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SYNTHESIS OF DISPERSIBLE POWDERS FOR SILICIDES METALS OF VIB GROUP BY ELECTROLYSIS OF HALOGENITE-OXIDE FUSIONS

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The conditions of synthesis for silicides of chrome, molybdenum and tungsten as superfine powders by the electrolysis of halogenide-oxide fusions are found on the basis of study of electrochemical action of chrome- (molybdenum, tungsten) and silicon containing fusions.

Key words: chromium, molybdenum, tungsten, silicon, silicides, superfine powders, electrolysis of haligenide-oxide melts

Connections of silicon with the metals of VI B group present the important class of inorganic connections, possessing alongside valuable descriptions [1]. Most studied and practically important are desilicides MSi_2 (M = *Cr*, *Mo*, *W*). The most widespread method of their receipt a synthesis serves as from elements in the atmosphere of rare gas at a temperature 1273-1373 K. From other known methods it should be noted alumina- and magnesium-thermic renewal of corresponding oxides at a temperature 1873-2573 K. To, besieging from the gas phase of halogenides and, finally, electrolysis of molten salts, which is one of most perspective [2-4].

For the synthesis of fusions of silicides for chrome, molybdenum and tungsten, electrolysis used their oxygen connections, cut-in in mixtures of *KCl-KF* and *NaCl-*Na_3AlF_6. It allowed to realize the high-slays of current and apply graphite as anodic material without the danger of origin of anodic effect.

Besieging of dispersible powders electrolysis was executed in a quartz reactor. An anode the graphite crucibles of brand of МПГ-7 served as, by a cathode are tungsten bar. A product was extracted with a working cathode, dissociated from him and was reduced to powder. Silicides dissociated from salts the successive lixiviating hot water and heated to the temperature 50-60 °C with 10 % solution of sulphuric acid. After it sediment was washed by the distilled water, filtered and dried to permanent mass at a temperature 100-105 °C.

On the current-voltage curves of chloride-cryolite fusions there are two waves at the joint presence of molybdate of sodium and oxide of silicon, first from them answers the electroreduction of oxifluoride complex of molybdenum, second - oxyfluoride complex of silicon. An analogical picture takes place and in presence a

tungstate. These data confirm that the receipt of silicides will be carried out at electrolysis in the kinetic mode [5].

The process of synthesis for silicides can be described by next electrochemical and chemical equations:

- on a cathode

$$Mo_2F_4^{2-} + 6\bar{e} \rightarrow M + 2O^{2-} + 4F^-, \quad (1)$$

$$SiO_xF_y^{4-2x-y} + 4\bar{e} \rightarrow Si + xO^{2-} + yF^-, \quad (2)$$

$$M + zSi = MSi_z; \quad (3)$$

- on an anode

$$2O^{2-} - 4\bar{e} + C \rightarrow CO_2. \quad (4)$$

Duration of the first stage of synthesis depends on the amount of refractory metal in the system and closeness of cathode current. For the receipt of molybdenum or tungsten as superfine powder a closeness of current must be maximal.

The second stage begins as far as making of electropositive component.

Optimization of process of synthesis of fusions of silicides of molybdenum or tungsten electrolysis is taken to determination of concentration correlations, closeness of current, temperature and duration of process. From the concentration of salt in fusion (at i_k = const) depend duration of selection of metal on a cathode. For complete solidification of the distinguished molybdenum or tungsten content of Na_2MO_4 in fusion must not exceed 2 %.

Substantial influence at the synthesis of fusions of silicides of molybdenum and tungsten electrolysis is rendered by the temperature of process and closeness of current. Decline of temperature below 850 °C does not provide plenitude of co-operation of molybdenum (tungsten) and silicon, at the increase of temperature higher 950 °C silicides does not appear. At optimal composition of fusion clean foods get, when a closeness of current is 0.5-1.2 A/sm^2 for $MoSi_2$ and 0.5-1.5 A/sm^2 for WSi_2.

At the synthesis of fusions for silicides of molybdenum and tungsten electrolysis, as well as at direct co-operation of simple matters, a primary process is diffusion of silicon through the layer of metal. A metal here poorly participates in diffusion, and higher silicides appear in the system due to more subzero. Therefore on composition of the got foods substantially influence renders duration of process.

Washed from salts and silicon and dried up silicides of molybdenum and tungsten are fine disperse powders with the size of particles of 0.1-5.0 mcm. The specific surface of $MoSi_2$ and WSi_2 makes 6-15 m^2.

It is known that silicides of VI group are very chemically steady connections, and connection of $MoSi_2$ - most oxidation-resistant among all anoxic connections. A temperature of beginning of active oxidization for $MoSi_2$ is 1600, and for WSi_2 is 1400 °C [6].

Originally the electro synthesis of chrome silicides was carried out from molten mixture of $NaCl$-Na_3AlF_6-K_2CrO_4-SiO_2. Current-voltage dependences contain the waves of renewal for oxifluoride complexes of chrome and silicon at considerably different potentials. Depending on composition and parameters of electrolysis got the

phases of CrO_3, higher silicides of $CrSi_2$, silicides of Cr_3Si in mixture with connections of aluminium.

For optimization of receipt for chrome silicides not containing connection of aluminium, the electro synthesis of silicides was carried out in the system KCl-KF-K_2SiF_6-K_2CrO_4. His current-voltage dependences also mark the waves of renewal of oxifluoride complexes of *Cr* and *Si* at considerably different potentials. Depending on composition and parameters of electrolysis both the individual phases of CrO_3, Cr_3Si and $CrSi_2$ and mixtures of these phases, are got with small content of silicon.

The realizable analysis of reactions of Cr_2O_3 with silicon for the receipt of different silicides (Cr_5Si, Cr_3Si, $CrSi$, $CrSi_2$) and oxidization of silicon to his oxide or dioxide showed that the process of formation for higher silicides $CrSi_2$ flowed through the stages of formation of more subzero silicides and in the conditions of electro synthesis of silicides (700-900 °C) thermodynamics formation for silicides Cr_3Si and $CrSi_2$ and oxidization of silicon is most advantageous to his dioxide.

Conclusions. The mechanisms of high temperature electrochemical synthesis of chrome silicides are set, molybdenum and tungsten from halodenite-oxide fusions. The optimal conditions of receipt of the indicated connections are found, phase composition and properties of the got materials is researched.

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