UDC 546.261+621.357.1+669.1+669.2/8

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# EXPERIMENTAL METHODS OF CONTROL BY COVERAGE STRUCTURE IN TUNGSTATE-MOLYBDATE FUSIONS

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The methods of control (composition of atmosphere above electrolytic bath, application of the non-stationary current modes, condition and parameters of electrolysis) by a structure of molybdenum and tungsten coverages are experimentally in tungstate-molybdate fusions.

Keywords: molybdenum, tungsten, coverage, structure, atmosphere, mode of electrolysis, condition of electrolysis

*Introduction.* In literature [1-3] the methods of control for coverages a structure are known in the process of conduct of electrolysis for aquatic or molten electrolytes. The analysis of literary data shows that most effective for ionic fusions are treasons of composition of atmosphere above electrolytic bath, application of the non-stationary current modes of conduct of electrolysis, and also treason of conditions and parameters of electrolysis.

*Purpose of work.* Experimentally to confirm possibility and to define the method of control by molybdenum and tungsten coverage's a structure in tungstate-molybdate fusions.

*Method of experiment.* Experiments executed in the sealed metallic electrolyzer. By electrolytes served as molten mixtures of $Na_2WO_4$-3 mole % $MoO_3$, $Na_2WO_4$-5 mole. % $WO_3$, $Na_2WO_4$-$Li_2WO_4$-10 mole. % $WO_3$. Sedimentation investigated by metallography. The sizes of grains measured by means of microscopes of «*MIM*-8*M*» and «*Hitachi* 800» on the metallographic section of transversal section in the distance 40-50 mcm from basis. A microhardness was measured also on the metallographic section of transversal section by the device of ПМТ-3 on loading on an indenter 100 g. Texture of sediments was studied by means of the x-ray photography setting of «*ДРОН*-4» and diffractometer of «Rigacu of rA».

*Results and their discussions.* Change-out of air atmosphere by inert (argon) practically does not influence on a structure and sizes of grains of sediments. Only differences are more even verges of surface grains in bath with the atmosphere of inert gas.

Entry of carbon dioxide ($CO_2$) to the atmosphere above bath results in grindings of grains of molybdenum and tungsten sediments. Increase of its partial pressure during the electrolysis of fusion $Na_2WO_4$-$Li_2WO_4$-10 mole % $WO_3$ for

temperature 1023 K results in a regeneration in tungsten powder-like sediments and coprecipitate powders of carbon on a cathode.

The increase of temperature reduces influence of $CO_2$ and on 1173 K the continuous sediments of molybdenum and tungsten were got on atmospheres above bath which contains to 100 % $CO_2$.

One of methods of diminishing of sizes of grains there is imposition of impulses of current at the beginning of electrolysis or during its realization. Electrodeposition carried out on temperature 1173 K from fusions of $Na_2WO_4$ are 3.0 mole % $MoO_3$ і $Na_2WO_4$ is 5.0 mole % $WO_3$. As basis was an applied nickeliferous plate. Impulses of current were set by the special generator. The cathode density of direct-current in all experiments presented $7.5 \cdot 10^{-2}$ A/sm$^2$.

X-ray photography researches showed that initial impulses with a value to 30 A/sm$^2$ does not influence on the orientation of sediment. On imposition of impulses of current ~30 A/sm$^2$ during an electrolysis imperfectness of layers grows only, which is predefined by education of new embryos of metal on every grain of sediment,. During imposition of impulses of current with amplitude over 50 A/sm2 sediments regenerate on spongy and poorly coupled with basis.

Tungstates and molybdates of alkaline and alkaline-earch metals are typical ionic liquids: thermally resisting, the not high temperatures of melting, specific conductivity and potentials of decomposition have comparatively. Such properties of the mentioned electrolytes are important for the electrodeposition of high-heat metals and their alloys.

The condition of the kind cohesion of coverage with basis is more positive potential of corrosion comparatively with potential of sedimentation. Therefore for the estimation of possibility of causing of tungsten coverage on different bases was measured stationary potentials of copper, nickel, steel 3, noncorrodible steel, titan in select electrolytes in relation to the semielements of *KCl-NaCl*-2,5 mole % $PbCl_2$ | *Pb*, *NaCl*-5 mole % $Na_2WO_4$ | $O_2$, *Pt* and $Na_2WO_4$-20 mole % $WO_3$ | $O_2$, *Pt*.

Potential of sedimentation of tungsten is considerably electronegative for potentials of corrosion of copper and nickel in fusions of $KCl\text{-}NaCl\text{-}Na_2WO_4\text{-}NaPO_3$ of and $NaCl\text{-}Na_3AlF_6\text{-}Na_2WO_4$ that stipulates possibility of successful coverage. On steels from these fusions loose powder is sediment. In fusions of $Na_2WO_4$- $B_2O_3$, $Na_2WO_4$-$NaPO_3$ and $Na_2WO_4\text{-}Na_2S_2O_7$ stationary potentials of all electrodes considerably more electro-positive for potential sedimentation of tungsten and the coupled coverage appears on them. The same conformities to law a full degree touch analogical molybdeniumcontaining fusions and electrodeposition of molybdenum.

Tungsten coverage's in fusion of $KCl\text{-}NaCl\text{-}Na_2WO_4\text{-}NaPO_3$ appear, if correlation is executed $0.02 < [PO_3^-] / [WO_4^{2-}] \geq 0.18$. On the concentration $Na_2WO_4$ less than 1.0 mole % in loose sediment the admixtures of phosphides are educed, at concentrations over 10 % are tungsten of oxides. Tungsten coverage's in fusion of $NaCl\text{-}Na_3AlF_6\text{-}Na_2WO_4$ appear for the sodium tungstate concentrations of 1-15 %. On a large concentration begins sedimentation of dioxide of tungsten and tungsten bronze.

*Conclusions*.

1. Change-out of air atmosphere by inert atmosphere does not influence on a structure and sizes of grains of sediments during the electrolysis of tungstate-molybdate baths. Entry of carbon dioxide in an atmosphere above these fusions results in grinding of grain of sediment, regeneration of sediment on powder and coprecipitate powders of carbon with a metal that allows considerably to increase microhardness and thickness of sediment.

2. Imposition of cathode impulses of current to 30 $A/sm^2$ for the electrodeposition of molybdenum and tungsten from tungstate-molybdate fusions on own and foreign bases does not violate the all-epitaxial sediment. The condition of his implementation is incomplete impoverishment of cathode layer by dimeric ions. On foreign basis imposition of initial impulse results in diminishing of sizes of grains some increase of microhardness of sediment.

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