Determination of phase equilibria in alloys by electrochemical method

The study of phase equilibria (phase transition) is realize with many experimental methods. For example, the differential thermal analysis DTA and differential scanning calorimetric method DSC, structural study, resistivity measurements etc.

This problem can be also investigated by the methods used for the measurement of thermodynamic properties, for example, the electromotive force measurement of electrochemical cells which is used for the determination of partial free energy change one of components of solid or liquid solutions (alloys).

The equation describing relation between electromotive force of electrochemical cell and the partial free energy of components can be derive as follows.

The free energy change of the system in the isothermal-isobaric process (T=cons and p=const) can be realized by the reversible work and the change of volume work:

$$dG=W_r-pdV \tag{1}$$

On the other side the reversible work in the electrochemical cell when the infinite current flow by the cell is equal to the sum of electric and volume work changes and is given by the equation:

$$W_r=EdQ-pdV \tag{2}$$

In Eq. (2) E (EMF) is the electromotive force of cell, dQ is the number of ions transported by the cell and -pdV is the change of volume work.

Combining Eq. 2 and 1 we obtain the relation:

$$dG=-EdQ \tag{3}$$

and after its integration, one can obtain the following equation describing relation between the electromotive force of electrochemical cell and the change of free energy :

$$\Delta G=-E\Delta Q \tag{4}$$

Knowing that the charge of one mole of electrons transported in the cell is equal nF, where n is the number of electrons exchanged in the cell during the cell reaction and F is the Faraday constant, equation (4) can be developed to the following one:

$$\Delta G = -nFE \tag{5}$$

So, the main problem is to established the reaction (process) leading in the electrochemical cell.

Let assume that the chemical reaction in the cell is given by the equation:

$$\sum_{i=1}^{s} k_i B_i = 0 \tag{6}$$

In Eq.6 k_i are the stechiometric coefficients of substrates and products B_i . In case of products the coefficients k_i are positive and the substrates negative. The free energy change of reaction (6) is given as follows:

$$\Delta G = \sum_{i=1}^{s} k_i G_i = \sum_{i=1}^{s} k_i \left(G_i^0 + RTln(a_i)\right) \tag{7}$$

Where: R is the gas constant, T is the temperature and a_i is the activity of component *i* in the solution.

The electromotive force of electrochemical cell is a function of reaction occurred in the cell, thus combination of Eq. 7 and 5 gives the equation linking the electromotive force of cell with the thermodynamic properties of components reacting:

$$\Delta G = -nFE = \sum_{i=1}^{s} k_i G_i^0 + RT\sum_{i=1}^{s} k_i ln(a_i) = \sum_{i=1}^{s} k_i G_i^0 + RTln\prod_{i=1}^{s} a_i^{k_i} \tag{8}$$

Dividing both sides of Eq.(8) by –nF one obtains:

$$E = -\frac{1}{nF}\sum_{i=1}^{s} k_i G_i^0 - \frac{RT}{nF}\sum_{i=1}^{s} k_i ln(a_i) = -\frac{1}{nF}\sum_{i=1}^{s} k_i G_i^0 - \frac{RT}{nF} ln\prod_{i=1}^{s} a_i^{k_i} \tag{9}$$

If in the cell reaction the number of substrates is equal Ns and products Np Eq. 9 can be written as follows:

$$\frac{E = -\frac{1}{nF}\sum_{i=1}^{s} k_i G_i^0 - \frac{RT}{nF}\ln\left(\prod_{i=1}^{Ns} a_i^{k_i}\right)}{\prod_{j=1}^{Np} a_j^{k_j}} \tag{10}$$

Knowing that the change of the partial free energy of alloy component i is defined as follows:

$$\Delta\overline{G_i} = RTln(a_i) \tag{11}$$

the equation (10) can be written:

$$E = -\frac{1}{nF}\left(\sum_{i=1}^{s} k_i G_i^0 - \sum_{i=1}^{s} k_i \Delta\bar{G}_i\right) = E^0 - \sum_{i=1}^{s} k_i \Delta\overline{G_i} \tag{12}$$

The above equation is the most general form of relation describing the partial free energy of component i with the electromotive force of the electrochemical cell.

First part of Eq. 12 describes the EMF of cell in the case when the activities of substrates and products are equal to unity (a_i=1) and it is named the standard electromotive force (E^0).

Often the concentration cells are used for the determination of the partial free energy change of one of alloy components. Such cell consist of two electrodes: reference electrode which is very often the pure component A and the alloy electrode consists of two components (A+B) in the simples case and such cell can be presented by the following scheme:

$$M_a| \text{ electrolyte with the I ions } | (M_A+M_B)_{alloy} \tag{13}$$

The electromotive force of cell (13) according to the equation (12), is equal:

$$E = -\frac{1}{nF}\Delta\bar{G}_i \tag{14}$$

What means that the electromotive force (EMF) of the cell (13) divided by nF is equal to the change of the partial free energy of component i.

In one phase composition region of binary solutions and at T=const, $\Delta\bar{G}_i$ and the same the electromotive force E of cell (13) is a function of composition (number of freedom degree is equal 1) and in two phase region $\Delta\bar{G}$ and E are independent of the solution composition what means that in such concentration region the electromotive force is constant (number of freedom degrees is equal to zero). It is the consequence of fact that in the equilibrium state between two phases the values of the partial free energy of component i in both phases is the same $〖\Delta \bar{G}〗_{\downarrow} i' = 〖\Delta \bar{G}〗_{\downarrow} i''$. Thus measuring the electromotive force E for many solutions of different composition one can determine the phase regions in A-B solutions (alloys). Because such experiments are conducted in the equilibrium conditions the concentration phase boundary obtained at given temperatures determine the ranges of phase coexistence that is the phase equilibria.

Let’s assume that the electromotive forces are measured for the system with the monotectic phase transition as shown in Fig. 1.

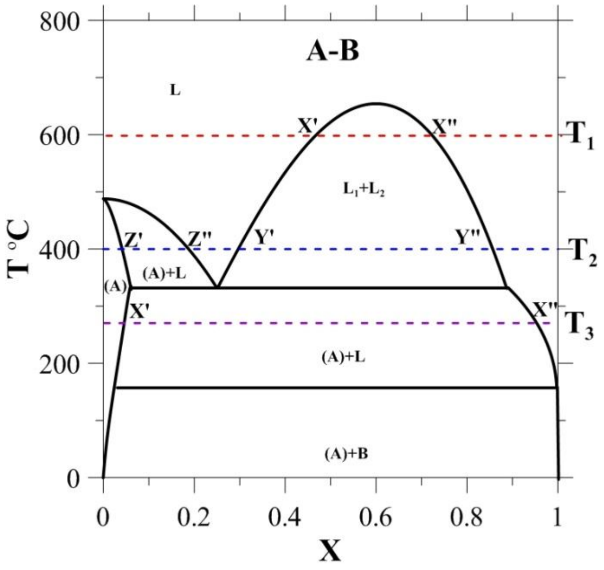


Fig. 1 . The hypothetical A-B phase diagram with the monotectic phase transition.

For this system at the temperature T_1, T_2 and T_3 two-phase regions are between X’-X”, Z‘-Z” and Y’-Y” concentrations. Because the others concentration regions are mono-phase the shape of measured electromotive forces in the entire range of composition will be such as it is seen in Fig.2a, 2b and 2c. In the two-phase concentration regions the EMF is constant because in these regions the number of freedom degrees is equal zero. For the solutions of the composition between or out of the two-phase region the number of freedom degrees is equal 1 and the EMF and $\Delta\overline{G}_i$ is dependent on the concentration of solution. Measuring the EMF for many solutions of the composition between 0<X<1 (X is the molar fraction of component B) and in fixed temperature range one can determine the concentration ranges and temperature of phase transitions.

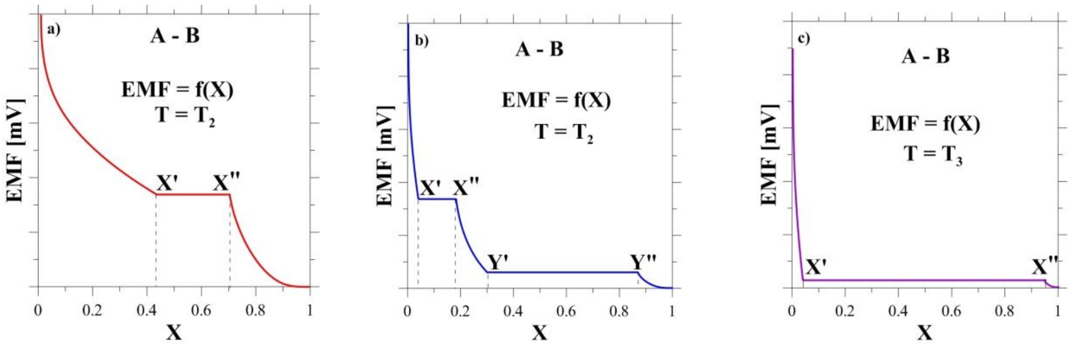
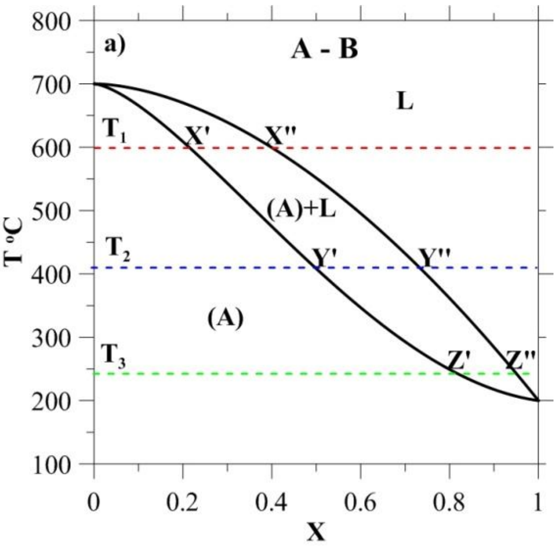


Fig.2. Concentration dependence of electromotive force for the A-B system at temperatures at temperatures T1 (a), T2(b) and T3(c).

In case of the system with the unlimited solubility in the solid and liquid solutions (Fig. 3a) the measured concentration dependencies of electromotive forces at constant temperatures have shapes as it was shown in Fig. 3b. Determining from the EMF measurements the alloy concentration of the beginning and the end of two-phase regions (straight line(s)) at several fixed temperatures one can find the liquidus and solidus in the A-B system.



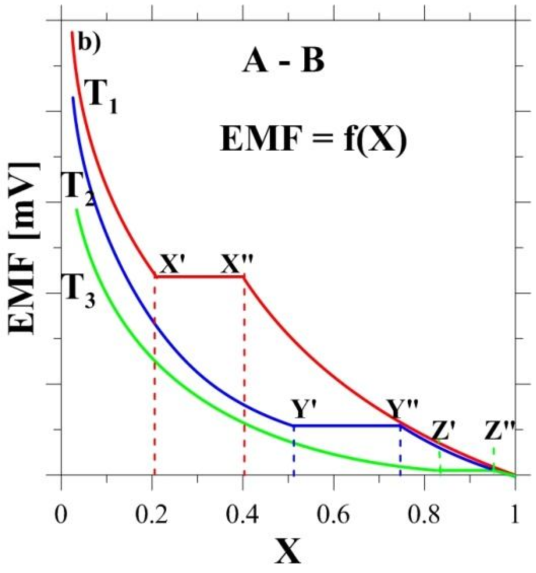


Fig. 3a. Hypothetical A-B system with the unlimited solubility in the solid and liquid state.

Fig. 3b. EMF concentration dependences for the A-B system at temperatures T1, T2 and T3 (Fig. 3a).

A bit more complicated plot of the electromotive force is observed for the binary A-B systems with intermetallic compounds. The phase diagram of such hypothetical A-B system is presented in Fig. 4. It possesses three intermetallic phases. Two phases are characterised by very narrow homogenous region (A_3B, A_3B_2) (they are drawn in Fig. 4 as lines) and the phase (AB) which is distinguished by the homogenous region in the vicinity X=0.5. Additionally, at the presented phase diagram two eutectic transitions are observed. In such binary system, the electromotive force graphs as a function of the concentration are shown in Fig. 5a, 5b and 5c at temperatures T1, T2, T3, respectively. In all cases the electromotive force is characterised by the constant value in two-phase regions, similar as in the earlier discussed systems (Fig. 1 and 3a).

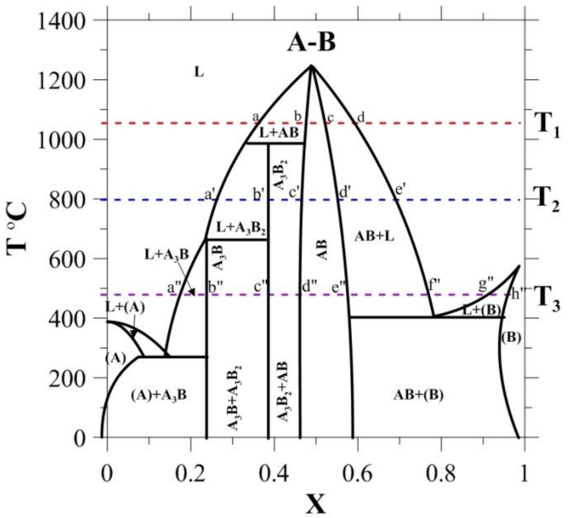


Fig.4. The hypothetic A-B system with three intermetallic phases and two eutectic phase transitions.

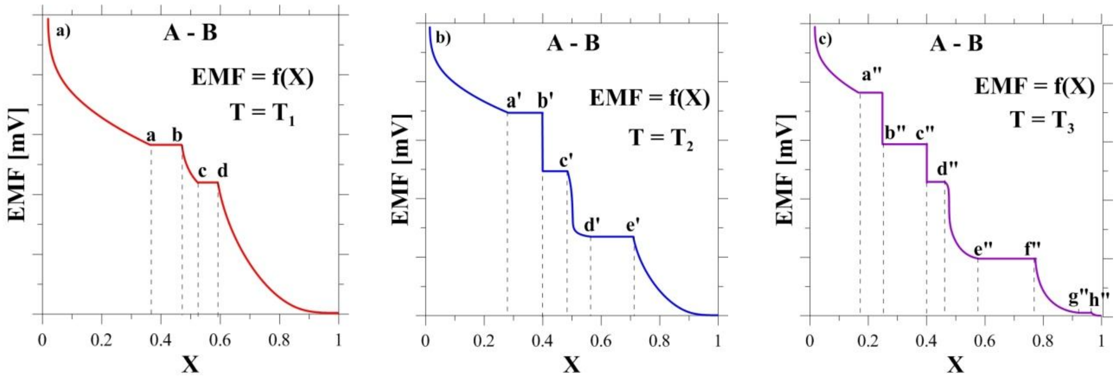


Fig. 5. Plots of EMFs for the A-B system, shown in Fig. 4, at established temperatures T_1(a), T_2(b) and T_3(c).

By crossing the composition of the intermetallic phase with the very narrow homogenous region very sharp drop of the electromotive force is observed at the isotherm EMF graph what is visual in Fig. 5b (X=b') and in Fig. 5c (X=b" and X=c"). In the homogenous region of intermetallic phase the EMF plot possesses the point of inflection in the composition of molecular formula (AB) (Fig.4).

Examples of graphs the measured electromotive force vs. alloy composition are presented in figures 6 and 7 for the Li-Sn [1] and the Mg-Li [2] system, respectively. They were used for the determination of the phase boundary of existing intermetallic phases and next for the critical evaluation of the thermodynamic properties and calculation of the phase equilibria in the lithium-tin and lithium-magnesium system. In the course of investigations the Li-Sn system the titration technique was used. It enabled to determine the EMF data for great number of Li-Sn alloys. This technique is based on the many times electrochemical deposition of lithium at the surface of the alloys (alloy electrode) starting from the pure second component (Sn). The concentrations of successive alloys are calculated basing on the mass of second component (Sn) and the cumulative deposited mass of Li in the alloy electrode which is calculated basing on the Faraday's equation. This method gives the possibility of very exact control of the alloy electrode composition and simultaneously very small changes of the alloy concentration. Therefore, it is very helpful for the determination of phase boundaries, specially, in such systems in which the number of intermetallic phases is numerous in the narrow concentration (see Fig.6).

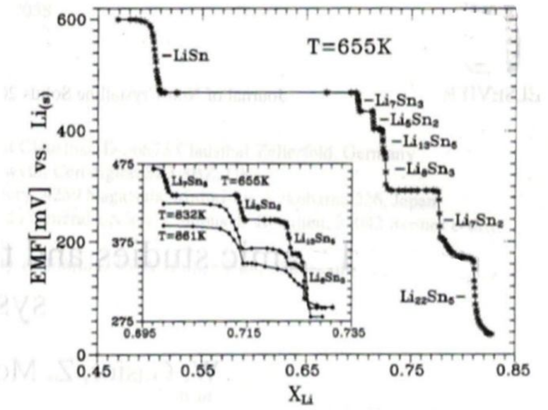


Fig. 6. Coulometric titration curves for the Li-Sn system at various temperatures.

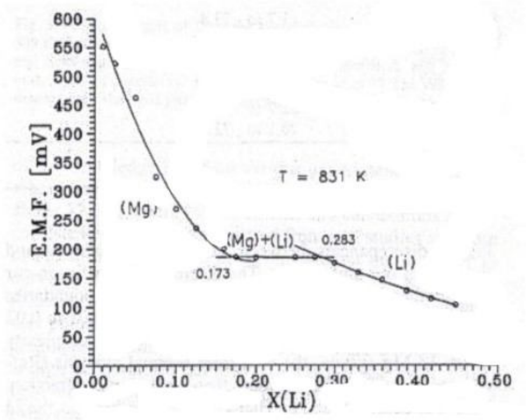


Fig. 7. An example of the determination of the phase boundaries at (Li)/[(Mg)+(Li)] and (Mg)/[(Mg)+(LI)] in the solid phase of the Li-Mg system from emf studies.

In case of the Li-Mg system (Fig. 7) the experiments were conducted for individual alloys and in the fixed temperature range. Basing on the temperature dependences of electromotive forces for many alloys, the values of EMF at the given temperature were analysed and the phase boundaries were determined by the graphical method presented in Fig. 7.

The titration technique can be used for the system and at temperatures when electrochemical cell reached fast the equilibrium state. The second method can be used in the case when the equilibrium state is reached in the measurement cell slowly. Both experimental techniques are very useful in the measurements of thermodynamic properties of alloys and determination of phase boundaries (phase equilibria).

References

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2. W.Gąsior, Z.Moser, W.Zakulski and G.Schwitzgebel, *Thermodynamic Studies and the Phase Diagram of the Li-Mg System*, Metallurgical and Materials Transaction A, 27A(1996)2419-2428.