ELSEVIER
Thermochimica Acta 314 (1998) 299–306
thermochimica acta

Liquidus surface and association in eutectic ternary alloys

K.Yu. Shunyaev[a,*], N.C. Tkachev[b], N.A. Vatolin[a]

[a] *Institute of Metallurgy, Ural Division of Russian Academy of Sciences, 101, Amundsen str., Ekaterinburg, 620016, Russian Federation*
[b] *Institute of High Temperature Electrochemistry, Ural Division of Russian Academy of Sciences, 20, S. Kovalevskoi str., Ekaterinburg, 620219, Russian Federation*

Received 13 August 1997; received in revised form 6 February 1998

Abstract

The model of ideal solution of self-associates is applied to analyze possible shapes of the liquid surface for ternary eutectic alloys. The interaction parameters of the constituents that can be expressed by means of melting temperatures have found to have much influence upon this shape. A discussion of that feature in comparison with possible differences in crystal structures is presented. Estimations of the liquids surface for the Ag–Bi–Cu and Bi–Cd–Sn ternaries were carried out. Different reasons found to be important for this three-fold surface have been considered. © 1998 Elsevier Science B.V.

Keywords: Associated solution; Liquidus surface; Ternary eutectic alloys; Ag–Bi–Cu; Bi–Cd–Sn

1. Introduction

Development of the associated solution model follows two main directions: a) to account for the interactions between complexes (regular associated solution [1–3] and (or) b) refinement of stoichiometric composition of the associates embedded in liquid phase [4,5]. It is necessary to emphasize that the introduction to the theory of such additional species, which are not evident from the phase diagram, seems to us as a quite artificial and ambiguous recourse. One needs to look only for comparison the recommended variety of the associates' stoichiometry in [4,5] that were considered by these authors for common systems [6]. We mention in passing that up to now the ability of self-association in binary melts was the subject of investigation only in a few works [7,8].

A detailed analysis of the consequences of taking into account the distribution of associates upon sizes and conformations within self-association has been undertaken by us for simple metallic liquids [9] as well as for the binary liquid alloys of eutectic type [10–12]. This approach is consistent in estimations of both melting and mixing thermodynamics. Namely, at first, to obtain the melting entropy as the function of the geometry of nearest neighborhood of the related solid. At second, to express explicitly dependencies of the thermodynamic mixing functions upon concentration in terms of only the melting temperatures of the pure components. At third, to carry out the evaluation of the eutectic liquidus curves. For the single component system the entropy of melting was found to be the universal quantity, i.e. their value is the same for the elements of matched crystal structures. The predictions of such a theory for metals and inert elements are in satisfactory agreement to the experimentally observed data [13,14]. For the binary eutectic alloys

---

*Corresponding author.

PII S0040-6031(98)00281-0

this model allows us to describe properly the qualitative features of the thermodynamics during mixing, if its deviation from the ideal mixture turned out to be positive and similarly for the shapes of the liquidus curves. In certain cases, especially for the liquidus curves, the agreement was found to be quantitative.

It is obvious that the trial-and-error method within appropriate stoichiometric compositions of the associates has more evidently displayed limitation in application to ternary systems, because the total number of the distinguished complexes in the constituent boundary two-component alloys should be rather large. Besides, it could be necessary also to consider mixed ternary associates that might be formed due to chemical equilibria between binary species. If one goes on another way of applying the regular associated solution theory, then the number of adjustable parameters must rise unambiguously.

In contrast, our version of the associated model, that still remains the ideal alternative, permits us to keep the minimal number of such parameters. In particular, the binary eutectic description requires two energies of pair bonds, which as a virtue, can be easily determined by the melting temperatures of the pure components. Furthermore, this kind of model can be readily generalized for the case of multi-component eutectic systems.

Therefore, aim of the presented paper is to illustrate the convenient application of the associated solution model taking the only self-association at the estimation of the liquidus surface in simple ternary eutectic alloys into account. The analysis of the ternary eutectic point allocation in relation to the melting temperatures' mismatch of the pure components as well as their structures in the solid state seems to us as one of the central problems. On this ground we present also a number of the estimated examples of the liquidus surface as well as the comparison for the Ag–Bi–Cu alloys among them.

2. General theory

Let us consider the following multi-component mixture $A^{(1)}_{c_1}A^{(2)}_{c_2}\cdots A^{(p)}_{c_p}$, where c_k is the mole fraction of k-component, their sum being equal to unity. Each of the pure components is an associated liquid of ideal type consisting of complexes of different sizes and configurations $A^{(k)}_{n,L^k_n}$, where n is the number of atoms and L^k_n is the number of pair bonds of nearest neighbors between these atoms. For multi-component system, we suggest only the existence of these self-associates. The existence of the following equilibria is supposed: $nA^{(k)}_1 = A^{(k)}_n$, which have to be described by the necessary reaction constants:

$$K_{A^{(k)}_n} = \exp\left(\frac{-\alpha_{kk}L^{(k)}_n}{\mathrm{k_B T}}\right), \tag{1}$$

where α_{kk} stands for the corresponding energy of pair bond of nearest neighbors $A^{(k)}\ A^{(k)}$,$\mathbf{k}_\mathrm{B}$ is the Boltzmann constant and T is the absolute temperature. In order to derive these expressions it is necessary to start from the molar Gibbs free energy and to minimize it upon the numbers of complexes [15,16]. This approach gives rise to the set of equations of the Mass Action Law in the form of Eq. (1). The entropy term of the constants is absent because the rotational and vibrational degrees of freedom of the complexes are not considered in this approximation.

We account for the geometry of associates, which are related to the crystal structure fragments of the original solid (for the pure component). Hence the number of these pairs must vary between the boundaries: $n-1 \le L^{(k)}_n \le m^{(k)}_n$. Here the lower boundary corresponds to the 'chain configuration', and all of the others can be constructed by consecutive 'scrolling', i.e. by appending one bond, as long as the spatial form of the complex reaches the most closed-packed configuration ($m^{(k)}_n$) in terms of the given lattice geometry. It is meaningful, that $\lim_{n\to\infty}\frac{m^{(k)}_n}{n} = \frac{Z^{(k)}}{2}$, where $Z^{(k)}$ is the coordination number of nearest neighbors in the solid component. This relation gives the above-mentioned possibility to analyze the melting–crystallization process. Thus, $L^{(k)}_n$ is simply the running integer of the summation. The values $m^{(k)}_n$ for different classes of crystal structures have been listed in [9] for complexes consisting of up to 20 atoms.

If we accept the approximation of ideal associated solution then, as it was shown [13], the following expression for the chemical potential proves to be rigorous:

$$\mu^{(k)}_A = k_B T \ln x^{(k)}_{A_1}, \tag{2}$$

Where $x^{(k)}_{A1}$ is the mole fraction of the unbonded (free) atoms of a given component. Furthermore, consideration of the rotations (as the solid body) and the vibrations do not influence such general results. It is possible to include into the theory non-trivial entropy terms for the reaction constants [13–15], however this consideration is not of our current interest.

The system is determined by (p) equations for its determination, one of them is the normalisation-to-unity condition and the others are (p-1) equations of the material balance for (p-1) components.

$$\begin{cases} 1 = \sum_{k=1}^{p} \sum_n x_{A_n^{(k)}} \\ c_1 = \dfrac{\sum_n n x_{A_n^{(1)}}}{\sum_{k=1}^{p} \sum_n n x_{A_n^{(k)}}} \\ \ldots \\ c_{p-1} = \dfrac{\sum_n n x_{A_n^{(p-1)}}}{\sum_{k=1}^{p} \sum_n n x_{A_n^{(k)}}} \end{cases} \tag{3}$$

The rules of summation are as follows:

$$\sum_n n x_{A_n^{(k)}} \equiv \sum_{n=1}^{M} n x_{A_1^{(k)}} \sum_{L_n^{(k)}=n-1}^{m_n^{(k)}} \times \exp\left(-\alpha_{kk} L_n^{(k)}/k_B T\right). \tag{4}$$

M is an upper boundary, that usually proves to be 20–25 for practical purposes under consideration. Alternatively, it could be equal to infinity if the numbers $m_n^{(k)}$ are approximated by some analytical expression to make up the summation in an explicit way. In order to obtain the condition of the solid–liquid equilibrium one might turn to a requirement of convergence of such series, for example, the D'Alembert requirement:

$$\begin{aligned} &\lim_{n\to\infty} \frac{\exp(\alpha_{kk} L_{n+1}^{(k)}/k_B T) x_{A^{n+1}_{1(k)}}}{\exp(\alpha_{kk} L_n^{(k)}/k_B T) x^n_{A_1^{(k)}}} \\ &= x_{A_1^{(k)}} \lim_{n\to\infty} \exp[\alpha_{kk}/k_B T(m_{n+1}^{(k)} - m_n^{(k)})] \\ &= x_{A_{1(k)}} \exp[\alpha_{kk} Z^{(k)}/2k_B T] < 1 \end{aligned} \tag{5}$$

The equilibrium between the complex of infinite size (the solid phase) and the associated liquid is reached at the temperature imposing the equality sign in the last expression. Numerical values of α_{kk} can now be easily expressed in terms of corresponding melting temperatures [15,16]:

$$-\frac{\alpha_{kk} Z_{kk}}{2} = k_B T_{A_k}^{m} \ln x_{A_k}^{0} \tag{6}$$

Where $T_{A_k}^m$ is the melting temperature of the pure component $A_k, x_{A_k}^0$ is the mole fraction of the free atoms in the liquid at this temperature. α_{kk} and $x_{A_k}^0$ must be found self-consistently by solving Eq. (6) together with the equation describing the normalization-to-unity condition for pure A_k. Hence, the bond energies for the different pairs are non-adjustable parameters and can be simply expressed through the melting temperatures of the involved species. Thus, the results of estimations presented below have been obtained without fitting of any parameters to the liquidus curves under consideration.

3. Ternary eutectic alloys

Let us consider a ternary system $A_{c_A} B_{c_B} D_{1-c_A-c_B}$ containing only self-associates. Our thermodynamic approach makes it possible to described both the liquidus surface and the liquid-phase thermodynamics at mixing. In doing so, we need only the melting temperatures of pure metals and their structures in the solid.

3.1. Liquidus surface estimation

Separate treatment of the solid–liquid equilibrium conditions for each component allows to evaluate the liquidus surface range adjacent to this component, if the equation system of material balance Eq. (3) is applied.

The equilibrium between the solid component A and the liquid phase is given by: $\mu_A^L(T_{LA}, c_A, c_B) = \mu_A^S$, where T_{LA} stands for the part of the liquidus surface adjacent A. It can be easily seen that Eq. (5) results in the following equation:

$$-\frac{\alpha_{AA} Z_A}{2} = R T_{\mathrm{LA}} \ln x, \tag{7}$$

where $x \equiv x_{A_1}(T_{LA}, c_A, c_B)$. By substitution of Eq. (7) into Eq. (3), we have a system of equations which allows to estimate the values of x, $y \equiv y_{B_1}(T_{LA}, c_A, c_B)$ and $z \equiv z_{D_1}(T_{LA}, c_A, c_B)$ as functions of temperature and pairs of independent concentrations (c_A and c_B). Hence, we obtain for this part of the liquidus surface:

$$\left\{\begin{aligned} 1 &= \sum_{n=1}^{M} x^n \sum_{L_n=n-1}^{m_n^{(A)}} x^{-2L_n/Z_A} + \sum_{n=1}^{M} y^n \sum_{L_n=n-1}^{m_n^{(B)}} x^{-2\alpha_{BB}L_n/\alpha_{AA}Z_A} + \sum_{n=1}^{M} z^n \sum_{L_n=n-1}^{m_n^{(D)}} x^{-2\alpha_{DD}L_n/\alpha_{AA}Z_A} \\ c_A &= \frac{\sum_{n=1}^{M} nx^n \sum_{L_n=n-1}^{m_n^{(A)}} x^{-2L_n/Z_A}}{\sum_{n=1}^{M} nx^n \sum_{L_n=n-1}^{m_n^{(A)}} x^{-2L_n/Z_A} + \sum_{n=1}^{M} ny^n \sum_{L_n=n-1}^{m_n^{(B)}} x^{-2\alpha_{BB}L_n/\alpha_{AA}Z_A} + \sum_{n=1}^{M} nz^n \sum_{L_n=n-1}^{m_n^{(D)}} x^{-2\alpha_{DD}L_n/\alpha_{AA}Z_A}} \\ c_B &= \frac{\sum_{n=1}^{M} ny^n \sum_{L_n=n-1}^{m_n^{(B)}} x^{-2\alpha_{BB}L_n/\alpha_{AA}Z_A}}{\sum_{n=1}^{M} ny^n \sum_{L_n=n-1}^{m_n^{(B)}} x^{-2\alpha_{BB}L_n/\alpha_{AA}Z_A} + \sum_{n=1}^{M} nx^n \sum_{L_n=n-1}^{m_n^{(A)}} x^{-2L_n/Z_A} + \sum_{n=1}^{M} nz^n \sum_{L_n=n-1}^{m_n^{(D)}} x^{-2\alpha_{DD}L_n/\alpha_{AA}Z_A}} \end{aligned}\right. \tag{8}$$

Parallel description for x, y, and z can be obtained for the parts adjacent to B and C components.

The interaction of each pair of these surfaces, which have the origins at the melting points of the pure components lies along a valley. For the evaluation of this valley it is necessary to complete the system of Eq. (8) by one more equilibrium condition for second component similar to Eq. (7). The starting point of the valley coincides with the eutectic point in related binary and this line terminates at the ternary eutectic point. The valley between constituents A and B is given by:

$$\left\{\begin{aligned} 1 &= \sum_{n=1}^{M} x^n \sum_{L_n=n-1}^{m_n^{(A)}} x^{-2L_n/Z_A} + \sum_{n=1}^{M} x^{\rho n} \sum_{L_n=n-1}^{m_n^{(B)}} x^{-2\alpha_{BB}L_n/\alpha_{AA}Z_A} + \sum_{n=1}^{M} z^n \sum_{L_n=n-1}^{m_n^{(D)}} x^{-2\alpha_{DD}L_n/\alpha_{AA}Z_A} \\ c_A &= \frac{\sum_{n=1}^{M} nx^n \sum_{L_n=n-1}^{m_n^{(A)}} x^{-2L_n/Z_A}}{\sum_{n=1}^{M} nx^n \sum_{L_n=n-1}^{m_n^{(A)}} x^{-2L_n/Z_A} + \sum_{n=1}^{M} x^{\rho n} \sum_{L_n=n-1}^{m_n^{(B)}} x^{-2\alpha_{BB}L_n/\alpha_{AA}Z_A} + \sum_{n=1}^{M} nz^n \sum_{L_n=n-1}^{m_n^{(D)}} x^{-2\alpha_{DD}L_n/\alpha_{AA}Z_A}} \end{aligned}\right. \tag{9}$$

Here $\rho = \alpha_{BB}Z_B/\alpha_{AA}Z_A$.

The calculation of the ternary eutectic point requires a third equation of the type Eq. (7) for the remaining component C. This leads us to a single equation of the form:

$$\begin{aligned} 1 = {} & \sum_{n=1}^{M} x^n \sum_{L_n=n-1}^{m_n^{(A)}} x^{-2L_n/Z_A} + \sum_{n=1}^{M} x^{\rho n} \sum_{L_n=n-1}^{m_n^{(B)}} \\ & \times x^{-2\alpha_{BB}L_n/\alpha_{AA}Z_A} + \sum_{n=1}^{M} x^{\xi n} \sum_{L_n=n-1}^{m_n^{(D)}} \\ & \times x^{-2\alpha_{DD}L_n/\alpha_{AA}Z_A}, \end{aligned} \tag{10}$$

where $\xi = \alpha_{DD}Z_D/\alpha_{AA}Z_A$.

3.2. Thermodynamics of mixing

The enthalpy of mixing is given with the above sum of products Eq. (9) in mixture of a given concentration with respect to the pure components.

$$\begin{aligned} \Delta H^M &= H(c_A, c_B) - c_A H_A - c_B H_B \\ &\quad - (1 - c_A - c_B) H_D \\ &= -\frac{\alpha_{AA} S_3^A + \alpha_{BB} S_3^B + \alpha_{DD} S_3^D}{S_2^A + S_2^B + S_2^D} \\ &\quad + c_A \alpha_{AA} \frac{S_3^{A0}}{S_2^{A0}} + c_B \alpha_{BB} \frac{S_3^{B0}}{S_2^{B0}} \\ &\quad + (1 - c_A - c_B) \alpha_{DD} \frac{S_3^{D0}}{S_2^{D0}} \end{aligned} \tag{11}$$

The superscript 0 is related to the pure components at the same temperature. The sums Eq. (11) are as follows:

$$S_2^k = \sum_{n=1}^{M} n \sum_{L_n^k=n-1}^{m_n^k} x_{L_n^k},\; S_3^k = \sum_{n=1}^{M} \sum_{L_n^k=n-1}^{m_n^k} L_n^k X_{L_n^k} \tag{12}$$

The enthalpy dependence on temperature is implicitly included in terms of the reaction constants Eq. (1). For the calculation of $x_{L_n^k}$ one needs the material balance Eq. (3).

Activities of the associated components can be found by means of chemical potentials starting from Eq. (2): $a_k = x_{k_1}/x_{k_1^0}$, with $x_{k_1^0}$ the mole fraction of the free atoms in pure liquid at the temperature of interest. The molar Gibbs free energy can be calculated by:

$$\begin{aligned} \Delta G^M &= RT[c_A \ln a_A + c_B \ln a_B \\ &\quad + (1 - c_A - c_B) \ln a_D] \end{aligned} \tag{13}$$

Other thermodynamic quantities of mixing, for example, the entropy can be found as usual.

4. Results and discussion

In order to solve the systems of Eqs. (4),(5) and (7) for plotting the liquidus surface, the intersections (valleys) and the ternary eutectic point, we have used the iteration method of Newton–Raphson. To investigate the influence of different effects upon the shape of the liquidus surface, calculations were carried out for various possible situations. First, for different melting temperatures of the components, but for the same local geometry, and, secondly, et vice versa, for the same melting temperatures, but for different crystal structures. For comparison with experimental data the system of Ag–Cu–Bi was chosen, which has only eutectic boundary binaries.

In Fig. 1(a) the configuration of the liquidus surface is depicted for the case of ternary alloys which have T_A=T_B=1000 K, T_D=800 K. The structure of the solid components was faced centered cubic. Fig. 1(b) illustrates the ternary diagram for the case of T_A=T_B=1000 K, T_D=1500 K, the components A and D have a local fcc structure as B constituent has the diamond-type structure. These figures show that the association model is qualitatively quite feasible. The main feature of the phase diagrams is the displacement of the ternary eutectic point to the side of the species with a lower melting point. In Table 1, we have presented the position of this point for different combinations of three structure types: face centered cubic (F.C.C.), diamond and β-Sn within the same (1000 K) melting temperatures for each component.

Table 1
Location of the ternary eutectic point as function of various types of local structure. The numbers 1, 2 and 3 correspond to F.C.C., diamond and ß-Sn lattices, respectively; T_A=T_B=T_D=1000 K.

	1-1-1	1-1-2	1-1-3	1-2-3
T_e/K	668	659	657	648
c_A^e	0.333	0.305	0.316	0.370
c_B^e	0.333	0.305	0.316	0.290

Results of the liquidus surface estimation for the Bi–Cd–Sn alloys are presented on Fig. 2(a). The melting temperatures of these metals are in the same range, therefore the ternary eutectic point is located near the center of the composition triangle. The experimental data (Fig. 2(b)) support this conclusion. The theory represents satisfactorily the curvature of the liquidus isotherms in contrast to the calculation of [19] (Fig. 2(b)). The results of another work [20] agree quite well with the experiment even at the quantitative level. However, it is remarkable that the authors have

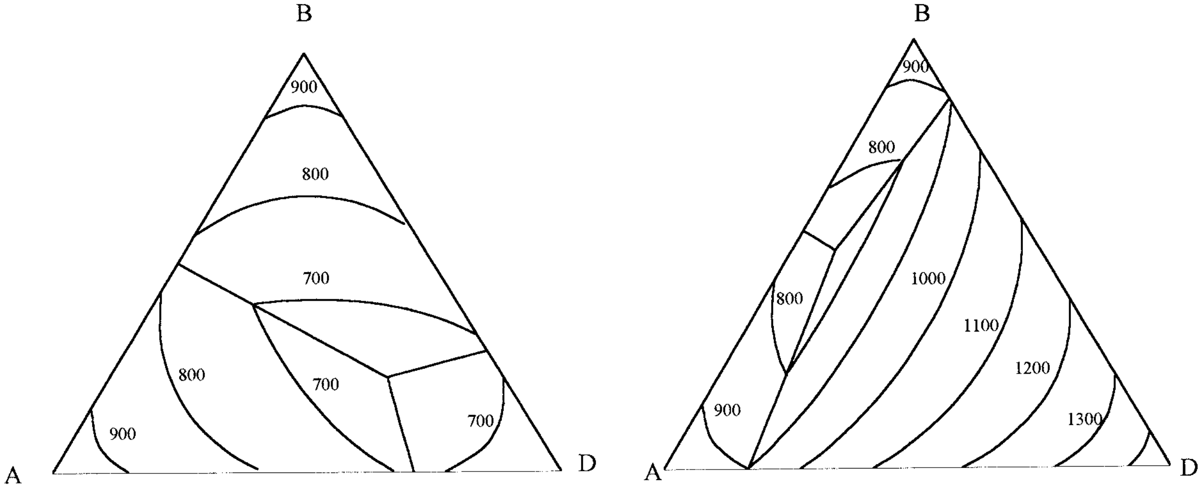

Fig. 1. Two examples of liquidus surface related to difference in melting temperatures: a) T_A=T_B=1000 and T_D=800 K for one and the same (F.C.C.) crystal structure; b) T_A=T_B=1000 and T_D=1500 K A-F.C.C., B-diamond and D-F.C.C. structure.

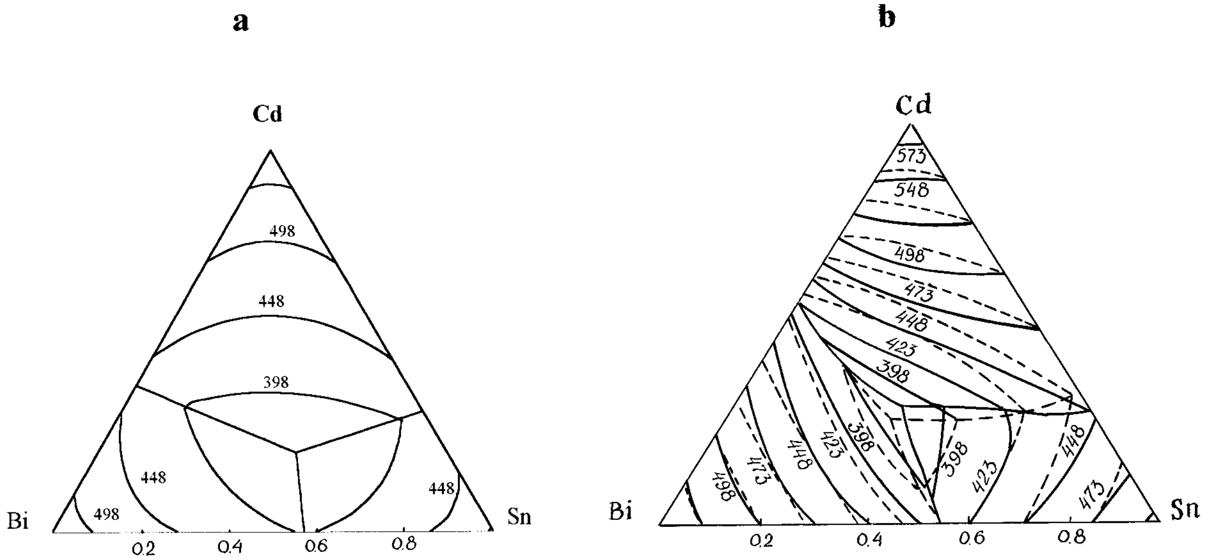

Fig. 2. Present estimation of liquidus temperatures for Bi–Cd–Sn ternary alloys (a) in Comparison with (b) experimental [18] and calculated data [19]. Solid curves correspond to the calculations taken from [19] and the dashed ones related to the experimental data.

used a lot of experimental information on thermodynamic properties of the corresponding binaries.

Fig. 3(a) and 3b show calculated results for the system Ag–Cu–Bi together with the experimental data. In previous work, we have reached a satisfactory agreement with the experimental liquidus for the corresponding binaries Ag–Cu and Cu–Bi [11] (Fig. 4(b) and 4c). The largest discrepancies from the experiment were found for the Ag–Bi binary (Fig. 4(a)). These deviations are displayed also in the shape of the ternary liquidus surface. The isotherms of the calculated diagram (Fig. 3(a)) are monotonic, whereas the experimental data differs noticeably, especially in the Bi-rich region.

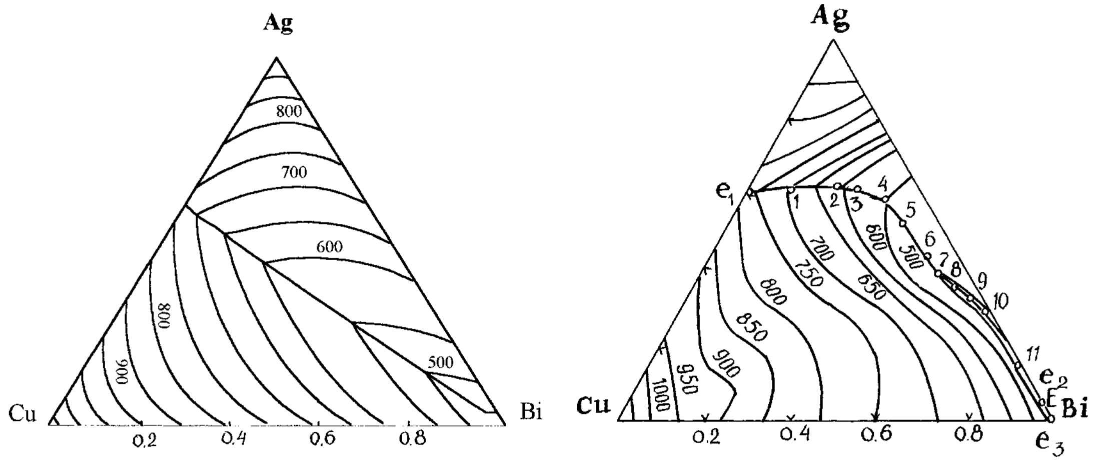

Fig. 3. Calculated (a) and experimental [17] (b) values of liquidus temperatures for Ag–Bi–Cu alloys.

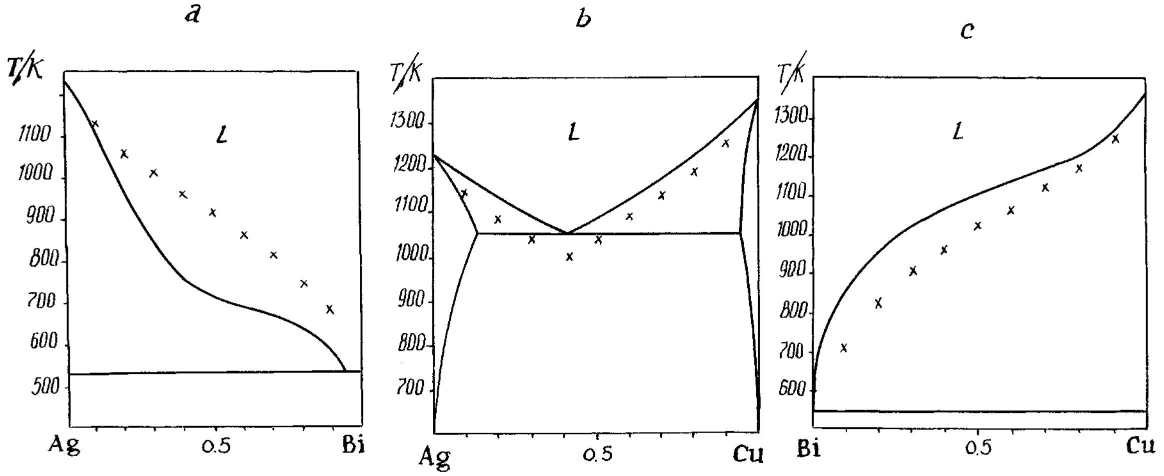

Fig. 4. Liquidus curves for the binary systems Ag–Bi (a), Ag–Cu (b) and Bi–Cu (c) (x calculated from theory, solid line corresponds to the experimental data [21]).

Bearing in mind the non-empirical character of presented estimations we consider this agreement as satisfactory: At first, the model describes qualitatively the observed trends for the eutectic liquidus surfaces. At second, there are perspectives of theory improvements, for example, to take into account the rotational and vibration degrees of freedom of the embedded complexes, the Flory type mixing entropy (volume dependence of the reaction constants), electronic subsystem etc.

5. Conclusion

The model of associated solutions enables us to give an analysis of some peculiarities of the liquidus surface description in ternary eutectic alloys. The first feature is associated with the interaction parameter mismatch between the pure components. The shape of the liquidus surface in ternary diagrams is very sensitive to this difference. On the contrary, unlike crystal structures of constituent metals influence upon the shape much less.

Non-monotonic shapes of experimental curves are probably lying out of the ideal association description. In our opinion, the reason might be the size mismatch of metallic atoms that has not been yet taken into account. Perhaps this size difference combined with local geometry could be responsible for these anomalies. At first glance, the Flory approximation would be able to improve the predictions. There is one more result. It is well known [13] that for binary eutectic systems with low-melting-entropy species the semi-empirical rule of Van Laar works quite well. So the tangent of the liquidus curve at small concentrations corresponds to the concave shape of the latter. This behaviour seems to hold for ternary systems as well. The calculated results are in agreement with this rule, because our earlier estimations of the melting entropy (more rigorously, its configurational part) and binary liquidus have supported this point of view. Finally, for understanding experimental trends of the liquidus surface and for a rough estimation of why some eutectic alloys have an anomalous behaviour, the present analysis is a fortunate compromise between the simplicity of computational attempts and the possibility to explore multi-component eutectic systems.

Acknowledgements

The authors are thankful to the Russian Fundamental Researches Foundation for financial support (grant N 96-03-32107).

References

[1] F. Sommer, Z. Metallkd. 73 (1982) 72.
[2] C. Bergman, R. Castanet, H. Said, M. Gilbert, J.-C. Mathieu, J. Less-Common Met. 85 (1982) 121.
[3] R. Schmid, Y.A. Chang, CALPHAD 9 (1985) 363.
[4] K. Wasai, K. Mukai, J. Jap. Inst. Metals 46 (1982) 266.
[5] A.G. Morachevsky, A.G. Mokrievich, E.A. Mayorova, J. Appl. Chem. (in Russ.) 66 (1993) 1441.
[6] K. Yu. Shunyaev, N.A. Vatolin, in: E.A. Pastuhov (Ed.), Physical Chemistry and Technology in metallurgy (in Russ.), Ekaterinburg, 1966, p. 91.
[7] M. Ivanov, Z. Metallkd. 82 (1991) 53.
[8] R.N. Singh, F. Sommer, Z. Metallkd. 83 (1992) 533.
[9] N.C. Tkachev, K.Yu. Shunyaev, A.N. Men, N.A. Vatolin, Melts 2 (1988) 1.
[10] N.C. Tkachev, K.Yu. Shunyaev, A.N. Men, N.A. Vatolin, Rep. Acd. Sci. USSR (in Russ.) 302 (1988) 153.
[11] K.Yu. Shunyaev, N.A. Vatolin, Melts (in Russ.) 5 (1993) 28.
[12] K.Yu. Shunyaev, N.A. Vatolin, Metals (in Russ.) 5 (1995) 96.
[13] I. Prigogine, R. Defay, Chemical Thermodynamics, Longmans Green and Co., London, 1954.
[14] V.M. Glazov, A.A. Aivazov, Melting entropy of metals and semiconductors (in Russ.), Metallurgy, Moscow, 1980.
[15] N.C. Tkachev, K.Yu. Shunyaev, A.N. Men, Phys. Chem. Liquids 15 (1986) 271.
[16] N.C. Tkachev, K.Yu. Shunyaev, A.N. Men, High Temp. -High Press. 22 (1990) 207.
[17] S. Liu, W. Sun, Acta Met. Sin. 24 (1988) B376.
[18] H.J. Bray, F.D. Bell, S.J. Harris, J. Inst. Met. 90 (1961) 24.
[19] A.D. Pelton, C.W. Bale, CALPHAD 1 (1977) 253.
[20] A.S. Bhansali, A.K. Mallik, CALPHAD 11 (1987) 105.
[21] R. Hultgren, P.D. Desai, D.T. Hawkins, M. Gleiser, K. Kelley, Selected values of the thermodynamic properties of binary alloys, Metal Park, Ohi: ASM, 1973.