

Nanocomposites and nanomaterials

High-temperature electrochemical synthesis of chromium, molybdenum, and tungsten borides in halide-oxide melts

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When comparing the electrodeposition potentials of Cr, Mo, and W in chloride-cryolite melt containing sodium chromate (molybdate, tungstate) with electroreduction potentials of boron oxyfluoride complexes, it is easy to assume that the joint electroreduction of metal and boron cannot be achieved. The potential difference reaches 0.7-0.8 V. These data support the possibility of electrochemical synthesis of borides in the kinetic mode. High-temperature electrochemical synthesis of chromium borides was carried out in molten mixture $\text{NaCl-Na}_3\text{AlF}_6\text{-K}_2\text{CrO}_4\text{-B}_2\text{O}_3$. Depending on melt composition and electrolysis parameters, both individual phases Cr_2O_3 , Cr_2B , CrB , CrB_4 , and mixtures of these phases were obtained. Unlike high-temperature electrochemical synthesis of molybdenum and tungsten borides, in this synthesis procedure, Cr_2O_3 is deposited instead of elementary chromium, and the boron is the reducing agent of this oxide. The yield of the single-phase product CrB_4 was $0.14\text{-}0.21 \text{ g(Ah)}^{-1}$, and the particles size – 55-90 nm.

High-temperature electrochemical synthesis of molybdenum and tungsten borides was realized from the molten mixture $\text{NaCl-Na}_3\text{AlF}_6\text{-Na}_2\text{MoO}_4(\text{MO}_3)\text{-B}_2\text{O}_3(\text{Na}_2\text{B}_4\text{O}_7)$. Optimization of synthesis process lies in the determination of the modes for higher boride MB_4 obtaining. The optimum concentration of MO_3 or Na_2MoO_4 was 0.75-1.5 wt. %. At higher concentrations, due of the instability of metal-salt "pear", complete boriding of deposited refractory metal was not achieved. Within the concentration range of B_2O_3 and/or $\text{Na}_2\text{B}_4\text{O}_7$ 10-20 wt.%, complete boriding of deposited refractory metal is achieved giving phases MoB_4 or WB_4 . The yield of the single-phase product MoB_4 and WB_4 was 0.2-0.3 and 0.3-0.45 g(Ah)^{-1} , respectively. The particles size for powders MoB_4 and WB_4 was 40-85 nm.