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PHASE DIAGRAM CALCULATION IN THE Te-Bi-Sb TERNARY SYSTEM

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Résumé. — On calcule le diagramme de l'équilibre liquide-solide dans le système ternaire Te-Bi-Sb par une théorie de solution régulière associée, utilisée par Laugier.

Abstract. — On the basis of the theory of regular associated solutions the equilibrium phase diagram of the ternary system Te-Bi-Sb was calculated by Laugier's method.

1. Introduction. — Chalcogenide systems, among which tellurium alloys represent the most numerous group, are increasingly often employed, mainly in electronics, both in the crystalline and noncrystalline states [1-3]. They show the interesting property of the dependence of the energy gap on alloy composition, which has been intensively investigated for the Te-Sn-Pb system [1, 4, 5]. Control of the composition of the alloy permits gaining control of its electronic properties. Since different techniques for growing alloy crystals have already been developed [6-10], it is now of interest to determine the dependence of the concentration on temperature. This can be achieved either by means of time- and labor-consuming measurements which permit plotting the equilibrium diagram [8], or — even more frequently — by means of theoretical calculations of equilibrium curves on the basis of the thermodynamics of non-ideal solutions [10, 11, 12]. There is no general calculation method being common for various systems. However, in the case of some types of systems, the application of well-founded assumptions and simplifications affords results consistent with the experimental ones [9, 13]. Consequently, these methods are utilized also for systems which have not been experimentally studied. In this manner equilibrium diagrams have been determined for a number of binary systems. Recently, the methods has been applied also to many ternary systems [e. g. 7, 10, 12].

2. Method of calculation. — **2.1 SYSTEM Te-Bi-Sb.** — The aim of the present study was to calculate the equilibrium diagram for the Te-Bi-Sb system which is homologous to the system Te-Sn-Pb. There is a simi-

larity in the shape of the equilibrium curves in the partial binary systems (Te-Bi, Te-Sb, Bi-Sb and Te-Sn, Te-Pb, Sn-Pb, respectively [14-15]), and in the pseudobinary systems formed by the stoichiometric compounds (Bi_2Te_3 - Sb_2Te_3 [16] and SnTe - PbTe [11, 17], respectively). Both systems exhibit a continuous change in the composition of the pseudobinary compound ($\text{Bi}_x\text{Sb}_{1-x}$) $_2\text{Te}_3$ [18] and ($\text{Sn}_x\text{Pb}_{1-x}$)Te [6], which is associated with a continuous change in electronic properties [14].

Both systems, Te-Bi-Sb and Te-Sn-Pb, satisfy the conditions for application of the theory of regular associated solutions to calculation of the equilibrium diagram. These conditions are as follows [7, 9-10]:

— lack of solubility in the binary systems Te-A^{V} (Te-Bi, Te-Sb) and Te-A^{IV} (Te-Sn, Te-Pb), and complete solubility in the binary systems Bi-Sb and Sn-Pb [14-15],

— the pseudobinary systems formed by the stoichiometric compounds Bi_2Te_3 - Sb_2Te_3 and SnTe - PbTe [16, 17] exhibit complete miscibility in both liquid and solid states, and form a continuous series of solid solutions satisfying Vegard's law, while the liquidus and solidus curves follow a monotonic course and are situated at a short distance from each other.

Since the above conditions are satisfied, the liquid state can be considered an equilibrium mixture of five kinds of species: Te, Bi, Sb, Bi_2Te_3 , Sb_2Te_3 in the system Te-Bi-Sb, and Te, Sn, Pb, SnTe , PbTe in the system Te-Sn-Pb, respectively, and the solid state can be regarded as an equilibrium mixture of two kinds of species: Bi_2Te_3 , Sb_2Te_3 in the system Te-Bi-Sb, and SnTe , PbTe in the system Te-Sn-Pb, respectively.

The respective relationships between the total num-

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bers of moles of the components A , B and C of the ternary system (n_1 , n_2 , n_3 , respectively) and the numbers of moles of the species $A_2 C_3$, $B_2 C_3$, A , B , C are :

$$\begin{aligned} n_1 &= n_A + 2 n_{A_2 C_3} ; \quad n_2 = n_B + 2 n_{B_2 C_3} ; \\ n_3 &= n_C + 3 n_{A_2 C_3} + 3 n_{B_2 C_3} . \end{aligned} \quad (1)$$

Expressions for the molar fractions related to the respective numbers of moles are as follows :

$$\frac{n_i}{x_i} = n_1 + n_2 + n_3 \quad (i = 1, 2, 3) ; \quad (2)$$

$$\frac{n_j}{x_j} = n_A + n_B + n_C + n_{A_2 C_3} + n_{B_2 C_3} , \quad (j = A, B, C, A_2 C_3, B_2 C_3) . \quad (3)$$

2.2 SYSTEM OF EQUATIONS FOR THE SOLIDUS AND LIQUIDUS CURVES. — The dependence of the compositions of the solid state and liquid state on the temperature was derived according to [10], with consideration of the changes upon transition to a system forming associates of type $A_2 C_3$ and $B_2 C_3$ instead of type AC and BC . At the solid state-liquid state equilibrium the following relationships between chemical potentials $\mu_{A_2 C_3}^s$ ($\mu_{B_2 C_3}^s$) in the solid state and chemical potentials μ_A , μ_C (μ_B , μ_C) in the liquid state hold true :

$$\begin{aligned} \mu_{A_2 C_3}^s &= 2 \mu_A + 3 \mu_C ; \\ \mu_{B_2 C_3}^s &= 2 \mu_B + 3 \mu_C . \end{aligned} \quad (4)$$

The chemical potentials of $A_2 C_3$, $B_2 C_3$ in the solid state are expressed as follows :

$$\begin{aligned} \mu_{A_2 C_3}^s &= \mu_{A_2 C_3}^{s,0} + RT \ln \gamma_{A_2 C_3}^s y ; \\ \mu_{B_2 C_3}^s &= \mu_{B_2 C_3}^{s,0} + RT \ln \gamma_{B_2 C_3}^s (1 - y) ; \end{aligned} \quad (5)$$

where y is the mole fraction of $A_2 C_3$ in solid state, $\mu_{A_2 C_3}^{s,0}$ is the chemical potential of pure $A_2 C_3$ in solid state.

The following formula developed by [19] expresses $\mu_{A_2 C_3}^{s,0}$ as a function of the chemical potentials of A , C in the stoichiometric liquid solution — μ_A^* , μ_C^* , the melting point of $A_2 C_3$ — T_{m1} , the entropy of fusion of $A_2 C_3$ — ΔS_{m1} , and the specific heat difference of $A_2 C_3$ in the solid and the liquid states — ΔC_{p1} :

$$\begin{aligned} \mu_{A_2 C_3}^{s,0} &= 2 \mu_A^* + 3 \mu_C^* - \Delta S_{m1} (T_{m1} - T) + \\ &+ \Delta C_{p1} \left(T_{m1} - T - \ln \frac{T_{m1}}{T} \right) . \end{aligned} \quad (6)$$

An analogous formula can be written for $B_2 C_3$. The term in the last bracket is small and can be neglected. Consequently :

$$\begin{aligned} \mu_{A_2 C_3}^{s,0} &= 2 \mu_A^* + 3 \mu_C^* - \Delta S_{m1} (T_{m1} - T) ; \\ \mu_{B_2 C_3}^{s,0} &= 2 \mu_B^* + 3 \mu_C^* - \Delta S_{m2} (T_{m2} - T) . \end{aligned} \quad (7)$$

From (4), (5), (7) we obtain :

$$\begin{aligned} y \gamma_{A_2 C_3}^s &= \frac{a_A^2 a_C^3}{a_A^{*2} a_C^{*3}} \exp \frac{\Delta S_{m1}}{R} \left(\frac{T_{m1}}{T} - 1 \right) ; \\ (1 - y) \gamma_{B_2 C_3}^s &= \frac{a_B^2 a_C^3}{a_B^{*2} a_C^{*3}} \exp \frac{\Delta S_{m2}}{R} \left(\frac{T_{m2}}{T} - 1 \right) . \end{aligned} \quad (8)$$

Expressions for the dissociation constants K_1 and K_2 are as follows :

$$\begin{aligned} K_1 &= \frac{a_A^2 a_C^3}{a_{A_2 C_3}} = \frac{x_A^2 x_C^3}{x_{A_2 C_3}} \frac{\gamma_A^2 \gamma_C^3}{\gamma_{A_2 C_3}} ; \\ K_2 &= \frac{a_B^2 a_C^3}{a_{B_2 C_3}} = \frac{x_B^2 x_C^3}{x_{B_2 C_3}} \frac{\gamma_B^2 \gamma_C^3}{\gamma_{B_2 C_3}} . \end{aligned} \quad (9)$$

From these expressions we obtain :

$$\frac{a_A^2 a_C^3}{a_A^{*2} a_C^{*3}} = \frac{a_{A_2 C_3}}{a_{A_2 C_3}^*} ; \quad \frac{a_B^2 a_C^3}{a_B^{*2} a_C^{*3}} = \frac{a_{B_2 C_3}}{a_{B_2 C_3}^*} . \quad (10)$$

From (1), (2), (3), we obtain :

$$\begin{aligned} x_A &= x_1 (1 + 4 x_{A_2 C_3} + 4 x_{B_2 C_3}) - 2 x_{A_2 C_3} ; \\ x_B &= x_2 (1 + 4 x_{A_2 C_3} + 4 x_{B_2 C_3}) - 2 x_{B_2 C_3} ; \\ x_C &= x_3 (1 + 4 x_{A_2 C_3} + 4 x_{B_2 C_3}) - 3 x_{A_2 C_3} - 3 x_{B_2 C_3} . \end{aligned} \quad (11)$$

The degrees of dissociation are defined as follows :

$$d_1 = \frac{n_A + n_C}{n_1 + n_3} ; \quad d_2 = \frac{n_B + n_C}{n_2 + n_3} . \quad (12)$$

Using (1), (2), (3), (11), (12) one can express $x_{A_2 C_3}$, $x_{B_2 C_3}$ in terms of d_1 , d_2 , x_1 , x_2 :

$$\begin{aligned} x_{A_2 C_3} &= \frac{3(1 - d_2)(1 - x_1) - 5(1 - d_1)(1 - x_2)}{-\{8[(1 - d_2)(1 - x_1) + (1 - d_1)(1 - x_2)] - 16\}} ; \\ x_{B_2 C_3} &= \frac{3(1 - d_1)(1 - x_2) - 5(1 - d_2)(1 - x_1)}{-\{8[(1 - d_2)(1 - x_1) + (1 - d_1)(1 - x_1)] - 16\}} . \end{aligned} \quad (13)$$

Now we introduce the parameters β_1 , β_2 — representing the values of d_1 , d_2 for the stoichiometric liquid. Thus, from (9) we obtain :

$$\begin{aligned} K_1 &= \frac{\gamma_A^2 \gamma_C^3}{\gamma_{A_2 C_3}} \frac{[x_1(1 + 4 x_{A_2 C_3} + 4 x_{B_2 C_3}) - 2 x_{A_2 C_3}]^2}{x_{A_2 C_3}} \times \frac{[x_3(1 + 4 x_{A_2 C_3} + 4 x_{B_2 C_3}) - 3 x_{A_2 C_3} - 3 x_{B_2 C_3}]^3}{x_{A_2 C_3}} = \\ &= \frac{\gamma_A^{*2} \gamma_C^{*3}}{\gamma_{A_2 C_3}^*} \frac{(2 \beta_1)^2 (3 \beta_1)^3}{(1 + 4 \beta_1)^4 (1 - \beta_1)} . \end{aligned} \quad (14)$$

FIG. 1. — Comparison of the calculated and the experimental liquidus curves for parts of the binary systems Te-AV.

Analogous expressions can be written for B_2C_3 . To obtain expressions for $x_{A_2C_3}$, $x_{B_2C_3}$, we assume very strong association, i. e. $\beta_1 \ll 1$, $\beta_2 \ll 1$. In this case the right side of equation (14) vanishes and we obtain the following expressions for $x_{A_2C_3}$, $x_{B_2C_3}$:

$$x_{A_2C_3} = \frac{x_1}{2 - 4(x_1 + x_2)}; \quad x_{B_2C_3} = \frac{x_2}{2 - 4(x_1 + x_2)}. \quad (15)$$

However, upon acceptance of the above assumption, no expressions for the respective molar equations are obtained when $x_3 < 0.6$. This is so, because at $x_3 > 0.6$, $\beta_1, \beta_2 \ll 1$ is equivalent to $x_A, x_B \cong 0$, whereas, at $x_3 < 0.6$, $\beta_1, \beta_2 \ll 1$ is equivalent to $x_C \cong 0$. Thus, by assuming very strong association (β_1, β_2 negligibly small) we obtain at $x_3 > 0.6$ two constraints, which enables us to find $x_{A_2C_3}$, $x_{B_2C_3}$. At $x_3 < 0.6$ we have only one constraint, $x_C \cong 0$, and thus only $x_{A_2C_3} + x_{B_2C_3}$ can be determined.

The next problem is to choose a form of $\gamma_{A_2C_3}$,

$\gamma_{B_2C_3}$ as a function of composition. We assume an empirical form of $\ln \gamma_{A_2C_3}$ ($\ln \gamma_{B_2C_3}$) in the binary solution (quadratic function):

$$RT \ln \gamma_{A_2C_3}^I = \alpha_1 x_1^2 + \alpha x_1 + c. \quad (16)$$

As can be seen from figure 1, this function fits the binary liquidus quite well.

The expression for $\ln \gamma_{A_2C_3}^I$ ($\ln \gamma_{B_2C_3}^I$) in the ternary solution (which in the particular case of a binary solution takes the form presented in (16)), satisfies the boundary conditions (17):

$$\gamma_{A_2C_3}^I \rightarrow 1 (\gamma_{B_2C_3}^I \rightarrow 1) \quad \text{for } x_3 \rightarrow 0.6; \quad (17)$$

is as follows:

$$RT \ln \gamma_{A_2C_3}^I = \alpha(x_1 + x_2)^2 + \alpha'(x_1 + x_2) - 0.16\alpha - 0.4\alpha'. \quad (18)$$

When substituting (18) and the expression for $x_{A_2C_3}$, $x_{B_2C_3}$ calculated from (13) in (10), we obtain:

$$\begin{aligned} \frac{a_{A_2C_3}}{a_{A_2C_3}^*} &= \frac{x_{A_2C_3} \gamma_{A_2C_3}}{x_{A_2C_3}^* \gamma_{A_2C_3}^*} = x_{A_2C_3} \frac{1 + 4\beta_1}{1 - \beta_1} \exp \left\{ \frac{1}{RT} [\alpha_1(x_1 + x_2)^2 + \alpha'_1(x_1 + x_2) - 0.16\alpha_1 - 0.4\alpha'_1] \right\}; \\ \frac{a_{B_2C_3}}{a_{B_2C_3}^*} &= \frac{x_{B_2C_3} \gamma_{B_2C_3}}{x_{B_2C_3}^* \gamma_{B_2C_3}^*} = x_{B_2C_3} \frac{1 + 4\beta_2}{1 - \beta_2} \exp \left\{ \frac{1}{RT} [\alpha_2(x_1 + x_2)^2 + \alpha'_2(x_1 + x_2) - 0.16\alpha_2 - 0.4\alpha'_2] \right\}. \end{aligned} \quad (19)$$

From (8), (15), (19) we obtain the ternary solidus-liquidus equations (the solid solution is assumed to be regular, i. e. $\Delta y^{xs} = w(1 - y)$):

$$y \exp \left[\frac{w}{RT} (1 - y)^2 \right] = \frac{1 + 4\beta_1}{1 - \beta_1} \frac{x_1}{2 - 4(x_1 + x_2)} \exp \left[\frac{\Delta S_{m1}}{R} \left(\frac{T_{m1}}{T} - 1 \right) \right] \times \\ \times \exp \left\{ \frac{1}{RT} [\alpha_1(x_1 + x_2)^2 + \alpha'_1(x_1 + x_2) - 0.16\alpha_1 - 0.4\alpha'_1] \right\}; \\ (1 - y) \exp \left(\frac{w}{RT} y^2 \right) = \frac{1 + 4\beta_2}{1 - \beta_2} \frac{x_2}{2 - 4(x_1 + x_2)} \exp \left[\frac{\Delta S_{m2}}{R} \left(\frac{T_{m2}}{T} - 1 \right) \right] \times \\ \times \exp \left\{ \frac{1}{RT} [\alpha_2(x_1 + x_2)^2 + \alpha'_2(x_1 + x_2) - 0.16\alpha_2 - 0.4\alpha'_2] \right\}. \quad (20)$$

For the pseudobinary liquidus: $x_1 = 0.4x$; $x_2 = 0.4(1 - x)$; $d_1 = \beta_1$; $d_2 = \beta_2$. $x_{A_2C_3}$, $x_{B_2C_3}$ are expressed by (13). As we assume $\beta_1, \beta_2 \ll 1$, we can write $1 - \beta_1 \cong 1 - \beta_2 \cong 1 - \beta$; $1 + 4\beta_1 \cong 1 + 4\beta_2 = 1 + 4\beta$.

Hence we obtain:

$$x_{A_2C_3} = x \frac{1 - \beta}{1 + 4\beta}; \quad x_{B_2C_3} = (1 - x) \frac{1 - \beta}{1 + 4\beta}. \quad (21)$$

From (8), (15), (19), (21), the pseudobinary solidus-liquidus equations are:

$$y \exp \left[\frac{w}{RT} (1 - y)^2 \right] = x \exp \left[\frac{\Delta S_{m1}}{R} \left(\frac{T_{m1}}{T} - 1 \right) \right]; \\ (1 - y) \exp \left(\frac{w}{RT} y^2 \right) = (1 - x) \exp \left[\frac{\Delta S_{m2}}{R} \left(\frac{T_{m2}}{T} - 1 \right) \right]. \quad (22)$$

2.3 THERMODYNAMIC DATA AND PARAMETERS REQUIRED FOR CALCULATION OF PHASE DIAGRAM. — Data on the melting entropy of the compounds A_2C_3 and B_2C_3 , as well as on the respective melting temperatures were obtained from ref. [20]. The phase diagrams for the systems Bi-Te and Sb-Te were taken from [15] and for the pseudobinary system Bi_2Te_3 - Sb_2Te_3 from [16]. The numerical data are recorded in table I.

TABLE I

Values of entropy of melting and melting temperatures for the systems Bi_2Te_3 and Sb_2Te_3

Compound	T_m [°C]	S_m [eu]
Bi_2Te_3	588.5 ± 1.0	6.58
Sb_2Te_3	618.5 ± 1.0	5.31

The parameters $\alpha_1, \alpha'_1, \alpha_2, \alpha'_2, \beta_1, \beta_2$ were determined by the least squares method, to obtain a set of equations (20) giving a best fit to the liquidus curves for

the binary systems. The interaction parameter w was determined on the basis of the set of equations (22). These parameters are presented in table II.

3. Results of phase diagram calculations. — The phase diagram for the Te-Bi-Sb system calculated by the method described above is recorded in figure 2; the experimental results obtained for this system [8] are also shown in the figure. As can be seen in figure 2, the experimental and calculated results are consistent.

The calculated values of parameters seem to justify the abovementioned assumptions. The value of the interaction parameter w in the solid state is small. This confirms the validity of considering the solid state to be a regular solution.

The small values of the dissociation parameters in the liquid state justify the acceptance of the assumption of very strong association.

As regards the activity coefficient in the liquid state, the parameter values occurring in the expression for $\gamma_{A_2C_3}^1$ of the compound cannot be compared with the

TABLE II

Parameters used in calculations

System	α [kcal/mol]	α' [kcal/mol]	β	System	w [kcal/mol]
Bi-Te	- 22.0	2.96	0.024 4	Bi_2Te_3 - Sb_2Te_3	0.115
Sb-Te	- 29.3	6.44	0.012 8

FIG. 2. — Phase diagram calculated for the system Bi-Sb-Te, with indication of the experimental values (dashed curves).

respective values obtained for other systems (forming compounds AC), on account of the different form of this expression. However, the fit this expression is rather good for binary systems.

4. Summary. — The phase diagram for the Bi-Sb-Te system has been calculated using the approach of the theory of regular associated solutions, with a modification of the system of equations applied in ref. [10]. The necessary parameters were determined by the least squares method.

Comparison of the calculated values with the experimental results points to their fairly good agreement.

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Note. — Thanks to the reviewer's kind help, most recent Szapiro's [12] extension of the RAS model to ternary systems came to our attention. Although both Laugier's [10] and Szapiro's [12] treatments refer to systems forming compounds AC and BC and are based on the same SLE equations, their equations for the activity coefficients in the liquid phase are different. Furthermore, Szapiro's mole fractions x_{AC} and x_{BC} are established numerically, while Laugier's are calculated analytically by assuming very strong association. Szapiro has accounted for the variation of the dissociation parameters with temperature.

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