Potassium—Cesium Molybdenum Oxide Bronzes

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Abstract — The electrochemical synthesis of potassium—cesium molybdenum oxide bronzes in ionic melts of the potassium—cesium molybdates of the ternary system $K_2MoO_4–Cs_2MoO_4–MoO_3$ is investigated. Two regions for compositions of the electro-crystallization of two alkaline bronzes $K_xCs_yMoO_3$ are revealed. The electrical conductance of corrosion-proof bronzes in solutions of strong electrolytes is studied, along with the application of a 2D protective coating to metals.

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INTRODUCTION

Oxygen multialkaline bronzes of transition metals, including molybdenum, arouse considerable interest as new inorganic compounds of varying composition which are promising for use as current-conducting corrosion-proof coatings; hemichrome and ion-selective electrode materials; in fuel cells and electronics; as catalysts of organic synthesis; and in nuclear power [1—3]. Among the new state-of-the-art methods for their manufacture, electrochemical synthesis in ionic melts, which makes considerably better use of existing technologies, is highly productive. Physicists and chemists have in recent years given a great deal of attention to interpreting of mechanisms of electroreduction during the electrodeposition of compounds of the VI—A group from ionic melts [4] based on multiple electronic processes for the separation of nonmetal and metal products, based on the discharge of oxygen ions of the polysalts of molybdenum and tungsten.

In this work, we systematically investigate multialkaline bronzes with the general formula $M^+EO_4^–$ $M'^+EO_4^–$ $EO_3^–$ (where $M$ and $M'$ are alkaline elements, and E is Mo and W), obtained on the basis of the feasibility curves for ternary oxide—salt systems consisting of two molybdates of alkaline metals and molybdenum (tungsten) trioxides. We consider the electrosynthesis of potassium—cesium molybdenum oxide bronzes $K_xCs_yMoO_3$ from melts of the system $K_2MoO_4–Cs_2MoO_4–MoO_3$. The sides of the phase diagrams of the system are represented by polysalts of types $K_2MoO_4⋅nMoO_3$ ($n = 1, 2, 4, 6$), $Cs_2MoO_4⋅nMoO_3$ ($n = 1, 2, 4, 6$).

The system $K_xMoO_4–Cs_yMoO_3$ is studied for the first time. We determine the formation of a number of continuous solid solutions with a minimum at 50 mol % of components and 860°C during crystallization from a melt, which is characteristic also for the low-temperature modification of salts in the region of the solidus below 570°C. The stability of these isomorphous mixtures is verified also in the ternary system $K_2(Cs_2)MoO_4–MoO_3$. The second zone of continuous solid solutions of potassium—cesium trimolybdates with a monoclinic system is presented in narrower region (Table 1). The remaining fields also correspond to side junctions. One feature of the cesium side system is its lack of tetramolybdate, which is found in $K_2MoO_4–K_2MoO_4$. The figure represents the electrocrystallization region for potassium—cesium molybdenum bronzes in the phase diagram of the ternary system $K_2MoO_4–Cs_2MoO_4–MoO_3$.

EXPERIMENTAL

Methods of bronze production and investigating their chemical composition and properties are given in [1, 5, 6]. The identification of mono- and two-alkaline potassium and cesium bronzes by means of X-ray phase analysis verify their structural types of blue and red potassium and cesium molybdenum bronzes with a monoclinic system [6]. Molybdenum oxide bronzes in binary combinations of alkaline elements K(Rb), K(Cs), Rb(Cs) were obtained for the first time. The figure represents the electrocrystallization region for potassium—cesium molybdenum bronzes in the phase diagram of the ternary system $K_2MoO_4–Cs_2MoO_4–MoO_3$.

In the range of 75—80 mol% MoO_3, we established the formation of cesium penta- and heptapolymolybdates $Cs_5MoO_{16}$ and $Cs_7MoO_{22}$, melting incongruently in the initial stage of crystallization. These correspond to small fields in the ternary system, verifying the possibility raised by Solodovnikov that compounds unstable in binary systems can exist in ternary systems. Isupov believes that these higher molybdates belong to a kind of lamellar structure formed on the basis of MoO_6 octahedrons with different thicknesses [7].
of alkaline metal oxymolibdates, MoO₃, and corresponding oxide bronzes.

Alkaline molybdenum oxide bronzes KₓCs₁₋ₓMoO₃ were obtained electrochemically from melts of the ternary system K₂(Cs₂)MoO₄–MoO₃ in a range of 75–82 mol % MoO₃ at a temperature of 535–550°C, which was higher than the melting point by 20–30°C. Our electrodes were platinum plates. The initial cathode current density in 0.05–0.3 A cm⁻² was maintained during tests. The findings from our investigation are presented in Table 2.

Potassium and cesium molybdenum bronzes (Table 2) were crystallized in blue (nos. 1–5) and red (nos. 6, 7) structures, and the crystal system was monoclinic. The maximum x and y for potassium and cesium were 0.30, despite a difference of 26% for ionic radii in the formulas of the bronzes. Cesium dominated in the K–Cs pairs for samples 3–5 and 2–4, or it was close to potassium by x. This showed the similarity of the compositions of bronzes KₓCs₁₋ₓMoO₃ and KₓRbₓMoO₃ presented in [6], which was probably associated with the equitype monoclinic structures. Ions K⁺ and Cs⁺ were arranged statistically in channels of a polygon–mesh framework of bronze crystals; both were actively incorporated into the lattice of two-alkaline molybdenum bronzes. We considered the mechanism of cathode processes of bronze electrosynthesis as the example of K₀.₃₃MoO₃ in [6] with the participation of polyanionic molybdate complexes. During electrolysis, this is probably accompanied by MoO₃ oxide found in the composition of the salts transitioning to the nonstoichiometric lower MoO₃–δ oxides of the monoclinic system (e.g., Mo₈O₂₃).