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Reasons for Contradiction of T-X-Y Diagram Au-Bi-Sb in "Atlas of Phase Diagrams for Lead-Free Soldering"

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The paper describes how 3D computer models of phase diagrams may be used for searching and correction of mistakes in projections and sections of phase diagrams, designed by known thermodynamic methods. The system Au-Bi-Sb from the Atlas of Phase Diagrams for Lead-Free Soldering is an example to demonstrate searching of mistakes and reconstruction of missing surfaces and phase regions with a help of 3D computer model of its T-x-y diagram.

Keywords: Nano- and Microstructures, Lead-Free Solders, 3D Computer Model of Phase Diagram.

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1. INTRODUCTION

Computer images of phase diagrams give a possibility to testify agreement of data about topological and geometrical features with initial thermodynamic models of phases and to understand reasons of their contradictions [1, 2].

So, the Atlas of binary and ternary systems phase diagrams for lead-free soldering have been published as a result of very expensive project of European Science Foundation [3]. It includes phase diagrams of 53 binary and 20 ternary systems. Nine ternary T-x-y diagrams with the simplest topology have from one (plus miscibility gap) to five liquidus surfaces and not more then two binary compounds, five of them have immiscibility of liquid or decomposition of solid solution. Number of liquidus surfaces in another 11 diagrams is varying from 7 to 17, all of them have binary compounds and 4 diagrams have not only binary but ternary compounds too. All binary compounds in 14 ternary diagrams have their own liquidus surfaces, but in 6 diagrams some compounds exist only in sub-solidus. The only binary compound in the Ag-Cu-In diagram, two compounds in Au-In-Sb and three compounds in Ag-Cu-Sn have no own liquidus surfaces and Cu-Ni-Sn and Au-In-Sn diagrams have five and Cu-In-Sn has six such binary compounds. A ternary compound does not have its own primary crystallization field in systems Cu-Ni-Sn and Cu-In-Sn.

Atlas authors have carry out thermodynamic agreement of calculated and experimental data of every system. However in spite of big efforts and costs the description of every ternary phase diagram is limited by liquidus projections and a few isothermal sections and isopleths only. Some sections have incomprehensible details and it is impossible to explain them without a special 3-dimensional computer model. For instance:

1) The only homogeneous region of solid solution Bi(Sb)=B(C) exists at 240°C in the binary system Bi-Sb=B-C (Fig. 1,a), but it can be seen the sections of three 2-phase regions B(C)+R2, L+B(C), B(C)+R1 on the isothermal section at the same temperature of the ternary system Au-Bi-Sb=A-B-C and all of them adjoin to the binary system Bi-Sb (Fig. 1,d). While compounds R1=Au_2Bi and R2=$AuSb_2$ do not even belong to the system Bi-Sb!

2) The binary system Bi-Sb has the 2-phase region B+C=Bi+Sb of solid solution B(C)=Bi(Sb) decomposition to B=Bi and C=Sb (Fig. 1,a). It is under surface of miscibility gap in the ternary system and it can be seen its sections in isopleths (Fig. 1,b) and (Fig. 1,c). However this 2-phase region in these isopleths is wrongly denoted as a 3-phase region B+C+R2= =RHOMBO_A7+RHOMBO_A7+AUSB2. There is the region B(C)+R2=Bi(Sb)+$AuSb_2$ above the miscibility gap surface. If to suppose that these regions are incorrectly denoted in the Atlas and it is need to erase R2, then the law of adjoining phase regions is broken: it is not permitted if 1-phase region B(C) have as neighbors 3-phase regions B(C)+R1+R2 and A+B(C)+R2.

To answer these questions it is necessary to analyze all known experimental data and to construct its 3D computer model.

2. THE SYSTEM Au-Bi-Sb INVESTIGATION HISTORY

Six isopleths ($z_{1(Au)}$=0.2, $z_{1(Au)}$=0.7, $z_{2(Bi)}$=0.2, $z_{1(Bi)}$=0.6, $z_{3(Sb)}$=0.2, $z_{1(Sb)}$=0.7) of the system have been published by Prince with colleagues and then they have been included to the MSIT data base [4]. Wang et al [5] have reproduced them later. They investigated the system by experimental studying simultaneously with thermodynamic calculations with the program ThermoCalc. Results of the same system analogous investigations and calculations by ThermoCalc have been published in a year [6], where Manasijevića et al have presented 3 isopleths: from every top of the concentration triangle to the middle of its opposite side.

After careful selection of data for the Atlas its authors have preferred results of the paper by Wang et al [5]. However the analysis of isothermal sections and isopleths, published in [3-6] does not answer to the formulated above questions.

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Isopleths of Prince et al [4] and Wang et al [5] has sections of the solid solution B(C)=Bi(Sb) region and adjoining with it 2-phase regions L+B(C), B(C)+R2. But isopleths of Manasijevića et al [6] and the Atlas [3] (they say that it includes results of Wang et al [5]) have no these regions. As it already said, regions B+C+R2=RHOMBO_A7+RHOMBO_A7+AUSB2B and B(C)+R2=RHOMBO_A7+AUSB2 adjoin to B-C=Bi-Sb instead of them. Obviously it was considered that regions B(C) and B+C are degenerated and therefore they can not appear in isopleths. Authors of papers [3, 5, 6] used the same data [7] of the system B-C=Bi-Sb. But Wang et al [5] do not work below temperature 400 K, whereas the solid solution decomposition curve is below (Fig. 1,a). It is possible that the region B(C)=Bi(Sb) isn't degenerated in the paper by Wang et al [5].

Isothermal sections have analogous contradictions. So, the section 300°C has been designed in four publications: in [3, 5, 6] and calculated [7] by "convex hulls" method [8, 9]. The region B(C)=Bi(Sb) section joins to B-C=Bi-Sb in two of them [5, 7] and the region B(C)+R2=Bi(Sb)+$AuSb_2$ section joins to B-C=Bi-Sb in another publications [3, 6].

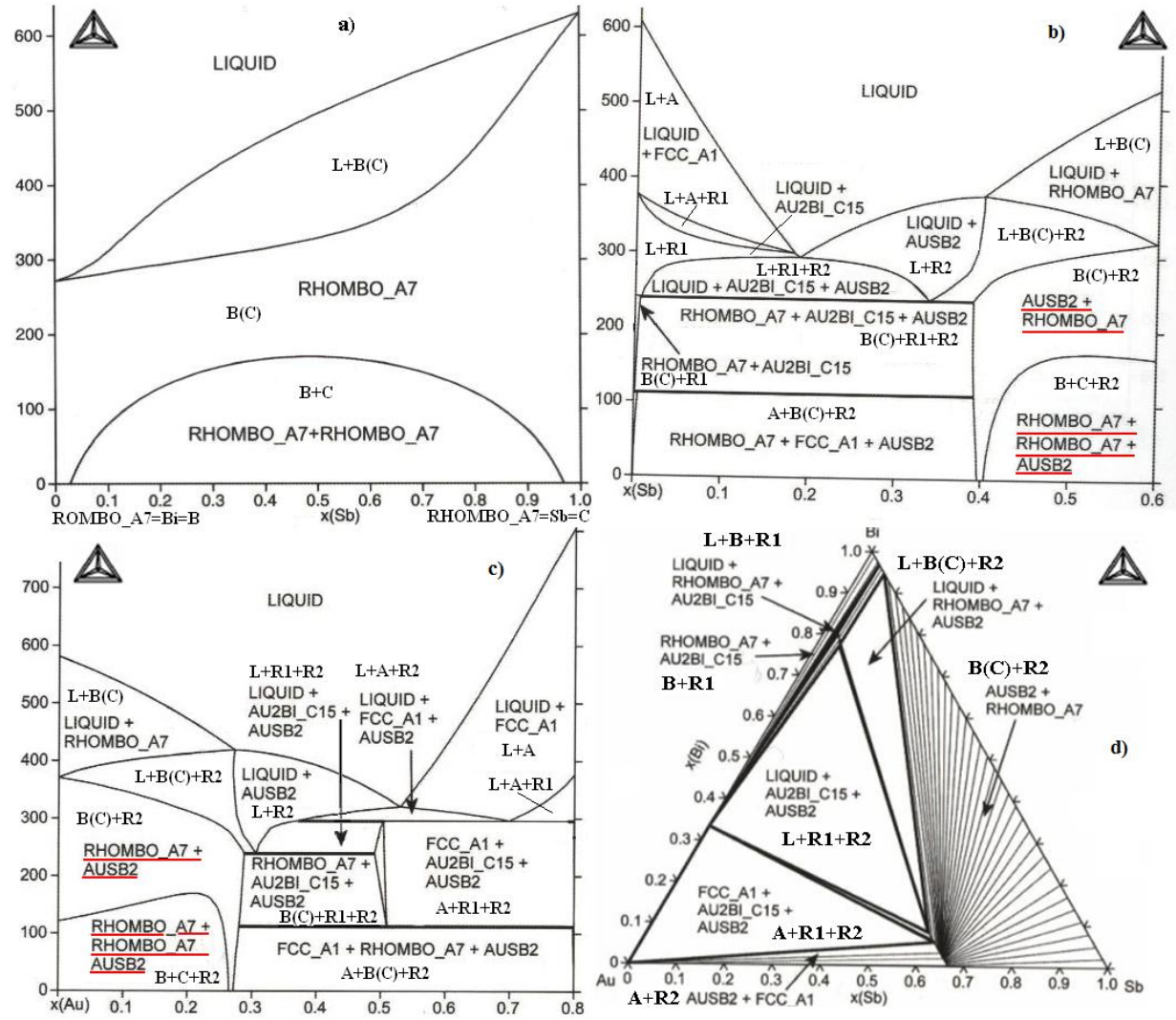

Fig. 1 – Binary system Bi-Sb (a), isopleths $z_{2(Bi)}$=0.4 (b), $z_{2(Bi)}$=0.8 (c) and isothermal section 240°C (d) of the system Au-Bi-Sb [3]

3. D COMPUTER MODEL OF THE SYSTEM Au-Bi-Sb T-x-y DIAGRAM

Design of the 3D computer model is fulfilled in some stages. Firstly after liquidus reconstruction it is necessary to understand reasons of contradictions in the Atlas contained sections. For this purpose the model of simplest diagram A-B-C, formed by two binary eutectic systems A-B and A-C and one binary system B-C with continuous series of solid solutions, is constructed (Fig. 2,a). Then the model becomes more complicated due to binary non-stoihiometric compounds R1 and R2 in systems A-B and A-C, correspondingly (Fig. 3,a). Its liquidus coincides with the system Au-Bi-Sb liquidus but another surfaces, included solidus and solvus, are not degenerated to edge or face of the prism (until both compounds are not stoihiometric). Final design of the Au-Bi-Sb T-x-y diagram 3D model is completed by comparison of its sections with the Atlas sections (Fig. 4).

3.1 Simplest T-x-y Diagram with Miscibility Gap

3D computer model of the simplest T-x-y diagram is complicated by the immiscibility of solid solution B(C) to B and C in a binary system B-C, as in the system Bi-Sb (Fig. 1,a). If a curve of miscibility gap in a binary system causes the miscibility gap surface "i" (Table 1) in a ternary system, then is it possible to suppose "interactivity" of the binary miscibility gap of solid solution B(C) with the solvus surface, formed by curves of binary solvus $B_AB^0_A$ and $C_AC^0_A$ (Fig. 2,c)? No, it is impossible, because in this case a vertical section of the miscibility gap surface divides two 2-phase regions A+B(C) and B+C (Fig. 2,d).

3.2 3D Computer Model of T-x-y Diagram without Surfaces Degeneration

If to approach to the Au-Bi-Sb phase diagram topology and to move points B_A and C_A as close as possible to B and C edges, correspondingly, then solvus can not be intersected with the solid solution miscibility gap surface in any case (Fig. 3) because otherwise analogous mistakes appear in sections (Fig. 1,b-d).

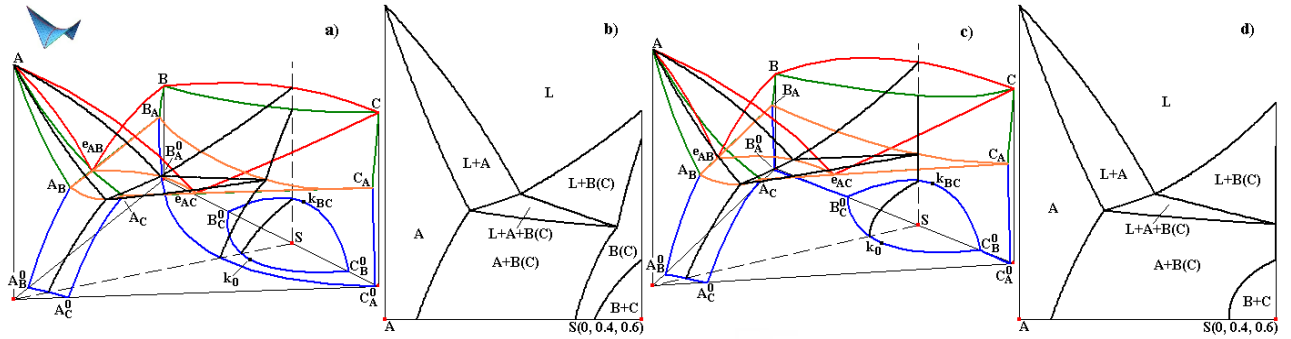

Fig. 2 – Simplest diagram with "correct" (a) and "incorrect" (c) solvus surfaces: curves of solidus BB_A and CC_A, solvus $B_AB^0_A$ and $C_AC^0_A$ are moved nearer to prism edges B and C in the system Au-Bi-Sb=A-B-C; isopleths A-S(0, 0.4, 0.6): correct (b) and wrong - 2-phase regions A+B(C) and B+C can not be adjoined (d)

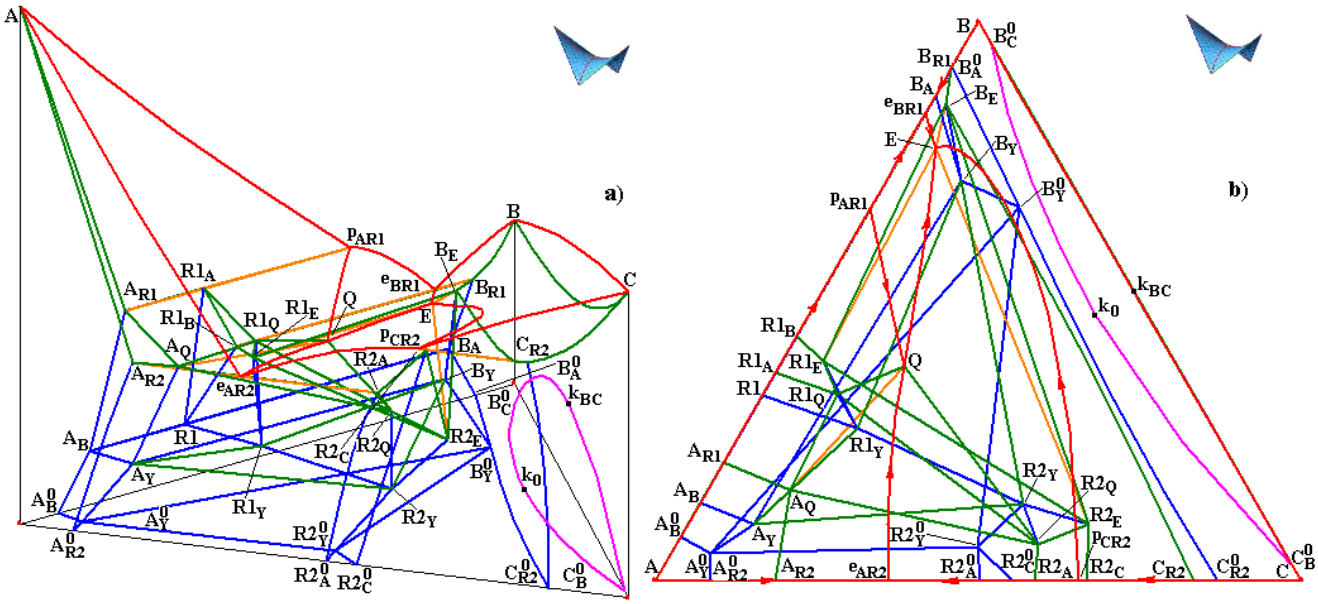

Fig. 3 – T-x-y diagram (a) and its x-y projection (b) for the hypothetical system without degeneration of curves BB_{R1}, CC_{R2}, $C_{R2}C^0_{R2}$ to the prism edges

3.3 T-x-y Diagram 3D Computer Model of the System Au-Bi-Sb

And finally – 3D model of the real system Au-Bi-Sb T-x-y diagram. Compound R1=Au2Bi is stoihiometric. Regions A+B=Au+Bi and A+R1=Au+Au2Bi are degenerated. However solidus $s_{B(C)}$ and two surfaces of solvus $v_{B(C)R2}$ and v_{BR1} are borders of the B(C) region as before. As a result, solidus $s_{B(C)}$ and solvus $v_{B(C)R2}$ have been missed in the Atlas. In spite of the binary system Au-Sb curves CC_{R2} and $C_{R2}C^0_{R2}$ are degenerated to the C edge and the point B_E practically belongs to the B-B=Bi-Sb face, solidus and solves surfaces themselves can not be degenerated (be closed to the B-C=Bi-Sb face), because the miscibility gap surface of solid solution B(C) must be between the prism face and these surfaces (Fig. 3,a).

As a result, the T-x-y diagram of the system Au-Bi-Sb consists of 60 surfaces (Table 1) and 24 phase regions (Table 2). Sections of new founded surfaces of solidus and solves give curves dividing the region B(C) from L+B(C) and B(C)+R2 (Fig. 4).

Table 1 – Liquidus and surfaces – borders of the phase region B(C)* (Fig. 3)

Surface	Contour	Surface	Contour
q_A	$Ap_{AR1}Qe_{AR2}$	$s_{B(C)}$	$BB_{R1}B_EC_{R2}C$
$q_{B(C)}$	$Be_{BR1}Ep_{CR2}C$	v_{BR1}	$B_{R1}B_AB_EB_Y$
q_{R1}	$p_{AR1}QEe_{BR1}$	$v_{B(C)R2}$	$B_EB_YB^0{}_YC^0{}_{R2}C_{R2}$
q_{R2}	$e_{AR2}QEp_{CR2}$	v_{BA}	$B_AB^0{}_AB^0{}_YB_Y$
		i	$k_{BC}B_{C0}k_0C_{B0}$

* Surfaces are denoted as: q – liquidus, s – solidus, v – solvus, ruled surfaces have upper index "r", i - immiscibility

Table 2 - Phase regions, adjoining with the region B(C) (Fig. 3)

Phase region	Borders	Adjoining phase regions
L+B(C)	$q_{B(C)}$, $s_{B(C)}$, $q^r{}_{BR1}$, $q^r{}_{B(C)R2}$	L, B(C), L+B(C)+R1, L+B(C)+R2
B(C)	$s_{B(C)}$, v_{BA}, v_{BR1}, $v_{B(C)R2}$, i	L+B(C), B(C)+R1, B(C)+R2
L+B(C)+R2	$q^r{}_{B(C)R2}$, $q^r{}_{R2B(C)}$, $s^r{}_{B(C)R2}$, h_{BR2E}	L+B(C), L+R2, B(C)+R2
B(C)+R2	$v_{B(C)R2}$, v_{R2C}, $s^r{}_{R2B(C)}$, $v^r{}_{BR2(E)}$, $v^r{}_{BR2(Y)}$	B(C), R2, L+B(C)+R2, A+B(C)+R2, B(C)+R1+R2
B+C	i	B(C)

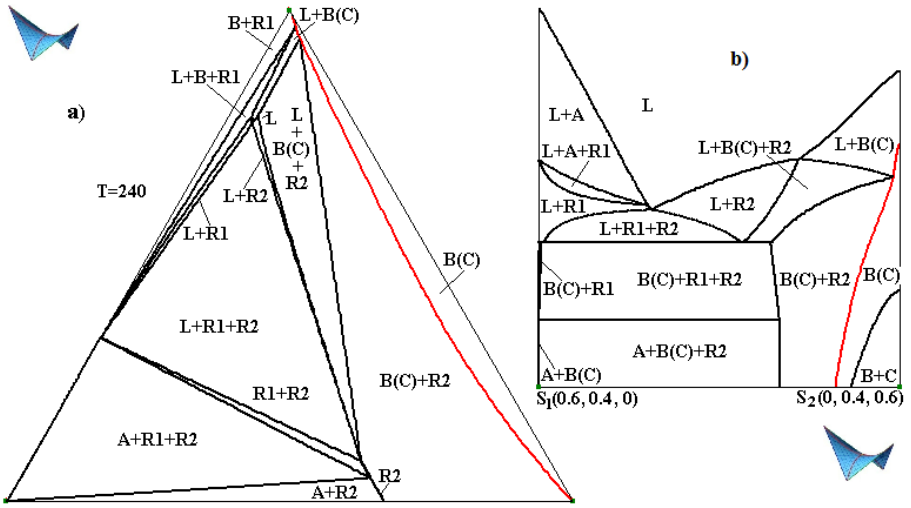

Fig. 4 – Improved (Fig. 1,b,d) isothermal section 240°C (a) and isopleth $z_{2(Bi)}$=0.4 (b) of the system Au-Bi-Sb

4. CONCLUSIONS

Phase diagram lightens design of materials in the ternary metal systems. It is possible that traditionally constructed with a help of thermodynamical assessment of experimental data phase diagrams have mistakes. So, it is conveniently to apply for correction and explanation of some contradictions 3-dimensional computer models [11, p. 150]. This sort of 3D models helped to find two surfaces and two phase regions in sections of the Au-Bi-Sb T-x-y diagram, missed in the *Atlas of Phase Diagrams for Lead-Free Soldering* [3].

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REFERENCES

1. V. Lutsyk, *Proc. of 1-st Intern. Conf. "Nanomaterials: applications & properties (NAP-2011)*" (Alushta, Crimea, Ukraine) **2** Part 1 11 (2011)
2. V.I. Lutsyk, V.P. Vorob'eva, *IOP Conf. Ser.: Mater. Sci. Eng.* **18** No 9 (2011)
3. A. Dinsdale, A. Watson, A. Kroupa et al, *Atlas of phase diagrams for lead-free soldering* (Czech Rep., Brno: Vydavatelstvi KNIHAR: 2008, V. 1).
4. A. Prince, G.V. Raynor, D.S. Evans (Inst. Met., London: 1990) SpringerMaterials - The Landolt-Börnstein Database
5. J. Wang, F.G. Meng, H.S. Liu et al, *J. Electron Mater.* **36** No 5, 568 (2007).
6. D. Manasijevića, D. Minićb, D. Živkovića et al, *J. Phys. Chem. Solids* **69** No 4, 847 (2008).
7. H. Ohtani, K. Ishida, *J. Electron. Mater.* **23**, 747 (1994).
8. http://td.chem.msu.ru/?page_id=638.
9. G.F. Voronin, *Rus. J. Phys. Chem.* **77** No 10, 1685 (2003).
10. V.A. Prostakova, V.I. Goryacheva, I.B. Kutsenok, *Vestnik Moskow State University, Series 2 – Chemistry* **52** No 2, 83 (2011) (In Russian).
11. J. Vrestal, A. Kroupa, P. Broz, *CALPHAD* **34**, 138 (2010).