Joint electrodeposition of molybdenum and tungsten and molybdenum-tungsten alloys production from oxihalide melts

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From literature data it is known that sodium oxifluoromolibdate is not stable in halide melts. We tried to determine the range of concentrations of an oxihalide melt in which the oxifluoride complex $MoO_2F_4^{2-}$ is stable. Also the processes of joint electroreduction of tungsten and molybdenum oxifluoride complexes in chloride-fluoride melts have been investigated.

The electrochemical behaviour of the KCl-NaCl-NaF(2.5-7.5 wt. %)-$Na_3MoO_3F_3$-$Na_3WO_3F_3$ system has been studied at 750°C by methods of linear and cyclic voltammetry.

We suppose that two kinds of electrochemically active species - $MoOF_6^{2-}$ and $MoO_2F_4^{2-}$ are formed in the KCl-NaCl-NaF-$Na_3MoO_3F_3$ melt when the ratio $[F^-]/[MoO_3]$ is higher than 25. Two waves at potentials –0.6-0.75 V and –1.0-1.1 V versus quasi-reversible platinum/oxygen reference electrode corresponding to the reduction processes of $MoOF_6^{2-}$ and $MoO_2F_4^{2-}$-ions are observed in the voltammograms. When the ratio $[F^-]/[MoO_3]$ is lower than 25, the reduction of a more stable complex $MoO_2F_4^{2-}$ at potentials –0.9-1.0 V takes place.

The reduction process of the complex $WO_2F_4^{2-}$ in the KCl-NaCl-NaF-$Na_3WO_3F_3$ melt proceeds in a similar way at potentials –1.0-1.1 V. Small additions of $Na_3MoO_3F_3$ to the melt do not lead to the appearing of new waves in the voltammogram, neither cathodic nor anodic. These additions only make the reduction wave shift to the area of more positive potentials by 0.1-0.15 V, and decrease its slope.

Similar processes happen when $Na_3WO_3F_3$ is added to the melt containing $Na_3MoO_3F_3$. Sodium tungstenate additions to the melt allow to prevent the formation of intermediate $MoOF_6^{2-}$ complex, which is unstable, and the process becomes more stable.

Therefore, controlling fluoride- and oxide-ions` activities, it is possible to realise the processes of joint electroreduction of $WO_2F_4^{2-}$ и $MoO_2F_4^{2-}$ complexes and obtain tungsten-molybdenum alloys.