Nanocomposites and nanomaterials

High-temperature electrochemical synthesis of chromium, molybdenum, and tungsten silicides from halide-oxide melts

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For chromium silicides obtaining, high-temperature electrochemical synthesis (HTES) was realized in molten mixture NaCl-KF-K_2SiF_6-K_2CrO_4. Depending on the melt composition and electrolysis parameters, both individual phases of Cr_2O_3, Cr_3Si, $CrSi_2$, and mixtures of these phases with low silicon content were obtained. Analysis of interactions of Cr_2O_3 with Si using reference data for obtaining of various silicides (Cr_5Si_3, Cr_3Si, CrSi, $CrSi_2$) and for oxidation of Si to SiO or SiO_2 has shown that the higher silicide $CrSi_2$ formation process proceeds through lower silicides formation steps, and, under HTES conditions (973-1173 K), Cr_3Si and $CrSi_2$ silicides formation, and also oxidation of Si to SiO_2, are thermodynamically the most favorable processes. Experimental data have shown that the process of silicothermic reduction of Cr_2O_3 depends on several factors, among which the decisive role is played by the temperature and duration of the process. With the synthesis temperature 1123-1223 K and with the current density 0.5-1.5 $A \cdot cm^{-2}$, chromium silicide powders were obtained with particles size 30-80 nm.

Electrochemical synthesis of molybdenum and tungsten silicides was carried out from molten mixture NaCl-KF-K_2SiF_6-Na_2MO_4 (where M - Mo W). The first step of the electrolysis process is the formation of the metal-salt "pear" and the silicon deposition process begins with transformation of refractory metal oxisalt. For the HTES, essential are temperature and current density. With the temperature decrease below 1123 K, the completeness of interaction between Mo (W) and Si is not provided, and with the temperature increase above 1223 K, the metal-salt "pear" stability falls, and silicides do not form. With the optimal composition of the melt, pure disilicides $MoSi_2$ and WSi_2 were obtained with cathode current density i_k = 0.5-1.2 $A \cdot cm^{-2}$ for $MoSi_2$ and 0.5-1.5 $A \cdot cm^{-2}$ for WSi_2. The average particles size of obtained powders was 35-70 nm. The yield of $MoSi_2$ was 0.2-0.3, and those of WSi_2 – 0.3-0.45 $g \cdot (A \cdot h)^{-1}$.