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ELECTRODEPOSITIONS OF TUNGSTEN COVERAGES FROM TUNGSTEN-PYROSULFATE FUSIONS AND THEIR INFLUENCE ON ELECTROCHEMICAL AND CORROSIVE ACTION OF TITAN

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The of possibility to increase titanium corrosion resistance by tungsten galvanic coatings deposition from melts was investigated. Methods of of potentiometry, voltammetry, potentiostatic and galvanostatic electrolysis were used to study the electrochemical behaviour of tungstate - pyrosulphate melts. It of was shown that, in of Na2WO4 - Na2S2O7 of melt, multi - electron equilibria and processes can be implemented involving ditungstate ions. It of is determined that effectiveness of the cathodic process at the coating surface is higher than at the tungsten by itself which allows to passivate titanium and to provide electrochemical protection.

Key of words : tungsten, electrolysis, melt, coating, corrosion

Alloying of titan by a molybdenum successfully arrive, for example, superficial alloying of titanic samples by a molybdenum with the use of method of vacuum deposition. The method of high temperature electrometallurgy synthesis (NES) from ionic fusions allows to reduce the temperature of alloying of titan by molybdenum, tungsten and their carbides to 1073-1173 K and substantially to shorten duration of process.

A tungsten did not find wide industrial application as construction material in a kind a scarceness, but is an essential alloying component during overcoating.

For the study of treason of activity of components in tungstened fusion by method at balanced terms it is studied the method of EMF for next cells:

$$Pt,O_2 \left|\, 1-x \;\; Na_2WO_4 - xNa_2S_2O_7 \right|\left| Na_2WO_4 - 0{,}2WO_3 \right| O_2,Pt\,, \tag{1}$$

$$W \left|\, 1-x \;\; Na_2WO_4 - xNa_2S_2O_7 \right|\left| Na_2WO_4 - 0{,}2WO_3 \right| O_2,Pt\,,\;, \tag{2}$$

where x – мольная part $Na_2S_2O_7$ in this fusion.

Galvanic deposition of tungsten on the titanic samples of mark WT 1-0 carried out by the method of NES from fusions 85 mol. % Na_2WO_4 - 15 mol. % $Na_2S_2O_7$ for temperatures 1073-1248 K and cathode density of current 0.04-0.15 A/sm^2 on air. The maximal thickness of coverage folded 500 mcm.

As known, in clean tungstened fusion there is an equilibrium:

$$W_2O_7^{2-} + O^{2-} \Leftrightarrow 2WO_4^{2-} \tag{3}$$

with the constant of equilibrium $K=\left[WO_4^{2-}\right]^2/\left[O^{2-}\right]\left[W_2O_7^{2-}\right]$.

During adding of oxygen ion of $Na_2S_2O_7$ acceptors to fusion of tungstate of sodium it is possible motion of reaction:

$$WO_4^{2-}+S_2O_7^{2-}\Leftrightarrow W_2O_7^{2-}+SO_4^{2-}\ . \tag{4}$$

Probability of flowing of reaction (4) is confirmed by a thermodynamics calculation its free energy ΔG. Derived value ΔG for temperatures 1173 K, which folds is 55.82 kJou/mol. Deposition part of all «participants» of equilibrium (3) through «n» and having regard to ionic balance after a tungsten: $nWO_4^{2-}+2nW_2O_7^{2-}=1$ it is possible to take out out equation of dependence of potential of platinum-oxygen electrode from the concentration of pyrosulfate of sodium. In fusions to which enter pyrosulfate of sodium, ions $W_2O_7^{2-}$ appear after a reaction (4). In this case, the quantity of grammes ions $n\ W_2O_7^{2-}$ of equals the amount of added moles $n\ S_2O_7^{2-}$. Accordingly, molal-shaie concentrations of tungstate ions and ditungsten is determined thus:

$$\left[WO_4^{2-}\right]=1-n\left[S_2O_7^{2-}\right]\ ; \tag{5}$$

$$\left[W_2O_7^{2-}\right]=n\left[S_2O_7^{2-}\right]\ . \tag{6}$$

Such supposition is confirmed by straight proportional character of dependence of current lance of electroreduction of ions $W_2O_7^{2-}$ from the concentration $S_2O_7^{2-}$.

Dropping mathematical transformations, get:

$$E_{O^{2-}}=E^{+}-\frac{27RT}{2F}\cdot lg\,\frac{K\cdot nS_2O^{2-}}{1-2nS_2O^{2-}\ {}^{2}}=E^{+}-\frac{27RT}{2F}\cdot \lg\left[\frac{nS_2O^{2-}}{1-2nS_2O^{2-}\ {}^{2}}\right]. \tag{7}$$

From equation of constant of equilibrium K for a reaction (3) determine there is balanced concentration of electro-active particles, which presents $W_2O_7^{2-}$ = 10^{-5}-10^{-7} mol. % and limits of sensitiveness of tungstenpyrometry are considerably below. Pyrosulfate of sodium, as an oxygen ion acceptor, displaces the equilibrium of reaction (3) to the left. The concentration of electro-active particles $W_2O_7^{2-}$ rises in fusion, here their renewal takes place at potentials -(1.1-1.2) V, that is more positive, than proceeding in the ions of tungstate at -(1.8-2.0) V. Total electrode process has the appearance of reaction (9).