

ELECTRODEPOSITION OF ALLOYS AND INTERMETALLIC COMPOUNDS OF MOLYBDENUM (TUNGSTEN) WITH OTHER METALS FROM TUNGSTATE-MOLYBDATE MELTS

Malyshev V.V., Uskova N.N., Shakhnin D.B., Grabchikov S.S.⁽¹⁾

V.I. Vernadsky's Institute of General and Inorganic Chemistry, NAS of Ukraine
32/34 Palladin Ave., Kyiv 03142, Ukraine, victor_malyshev@mail.ru

⁽¹⁾SA "Scientific and Practical Center for Materials Science of NAS of Belarus"
19 P. Brovka St., 220072 Minsk, Republic of Belarus

During the cathode codeposition of metals with molybdenum (tungsten) from oxide tungstate-molybdate melts, determining factors are the following: the difference of standard electrode potentials of the alloy components (ΔE^0); similarity of their crystal lattices; rate of mutual diffusion of the alloy components.

At close values of standard electrode potentials ($\Delta E^0 < 0,2$ B) of codeposited metals and their similar crystal lattices (case of Mo-W pair), cathode process takes place under conditions close to equilibrium. In this case, it is possible to produce continuous deposits of alloys of components over the entire range of compositions.

In case of $\Delta E^0 > 0,2$ B and with heterogeneous crystal lattices (cases of Mo (W)-Ag (Cu) pairs), cathode process occurs under conditions being considerably far from the equilibrium. In this case, the formation of deposits of three types is possible, namely, of sponge, of one component germinated by dendrites of other component, and of needles.

In case of $\Delta E^0 < 0,2$ B and with heterogeneous lattices (cases of Mo (W)-Ni (Co) pairs), cathode process proceeds, as in the first case, under conditions close to equilibrium. In this case, continuous intermetallic deposits obtaining is possible.

In case of $\Delta E^0 > 0,2$ B and with similar crystal lattices (cases of Mo(W)-Re pairs), cathode process occurs under conditions being far from the equilibrium. In this case, in adherent powder deposits are usually formed.

During the alloys formation, low rate of mutual diffusion at electrolysis temperatures (e.g., of refractory molybdenum (tungsten) and rhenium) contributes to poor adhesion between phases crystallites and formation of powder-like deposits. For more low-melting systems (molybdenum (tungsten) - nickel (cobalt)), promoting interdiffusion can lead to a stronger adhesion of phases crystals in deposits and to the formation of a continuous layer.

Co-deposition of molybdenum (tungsten) and nickel from oxide tungstate-molybdate melts is a typical case of electrodeposition of alloys which components have heterogeneous crystalline lattices and similar values of electrode potentials.

Adding of molybdenum oxide (VI) to the nickel-containing tungstate melt leads to the appearance of dimolybdate ion reduction wave. The difference in the potentials of nickel and molybdenum deposition in this case is 0,090-0,115 V at 1173 K. The electrodeposition was performed with cathode current density 0.05-0.1 A/cm² within the temperature range 1123-1173 K. Concentrations of NiO and MoO₃ was changed within intervals 0,025-1,0 and 0.05-1.5 mol. %, respectively. With different ratios of concentrations of MoO₃ and NiO, deposition of continuous layers of intermetallics MoNi, MoNi₃, and MoNi₄ is possible. These layers are characterized by fine crystalline or layered structure. Deposit microhardness decreases from the first to the third intermetallic from 715 to 345 kg/mm².

From melts containing no MoO₃ with current densities up to 0.05 A/cm², nickel layers up to 40-50 microns thick are formed having block or columnar-block structure and microhardness 115-120 kg/mm². Building-up of nickel coatings or increase of current density above 0.05 A/cm² leads to their degeneration into the dendrites.

Patterns described above are also typical for the deposition of tungsten-nickel alloys. Depending on the ratio of concentrations of WO₃ and NiO, on temperature, and on cathode current density, complex layers of tungsten, WNi, WNi₃, WNi₄, and nickel of various composition were obtained from molten Na₂WO₄ - WO₃ - NiO.

One of the main factors of the coatings deposition is the proximity of the electrode potentials of co-deposited metals. In this case, cathodic process proceeds under conditions close to equilibrium.