CONSTRUCTION PRINCIPLE OF COMPLEX ELECTROCHEMICAL SYNTHESIS (ES) DIAGRAMS ON THE EXAMPLE OF THE Ti-B SYSTEM

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ABSTRACT

The concept and algorithm of constructing electrochemical synthesis (ES) diagrams is summarized in this paper. The ES diagrams show the phases synthesized, as a function of $\Delta E$ and the logarithm of cathodic current density at the temperature and composition of the melt fixed (where parameter $\Delta E$ is the difference between equilibrium deposition potentials of the two components, A and B, on an inert cathode). The ES diagrams are built using basic information such as standard Gibbs energies of formation of all the phases $A_xB_{1-x}$ in the given A-B system, the exchange current densities and the diffusion limiting current densities of components A and B. As an example, the ES diagram in the Ti-B system is presented, showing five 1-phase regions ($\text{Ti}$, $\text{TiB}$, $\text{Ti}_3\text{B}_4$, $\text{TiB}_2$, $\text{B}$) and different 2-phase regions.

INTRODUCTION

Electrochemical synthesis (ES) is one of the most promising technologies to produce high temperature compounds in the form of coatings or powders from molten salts, by joint electrodeposition of two or more components. By the ES technology intermetallic compounds, borides, carbides, nitrides, silicides, etc. can be produced (reviews on intermetallides of Ti and boride phases are given in (1, 2)). However, as a rule, in those systems phase equilibria are very complex, and thus depositing the same two atoms A and B from molten salts of different composition, at different temperatures and at different current densities, different phases are formed. Therefore, the need in the ES diagrams showing the phases to be formed under different conditions is obvious. The principles to construct EES (equilibrium electrochemical synthesis diagrams) were developed by us earlier (3-4), and EES diagrams for the binary Ti-B system (3, 4), for the ternary Ti-Al-B system (5) and for the binary Al-Gd, La-B, Gd-B, and Al-La systems (6) have been developed. However, those diagrams are valid only in equilibrium, i.e. at zero current density. During real processing, however, realistic current densities are taking place (usually above 10 mA/cm$^2$). Hence, there is a need to develop the complex ES (electrochemical synthesis) diagrams, taking into account also kinetic effects. In the present paper the kinetic limitations due to the charge transfer and due to diffusion limitations of ions in the melt will be taken into account. The ES diagrams will have the following two axes:
i. the difference of deposition potentials of the components at an inert cathode, providing thermodynamic limitations to the formation of the given compound (for simplicity it will be denoted as $\Delta E$, and defined as $\Delta E = E_B - E_A$)

ii. the logarithm of the current density, providing kinetic limitations to the formation of the given compound.

Having the above two axes, the goal is to fill the diagram with areas of existence of different 1-phase, 2-phase, etc. regions, similarly to the classical (composition-temperature) phase diagrams. As the ES diagrams will be constructed at constant temperature and pressure, according to the phase rule, the maximum number of co-existing phases will equal the number of deposited components. Thus, in a 2-component A-B system only 1-phase and 2-phase regions will exist. However, when a cation of the solvent electrolyte (such as Na or K) is deposited as well at higher current densities, 3-phase regions become possible, too.

First, the ES diagram will be drawn schematically, supposing that only one compound, $A_pB_q$ is formed in the A-B phase diagram. This simplified example will help to understand the basic features of the ES diagrams. After that, the specific Ti-B ES diagram will be constructed, with three phases formed in it ($TiB$, $Ti_3B_4$ and $TiB_2$) (7, 8). This diagram can be considered as an extension of the previously constructed Ti-B EES diagram (3, 4).

CONSTRUCTION OF A GENERAL ES DIAGRAM FOR THE A-B SYSTEM WITH TAKING INTO ACCOUNT ONLY ONE COMPOUND $A_pB_q$

First, thermodynamic and then, kinetic limitation will be considered.

**Thermodynamic Limitations**

Let us study a 2-component A-B system, having one compound $A_pB_q$, where $p$ and $q$ are integer numbers, the so called stoichiometric coefficients of the compound. The compound will be considered as a ‘line compound’, i.e. having negligible homogenous ranges in the phase diagram. The composition of the compound will be expressed through one single variable – the atomic fraction of component $A$ in the compound, $x$. Thus, it will be written as $A_xB_{1-x}$, with $x = p/(p + q)$. The compound is characterized by its own standard Gibbs energy of formation, denoted here as $\Delta G$ [kJ/g-atom]. It is related to the standard Gibbs energy of formation [kJ/mol] by the relationship: $\Delta G = \Delta G_{A_pB_q}^0/(p + q)$.

Let us consider a molten salt system consisting of $A^{m+}$ and $B^{n+}$ ions, discharging at an inert cathode at potentials $E_A$ and $E_B$. Both of these quantities are functions of the molten salt composition and temperature. Now, let the $A_xB_{1-x}$ compound form at the cathode from the $A$ and $B$ ad-atoms, with a synthesis potential $E_S$. Then, the energy of the compound formation $\Delta G$ is spent on shifting the deposition potential of $(1-x)$ moles of component $B$ from $E_B$ to $E_S$, and on shifting the deposition potential of $x$ moles of component $A$ from $E_A$ to $E_S$. Hence, the following equations can be written:

$$-\Delta G = n \cdot x \cdot F \cdot (E_S - E_A) + m \cdot (1-x) \cdot F \cdot (E_S - E_B)$$

[1]
where $F$ = the Faraday number.

Introducing the potential difference $\Delta E = E_B - E_A$, the equilibrium synthesis potential $E_s$ can be expressed from the above equation, relative to the deposition potential of component A, as:

$$E_s - E_A = -\frac{\Delta G}{c \cdot F} + \frac{m \cdot (1 - x)}{c} \cdot \Delta E$$  \[2\]

where $c = n \cdot x + m \cdot (1 - x)$.

In Figure 1, the synthesis potential of the compound is drawn in a coordinate system $(E - E_A) - \Delta E$, according to Eq. [2]. The deposition potentials of components A and B are also shown in Figure 1. The compound will be formed as the first cathodic product, if $E_s > E_A$ and if $E_s > E_B$. Substituting these conditions into Eq. [2], the range of $\Delta E$ can be found, in which $A_xB_{1-x}$ will be the first cathodic product:

$$\Delta E_b = \frac{-\Delta G}{n \cdot x \cdot F} > \Delta E > \frac{\Delta G}{m \cdot (1 - x) \cdot F} = \Delta E_a$$  \[3\]

The ‘a’ and ‘b’ points are shown in Figure 1. The intervals of the $\Delta E$ values, within which the compound and the two components are formed, are shown in Figure 1. These intervals are functions of the temperature only (the pressure dependence becomes significant only at $p > 1,000$ bar). Thus, the previous EES diagrams (3-6) were constructed by us in the $T - \Delta E$ coordinates, and those EES diagrams are valid for any molten salt system of any composition, consisting of some $A^{n+}$ and $B^{m+}$ ions. As the value of $\Delta E$ is function of both composition and temperature, to each particular composition and temperature a ‘working point’ will correspond on the EES diagrams. Thus, the equilibrium phase at low current densities will be a function of temperature and melt composition only (at least, below 1,000 bar).

**Figure 1.** The relative (to $E_A$) deposition and synthesis potentials ($E$) as functions of parameter $\Delta E$. The intervals of $\Delta E$ values, within which phases A, $A_xB_{1-x}$ and B as first cathodic products form, are shown at the top of the figure.
Kinetically, the highest current densities are achieved at lowest depolarizations, i.e. along lines a-0 and 0-b in Figure 1. Thus, the minimum partial depolarization values ensuring the formation of the compound can be written as:

\[
\begin{align*}
\text{at } \Delta E < 0 & \rightarrow \Delta E_A \geq 0, \Delta E_B \geq -\Delta E \quad [4.a] \\
\text{at } \Delta E > 0 & \rightarrow \Delta E_A \geq \Delta E, \Delta E_B \geq 0 \quad [4.b]
\end{align*}
\]

The above equations will be applied when deriving kinetic limitations to the ES diagram.

**Kinetic Limitations, due to the Charge Transfer during Deposition of the Components**

In the first approximation we will assume that the rate of formation of compound \( A_xB_{1-x} \) is limited only by the charge transfer during the deposition of \( A \) and \( B \) atoms. Then, the rate of deposition of \( A \) and \( B \) atoms can be written as:

\[
\begin{align*}
v_A &= \frac{i_A^o}{n \cdot F} \cdot \exp \left( -\frac{\alpha_A \cdot n \cdot F}{R \cdot T} \cdot \Delta E_A \right) \quad [5.a] \\
v_B &= \frac{i_B^o}{m \cdot F} \cdot \exp \left( -\frac{\alpha_B \cdot m \cdot F}{R \cdot T} \cdot \Delta E_B \right) \quad [5.b]
\end{align*}
\]

where \( v_A \) and \( v_B \) - the rates of deposition of components \( A \) and \( B \) onto the unit surface of the cathode (mol s\(^{-1}\) cm\(^{-2}\)),

\( i_A^o \) and \( i_B^o \) - exchange current densities of components \( A \) and \( B \) (A/cm\(^2\)),

\( \alpha_A \) and \( \alpha_B \) - cathodic parameters of charge transfer,

\( R \) - gas constant (8.314 J/molK),

\( T \) - absolute temperature (K).

Generally, atoms \( A \) and \( B \) will not appear in stoichiometric ratios \( A_xB_{1-x} \) on the cathodic surface. However, as both depolarization values \( \Delta E_A \) and \( \Delta E_B \) are functions of \( \Delta E \), there is a certain value of \( \Delta E^* \) at which this stoichiometry is ensured, i.e. the following condition is fulfilled:

\[
\frac{v_A}{v_B} = \frac{x}{1-x} \quad [6]
\]

Substituting Eq-s [5.a-b] into Eq-[6] and taking into account Eq-s [4.a-b], the value of \( \Delta E^* \) can be found as follows:

\[
\begin{align*}
\text{at } \Delta E < 0: \\
\Delta E^* &= \frac{R \cdot T}{\alpha_B \cdot m \cdot F} \cdot \ln \left[ \frac{i_A^o \cdot m \cdot (1-x)}{i_B^o \cdot n \cdot x} \right] \quad [7.a]
\end{align*}
\]
at $\Delta E > 0$:  

$$\Delta E^* = \frac{R \cdot T}{\alpha_A \cdot n \cdot F} \cdot \ln \left[ \frac{i^o_A \cdot m \cdot (1-x)}{i^o_B \cdot n \cdot x} \right]$$ \hspace{1cm} [7.b]

Analyzing Eq-s [7.a-b] one can find that they correspond to the conditions:

$\Delta E^* \leq 0$, if  

$$i^o_A \cdot m \cdot (1-x) \leq i^o_B \cdot n \cdot x$$ \hspace{1cm} [8.a]

$\Delta E^* \geq 0$, if  

$$i^o_A \cdot m \cdot (1-x) \geq i^o_B \cdot n \cdot x$$ \hspace{1cm} [8.b]

The maximum values of the current densities of the compound synthesis $i = i^*$ can be calculated as:

at $\Delta E^* \leq 0$:  

$$i^* = i^o_A \cdot \left[ 1 + \frac{m \cdot (1-x)}{n \cdot x} \right]$$ \hspace{1cm} [9.a]

at $\Delta E^* \geq 0$:  

$$i^* = i^o_B \cdot \left[ 1 + \frac{n \cdot x}{m \cdot (1-x)} \right]$$ \hspace{1cm} [9.b]

If $\Delta E < \Delta E^*$, i.e. if the condition of stoichiometry [6] is not appearing at the surface during the same period of time. Hence, the excess amount of component A will be dissolved back at $E > E_A$, and the brutto current density of synthesis will be determined by the rate of deposition of component B. Thus, the maximum current density of the synthesis of compound $A_xB_{1-x}$ can be written as:

at $\Delta E \leq \Delta E^*$:  

$$i_{max} = i^* \cdot \exp \left[ \frac{\alpha_A \cdot m \cdot F}{R \cdot T} \cdot (\Delta E - \Delta E^*) \right]$$ \hspace{1cm} [10.a]

On the other hand, if $\Delta E > \Delta E^*$, B atoms will be in excess on the surface, i.e. the brutto current density will be determined by the rate of deposition of component A. Thus, the maximum current density of the synthesis of compound $A_xB_{1-x}$ can be written as:

at $\Delta E \geq \Delta E^*$:  

$$i_{max} = i^* \cdot \exp \left[ \frac{\alpha_A \cdot n \cdot F}{R \cdot T} \cdot (\Delta E^* - \Delta E) \right]$$ \hspace{1cm} [10.b]

From Eq-s [10.a-b] one can see that the logarithm of the maximum current densities of synthesis of compound $A_xB_{1-x}$ decreases linearly with the absolute difference between $\Delta E$ and $\Delta E^*$ values. Schematically the logi - $\Delta E$ diagram is shown in Figure 2. The area of stable synthesis of compound $A_xB_{1-x}$ is limited by four lines. The two vertical lines are identical to the broken vertical lines shown in Figure 1 and have thermodynamic origin. The two other lines correspond to Eq-s [10.a-b], with the crossing point at $\Delta E^*$ - logi* described by Eq-s [7.a-b, 9.a-b]. Above those lines two 2-phase regions are situated: the $(A_xB_{1-x} + A)$ region and the $(A_xB_{1-x} + B)$ region. Outside the region of the synthesis of $A_xB_{1-x}$ compound the deposition of A and B components are taking place.
Additional Kinetic Limitations, due to the Diffusion of Ions in the Melt

At high current densities the rates of the electrochemical synthesis and deposition are also limited by the diffusion of ions in the molten salt. If the diffusion limiting current densities of components A and B are denoted as $i_{Ad}$ and $i_{Bd}$, and if these values are below the value of $i^*$, the following changes should be introduced into Figure 2 (see Figure 3):

i. at the B-side of the diagram the horizontal line will separate the one phase region B from the two-phase region $B + A_x B_{1-x}$ at $i = i_{Bd}$,

ii. at the A-side of the diagram the horizontal line will separate the one phase region A from the two-phase region $A + A_x B_{1-x}$ at $i = i_{Ad}$,

iii. the region of the $A_x B_{1-x}$ compound synthesis will be limited by a horizontal line, depending on whether the quantity $i_{Ad}^{ds}$ defined below is larger or smaller than the quantity $i_{Bd}^{ds}$ defined below (for definition see also Eq-s [9.a-b]):

\[
\begin{align*}
 i_{A}^{ds} &= i_{A}^{d} \cdot \left[ 1 + \frac{m \cdot (1-x)}{n \cdot x} \right] \\
 i_{B}^{ds} &= i_{B}^{d} \cdot \left[ 1 + \frac{n \cdot x}{m \cdot (1-x)} \right]
\end{align*}
\]  

[11.a]  
[11.b]

In Figure 3 the case when $i_{A}^{ds} > i_{B}^{ds}$ is shown. Then, the first phase boundary inside the synthesis interval will be drawn at $i = i_{B}^{ds}$, separating the region of synthesis of single phase $A_x B_{1-x}$ from the region of the 2-phase region $A_x B_{1-x} + A$. The same horizontal line will be drawn towards the B-side of the diagram, as due to stoichiometric limitations no more free B can be formed above this line, and thus the 2-phase region ($A_x B_{1-x} + B$) is replaced by the 2-phase region ($A_x B_{1-x} + A$).
The schematic form of the ES diagram (if only one compound is formed between the components, the synthesis is limited both by the charge transfer and the diffusion of the components in the molten salt and if $i^* > i_{A\text{ds}} > i_{B\text{ds}}$)

The 2-phase ($A_xB_{1-x} + A$) region will be limited by a horizontal line at the $i = i_{A\text{ds}}$ value. However, it might be that the value of $i = i_{A\text{d}} + i_{B\text{d}}$ is lower than the $i_{A\text{ds}}$ value; in this case the upper horizontal line is drawn at $i = i_{A\text{d}} + i_{B\text{d}}$. Above this line the cations of the basic electrolytes will be discharged (such as Na or K, depending on the composition), denoted generally as ‘Me’ in Figure 3. Correspondingly, it gives a 3-phase region ($A_xB_{1-x} + A + Me$). If, opposite to what is shown in Figure 3, $i_{A\text{ds}} < i_{B\text{ds}}$, the phases change accordingly, and at high current densities the 3-phase region ($A_xB_{1-x} + B + Me$) will be stable. Thus, in contrary to the EES diagrams, the form of the ES diagrams will depend on the composition of the melt, as the diffusion limiting current densities are proportional to the concentrations of ions $A^{n+}$ and $B^{m+}$, respectively. It will be also the function of temperature, as the limiting current densities are proportional to the temperature dependent diffusion coefficients. In other words, the ES diagram should be constructed specifically for the given melt composition and temperature.

CONSTRUCTION OF ES DIAGRAM FOR THE Ti-B SYSTEM

Thermodynamic Limitations

There are three stable compounds in the Ti-B phase diagram (7), with basic thermodynamic properties given in Table 1 (8) ($A = Ti$, $B = B$, $n = 4$, $m = 3$). The thermodynamic parameters are given in Table 1. The intervals of $\Delta E$-values corresponding to the stability of different phases are given in Table 2. Values given in Table 2 correspond to the EES Ti-B diagram published by us earlier (3, 4). However, in Table 2 the intervals of stability of each compound is divided into two parts, as the equations of depolarization of Ti and B are different in these parts.
Table 1. Thermodynamic parameters of the Ti-B system at 1,000 K

| Phase | p  | q  | x   | c | ΔG, kJ/g-atom (8) | E<sub>S</sub> - E<sub>A</sub>, V (Eq.[2]) |
|-------|----|----|-----|---|-----------------|-----------------------------------------|
| Ti    | 1  | 0  | 1   | 4 | 0.0             | 0                                       |
| TiB   | 1  | 1  | 1/2 | 3.5| -88.2           | 0.2612 + 0.4286 ΔE                      |
| Ti<sub>3</sub>B<sub>4</sub> | 3  | 4  | 3/7 | 3.429| -96.4           | 0.2914 + 0.5 ΔE                         |
| TiB<sub>2</sub> | 1  | 2  | 1/3 | 3.333| -104.8          | 0.3259 + 0.6 ΔE                         |
| B     | 0  | 1  | 0   | 3 | 0.0             | ΔE                                      |

Table 2. The stable phases (at i = 0) and the partial depolarization values needed for their synthesis in different intervals of ΔE

| ΔE interval, V | phase at i = 0 | ΔE<sub>Ti</sub>, V | ΔE<sub>B</sub>, V |
|----------------|-----------------|---------------------|-------------------|
| ΔE < -0.6094   | Ti              | 0                   | < - ΔE            |
| -0.6094 < ΔE < -0.5828 | TiB        | 0                   | > - ΔE            |
| -0.5828 < ΔE < -0.4232 | TiB      | > 0.2914 + 0.5 ΔE  | > 0.2914 - 0.5 ΔE |
| -0.4232 < ΔE < -0.3773 | Ti<sub>3</sub>B<sub>4</sub> | > 0.2612 + 0.4286 ΔE | > 0.2612 - 0.5714 ΔE |
| -0.3773 < ΔE < -0.3447 | Ti<sub>3</sub>B<sub>4</sub> | > 0.3259 + 0.6 ΔE | > 0.3259 - 0.4 ΔE |
| -0.3447 < ΔE < 0.5828 | TiB<sub>2</sub> | > 0.2914 + 0.5 ΔE | > 0.2914 - 0.5 ΔE |
| 0.5828 < ΔE < 0.8146 | TiB<sub>2</sub> | > ΔE                | 0                 |
| ΔE > 0.8146    | B               | < ΔE                | 0                 |

Figure 4. The ES diagram for the Ti-B system (A = Ti, B = B, n = 4, m = 3, T = 1,000 K, i<sub>Ti</sub><sup>0</sup> = 100 A/cm<sup>2</sup>, i<sub>B</sub><sup>0</sup> = 50 A/cm<sup>2</sup>, α<sub>Ti</sub> = α<sub>B</sub> = 0.5, i<sub>Ti</sub><sup>d</sup> = 1 A/cm<sup>2</sup>, i<sub>B</sub><sup>d</sup> = 0.5 A/cm<sup>2</sup>)
(region C = Ti<sub>3</sub>B<sub>4</sub> + TiB, region D: TiB<sub>2</sub> + Ti<sub>3</sub>B<sub>4</sub>)

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Table 3. The coordinates of the starting and ending points of the lines in Figure 4

| Line | Starting Point | Ending Point | Phases left/down from the line | Phases right/up from the line |
|------|----------------|--------------|--------------------------------|-------------------------------|
| 1    | -0.6094 V      | -0.6094 V    | Ti                             | TiB                           |
| 2    | -0.4232 V      | -0.4232 V    | TiB                            | Ti₃B₄                         |
| 3    | -0.3447 V      | -0.3447 V    | Ti₃B₄                         | Ti₂B                          |
| 4    | +0.8146 V      | +0.8146 V    | TiB                            | B                             |
| 5    | -0.6094 V      | 0            | Ti                             | Ti + TiB                      |
| 6    | -0.6094 V      | 0.176 V      | Ti + TiB                       | Ti + TiB + Me                 |
| 7    | -0.5828 V      | -0.5828 V    | TiB                            | Ti + TiB                      |
| 8    | -0.4232 V      | -0.4232 V    | TiB                            | Ti + TiB                      |
| 9    | -0.3447 V      | -0.3447 V    | TiB                            | Ti₂B + TiB                   |
| 10   | -0.3773 V      | -1.605 V     | TiB                            | Ti₂B + TiB                   |
| 11   | -0.4232 V      | -1.737 V     | Ti₂B₄ + TiB                   | Ti + TiB                      |
| 12   | -0.3773 V      | -1.538 V     | Ti₂B₄ + TiB                   | Ti + TiB                      |
| 13   | -0.3447 V      | -1.586 V     | Ti₂B₄ + TiB                   | Ti + TiB                      |
| 14   | -0.3447 V      | -1.507 V     | TiB + Ti₂B₄                   | TiB + Ti₂B₄                   |
| 15   | -0.3447 V      | -1.440 V     | TiB + Ti₂B₄                   | Ti + TiB                      |
| 16   | -0.0292 V      | -0.392 V     | TiB + Ti₂B₄                   | TiB₂ + TiB + B               |
| 17   | +0.5828 V      | -3.477 V     | TiB₂                          | TiB₂ + B                      |
| 18   | -0.0292 V      | -0.0791 V    | TiB₂                          | TiB₂ + Ti₂B₄                 |
| 19   | -0.0292 V      | 0.000 V      | TiB₂ + Ti₂B₄                 | TiB₂ + TiB + B               |
| 20   | -0.0292 V      | 0.067 V      | TiB₂ + TiB + B               | TiB + TiB                     |
| 21   | -0.0292 V      | -0.392 V     | different                     | different                     |
| 22   | +0.8146 V      | -0.301 V     | B                             | TiB₂ + B                      |

Kinetic Limitations

The ES diagram shown in Figure 4 has been constructed with the following kinetic parameters: \( i_{\text{Ti}}^0 = 100 \text{ A/cm}^2 \), \( i_{\text{B}}^0 = 50 \text{ A/cm}^2 \), \( \alpha_{\text{Ti}} = \alpha_B = 0.5 \), \( i_{\text{Ti}}^d = 1 \text{ A/cm}^2 \), \( i_{\text{B}}^d = 0.5 \text{ A/cm}^2 \). In Table 3 each line of the ES diagram of Figure 4 is specified.

Let us briefly describe how the 22 lines appeared in Figure 4 and Table 3. The four vertical lines (vertical lines 1, 2, 3, 4 in Table 3) correspond to the thermodynamic conditions (see Table 2), and divide the diagram at low current densities into five 1-phase regions; from left to right: Ti, TiB, Ti₃B₄, TiB₂ and B. The phases follow each other in the same order as in the common 'x-T' Ti-B phase diagram (7). All the other lines in Figure 4 correspond to kinetic conditions. The diagram should be rationalized from bottom to top, as \( i \) increases, while \( \Delta E = \text{const} \). It also corresponds to the physical reality, as the temperature and composition of the melt determine the form of the diagram and the value of \( \Delta E \). The latter determines the equilibrium phase to be synthesized/deposited at low \( i \). By increasing the current density, kinetic limitations will lead to the formation of different 2-phase regions instead of the formation of a 1-phase region.
In the Interval at $\Delta E < -0.6094$ V, pure Ti will be deposited at low current densities, up to $i_T^d = 1$ A/cm$^2$. Above this value boron will be deposited. However, according to the Ti-B phase diagram, the first compound on the Ti-side is TiB, thus B will be deposited in the form of TiB. Hence, horizontal line 5 at $i = 1$ A/cm$^2$ separates the 1-phase region of Ti-deposition from the 2-phase region of (Ti + TiB) deposition. Increasing the current density further, the B-content of the deposit will gradually increase. Principally the B-content of the deposit can be increased above the stoichiometry of TiB if $i_B^d$ is higher than the current density of B-deposition corresponding to this compound:

$$i_B = \frac{m \cdot (1 - x)}{n \cdot x} \cdot i_T$$  \[12\]

At $i_T^d = 1$ A/cm$^2$, for TiB $x = 0.5$, $n = 4$, $m = 3$, from Eq.[12]: $i_B = 0.75$ A/cm$^2$, which is higher than $i_B^d = 0.5$ A/cm$^2$, and thus the composition of the 2-phase region (Ti+TiB) will never reach the stoichiometry of TiB. Therefore, when the current density is increased above the level of $i_T^d + i_B^d = 1.5$ A/cm$^2$, the potential will be shifted to the potential of deposition of an alkali metal Me from the basic electrolyte. Therefore, at $i = 1.5$ A/cm$^2$ horizontal line 6 will separate the 2-phase region (Ti + TiB) from the 3-phase region (Ti + TiB + Me). This line will be drawn at any value of $\Delta E$ (see below).

In the Interval between $-0.6094$ V < $\Delta E$ < $-0.4232$ V, the primary phase synthesized at $i = 0$ will be TiB. First, let us calculate the maximum current density of pure TiB synthesis at $\Delta E = -0.6094$ V. This value principally can be limited by four different processes:

i. charge transfer of Ti (see Eq-s [5.a, 9.a]):

$$i(Ti - \text{charge}) \leq i_T^* \cdot \left[ 1 + \frac{m \cdot (1 - x)}{n \cdot x} \right] \cdot \exp \left( \frac{-\alpha_n \cdot n \cdot F}{R \cdot T} \cdot \Delta E_n \right)$$  \[13.a\]

ii. charge transfer of B (see Eq-s [5.b, 9.b]):

$$i(B - \text{charge}) \leq i_B^* \cdot \left[ 1 + \frac{n \cdot x}{m \cdot (1 - x)} \right] \cdot \exp \left( \frac{-\alpha_b \cdot m \cdot F}{R \cdot T} \cdot \Delta E_b \right)$$  \[13.b\]

iii. diffusion of Ti – see Eq.[11.a] (equal 1.75 A/cm$^2$),

iv. diffusion of B – see Eq.[11.b] (equal 1.17 A/cm$^2$).

Substituting the depolarization values $\Delta E_T$ and $\Delta E_B$ from Table 2 at $\Delta E = -0.6094$ V into Eq-s.[13.a-b], $i(Ti$-charge) = 175 A/cm$^2$, $i(B$-charge) = 0.00288 A/cm$^2$. Thus, $i = 0.00288$ A/cm$^2$ is the lowest of the four possible current densities at $\Delta E = -0.6094$ V, and thus, the 1-phase region of TiB synthesis will be limited by this current density. This point will be the starting point of line 7.

Repeating the same procedure as above in the whole interval, the limiting current density of the 1-phase region of TiB synthesis can be found. As this interval consists of
two parts (see Table 2), line 7 and line 8 will be the limiting lines (see Table 3). It can be shown that the charge transfer of B is limited most in the whole interval. Thus, lines 7-8 will separate the 1-phase region of TiB synthesis from the 2-phase region, where some extra Ti is deposited in addition to TiB, as the B-deposition is limited due to its charge transfer. This 2-phase region (TiB + Ti) joins the 2-phase region (Ti + TiB) discussed above.

In the Interval between \(-0.4232 \text{ V} < \Delta E < -0.3447 \text{ V}\), the primary phase synthesized at \(i = 0\) will be TiB4. If the analysis shown above is repeated here, it can be shown that in the whole region the rate limiting step is the charge transfer of B atoms. This interval is also sub-divided into two parts (see Table 2). This sub-division is hardly visible in Figure 4, but it is indicated by the presence of two lines 9-10 in Table 3. As the charge transfer of B-deposition is limited above lines 9-10, some extra Ti will be deposited on the top of TiB4 phase, leading to the formation of the 2-phase (TiB4 + TiB) region (denoted by region 'C' in Figure 4), according to the phase diagram (7). The 2-phase region will be converted to the 1-phase (TiB), when the stoichiometric amount of extra Ti is deposited, according to the reaction: \(\text{TiB}_4 + \text{Ti} = 4 \text{TiB}\). Hence, 1 mole of TiB4 (i.e. \(3*4 + 4*3 = 24\) mole electrons) corresponds to 1 mole of extra Ti (4 moles of electrons). Therefore, line 11 should be drawn parallel to line 9, multiplying the corresponding \(i\)-values of line 9 by coefficient \((1 + (4/24)) = 1.1667\). Similarly, line 12 should be drawn parallel to line 10, multiplying the corresponding \(i\)-values of line 10 by the same coefficient 1.1667. Above lines 11-12 the 2-phase region TiB + Ti is situated, which is joined with the same (TiB + Ti) regions discussed above. It should be noted that lines 11-12 are not exactly straight in the semi-logarithmic coordinates of Figure 4, but the deviation is hardly visible.

In the Interval between \(-0.3447 \text{ V} < \Delta E < +0.8146 \text{ V}\), the primary phase synthesized at \(i = 0\) will be TiB2. If the analysis shown above is repeated here, it can be seen that in this interval the B-charge limitation will change to Ti-charge limitation at a certain value of \(\Delta E\), being somewhere around \(\Delta E = 0\), and denoted as \(\Delta E^*\) (see above). Hence, first this turning point should be found, and then the interval should be considered in two sub-intervals.

In order to find the value of \(\Delta E^*\), Eq-s [5.a-b, 7.a-b] should be applied. According to Table 2, the depolarization equations corresponding to the part of the interval -0.3447 < \(\Delta E\) < 0.5828 should be applied. Substituting these values into Eq-s [5.a-b, 7.a-b], \(\Delta E^* = -0.0292 \text{ V}\) is found. Substituting this value back into Eq-s [13.a-13.b]: \(i^* = 0.405 \text{ A/cm}^2\) is obtained. This \('*\) point will divide the discussed interval into two sub-intervals. Before going on with the discussion, let us check if this maximum \(i^*\) value is permitted by the diffusion limiting current densities. 1 mole of TiB2 is deposited by transferring 10 moles of electrons: 4 moles of electrons for depositing 1 mole of Ti plus \(2*3 = 6\) moles of electrons for depositing 2 moles of B. Thus, the partial current densities of Ti and B at the \('*\) point can be calculated as: \(i_{\text{Ti}}^* = 0.4 \cdot i^* = 0.162 \text{ A/cm}^2\) (< \(i_{\text{Ti}}^d = 1 \text{ A/cm}^2\)), \(i_{\text{B}}^* = 0.6 \cdot i^* = 0.243 \text{ A/cm}^2\) (< \(i_{\text{B}}^d = 0.5 \text{ A/cm}^2\)). As the diffusion limiting current densities for both components are higher than the partial current densities of the components at point \('*\)', the \('*\) point will actually appear in the ES diagram (see Figure 4). Otherwise this point would be a virtual point, overdrawn by lines corresponding to the diffusion control of one of the components.
In the Sub-Interval between \(-0.3447 \, V < \Delta E < -0.0292 \, V\), the primary phase is TiB\(_2\) at \(i = 0\), and the first limitation is the charge transfer of component B. According to Table 2, this sub-interval is not divided into two parts, from point of view of the depolarization equations. Thus, a single line 13 will indicate the highest current density values at which the single compound TiB\(_2\) can be deposited. This line will end at the ‘**’ point, and will start at \(\Delta E = -0.3447 \, V\). When the current density is higher than that indicated by line 13, some extra Ti will be deposited onto TiB\(_2\), and thus, according to the Ti-B phase diagram, the 2-phase region TiB\(_2\)-Ti\(_3\)B\(_4\) will be formed (7), indicated by ‘region D’ in Figure 4. This 2-phase region will become a 1-phase Ti\(_3\)B\(_4\), when the reaction 2TiB\(_2\) + Ti = Ti\(_3\)B\(_4\) reaches its stoichiometry. Thus, 2 moles of TiB\(_2\) (i.e. 20 moles of electrons) is in stoichiometry with 1 mole of Ti (i.e. 4 moles of electrons). Therefore, line 14 will be parallel to line 13, but situated at current density, being higher by \((1+4/20) = 1.2\). Above line 14 the 2-phase region TiB\(_2\)-Ti will be situated (denoted as ‘region C’ in Figure 4). It will terminate to a 1-phase region TiB at current density higher by \((1+4/24) = 1.1667\) (see above). This will be line 15, above which the 2-phase region TiB+Ti is situated, what is joined with the other TiB+Ti regions of the diagram. In fact, lines 14 and 15 are not exactly straight in the semi-logarithmic coordinates of Figure 4, but this effect is hardly visible in Figure 4.

In the Sub-Interval Between \(-0.0292 \, V < \Delta E < +0.8146 \, V\), the synthesis of TiB\(_2\) will be limited by the charge transfer of Ti, i.e. Eq.[13.a] will be applied. This sub-interval is divided into two parts, according to Table 2. Lines 16 and 17 will be limiting the 1-phase region of TiB\(_2\) synthesis. Above lines 16-17 some extra B will be deposited above the stoichiometry of TiB\(_2\). As between the phases TiB\(_2\) and B there are no more phases in the Ti-B phase diagram (7), this region will be limited by the diffusion of B\(^{3+}\) ions corresponding to the current density \(i_\text{Bd}^{\alpha}\), to be found by Eq.[11.b]. For this case \(i_\text{Bd}^{\alpha} = 0.833 \, A/cm^2\). Then, the partial current density of Ti is \(0.833 - 0.5 = 0.333 \, A/cm^2\), being below the \(i_{\text{iTi}}^{\alpha} = 1 \, A/cm^2\) value, i.e. this process is not limited by the diffusion of Ti\(^{3+}\) ions. Then, the (TiB\(_2\) + B) 2-phase region will be limited from the top by horizontal line 18 at \(i = 0.833 \, A/cm^2\), lasting from \(\Delta E = \Delta E^* = -0.0292 \, V\) till \(+\infty\).

Above line 18, excess Ti will be deposited on the top of TiB\(_2\). Then, as it was shown above, a parallel line at current density, higher by a coefficient of 1.2 will limit the (TiB\(_2\) + Ti\(_3\)B\(_4\)) 2-phase region, shown as ‘region D’ in Figure 4. This horizontal line 19 will be drawn at \(i = 0.9996 \, A/cm^2\), lasting from \(\Delta E = \Delta E^* = -0.0292 \, V\) till \(+\infty\). Above line 19, excess Ti will be deposited on the top of Ti\(_3\)B\(_4\). Then, as it was shown above, a parallel line at current density, higher by a coefficient of 1.1666 will limit the (Ti\(_3\)B\(_4\) + TiB) 2-phase region, shown as ‘region C’ in Figure 4. This horizontal line 20 will be drawn at \(i = 1.166 \, A/cm^2\), lasting from \(\Delta E = \Delta E^* = -0.0292 \, V\) till \(+\infty\). Above line 20 the (TiB + Ti) 2-phase region is formed, which is joined to the same regions discussed above. In order to separate the different regions situated at the left and right hand sides, but above the ‘**’ point, vertical line 21 is drawn from the ‘**’ point to \(i = 1.166 \, A/cm^2\).

In the Interval at \(\Delta E > +0.8146 \, V\), pure B will be deposited at low current densities, up to the diffusion limiting current density of B, \(i_\text{Bd}^{\alpha} = 0.5 \, A/cm^2\). Above this value Ti will be deposited. However, according to the Ti-B phase diagram (7), the first compound on the B-side is TiB\(_2\), therefore Ti will be deposited in the form of TiB\(_2\). Thus, at \(\Delta E > +0.8146 \, V\), horizontal line 22 at \(i = 0.5 \, A/cm^2\) separates a 1-phase region of B-
deposition from a 2-phase region of (B + TiB₂) deposition. This region is joined with the same region discussed above.

CONCLUSIONS

The general principle of constructing ES diagrams with taking into account thermodynamic and kinetic limitations (the latter with charge and diffusion limits) has been developed and presented on the example of the Ti-B system. It has been shown that while the EES (equilibrium ES) diagrams are unique diagrams for the given A-B system, the upper part of the ES diagrams are also dependent on the composition of the melt and temperature. Comparing the ES diagram with the EES diagram (see (3,4)) (or what is the same, with the bottom part of the ES diagram), one can see some serious changes in deposited/synthesized phases at higher current densities. It should be mentioned that the maximum point of the 1-phase region (point '*' in Figure 4) is situated several orders of magnitude lower than the current exchange densities of the components. The reason is the existence of more than one compound in the Ti-B phase diagram (7). Thus, in order to find the limiting current density of synthesis of a single compound, the thermodynamic properties of the neighboring phases should also be precisely known. The maximum current density of the synthesis of only one compound as a pure phase decreases as the difference between deposition potentials of the components increases. Thus, when the actual absolute value of ΔE is relatively large (above 0.2 - 0.4 V, depending on the system), two phases will be formed on the cathode during practical electrosynthesis (conducted usually above 10 mA/cm²), even if at i = 0 A/cm² only one phase should have been synthesized. This theoretical prediction is confirmed by experiments (9). In the future, a special series of synthesis experiments should be performed to confirm the theoretical ES diagrams.

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