T-X-Y DIAGRAMS OF LEAD-FREE SOLDERING SYSTEMS WITH THERMODYNAMIC CONTOURS OF MINIMAL SURFACES

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ABSTRACT

Alternative principle of the phase diagrams (PD) engineering has been offered: 1) before proceeding with the assembly of hypothetical or real PD, a space scheme of monovariant reactions (three-phase regions scheme) is to be elaborated; 2) contours of the surfaces with the unruled nature are to be closed and data of thermodynamic calculations are used on this stage; 3) surfaces should be approximated as the minimal ones, like the soap films, with the minimal area; 4) all geometrical elements (points, lines, surfaces, phase regions) are designated, and their "names" contain the meaning (reason) of these designations; 5) after the computer assembling the PD space model is a useful tool to solve different fundamental and applied tasks of materials science. E.g. solidification paths are confirmed by the mass balances: a vertical one - for the given centre of masses, and a horizontal one - for the isothermal state of isopleth. As computer model of PD saves information about system in compact form and permits to receive any projection, isotherm and isopleth with the decoding of intersected surfaces and phase regions, it helps also to enquire the errors and incorrectly interpreted experimental data, especially in the cases of surfaces' degeneration because of negligibly small sizes of homogeneous regions. To investigate a competition of tiny eutectical crystals with more large primary crystals of the same phase in the invariant reaction with melt, an idea of "disperse" tie-line is used, and as a result the microstructures can be located with large, small and with mixed type of crystals.

Key words: lead-free solders, microstructures of ceramics and alloys, 3D computer models of phase diagrams, competition of crystals with different dispersity, invariant reactions, three-phase regions with the surfaces of two-phase reactions

INTRODUCTION

Results of ESF COST 531 Project were published as T-x-y diagrams Atlas of systems, which could replace Pb-contained solders [1]. Though preparation of Atlas has been required many efforts, concerned with thermodynamic coupling of experimental data, the description of 20 ternary systems were finally reduced to liquidus projection, 2-3 isotherms and isopleths (sometimes

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in fragments) and a table of invariant reactions. Shortcoming of information is felt especially when diagrams have binary and ternary compounds only in sub-solidus. So it is necessary to reconstruct lead-free ternary systems in whole scope and to design the computer models for their T-x-y diagrams [2-3].

3D PHASE DIAGRAMS WITH KINEMATICAL SURFACES

In the process of PD computer models engineering (*Figure 1*) the mistakes and contradictions in their traditional explanations have been found. E.g., in three systems of eutectical type with different variants of liquid stratification cupola [4], the same error repeats with the unclosed contour of a solvus surface – lack of line $C^0_AC^0_E$ on a prism base (*Figure 2*).

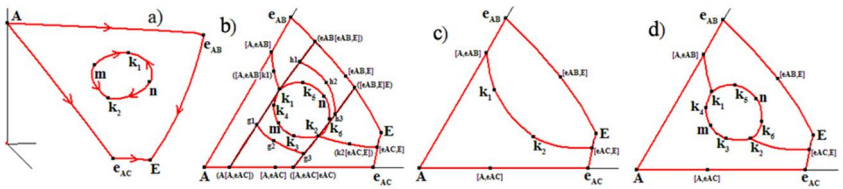

Fig. 1 – Forming of surface $Ae_{AB}Ee_{AC}$ with a hole k_1mk_2n (a): by the fragments $Ae_{AB}(e_{AB}[e_{AB},E])(A[A,e_{AC}])$, $(A[A,e_{AC}])k_1k_2([A,e_{AC}]e_{AC})$, $k_1(e_{AB}[e_{AB},E])([e_{AB},E]E)k_2$, $([A,e_{AC}]e_{AC})([e_{AB},E]E)Ee_{AC}$ (b); and by a template (c-d) with the directing curves $k_1k_4mk_3k_2$ & $k_1k_5nk_6k_2$ on hole's contour

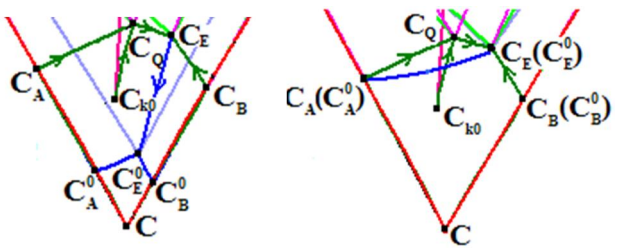

Fig. 2 – Solidus $CC_AC_QC_EC_B$ with a fold $C_{k0}C_Q$ and solvuses $C_BC_EC^0_EC^0_B$ & $C_AC_QC_EC^0_EC^0_A$ at auxiliary and orthogonal position of lines $C_AC^0_A$, $C_BC^0_B$, $C_EC^0_E$, projecting into points $C_A(C^0_A)$, $C_B(C^0_B)$, $C_E(C^0_E)$

Computer models of PD simplify the analysis of contradicting data on low-fusible systems with a lead and allow to predict their topological variants with decomposing of compounds and degeneration of solvus surfaces at low temperatures. Such diagrams are testing on their schemes (*Figure 3-5*).

Correcting the «eutectical» sections of Cd-Sn-Pb PD [5], contradicted with [6], W. Zhou [7] has given the sections of reaction R=A+B+C plane too, but didn't reach a success in the phase regions visualizing (*Figure 3*).

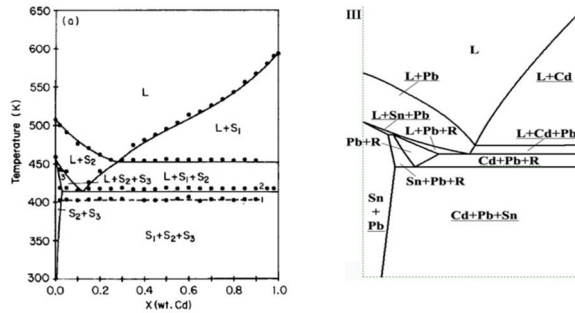

Fig. 3 – Isopleth of Cd(S1)-Sn(S2)-Pb(S3) diagram [7] and its scheme

Despite thermodynamic instability and decomposition at -46°, an incongruently melting compound R1=Pb_mBi was taken as a stable one in Pb-Sn-Bi PD [8], whereas a ternary compound R2 decomposes (*Figure 4* and *5*).

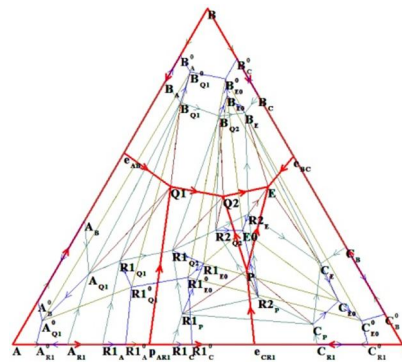

Fig. 4 - A scheme of diagram Pb(A)-Sn(B)-Bi(C) [8]

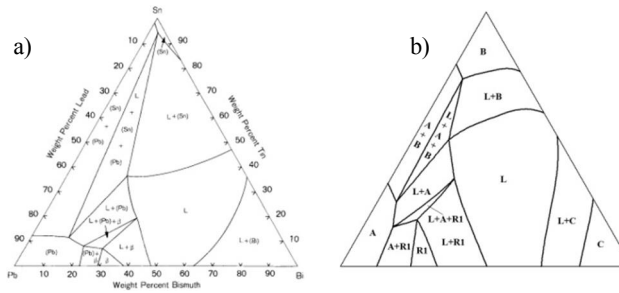

Fig. 5 – An isotherm of real [8] and schematical (Figure 4) diagram

MASS BALANCES INVESTIGATION

New results were received for the monovariant and invariant reactions. Besides confirming a horizontal position (*Figure 6*) for the surface of 3-phase reaction type change [9-10], new features of subsolidus 3-phase region were found (*Figure 7*). Investigation was validated by the mass balances.

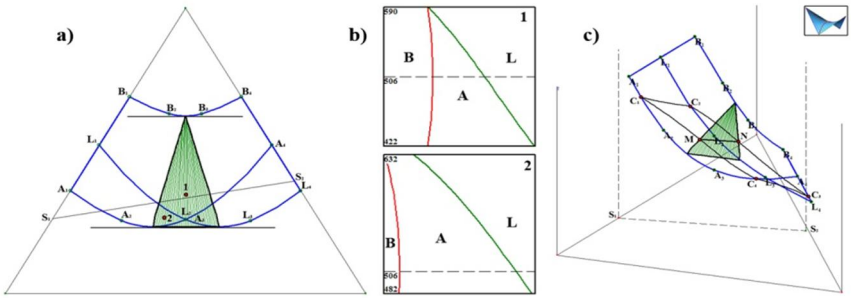

Fig. 6 – Horizontal plane of phase B mass increment sign changing for the parallelism of B_1B_4 curve tangent and common tangent of L_1L_4 & A_1A_4 curves (a); mass balances for compositions 1, 2 (b); isopleth S_1S_2 and surfaces cuts: $A_1L_1L_4A_4$ - curves C_1C_2&C_3C_4, $B_1L_1L_4B_4$ - C_2C_3, $A_1B_1B_4A_4$ - C_1C_4 (c)

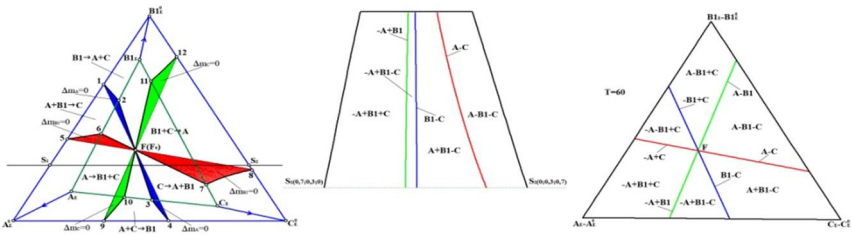

Fig. 7 – Three-phase region with 6 changes of the reaction type and its vertical and horizontal sections

As each phase in the process of cooling has its own density, it is important to recognize that real item belongs either one of 3 "eutectiodal" fragments, or 3 "peritectoidal" ones (*Figure 7*). And every such fragment will have its individual mechanism of development of the specific gravity.

Computer model of PD simplifies the solution of problems with microstructures design [11]. Field $Ae_{AB}FS$ of reaction $L+A^Q=B^Q+R^Q$ is broken by the lines Ke_{AB} and KA into the fragments $e_{AB}FK$, $Ae_{AB}K$ and ASK (Figure 8a). In the top fragment $e_{AB}FK$ microstructure contains a matrix $M=R^Q+B^Q+B^e$ and eutectical crystals A^e, in bottom fragment ASK – a matrix M and primary crystals A^1. The microstructure of medium fragment $Ae_{AB}K$ includes both types of crystals A: $M+A^1+A^e$. On the fragment $UH\equiv(A\text{-}Q)(e_{AB}Q)$ of isopleth BV the horizontal (isothermal) mass balances (Figure 8b-c) are constructed, before and

after reaction $L+A^{Q}=B^{Q}+R^{Q}$, where in intervals UH and $(e_{AB}\text{-}K)(A\text{-}K)$ the dividing of the crystals portions is executed: A into A^{e} & A^{1} and $A^{и}$ - into $A^{ие}$ & $A^{и1}$ ("и" means excess, «избыток» - in Russian, after the quasiperitectical invariant 4-phase reaction).

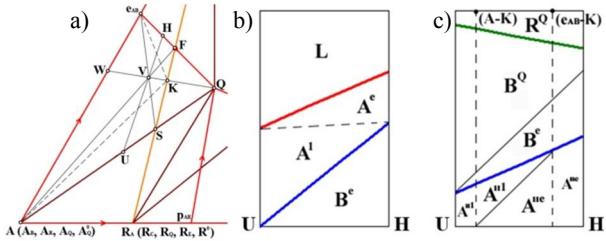

Fig. 8 - A concentration field $Ae_{AB}FS$ in PD with incongruently melting compound $R=A_nC$ (a); horizontal mass balances of isopleth UH at $T_Q+\delta$ (b) and $T_Q-\delta$ (c)

MINIMAL SURFACES

Main perspectives for the PD computer models are connected with the using of minimal surfaces. It is the well-known task to define a surface Z=Z(x,y) with the given borders. As the first step in this direction, a smooth surface of property above the whole concentration triangle ABC, (e.g. liquidus of the continuous row of solid solutions) is considered [3, p. 98]. As a surface behavior isn't known, it is possible to assume that its average curvature H=0 and to receive a one, which among all other surfaces with the same contour has a minimal area. The minimal surface searching on its given contour is named as the Plato's problem.

Average curvature of a surface is defined as $H=\frac{1}{2}\frac{EN-2FM+GL}{EG-F^2}$, where $E=1+z_x^2;\quad G=1+z_y^2;\quad F=z_x z_y;\quad L=Z_{xx}/\sqrt{1+z_x^2+z_y^2};\quad M=Z_{xy}/\sqrt{1+z_x^2+z_y^2};$ $N=Z_{yy}/\sqrt{1+z_x^2+z_y^2}$. If suppose $H\equiv 0$, we will receive $\frac{EN-2FM+GL}{EG-F^2}=0$ or $\frac{(1+z_x^2)z_{yy}-2z_x z_{xu} z_y+(1+z_y^2)z_{xx}}{(1+z_x^2+z_y^2)^{2/3}}=0$.

As the denominator isn't equal to zero, a problem solution is reduced to a linear differential equation of the second power with private derivatives of elliptic type $(1+z_x^2)z_{yy}-2z_x z_{xu} z_y+(1+z_y^2)z_{xx}=0$. (1)

Let's place a ternary system with a smooth surface in rectangular Cartesian system of coordinates (Figure 9), where binary systems are represented by the curves, described by the equations $z_{A-B}=\varphi_1(x,y)$, $z_{B-C}=\varphi_2(x,y)$,

$z_{A-C} = \varphi_3(x, y)$. On this contour it is required to find a surface $z = z(x, y)$, which is the solution of the equation (1). It may be solved by the numerical methods. For this purpose a triangle of composition is divided by a uniform grid with step λ, formed by the lines, parallel to the triangle sides.

Let's consider any knot with number ijk on a grid. On an axis i the content of component B changes, on j - component A, on k – component C. For again added axes a, b, c we will receive: $\frac{\partial z}{\partial x} = \frac{\partial z}{\partial a}$; $\frac{\partial^2 z}{\partial x^2} = \frac{\partial^2 z}{\partial a^2}$; $\frac{\partial z}{\partial y} = \frac{1}{\sqrt{3}}\left(\frac{\partial z}{\partial b} + \frac{\partial z}{\partial c}\right)$;

$\frac{\partial^2 z}{\partial y^2} = \frac{2}{3}\left(\frac{\partial^2 z}{\partial b^2} + \frac{\partial^2 z}{\partial c^2} - \frac{1}{2}\frac{\partial^2 z}{\partial a^2}\right)\frac{\partial^2 z}{\partial x \partial y} = \frac{1}{\sqrt{3}}\left(\frac{\partial^2 z}{\partial b^2} - \frac{\partial^2 z}{\partial c^2}\right)$ and the equation (1) will be copied in an equation

$$\frac{2}{3}\left[1+\left(\frac{\partial z}{\partial a}\right)^2\right]\left(\frac{\partial^2 z}{\partial b^2} + \frac{\partial^2 z}{\partial c^2} - \frac{1}{2}\frac{\partial^2 z}{\partial a^2}\right) + \left[1+\frac{1}{3}\left(\frac{\partial z}{\partial b} + \frac{\partial z}{\partial c}\right)^2\right]\frac{\partial^2 z}{\partial a^2} - \frac{2}{3}\frac{\partial z}{\partial a}\left(\frac{\partial z}{\partial b} + \frac{\partial z}{\partial b}\right)\left(\frac{\partial^2 z}{\partial b^2} - \frac{\partial^2 z}{\partial c^2}\right) = 0 .$$

Let's replace the private derivatives by the central differential schemes for a point ijk:

$$\frac{\partial z}{\partial a} = (z_{i,j+1,k-1} - z_{i,j-1,k+1})/2\lambda;$$

$$\frac{\partial z}{\partial b} = (z_{i+1,j+1,k} - z_{i-1,j-1,k})/2\lambda;$$

$$\frac{\partial z}{\partial c} = (z_{i+1,j,k+1} - z_{i-1,j,k-1})/2\lambda;$$

$$\frac{\partial^2 z}{\partial a^2} = (z_{i,j+1,k-1} - z_{i,j-1,k+1} - 2z_{ijk})/\lambda^2;$$

$$\frac{\partial^2 z}{\partial b^2} = (z_{i+1,j+1,k} - z_{i-1,j-1,k} - 2z_{ijk})/\lambda^2;$$

$$\frac{\partial^2 z}{\partial c^2} = (z_{i+1,j,k+1} - z_{i-1,j,k-1} - 2z_{ijk})/\lambda^2;$$

A system of K equations are produced:

$$\frac{2}{3}\left[1+\frac{(z_{i,j+1,k-1} - z_{i,j-1,k+1})^2}{4\lambda^2}\right]\left(\frac{z_{i+1,j+1,k} + z_{i-1,j-1,k} - 2z_{i,j,k}}{\lambda^2} + \frac{z_{i+1,j,k+1} + z_{i-1,j,k-1} - 2z_{i,j,k}}{\lambda^2} - \right.$$

$$\left. - \frac{1}{2}\frac{z_{i,j+1,k-1} + z_{i,j-1,k+1} - 2z_{i,j,k}}{\lambda^2}\right) + \left[1+\frac{(z_{i+1,j+1,k} + z_{i-1,j-1,k} - 2z_{i-1,j,k-1})^2}{12\lambda^2}\right] \times \frac{z_{i,j+1,k-1} + z_{i,j-1,k+1} - 2z_{i,j,k}}{\lambda^2} -$$

$$- \frac{2}{3}\frac{(z_{i,j+1,k-1} - z_{i,j-1,k+1})}{4\lambda^2} \times \frac{(z_{i+1,j+1,k} - z_{i-1,j-1,k} + z_{i+1,j,k+1} - z_{i-1,j,k-1})}{4\lambda^2} \times$$

$\times \frac{\left(z_{i+1,j+1,k} + z_{i-1,j-1,k} - z_{i+1,j,k+1} - z_{i-1,j,k-1}\right)}{\lambda^2} = 0$, where triangle sides have N equal segments and there are $K = \sum_{i=1}^{N-2}(n-i-1)$ unknown points within a triangle.

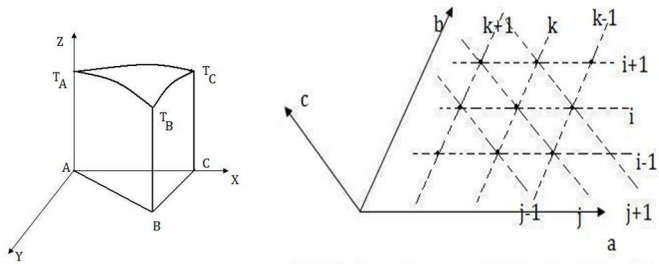

Fig. 9 - A surface and a central differential scheme for the equation (1)

The system solution – values of temperatures in K points within a triangle – is received by the Newton method. As initial approximation the values of temperatures in the grid knots, received for a plane, constructed on three points, are accepted: $A(0,0,T_A), B(1/2,\sqrt{3}/2,T_B), C(1,0,T_C)$.

At algorithm realization each point i, j, k in a triangle are considered in an environment of six others: (i-1) and (i+1), (j-1) and (j+1), (k-1) and (k+1). Accordingly in all these points seven derivatives and values of function in a point i, j, k are calculated. Received system of the K linear equations has been dared by the using of standard procedures.

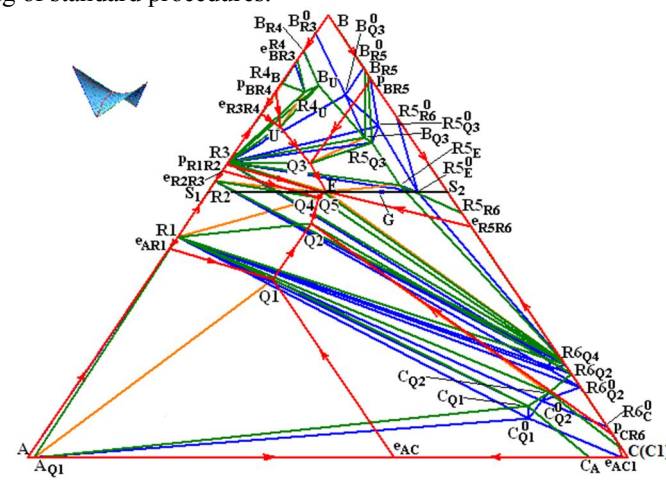

Fig. 10 – Bi(A)-In(B)-Sn(C) T-x-y diagram

RESULTS AND DISCUSSION

The Bi-In-Sn T-x-y diagram with binary compounds R1-R6, 155 surfaces and 60 phase regions (*Figure 10*) had been reconstructed by the data of binaries, liquidus projection, isotherm 56°, isopleths z_{In}=0.6 and z_{Bi}=0.2. Quality of reconstruction is confirmed by coincidence of simulated isopleths and isotherms with the given sections in the Atlas.

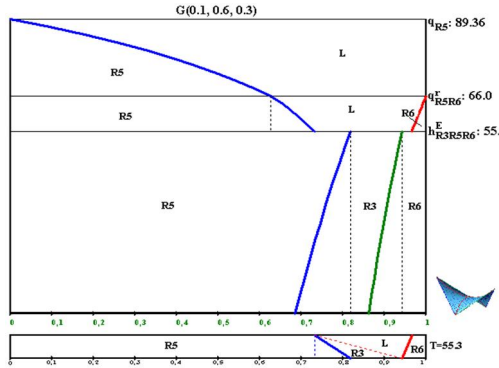

Fig. 11 – Mass balances for composition G (S_1S_2 isopleth of Figure 10)

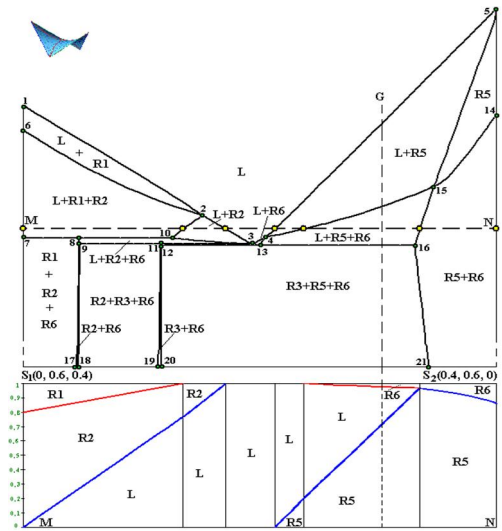

Fig. 12 - Mass balances for the isopleth z_{In}=0.6 at T=60° (Figure 10)

Two types of mass balances are considered to analyze the microstructure forming: 1) in all temperature diapason for a given concentration G (Figure 11), to show, which phase regions are intersected by the mass centre G and the

mass portions of the coexisting there phases, 2) for isothermal states of isopleth MN (Figure 12) to demonstrate the portions of phases in the phase regions intersected by MN at this temperature.

CONCLUSIONS

As a solder without Pb sometimes makes worse the quality of a microelectronic device, it is necessary to find methods to improve its microstructure by means of PD computer model.

PD computer model became an important tool to investigate physico-chemical systems. It permits to receive an adequate evaluation for the thermodynamic calculation and for the interpretation of experimental data.

An analysis of crystallization schemes in the system with only one ternary incongruently melting compound is characterized as very complicated one [12]. Meanwhile it was thoroughly interpreted by L.S. Palatnik, A.I. Landau [13]. In similar way the crystallization paths can be considered for any ternary system by means of computer model for its T-x-y diagram.

Computer design of materials gives a possibility to detect such nuances of microstructure formation as 3-phase transformation type change and competition of crystals with different disopersity.

Acknowledgements

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