was set that at the closeness of current from 0,04 to 0,10 And/см2 tungsten coverages have a columned structure and thickness to 150-200 mcm at a microhardness 3.33-4.12 GPa.

For the cathode coprecipitation of metals in an alloy a tungsten anode was replaced by cobalt, and electrolysis carried out at the cathode closenesses of current 0,05-0,12 A/sm^2 in the mentioned temperature interval. The concentration of WO_3 was supported in an interval 0.1-1.5 mol. %, and the concentration of CoO was changed from 0.01 to 1.0 mol. %. Increase of concentration of CoO or temperatures and decline of cathode closeness of current is conduced to the increase of cobalt content in sediment. From fusions, containing 0.08-1.0 mol. % CoO, at a temperature 1123-1173 K on a cathode the continuous layers of intermetallide CoW and Co_3W are consistently exuded. They have a fine-crystallineor stratified structure, and their microhardness diminishes from 8.24 to 4.90 GPa. From fusions, not containing WO_3, at the closenesses of current to 0.05 A/sm^2 appear continuous cobalt layers of sectional or columned-block structure in thick to 50 мкм with a microhardness 1.47-1.77 GPa. At the further encrease of cobalt coverages or increase of closeness of current higher 0.05 A/sm^2 they regenerate to dendrites. Introduction of molybdenum oxide (VI) in cobaltcontaining tungstate fusion has investigation wave of renewal of dimolybdate-ion:

$$4Mo2O_7^{2-} + 6e \Leftrightarrow Mo^0 + MoO_4^{2-} + 3O^{2-}\ . \tag{4}$$

The methods of deposition of alloys are analogical to described higher with a that only difference, that initial fusion of Na_2WO_4 served as – 5.0 mol. % MoO_3. Thus mechanism to law of deposition of alloys are analogical *W-Co*. Thus the molar relation of ions of molybdenum and cobalt changed from 500 to 0.05. From fusions, containing 0.1-0.8 mol. % *CoO*, at a temperature 1123-1173 K on a cathode the continuous layers of intermetallides *CoMo* and Co_3Mo are consistently distinguished. From fusions, not containing MoO_3, at the closenesses of current to 0.05 A/sm^2 appear continuous cobalt layers of block or columned-block structure.

Conclusions. Thus, molybdenum (tungsten)-cobalt alloys can be distinguished on a cathode from oxide fusions as continuous layers. It is possible to manage composition and structure of sediment, changing the concentrations of corresponding components in fusion, temperature and cathode closeness of current. General mechanism to law of electrodeposition of alloys is analogical to such for molybdenum (tungsten)-nickel alloys.

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