Nanocomposites and nanomaterials

High-Themperature Electrochemical Synthesis of Nanopowders of VIB Group Metals Silicides in Ionic Melts

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For synthesis of Cr, Mo, and W silicides, their oxygen compounds were dissolved in KCl-KF and NaCl-Na_3AlF_6 mixtures. In current-voltage curves for chloride-cryolite melts, under joint presence of sodium molybdate and silicon oxide, two waves are observed. The first of them is caused by electroreduction of molybdenum oxyfluoride complex, and the second one - by oxy-fluoride complex of silicon. Difference between half-wave potentials is 0.8-0.9 V. Sumilar situation is observed in presence of sodium tungstate (chromate), with the only difference that difference of half-waves potential is 100-150 mV lower. These data confirm that silicides synthesis could be carried out by electrolysis alone in kinetic regime. It causes the following sequence of steps for electrosynthesis of silicides of molybdenum and tungsten: deposition of more electropositive metals (chromium, molybdenum, or tungsten); deposition of the second component-silicon-on the surface of Cr_2O_3, Mo, or W deposited earlier; and silicon reaction diffusion into the depth of metal-salt "pear" with formation of silicides phases of different compositions up to higher silicides.

Duration of the first stage of synthesis depends on amount of refractory metal in system and on cathode current density. To obtain Cr_2O_3, molybdenum, or tungsten in form of fine powder, current density should be the maximum possible. The second stage begins with exhausting of electropositive component. Synthesis of silicides can be carried out only under conditions that Cr_2O_3, molybdenum, or tungsten powders deposit at cathode surface in form of metal-salt "pear" of such size and shape which allow it to be held firmly at the cathode without breaking. In case Cr_2O_3, molybdenum, or tungsten powders are falling out to the electrolyzer bottom, synthesis components are not in contact with each other, and silicides synthesis does not occur.