

ELECTROCHEMICAL SYNTHESIS MECHANISM TiB_2 MELT FROM HALOGEN COMPOUND.

I.V. ZARUTSKY, V.I. SHAPOVAL, S.V. VOLKOV

ACADEMY OF SCIENCE OF UKRAINE

INSTITUTE OF GENERAL AND INORGANIC CHEMISTRY,
KIEV

The possibility of titanium diboride electrochemical extraction from the melt, containing compounds of trivalency titanium and boron is known for a long time. We want to pay attention to separate peculiarities of this process. The finding out the peculiarities permit to understand the role of electrolyte composition in volume mechanism or electrochemical active particles formation. It is possible these particles directly take part in the charge transport reaction.

In Fig.1 the voltamperical dependences at individual and joint reaction compounds of titanium and boron from chloride-fluoride melt are given. Individual reduction is determined by equilibriums (1a), (1b), (2b) in the melt volume, charge transport delay stages (1c) and (2c) for titanium and boron accordingly. The typical features of the joint reduction process are:

a) The availability of one wave at more positive potentials then for separate components,

b) The absolute absence of polarization with exception of concentration polarization at current peak meaning achievement,

c) The accordance of synthesis limiting current to the sum of separate components limiting currents.

The indicated features permit to suppose the process of synthesis is determined in the main by the individual components diffusion and thermodynamics of titanium and boron interaction with a large gain of energy. However, more detailed research shows the point “c” is not observed in the wide interval of polarization rate. Fig.2.3. The polarization rate is greater the meaning of synthesis peak current, as compared with the individual processes, current sums is smaller. So there is no summed diffusion flows and separate reduction processes. There is enough slow chemical interaction of titanium and boron compounds in the melt with formation of electroactive particle. This particle has the phenomenal properties as it can receive nine electrons with the titanium diboride formation. Its properties is too well shown from the researches with the help of cyclic voltamperometry.

In Fig.4 voltamperical diagrams of titanium diboride synthesis taken off at the absence of fluorine too and at its addition are shown.

At the absence of potassium fluoride in the melt the cathode wave is considerably stretched on the potential: peak potential is shifted in the negative region as compared with the titanium diboride potential equilibrium and extraction potential. It is observed strong polarization at the anodic wave too. So, cyclic voltamperogram reflects phenomenon of autoinhibition.

The phenomenon is possible in the only case, when fluorine ions are released at electrolytic reduction of electrochemically active particle with titanium diboride formation. These ions lead to formation

of the new electrochemically unactive complex at the electrode surface.

Potassium fluoride ions addition in the melt leads to titanium diboride extraction potential shifting to the negative region and to polarization reduction for cathode wave as well as for anode one.

Observed phenomena permit to suppose:

a) At the absence of fluorine ions in electrolyte volume the reaction type (3a) with the formation of electrochemically active particle of $\text{TiB}_2\text{F}_8\text{Cl}_4^{3-}$ takes place,

b) At its electroreduction according to the reaction (3c) fluorine ions are released, which inhibit the cathode process. New coordinate compounds are formed (reaction 3b),

c) Potassium fluoride addition to the melt leads to the reactions (3b) in the whole electrolyte volume.

Calculation of ligands quantity (fluorine ions) according to the extraction potential shifting (fig.5) gave the meaning $N=4$, that corresponds to equilibrium (3b). Calculation of electrons quantity according to Nicolson-Shane Theory for the reversible processes gave the meaning "9" for reaction (3c).

There is all grounds to suppose the formation of complex coordinate particle of $\text{TiB}_2\text{F}_8\text{Cl}_4^{3-}$ type, which is electrochemically active one. It is necessary to find out its quantitative composition.