Investigation of the mechanism of the joint electrodeposition of molybdenum, tungsten and carbon in oxide and oxihalide melts

H.B. Kushchov, L.M. Beroeva, M.N. Adamokova
Department of Inorganic and Physical Chemistry,
Kabardino-Balkarian State University, Nalchik, Russia

Analysis of the literature data available shows that processes of the joint electrodeposition of W, Mo and C from ionic melts are not studied, although it can be the basis for the electrosynthesis of binary molybdenum and tungsten carbides. Processes of the joint electroreduction of $W_2O_7^{2-}$ and $Mo_2O_7^{2-}$-ions in tungstenate and chloride-tungstenate melts at 750-850°C have been previously studied by us [1, 2] using methods of linear and cyclic voltammetry.

The reduction potential of carbon dioxide is close to the potential of joint discharge of $W_2O_7^{2-}$ and $Mo_2O_7^{2-}$-ions in these melts, and this enables joint electroreduction of tungsten, molybdenum and carbon from tungstenate and chloride-tungstenate melts. In the Na_2WO_4-WO_3-MoO_3 and KCl-NaCl-Na_2WO_4(2,5-20 wt. %)-$Na_2W_2O_7$-$Na_2Mo_2O_7$ melts only one wave at potentials -0.9-1.0 V corresponding to the reduction of $W_2O_7^{2-}$ and $Mo_2O_7^{2-}$-ions is observed in the cathodic part of the voltammogram. Making an excessive pressure of carbon dioxide in the system does not bring about the appearing of an additional reduction wave, but the height of the single reduction wave as well as the difference between the cathodic and anodic wave potentials increase as the carbon dioxide pressure is increasing, while the potential of the wave shifts to the positive area. Changing the polarisation rate in the interval 0.01-1.0 V/s does not allow us to distinguish between different stages of the whole multi-electron process. In the KCl-NaCl-Na_2WO_4 melt the stability of electrochemically active species ($W_2O_7^{2-}$, $Mo_2O_7^{2-}$ and CO_2) is defined by the concentration of Na_2WO_4.

The product of electrolysis at the potentials of joint electroreduction of $W_2O_7^{2-}$, $Mo_2O_7^{2-}$ and CO_2 in tungstenate and chloride-tungstenate melts is binary carbide $(W, Mo)_2C$.

Based on the studies performed we can conclude that controlling acid-basic interactions in the melt it is possible to realise multi-electron processes of the joint electrodeposition of W, Mo and C. The process of joint electroreduction of $W_2O_7^{2-}$, $Mo_2O_7^{2-}$ and CO_2 proceeds in one stage in a thermodynamic mode.

1. Kushkhov Kh.B., Beroeva L.M., Vindizheva M.K., Zimin A.V. Studies of joint tungsten and molybdenum electrodeposition in oxide and oxyhalide melts. X Kola Seminar on rare metals electrochemistry. Apatity, 2000, p. 46.
2. V.I. Shapoval, A.N. Baraboshkin, Kh.B. Kushkhov, V.V. Malyshev. Particularities of electroreduction of molybdenum (VI) as oxy-forms on the base of tungstenate melt. Electrochemistry. 1987. No 7. Pp. 942-946.