TWO-COMPONENT SYSTEMS WITH LOW SOLUBILITY OF ELEMENTS IN THE SOLID α-PHASE

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The paper describes the analysis of two-component systems with low solubility of elements in the solid α-phase, which includes calculations of the maximum solubility of the poorly soluble component using the laws of interphase transformations and thermodynamic parameters of the components. Two different approaches to calculating the limiting solubility of poorly soluble components in the solid α-phase are considered: under the assumption of ideal behavior of the system and with deviation of the system from ideal dissolution, i.e. under the condition that the α-phase behaves as a regular solution. Parametric expressions for determining the solubility of poorly soluble components in the solid α-phase are described. The results of applying these expressions for calculating the solubility of the second component in individual systems based on cadmium, zinc, and tellurium are given. The scatter values of the obtained calculated data on the solubility of poorly soluble components in the solid α-phase when the systems deviate from ideal dissolution are given.

INTRODUCTION

The analysis of known state diagrams (DS) of binary metal systems [1, 2] shows that in many cases they form eutectics or peritectics based on pure elements (simple eutectics) from the main component. For some systems the mutual solubility of the components in the solid state is low (< 1 at.%), and complete insolubility of the components in the solid state is a limiting case. The solubility of components in the solid phase can be so small that at the accepted scales of plotting state diagrams regions of solid solutions are not detected and one gets the impression that not solid solutions but pure components participate in phase equilibria (Figure).

For such narrow areas of primary solid solutions of DS it is difficult to determine the ultimate solubility (construction of solidification curves) experimentally. Therefore, such areas of state diagrams remain either not studied at all or considered in a limited area of component concentrations.

Knowing the solubility regions in the solid state near the ordinates of the components is also of practical importance, especially for the processes of deep purification of substances by crystallization methods as well as doping of metals and semiconductors. Even a very small solubility has a large and often exceptionally strong effect on the electrophysical, mechanical and technological properties of materials.

One of the ways to determine the solubility in the solid phase can be a calculation method that takes into account the thermodynamics of phase equilibria and parameters of known liquidus lines of state diagrams as well as the use of only thermodynamic parameters of solution components.

The thermodynamic approach with the use of modern computational computer technology makes it possible to efficiently and with high accuracy calculate the unknown regions of solubility in the solid state in a wide range of concentrations.

FORMULATION OF THE PROBLEM

Consideration of the DS of eutectic systems allows us to note a number of significant contradictions characteristic of these diagrams. One of the contradictions is related to the idea of the mandatory limited mutual solubility of the components of eutectic compositions in the solid state and the position of the solidus line on the DS of those systems in which this solubility is very small [3]. Although thermodynamics does not prohibit the possibility of the existence of single-component phases in heterogeneous systems, such processes as thermal movement and diffusion provide a basis for denying absolute insolubility [4].

Modern research methods reveal solubility of the order of $10^{-3}...10^{-6}$% in systems in which the complete absence of mutual solubility was previously assumed. Systems with such low solubility can be attributed to systems with "degenerate" eutectics (see Figure). It is impossible to depict the region of primary solid solutions in them on the usual scales on the DS (the imaginary lines of the solidus coincide with the ordinate axis of the pure components). Visual presentation of such imaginary areas of limiting dissolution is possible when transitioning to logarithmic coordinates of the image [5, 6].
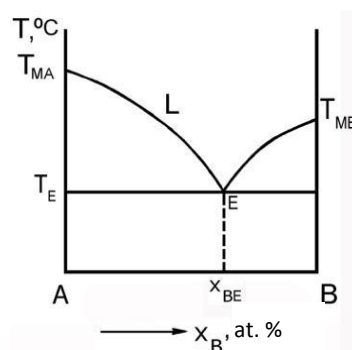
State diagram of system A–B with "degenerate" eutectic (schematic)

In the literature there is limited information on the solubility limit which characterizes state diagrams with "degenerate" eutectics. The development of ideas about the form of eutectic transformations of poorly soluble components will contribute to the construction and specification of DS of such systems.

The purpose of this work is to present the methods of calculating the limiting solubility of poorly soluble components in the solid α-phase of binary metal systems using the regularities of interphase transformations and thermodynamic parameters of the components.

METHODS OF CALCULATIONS AND THEIR DISCUSSION

Works [5, 6] describe the method of calculating the limiting solubility of poorly soluble components in the solid α-phase using the temperature dependence of the equilibrium distribution coefficient k_{0B} which is determined by the ratio of the concentration of component B in the solid x_{SB} and liquid x_{LB} phases under the assumption of ideal system behavior. In works [7, 8] the following expression for determining k_{0B} is given:

$$\ln k_{0B} = \ln \frac{x_{SB}}{x_{LB}} = \frac{T_{MA}}{T} \ln k_{0limB} - \frac{\Delta S_{MB}}{R}\left(\frac{T_{MA}}{T} - 1\right), \quad (1)$$

where k_{0limB} is the limiting coefficient of distribution of component B in A; T_{MA} is the melting point of the main component A; T is the temperature at the liquidus line; R – universal gas constant; ΔS_{MB} is the melting entropy of component B.

The issue of determining the limiting coefficient of distribution k_{0limB} for systems with extremely low solubility of impurity elements in the solid state was solved by the author and his colleagues [9, 10].

Using expression (1) and the value of the concentration of impurity component B at the liquidus line at a given temperature, it is possible to determine the concentration of dissolution of the component in the solid α-phase. Such calculations also make it possible to construct solidus lines of DS for poorly soluble components [5, 6].

It is of interest to determine the solubility of component B in the solid α-phase for systems with low solubility using the regularities of interphase transformations and thermodynamic parameters of the components. At the same time two different approaches are considered.

In the first approach the case of ideal dissolution is considered. The corresponding expression describes the limiting concentration x_{SB} of component B using such parameters as the change in enthalpy ΔH_B during melting of component B, the melting temperature of T_{MA} of the main component, the change in entropy ΔS_B during melting of component B, the universal gas constant R and the temperature-independent limiting coefficient of distribution k_{0limB} of component B in based on A.

In the second approach the deviation of the system from the ideal behavior is taken into account, that is, under the condition that the α-phase behaves like a regular solution. In this case an expression is used to determine x_{SB}, which includes the temperature-dependent partial enthalpy of dissolution $\Delta \overline{H}_B^{\alpha}$ of component B in the solid α-phase.

The work [11] describes the proposed approach for determining the dissolution enthalpy $\Delta \overline{H}_B^{\alpha}$, activity coefficients γ_B^{α} and activity a_B^{α} of binary metal systems with low solubility of components in the solid α-phase.

Analytical expressions for determining the solubility of components with low solubility in the solid α-phase are given below [12]. The expressions are based on the fundamental law of equality of chemical potential $\mu_{SA} = \mu_{LA}$ in solid and liquid phases at constant temperature. In conditions of equilibrium between solid and liquid solutions the law describes, for example, the distribution of impurities between the liquid and solid phases during crystallization. This is effectively used for the purification of materials by directional crystallization methods.

In [8] an expression for the solubility interval of component B in the liquid and solid phases depending on the temperature is given, taking into account the ideal behavior of the system.

$$x_{LB} - x_{SB} = \frac{\Delta H_{MA}}{R}\left(\frac{1}{T} - \frac{1}{T_{MA}}\right), \quad (2)$$

where ΔH_{MA} is the melting enthalpy of the main component; T_{MA} is the melting point of the main component A; T is the temperature of interphase equilibrium; R is a universal gas constant.

Solving (1) together with (2) and entering the appropriate parameters, the following parametric expression for the limiting solubility of component B in the solid α-phase is obtained [12]:

$$x_{SB} = \frac{D(T)e^{C(T)}}{1 - e^{C(T)}}, \quad (3)$$

where $D(T) = \frac{\Delta H_{MA}}{R}\left(\frac{1}{T} - \frac{1}{T_{MA}}\right), C(T) = \frac{T_{MA}}{T}\ln k_{0limB} - \frac{\Delta S_{MB}}{R}\left(\frac{T_{MA}}{T} - 1\right)$. All notations here have the same meanings as in (1) and (2).

To determine the solubility of the second component, taking into account the deviation from the ideal behavior of the system, another approach is considered. One of the values characterizing this deviation is the activity of the second component which is related to the partial enthalpy of dissolution of component B in the α-phase [11].

Based on consideration of the thermodynamic properties of component A in the solid α-phase and in the liquid phase, the following expression was given for the solubility of component B in the liquid phase x_{LB} in [13]:

$$\ln x_{LA} = \ln(1 - x_{LB}) = \frac{\Delta H_{MA}}{R}\left(\frac{1}{T_{MA}} - \frac{1}{T}\right), \quad (4)$$

where the notation is the same as in expression (2).

Equation (4) is the equation of the liquidus line for equilibrium with the α-phase. In the same place, in [13], under the condition of equality of chemical potentials $\mu_{LB} = \mu_{SB}$ at equilibrium the following expression was obtained for the ratio of concentrations of component B in the liquid and solid phases:

$$\ln \frac{x_{SB}}{x_{LB}} = \frac{\Delta H_{MB} - \Delta \overline{H}_B^{\alpha}}{RT} - \frac{\Delta S_{MB}}{R}, \quad (5)$$

where $\Delta \overline{H}_B^{\alpha}$ is the partial enthalpy of dissolution of the component in the solid α-phase; other values are the same as in expression (2).

Expressions (4), (5) are obtained under the condition that the α-phase behaves like a regular solution and the liquid phase which is in equilibrium with the α-phase above the eutectic temperature behaves like an ideal solution. Regular solutions are characterized by the fact that their enthalpy of mixing ΔH_{mix} is different from zero and the entropy of mixing ΔS_{mix} is exactly the same as for ideal solutions. Performing the same procedure as above, marking the right-hand parts in equations (4) and (5) with parameters D(T) and C(T), the following expression is obtained [12]:

$$x_{SB} = e^{C(T)}\left(1 - e^{D(T)}\right), \qquad (6)$$

where $D(T) = \dfrac{\Delta H_{MA}}{R}\left(\dfrac{1}{T_{MA}} - \dfrac{1}{T}\right)$, $C(T) = \dfrac{\Delta H_{MB} - \Delta \overline{H}_B^{\alpha}}{RT} - \dfrac{\Delta S_{MB}}{R}$.

The thermodynamic notations are those in (4) and (5). Expressions (3) and (6) are solved using the mathematical package Mathcad. Work [11] describes the developed calculation method for determining $\Delta \overline{H}_B^{\alpha}$ both for systems with known solubility and for systems with low solubility of component B in the solid α-phase.

The resulting equations (3) and (6) have an exponential form and are parametric expressions for determining the limiting solubility of component B in the solid α-phase. Expression (3) characterizes the ideal behavior of binary systems as it includes temperature-independent parameters. Equation (6) characterizes the deviation of the interaction of the components from the ideal due to taking into account the temperature dependence of the partial enthalpy of dissolution of the second component in the solid phase. The interval of application of equations (3) and (6) extends from the melting temperature of the pure component to the temperature of the eutectic transformation.

The Table shows the calculated solubility data of the B component in the A base for the indicated binary systems which are obtained using expressions (3) and (6). Calculations were made for the specified temperatures T, limiting coefficients of distribution k_{0limB} and partial enthalpies of dissolution $\Delta \overline{H}_B^{\alpha}$. Data on the values of parameters k_{0limB} and $\Delta \overline{H}_B^{\alpha}$ are taken from works [9, 10] and [11] respectively.

Calculated solubility values of x_{SB} components, at.% in the Cd-Tl, Zn-Sn, Te-As, Te-Cu systems and their relative spread δ, %

System	T, °C	$\Delta \overline{H}_B^{\alpha}$, J/mol	k_{0limB}	x_{SB}, at.% (3)	x_{SB}, at.% (6)	δ×100, %
Cd-Tl	295.09	15010		0.25	0.23	8.7
	256.08	15570	0.05	0.5	0.44	13.6
	222.55	16050		0.6	0.51	17.6
Zn-Sn	403.12	11830		0.21	0.25	16.0
	356.93	14400	0.07	0.61	0.55	10.9
	229.89	17940		0.66	0.52	26.9
Te-As	443.35	32180		0.015	0.015	0.0
	440.21	32280	0.006	0.022	0.021	4.7
	406.94	33370		0.071	0.064	10.9
Te-Cu	440.88	24660		0.18	0.17	5.8
	415.37	25150	0.05	0.62	0.55	12.7
	351.60	26380		1.2	0.95	26.3

As can be seen from the Table the values of the limit concentrations of solubility for the studied systems and the selected parameters which are obtained by different methods differ among themselves. The concept of the comparison criterion, %: $x_{SB}/x_{SB}(T) = 1 \pm \delta$ was used to estimate the dispersion of the obtained data.

The value of δ can be considered the "activity" of the second component when dissolving it in the solid phase when the system deviates from ideal dissolution. The given relative dispersions of values of dissolution concentrations δ, % range from 0% to a maximum of 26.3% for the Te-Cu system and 26.9% for the Zn-Sn system. It should also be noted that as the temperature of the solution decreases the values of the deviations increase significantly.

The dispersion of the obtained data on the solubility of components obtained by different calculation methods is explained by the difference in the choice of equilibrium conditions when deriving expressions of the dependence of dissolution on parameters, the accuracy of reference values of thermodynamic quantities, the

accuracy of experimentally constructed liquidus curves of state diagrams, etc., but the main one is the deviation from the ideal behavior of the systems. This can lead to errors in the results obtained by calculation methods.

CONCLUSIONS

Parametric expressions for determining the solubility of poorly soluble components in the solid α-phase are described, which are obtained on the basis of the laws of interphase transformations and the use of thermodynamic parameters of the components. Two different calculation approaches are considered: under the assumption of ideal behavior of the system and under the condition that the α-phase behaves like a regular solution. The results of applying these expressions for calculating the solubility of the second component for such systems as Cd-Tl, Zn-Sn, Te-As, Te-Cu are given. It is shown that the solubility of the second component in the studied systems is < 1 at.%. Values of limit concentrations of solubility for different approaches differ among themselves. As the temperature of the solution decreases the

deviations increase. The main reason for the dispersion of calculated data on solubility is the deviation from the ideal behavior of systems, which must be taken into account when performing such calculations.

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ДВОКОМПОНЕНТНІ СИСТЕМИ З МАЛОЮ РОЗЧИННІСТЮ ЕЛЕМЕНТІВ У ТВЕРДІЙ α-ФАЗІ

О.П. Щербань

Описано аналіз двокомпонентних систем з малою розчинністю елементів у твердій α-фазі, який включає розрахунки максимальної розчинності малорозчинного компоненту з використанням закономірностей міжфазних перетворень і термодинамічних параметрів компонентів. Розглянуті два різних підходи розрахунків граничної розчинності малорозчинних компонентів у твердій α-фазі: у припущенні ідеальної поведінки системи і з відхиленням системи від ідеального розчинення, тобто при умові, що α-фаза веде себе як регулярний розчин. Описані параметричні вирази для визначення розчинності малорозчинних компонентів у твердій α-фазі. Наведено результати застосування даних виразів для розрахунку розчинності другого компонента в окремих системах на основі кадмію, цинку і телуру. Приведені величини розкиду отриманих розрахункових даних щодо розчинності малорозчинних компонентів у твердій α-фазі при відхиленні систем від ідеального розчинення.