

Construction Principle of Complex Electrochemical Synthesis (ES) Diagrams on the Example of the Ti-B System

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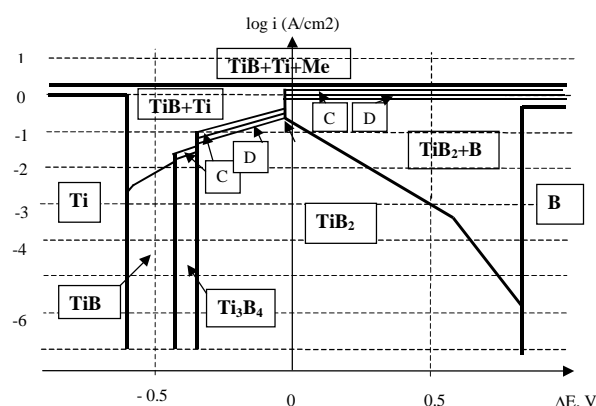
Molten salts are perfect media for the electrochemical synthesis of intermetallics and other metal-like compounds, such as borides, carbides and nitrides [1]. In the majority of A-B phase diagrams (where A is a metal, B is a metal, or carbon, boron, nitrogen) with at least one stable compound, there are several stable compounds are formed. Therefore, when ad-atoms of A and B are deposited at the cathode surface, they can combine into compounds of different stoichiometry, depending on thermodynamic and kinetic conditions. In order to provide a theoretical basis and an engineering tool for the technology of electrochemical synthesis, electrochemical synthesis diagrams should be constructed. In the past, the concept of EES (equilibrium electrochemical synthesis) diagrams were developed and applied to the variety of binary and ternary boron-containing systems [1-4]. The EES diagrams are based purely on thermodynamic approach, i.e. they are valid strictly only at infinitely low current density. However, real high-temperature technologies always apply current densities between 0.001 and 1 A/cm². Hence, complex ES (Electrochemical Synthesis) diagrams should be worked out, taking into account also the kinetic effects. In the present paper the construction principles of such ES diagrams will be presented, on the example of the Ti-B system. Only kinetic effects due to charge transfer of components and diffusion limitations in the melt will be considered (the kinetic role of nucleation and other effects will be neglected).

The ES diagrams will contain the same phases as the 'normal' (composition – temperature) phase diagrams, but in different coordinates. The 'x' coordinate will carry a thermodynamic, while the 'y' coordinate will carry the kinetic information. Therefore an 'x' coordinate will be the difference in deposition potentials of components B and A on an inert cathode, without any compound formation (ΔE). ΔE will be a function of the composition of the molten salt and temperature. Along the 'y' coordinate the logarithm of the current density ($\log i$) will be measured, as the basic electrochemical kinetic parameter. The ES diagrams are constructed at a constant temperature and pressure. Therefore, according to the phase rule, the maximum number of phases, which can co-exist in a given deposited material equals the number of components. In other words, the binary A-B ES diagrams can consist only 1-phase regions and 2-phase regions. If at high current density the cation of the solvent (Me) is also deposited, the system becomes 3-component (A-B-Me) and thus the existence of 3-phase regions is allowed, as well.

An example of the ES diagram is shown in the figure below for the Ti-B system, calculated with the following parameters. It is supposed that the deposition of Ti is taking place from Ti⁺⁴ ions, while the deposition of B from B⁺³ ions. Calculations are performed at 1,000 K and 1 bar. According to the Ti-B phase diagram, under these circumstances three stable compounds exist: TiB₂, TiB and Ti₃B₄, with the standard Gibbs energy of

formation of -314.4 kJ/mol, -176.4 kJ/mol and -674.8 kJ/mol, respectively (relative to pure Ti and pure B as reference materials). The exchange current densities are taken equal: $i_{Ti}^0 = 100$ A/cm², $i_B^0 = 50$ A/cm², the diffusion limiting current densities are taken equal: $i_{Ti}^d = 1$ A/cm², $i_B^d = 0.5$ A/cm², the cathodic charge transfer coefficients are taken equal: $\alpha_{Ti} = \alpha_B = 0.5$.

The ES diagram presented below can serve as a tool for planning experiments and technologies on electrochemical synthesis of materials with Ti and B content. If the desired region is chosen from the diagram, the $i - \Delta E$ values can be selected. The ΔE value can be reached with an appropriate selection of the molten salt composition and temperature (note: temperature causes a minor shift in the lines given in the ES diagram below).



The Electrochemical Synthesis Diagram of the Ti-B system (parameters see in the text)
(regions 'C' = Ti₃B₄ + TiB, 'D': TiB₂ + Ti₃B₄)

References

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