# Nanocomposites and nanomaterials

## High-temperature electrochemical synthesis of nanopowders of carbides of tungsten and molybdenum in oxide melts

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Nanopowders application allows solving the problem of obtaining of high strength ceramic and metal materials. Low solubility of $CO_2$ in halide-oxide melts allows for low current density usage to obtain powders with particles size 20-50 nm. Particles size reduction by increase of cathode current density is possible in oxide tungstate-molybdate-carbonate melts. Application of such melts can also eliminate the complex task of creation of electrolyzers working under high pressure.

Conditions for obtaining of tungsten carbide are as follows: electrolyte composition (mol. %): $Li_2CO_3$ – 10-20, $Li_2WO_4$ – 30-45, $Na_2WO_4$ – the rest; T = 1073-1173 K, cathode current density – 1.0-1.7 $A{\cdot}cm^{-2}$. The yield of product is 0.68-0.71 $g{\cdot}A^{-1}{\cdot}h^{-1}$, the current efficiency is 93-97%.

Electrochemical behavior of tungstate-carbonate melts was studied, and mechanism of high-temperature electrochemical synthesis of tungsten carbide was suggested. The mechanism of formation of electrochemically active particles can be described using the theory of cationic catalysis. Electrolysis of melt $Li_2WO_4$ (43 mol. %) - $Li_2CO_3$ (20 mol. %) - $Na_2WO_4$ at 973-1023 K with cathode current density 0.8-1.5 $A{\cdot}cm^{-2}$ allows to obtain a cathode precipitate consisting of $W_2C$ containing 2-5 wt.% of free carbon. $W_2C$ synthesis conditions differ from those of WC synthesis only by electrolysis temperature. Electrochemical synthesis of molybdenum carbide was performed in the following molten oxide electrolyte (mol. %): $Li_2MoO_4$ - 5-20, $Li_2CO_3$ - 10-25, $Na_2WO_4$ - 55-85. Process parameters were similar. The current efficiency was 95-98%.

Nanopowders often contain up to 5-7 wt. % of free carbon and also oxygen adsorbed on the surface which prevents the powders compacting and sintering. Annealing in the activated hydrogen medium removes free carbon (from 7 down to 0.1 wt. %) and reduces the oxygen content by one order of magnitude (from 5 down to 0.2-0.3 wt. %).