ANALYSIS OF SOLIDUS LINES OF BINARY METAL SYSTEMS WITH A LOW SOLUBILITY OF COMPONENTS

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The calculation procedure of the maximum solubility and construction of solidus lines of metal systems with a low solubility of components in the solid phase in the range from zero concentration of the second component up to the eutectic point $0 \leq x_{1,2} \leq 0.01\%$ was proposed. The calculation is based on a combination of the thermodynamic laws of phase equilibria and mathematical analysis of the liquidus on the phase diagrams. The examples of the use of proposed method for the constructing solidus lines of the some specific systems based on cadmium, zinc and tellurium have been provided. The retrograde solubility was revealed for Zn-Sn system of the second component in the solid state. The temperature and the maximal solubility at the retrograde nature of the solidus in the system Zn-Sn, as well as the limiting solubility of components at the point of eutectic in Cd-Sh, Te-Al, Zn-Sn systems have been determined.

INTRODUCTION

The eutectic equilibria were observed in the most of the known phase diagrams of (PD) of binary metallic systems [1, 2]. The common eutectics are those based on pure elements ("degenerate" eutectic), on the primary solid solutions (simple eutectic) or grounded on pure and primary solid solutions and intermediate phases – the chemical compounds of various types.

In the overwhelming majority of a binary metal systems the components exhibit a unlimited solubility in the liquid state, but for some systems the mutual solubility of components in the solid state is low (<1% at.), but the complete mutual insolubility of the components in solid state is a limiting case. The solid-phase solubility of the components may be so small at the scale adopted by the drawing of diagrams, that the areas of solid solutions are not resolvable, and it seems that the pure components but not solid solutions are involved in the phase equilibria (Fig. 1).

At the same time, for the narrow areas of primary solid solution of eutectic diagrams the solubility limit (the construction of the solidification curve) is difficult for experimental determination. Therefore, the areas of the PD are either completely unexplored or those have been considered in a limited range of the component concentrations.

The information about solubility areas in the solid state near ordinates of components has a practical importance, especially for the deep purification processes of substances by the crystallization methods, as well as for alloying metals and doping semiconductors. Even a very low solubility has a significant and often extremely strong influence on the electrical, mechanical and technological properties of materials.

One way to determine the boundaries of the saturated solution may be the calculation method, which takes into account the thermodynamics of phase equilibria and the parameters of the known liquidus lines of the phase diagrams. The thermodynamic approach by the use of modern computer technique allows calculate effectively and accurately the unknown segments of solid solubility lines in a wide range of concentrations.

PROBLEM STATEMENT

A critical examination of the PD eutectic systems in view of modern experimental facts and based of them the theoretical concepts allows denote some significant contradictions inherent to these diagrams. One of the contradicitions was associated with the idea of a mandatory limited mutual solubility of the components of the eutectic composition in the solid state and the position of the solidus line in the phase diagrams of those systems in which the solubility (in many cases alleged) is very small [3].

From the viewpoint of thermodynamics, it is necessary to accept a possibility of existence of single-component phase in heterogeneous systems, but the processes such as a thermal motion and a diffusion provide a basis for denial of absolute insolubility [4]. The low solubility due to the placement of atoms of dissolved element in clusters of vacancies, in dislocation tubes, on sub-boundaries and grain boundaries [5] has been observed always even in the case of a considerable dissimilarity of atoms and very unfavorable package design excluding the possibility of placing atoms in the lattice point or interstitial sites of the lattice A (and vice versa). However, the placement possibility of extrinsic atoms into the defect sites of the crystal lattice does not mean that these atoms always determine the state and properties of such systems, which are specific for true solid solutions.

Modern methods of investigation discover the solubility of the order of $10^3 - 10^6$ % in systems where the complete absence of mutual solubility were assumed previously. Thus, it was found that the solubility of aluminum in silicon in the Si-Al system in a solid state is not more than 0.01 at. % and the solubility of Ti and Au in a solid Ge is $\sim 2 \cdot 10^6$ at. % [3]. Systems with a low solubility can be attributed to the system with the "degenerate" eutectic (Fig. 1). The representation of the area of primary solid solutions of these systems in ordinary scale on the PD is not possible (imaginary solidus lines match with the vertical axis of pure components). The visual presentation of the imaginary areas of limited dissolution is possible during the transition to logarithmic coordinates. The existence of solubility areas near
to the ordinates of pure components also was proved in [4] by a thermodynamic method involving structural and kinetic considerations.

![Fig. 1. PD of A-B System is a “degenerate” eutectic (schematically)](image)

In modern literature, the information about the limited solubility, relating to PD of the systems with “degenerate” eutectic, is limited. The development of concepts about the form of the eutectic transformation of slightly soluble components will contribute to the clarification of the PD these systems.

The aim of this work is the development of methods for calculating the limiting solubility of the components in the solid phase and the construction of the solidus lines of binary metallic systems with low solubility of the components in the solid phase within the range from zero concentration of the second component to eutectic point.

**METHOD OF COMPUTATION**

In this paper, the basis of the performed calculations of limiting solubility of the components and the construction of the solidus is the combination of thermodynamic laws of phase equilibria and mathematical analysis of the parameters of the PD liquidus curves.

The value of the limiting solubility and parameters of liquidus curves within a concentration range from 0.1 at. % up to the point of eutectic 0.1 < x_{LB} ≤ x_{BE} at. % are determined from the temperature dependence of the equilibrium distribution coefficient (DC) on the assumption of supposing the ideal behavior of the system [6, 7] where the following expression is obtained:

where \( k_{0B}^A \) and \( k_{0LimB}^A \) – the equilibrium and limiting

\[
\ln \frac{x_i}{x_j} = \frac{T_{MA}}{T} \ln k_{0B}^A - \frac{\Delta S_{MB}}{R} \left( \frac{T_{MA}}{T} - 1 \right) \tag{1}
\]

distribution coefficients respectively; \( T_{MA} \) – the melting temperature of base component A; \( T \) – the temperature on the liquidus, \( \Delta S_{MB} \) - the melting entropy of impurity element, \( R \) – the universal gas constant.

Equilibrium distribution coefficients \( k_{0B}^A \) are the main parameters characterizing the distribution of the components in the solidification process, and they are equal to the ratio of equilibrium concentrations of the impurity elements in two neighboring solid (x_{SB}) and liquid phases (x_{LB}): \( k_{0B}^A = x_{LB}/x_{SB} \).

\[
\ln \frac{x_i}{x_j} = \frac{T_{MA}}{T} \ln k_{0LimB}^A - \frac{\Delta S_{MB}}{R} \left( \frac{T_{MA}}{T} - 1 \right) \tag{2}
\]

Coefficients \( k_{0B}^A \) are converted into limiting distribution coefficients \( k_{0LimB}^A \) at the tendency of the component B content to zero concentration.

For simple eutectic systems, one of the techniques for determining \( k_{0LimB}^A \) described in [7–9] is the method of mathematical analysis of the PD solidus and liquidus curves. Determination of the limiting distribution coefficients (DC) for systems with low solubility is a separate problem. In this connection, the authors of this work were proposed the calculation method for determining the limiting DC for such systems [10, 11].

The basis of calculation approach is the expression for the equilibrium DC in the following form [12]:

\[
k_{0B} = 1 + \frac{q_{LB} \Delta H_{MA}}{RT_{MA}^2}, \tag{3}
\]

where \( q_{LB} \) – the slope of the liquidus, \( \Delta H_{MA} \) – the melting enthalpy of pure component A (dissolvent), \( T_{MA} \) – the melting temperature of base component A.

Formula (3) is true for both the ideal and the real dilute solutions, and when the values \( k_{0B} \) are not very close to unity, it is very convenient for calculation. During the calculation of DC according to the expression (3), the values which relatively easy to obtain experimentally are used. Derivation of ratio (3) may be found, for example, in [6]. This expression was used also for determination of the distribution coefficient \( k_{0LimB} \) [13].

The magnitude \( k_{0LimB} \) depends on the concentration and in a limiting case, when \( x_i \to 0 \), the value \( q_L \) is determined explicitly at the melting point of pure component, it enables the transition from the equilibrium DC \( k_{0B} \) to its limiting value \( k_{0LimB} \).

The procedure for determining \( k_{0LimB} \) consists in the representation of the liquidus in the form:

\[
T_L = p_{LB} \cdot x_{LB}^2 + q_{LB} \cdot x_{LB} + T_{MA} \tag{4}
\]

where \( x_{LB} \) – the concentration of impurities in the approximating equations of liquidus, at. %; \( p_{LB} \) and \( q_{LB} \) – the regression coefficients; \( T_{MA} \) - the melting temperature of base component A.

The regression coefficients in (4) were calculated using mathematical package Maple by the method of least squares from value pairs \( T_L(i), x_{LB}(i) \) taken from PD [1, 2] on the liquidus.

Determining from (4) \( dT_L/dx_L \) at \( x_L \to 0 \)

\[
\frac{dT_L}{dx_L}_{x_L=0} = -q_{LB} \tag{5}
\]
and changing the concentration of atomic percent to
atomic mole fractions \( x_{LB} = x_{LB}/100 \), in final form for
the determination of \( x_{LB} \) the equation (3) is transformed
into the following expression [11, 12]:

\[
K_{0lim, B} = 1 + \frac{100 \cdot q_{LB} \cdot \Delta H_{MA}}{R \cdot T_{MA}^2}.
\]  

(6)

The resulting expression was used to determine
\( K_{0lim, B} \) of slightly soluble components of cadmium, zinc
and tellurium the values of which are given in [10, 11].

In this paper, the calculations of limiting solubility
of slightly soluble components are based on the use of
the values \( K_{0lim, B} \) both directly and as a parameter in the
expressions of equilibrium DC depending on temperature
and concentration of the dissolved component \( x_{LB} \)
on the liquidus line L.

It was shown in [11] that \( K_{0lim, B} \) seeks to continual limit-
ing value of \( x_{LB} \) at the concentration of the second component \( x_{LB} < 0.1 \text{ at.}\% \). Therefore, in the concentration
range \( 0 \leq x_{LB} < 0.1 \text{ at.}\% \) for the determination of
limiting solubility of the second component in the solid
state, the simple expression can be used:

\[
x_{SB} = K_{0lim, B} \cdot x_{LB}.
\]  

(7)

The results of the application (1) for determination of
the limiting solubility and construction of the solidus
on the section \( 0.1 < x_{LB} < x_{BE} \text{ at.}\% \) for certain binary
systems with low solubility on the basis of cadmium,
zinc and tellurium are given in [14].

Thus, based on the above-mentioned laws, the algo-
rithm for the determination of the limiting solubility and
the construction of solidus of eutectic systems with a
low solubility of components in the solid phase is pro-
posed and it consists in following:

- determination of the coefficients of the regression in approximating equations of the liquidus (the tangent
of slope angle of the liquidus in the melting point of the
basic component);
- determination of the limiting distribution coeffi-
cient \( k_A^{lim, B} \) via the tangent of slope angle of the li-
quidus in the melting point of the basic component;
- the calculation of the limiting solubility within the
concentration region \( 0 \leq x_{LB} < 0.1 \text{ at.}\% \) by the values of
concentration on the liquidus, extrapolated to zero
concentration of the impurity element;
- calculation of limiting solubility and construction of
the solidus in the concentration region of variable
values of equilibrium DC \( K_{0lim, B} \) \( 0.1 < x_{LB} \leq x_{BE} \text{ at.}\% \) di-
rectly by the liquidus line parameters obtained experimentally.

**RESULTS AND DISCUSSION**

As the example, Fig. 2 shows the results of calcula-
tions of the limiting solubility and construction of soli-
dus of binary eutectic systems with a low solubility of
components in the solid phase on the section of
\( 0 \leq x_{LB} \leq x_{BE} \text{ at.}\% \) for Cd-Sb, Zn-Sn, Te-Al systems. On
the plots, the concentration range of impurity element
from 0 to 0.1 at.\% (at the left) and the concentration
range of impurity element from 0.1 to \( x_{BE} \) at.\% (at the
right) are considered.

The thermodynamic parameters and coefficients
computed previously by the proposed method to get the
limiting solubility and construction of solidus are pre-
sented in Table.

For the Zn-Sn system the retrograde solubility was
detected, the maximum retrograde solubility is
1.82 at.\% at a temperature of 322.3 °C; while, in
the eutectic point at a temperature \( T_E = 198.5 \text{ °C} \) the solu-
bility is 0.78 at.\%. The limiting solubility of compo-
nents at a eutectic transformation in the Cd-Sb system is
3.5 at.\% at \( T = 290 \text{ °C} \); in the Te-Al system is 0.8 at.\%
at \( T = 432 \text{ °C} \), respectively.

The thermodynamic parameters and the calculated coefficients for the construction of the solidus
of investigated binary eutectic systems

<table>
<thead>
<tr>
<th>Syst.</th>
<th>( \Delta S_{MA} )</th>
<th>( \Delta S_{MB} )</th>
<th>( q_{LB} )</th>
<th>( q_{LB} )</th>
<th>( k_A^{lim, B} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd-Sb</td>
<td>10.43</td>
<td>21.98</td>
<td>-0.3080</td>
<td>-1.9179</td>
<td>0.6</td>
</tr>
<tr>
<td>Zn-Sn</td>
<td>10.59</td>
<td>13.94</td>
<td>0.1836</td>
<td>-5.0580</td>
<td>0.07</td>
</tr>
<tr>
<td>Te-Al</td>
<td>24.20</td>
<td>11.47</td>
<td>-0.0218</td>
<td>-2.2306</td>
<td>0.08</td>
</tr>
</tbody>
</table>

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**CONCLUSIONS**

The algorithm for the calculation of the limiting solubility and the construction of solidus of the phase diagrams of binary eutectic systems with a low solubility of the components in the solid state has been developed.

The limiting solubility of the second component is investigated in the range from zero concentration to 0.1 at.% and from 0.1 at.% to the eutectic point. The solidus curves of phase diagrams for binary eutectic Cd-Sb, Zn-Sn, Te-Al systems constructed by the proposed method in the indicated range of concentrations of the second component are given. The retrograde solubility has been revealed for the Zn-Sn system.

**REFERENCES**


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РАСЧЕТ ЛИНИЙ СОЛЮДУСА БИНАРНЫХ ЭВТЕКТИЧЕСКИХ СИСТЕМ С НИЗКОЙ РАСТВОРИМОСТЬЮ КОМПОНЕНТОВ

A.P. Щербанин, О.А. Даценко

Предложен алгоритм расчета предельной растворимости и построения линий солидуса бинарных эвтектических систем с низкой растворимостью примесей в твердом состоянии на участке от нулевой концентрации до концентрации второго компонента. В основу расчета положено сочетание термодинамических закономерностей фазовых равновесий и математического анализа линий ликвидуса диаграмм состояния. Приведены примеры использования предложенной методики для построения линий солидуса отдельных конкретных систем на основе кадмия, цинка и теллура. Для системы Zn-Sn выявлена ретроградная растворимость второго компонента в твердом состоянии. Определена температура и максимальная растворимость при ретроградном характере линий солидуса в системе Zn-Sn, а также предельные растворимости компонентов в точке эвтектических превращений в системах Cd-Sb, Te-Al, Zn-Sn.

РОЗРАХУНОК ЛІНИЙ СОЛЮДУСА БІНАРНИХ ЕВТЕКТИЧНИХ СИСТЕМ З НИЗЬКОЮ РОЗЧИННИСТЮ КОМПОНЕНТІВ

О.П. Щербанин, О.А. Даценко

Запропоновано алгоритм розрахунку граничної розчинності та побудови ліній солідуса бінарних евтектичних систем з низькою розчинністю домішок у твердому стані на ділянці від нульової концентрації другого компонента до точки евтектичного перетворення 0 ≤ xLB ≤ xBE ат. %. В основу розрахунку покладено поєднання термодинамічних закономірностей фазових рівноваг і математичного аналізу ліній ліквідусу діаграм станов. Наведено приклади використання запропонованої методики для побудови ліній солідуса окремих конкретних систем на основі кадмію, цинку і теллуру. Для системи Zn-Sn виявлена ретроградна розчинність другого компонента в твердому стані. Визначена температура i максимальна розчинність при ретроградному характері ліній солідуса в системі Zn-Sn, а також граничні розчинності компонентів в точці евтектичних перетворень в системах Cd-Sb, Te-Al, Zn-Sn.

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