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Computer models of eutectic-type *T–x–y* diagrams with allotropy

Two inner liquidus fields of two low-temperature modifications of the same component

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Abstract Using the eutectic-type *T–x–y* diagram as an example, it can be represented the analysis of its geometrical construction dependence on the temperature of a component two polymorphous modifications which participate in mono- and invariant metatectic and invariant eutectic (eutectoid) transformations above or below (and within) binary eutectics temperature intervals and below a ternary eutectic temperature. Computer models for considered phase diagrams have been designed. Such models help to solve applied tasks like visualization, isopleths and isothermal sections decoding, mass balances calculation and evaluation of phase and conglomerate concentration in microstructure.

Keywords Allotropy · Phase diagram · Metatectic equilibrium · Phase scheme with phases paths

Introduction

In spite of phase diagrams (PD) were initially created to visualize properties of *n*-component systems, the progress of the PD theory and discovery of laws of their geometrical construction had offered to the fact that PD itself had transformed from the visualization instrument of investigation results to the investigation object. At the same time, achievements of computer graphics had made possible to design more and more complicated geometrical constructions of not only multidimensional PD, but even at $n = 3$. As a result, on the one hand, some researchers either have stopped to use phase diagrams at all or limit they self by one-two sections and concentration projections because of too much PD complicity, and on the other hand, we can see the tendency to search another ways to formalize and to make simpler PD descriptions, for instance, with a help of graphs [1, 2] and matrixes [3].

Traditional visualization of phase diagrams investigation results with a help of thermodynamical calculations and agreement with experiments is limited usually by *x–y* projections, isotherms and isopleths. This sort of information is complemented sometimes by tables of either mono- and invariant phase reactions (including temperatures and types of reactions) or primary crystallization beginning temperatures with crystallizing phase names [4–6]. It is supplemented by 3D graphics now. Three-dimensional presentations of phase diagrams are drawn by the AutoCAD program [7] or by elaborated specially for these purposes program [8].

Nevertheless, PD is as before the best and perhaps the only instrument of experimental and calculated results visualization and the method of their agreement too. Moreover, PD accumulates huge information. The access to this information becomes simpler by means of PD computer models. Hence, PD computer models can and must help to understand the construction of even the most complicated diagram.

The first, primitive PD model may be designed even by limited set of thermal analysis data. For this purpose, it is enough to use base points (binary and ternary eutectics, peritectics and so on). Further, replenishment of the experimental information about the system and the model improvement by means of more precise definition of base points coordinates, lines and surfaces curvature, agreements of experimental results with thermodynamic

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calculations improves the computer model step-by-step. However, the model must be able to fulfill, independently on its accuracy and precision and on any stage of its construction, except its main function of visualization, another applied operations like design and decoding of isopleths and isothermal sections, calculation of mass balances and temperature-concentration conditions of phase reactions at different stages of crystallization, calculation of phase and conglomerate concentration of microstructure, correction of inaccurate interpretation of experimental data because of misunderstanding of some PD elements, especially at degeneration of bordering solid solubility regions surfaces.

To illustrate PD computer models possibilities, *T–x–y* diagrams with allotropy have been picked up because firstly they are insufficiently presented in literature since known publications either are not correct or have serious mistakes in experimental data estimation [9]; and second, they make possible to trace the logic of the surfaces and phase regions forming in dependence on temperature intervals of polymorphous transformations and as a result to understand total principles of the PD complicated construction formation from phase regions.

Eutectic-type *T–x–y* diagrams with two polymorphous modifications of the component B

Two types of polymorphous transformation with low-temperature modifications B1 and B2

$$B \rightarrow B1 + N, \tag{1}$$

$$B1 \rightarrow B2 + N, \tag{2}$$

where N is either liquid L or one of solid phases A or C, occur in different situations (Fig. 1): both transformations (a) or one of them (b, d) are monovariant metatectic; one transformation (b) or two (c, d, e, f, g) are invariant metatectic; one (g) or two (h) transformations are invariant eutectoid. In this case a point k of a binary metatectic is changed by a point e of a binary eutectoid. So it is possible to receive in dependence on temperature of reactions (1) and (2) eight variants of this diagram (Fig. 1): both transformations (1) and (2) take place above binary eutectics (a); the reaction (1) happens above binary eutectics and the reaction (2) between them (b) and (d); both transformations take place either between binary eutectics (c) and (e) or below binary eutectics but above the ternary eutectic (f) or below it (h); the transformation (2) has already descended below the ternary eutectic but the reaction (1) not yet (g). Another three cases, which are not showed in the Fig. 1, are possible when the transformation (2) takes a place below the ternary eutectic and the transformation (1) above it and simultaneously: above both binary eutectics, between them and below them.

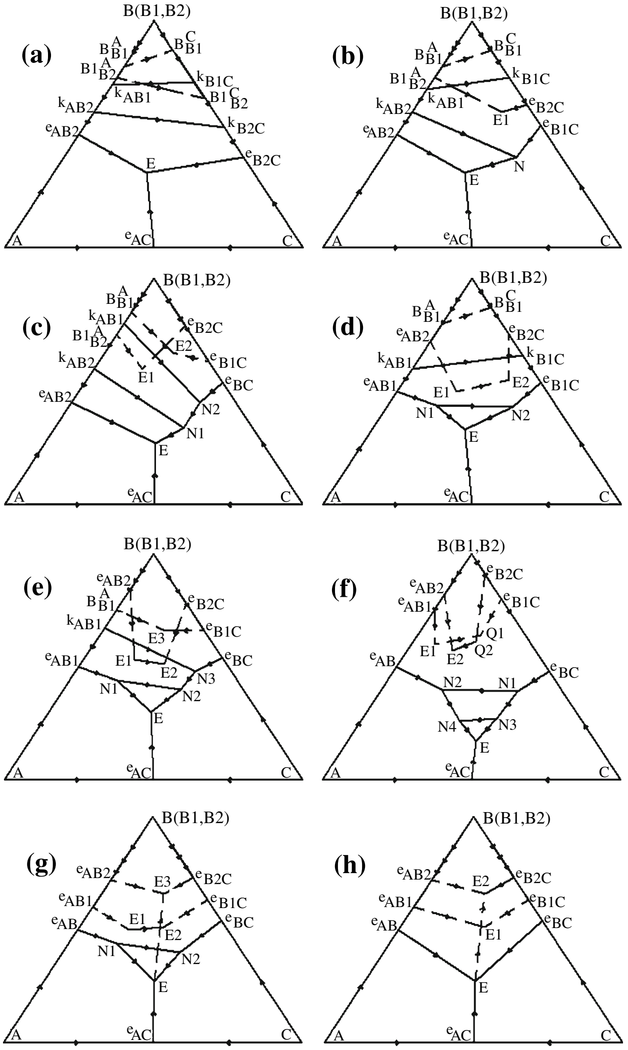

Fig. 1 Genesis of eutectic type *T–x–y* diagrams liquidus with two polymorphous modifications of the component B

Inner liquidus fields of B1 and B2 at the falling of polymorphous transformations temperatures shift from the concentration triangle sides and come nearer to the ternary eutectic. Pairs of transus surfaces are borders of phase regions B + B1 and B1 + B2 by analogy with two-phase regions L + J borders as the conjugated pair “liquidus-solidus”. The first transus surface of the “liquidus” type is the border of the vanished phase (which is in the left part of Eqs 1 and 2) and the second transus surface of the “solidus” type becomes the border of the formed phase (which is in the right part of Eqs. 1 and 2). Therefore, contours of transus surface-type “liquidus” at changing of the liquidus topology are changed too. Invariant points of eutectic (E) or quasi-peritectic (Q) type:

$$B(E) \rightarrow B1 + J + N,\ B1(E) \rightarrow B2 + J + N \quad \text{or}$$
$$B(Q) + J \rightarrow B1 + N, B1(Q) \rightarrow B2 + J + N,$$

where N = L, A, C and J = A, C, N ≠ J, appear on transus surfaces contours at the same time.

Eutectic-type T–x–y diagram with two inner liquidus fields of two low-temperature modifications of the component B

The T–x–y diagram with two inner liquidus fields (Fig. 1f) has most common and character features among considered eight liquidus models. Hence, its geometrical construction will be the discussion object of this article.

Monovariant states scheme

If the first task to give the form of liquidus and liquidus transus with supposed mono- and invariant transformations is not difficult one, then the second more difficult task may be formulated as “how to define numbers and types of all PD surfaces, to design them, and finally to create the PD computer model?” To get ready to the computer model design it is conveniently to take advantages of the monovariant states scheme (of three-phase regions) (Fig. 3). Every such scheme is the well known phase reactions scheme [10] supplemented by lists of three-phase transformations participations concentrations changing trajectories [11].

To compose the scheme, all base points have got the content designation. Except obvious and generally accepted names type A, e_{AB}, E and so on, these are some examples (Fig. 2a): the point name A_{B1} signifies that the point A_{B1} belongs to the binary system A–B and is in the same horizontal line that the eutectoid e_{AB1}, nearer A; the analogous point $B1_A$ is on the same horizontal nearer B; one of four the horizontal complex’s $Q1N1C_{Q1}B1_{Q1}$ tops, corresponding to the invariant transformation B(Q1) + C→B1 + L(N1), is named as C_{Q1}; the upper index “0” means that the point A^0_E belongs to the T–x–y concentration base.

As a result, the typical scheme of phase reactions, lined according to the temperature row, is enriched by information, which is able to predict all PD geometrical construction. As every horizontal complex of invariant transformation is always divided into four simplexes hence four arrows of monovariant transformations are always connected with it. So, the presence of h invariant transformations (complexes) and connected with them a arrows says that the T–x–y diagram includes $h \times 4$ horizontal planes (simplexes) and $a \times 3$ ruled surfaces.

Trajectories of three phases—participations of a monovariant transformation—are directing lines of ruled surfaces. Every directing line participates in the formation of two ruled surfaces and at one time belongs to two unruled surfaces, intercrossing on it. Trajectories of the phase L constitute the liquidus contour. Two other lines written to name the concentration changing of two solid phases, which take part in the three-phase transformation with the L participation, belong to contours of solidus surfaces. (Obviously, it is necessary to add to contour corresponding curves of binary systems, which are not taken into account in the monovariant states scheme). For instance, to put together the solidus A contour it is necessary to choose from the scheme records of lines: A_BA_{E1}, $A_{E1}A_{E2}$, $A_{E2}A_E$, A_CA_E—trajectories of the phase A concentrations changing in four monovariant transformations L → A + B, L → A + B1, L → A + B2, L → A + C—and to enclose the contour by curves AA_B and AA_C of binary systems (Fig. 2b).

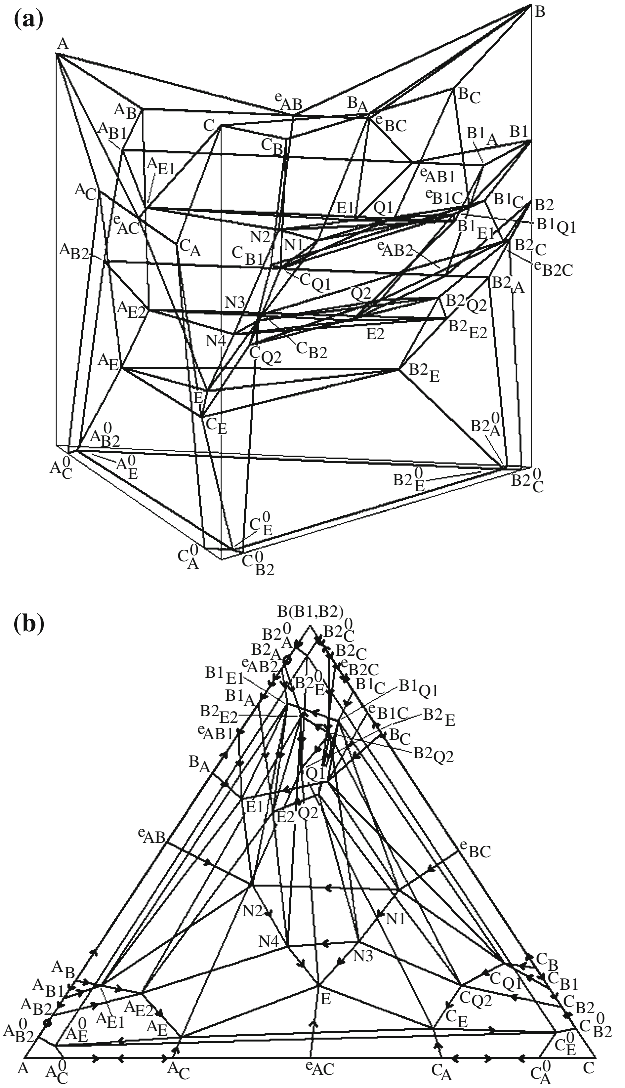

Fig. 2 Eutectic type T–x–y diagram with two inner liquidus fields of the component B two low-temperature modifications (**a**) and its x–y projection (**b**)

Contours of every pair of transus surfaces are written analogously to similar pairs of liquidus and solidus. For instance, the transus-type "liquidus" contour $B1e_{AB1}E1$-$Q1e_{B1C}$, dividing regions B and B + B1, is given likely the liquidus contour $Be_{AB}N2N1e_{BC}$, dividing regions L and L + B. It is given by points of binary and ternary transformations of eutectic and (quasi)peritectic type, too.

Usually, the solvus surface contour is composed from curves, marked by the index "0", and from common with corresponding solidus curves. However, it is worth to deliver to solvus also every pair of conjugated unruled surfaces, serving borders of the two solid phase's coexistence region, if one on them is the component low-temperature modification. Such surfaces do not lean to the concentration triangle and because their contours do not include curves with the index "0". In this case, paths of phases I and J concentration changing are copied out the scheme for all those three-phase transformations where these both phases participate at once. For instance, phases A and B meet simultaneously in the scheme (Fig. 3) only two times in records of monovariant transformations L → A + B and B → A + B1. Contours $A_BA_{E1}A_{B1}$ and B_AE1e_{AB1} are composed from record of their trajectories, bordering the region A + B of solvus surfaces.

Thus, the monovariant states scheme takes possible to determine types and numbers of all surfaces and a type of every surface. It is possible to know from the scheme about number of phase regions too. The number a of arrows in the scheme is equal to the number of three-phase regions: b—with liquid, c—without liquid, $a = b + c$. The number s of two-phase regions with liquid L + J is equal to appointed already from the scheme (or given by the scheme) number of liquidus surfaces. If k low-temperature polymorphous modifications have their inner liquidus fields, then, in agreement with the Palatnik law [12] of adjoining phase regions [13], the number of two- (r) and three-phase (b) regions with liquid L + J and L + I+J coincides with the number of homogeneous J and two-phase without liquid I + J regions, accordingly.

As a result, the T–x–y diagram consists of $s \times 2 + k \times 2 + (b - k) \times 2 + a \times 3 + h \times 4$ surfaces, including s liquidus and s solidus, k pairs of transus surfaces, b pairs of solvus, a ruled surfaces and $h \times 4$ horizontal simplexes. These surfaces are borders of $s \times 2 + b \times 2 + c$ phase regions, including s regions L + J and s regions J, b regions L + I + J and b regions I + J, c regions I + J + K.

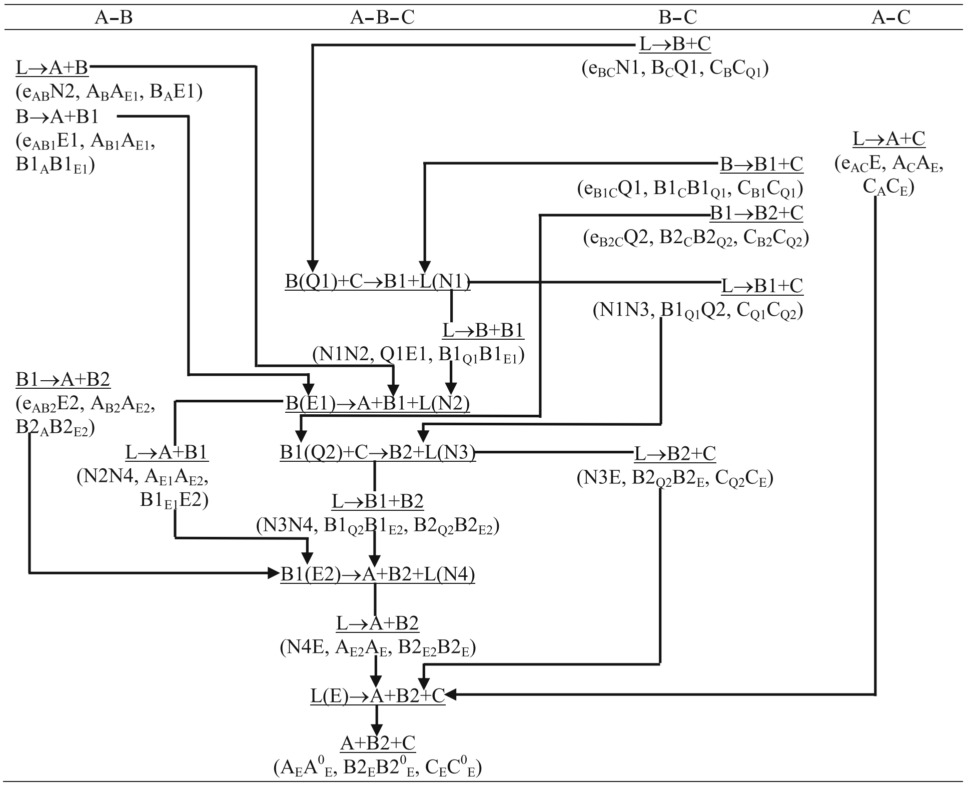

Fig. 3 Monovariant states scheme (of 3-phase regions) according to temperatures B > C>A > e_{BC} > e_{AB} > B1 > e_{AB1} > e_{AC} > e_{B1C} > - B2 > e_{B2C} > N1 > N2 > e_{AB2} > N3 > N4 > E (Fig. 2)

Surfaces

The considered *T–x–y* diagram is given by 55 points. Out of them every 3 points are on binary horizontals $\mathrm{e_{IJ}}$ ($\mathrm{e_{IJ}}$, $\mathrm{I_J}$, $\mathrm{J_I}$) of three eutectics ($\mathrm{e_{AB}}$, $\mathrm{e_{AC}}$, $\mathrm{e_{BC}}$) and four eutectoids $\mathrm{e_{AB1}}$, $\mathrm{e_{AB2}}$, $\mathrm{e_{B1C}}$, $\mathrm{e_{B2C}}$, in total 7 × 3=21 points. Every of five complexes of N1–N4 and E has four tops: 5 × 4=20 points. In three points, $\mathrm{I^0}$ ($\mathrm{I^0_E}$, $\mathrm{I^0_J}$, $\mathrm{I^0_K}$) are situated near tops A, B2, C of the concentration triangle, in total nine points. It is necessary to add to them points A, B, C, B1, B2 on the edges of the *T–x–y* prism at temperatures of phase transitions of components (Fig. 2a).

Enumerated points of the diagram are joined by 136 lines, including: in 6 lines on every of five simplexes, i.e. $h \times 6=5 \times 6=30$; in three directing curves for every monovariant transformations, i.e. $a \times 3=14 \times 3=42$; 55 lines and curves on the prism sides, out of them 9 in the A-C (in 2 curves of liquidus and solidus, two curves of solvus and three horizontals at $\mathrm{e_{AC}}$) and in 23 in the A–B and B–C (in three curves of liquidus and solidus, four transus and six solvus surfaces, in three horizontals $\mathrm{e_{BJ}}$, $\mathrm{e_{B1J}}$ and $\mathrm{e_{B2J}}$, where J = A, C); nine curves at $\mathrm{T_0}$: $\mathrm{A^0_CA^0_E}$ and $\mathrm{A^0_{B2}A^0_E}$, $\mathrm{B2^0_AB2^0_E}$ and $\mathrm{B2^0_CB2^0_E}$, $\mathrm{C^0_AC^0_E}$ and $\mathrm{C^0_{B2}C^0_E}$; $\mathrm{A^0_EB2^0_E}$, $\mathrm{A^0_EC^0_E}$, $\mathrm{B2^0_EC^0_E}$.

As it seen from the monovariant states scheme (Fig. 3) $h = 5$ invariant transformations are connected by $a = 14$ arrows and from 14 three-phase regions $p = 9$ regions with liquid L and $q = 5$ without it. From this it follows that the *T–x–y* diagram consists of $h \times 4=5 \times 4=20$ horizontal simplexes and $a \times 3=14 \times 3=42$ ruled surfaces. Thus, as there are $s = 5$ liquidus surfaces then the total number of surfaces is equal to

$$s \times 2 + k \times 2 + (b - k) \times 2 + a \times 3 + h \times 4$$
$$= 5 \times 2 + 2 \times 2 + 7 \times 2 + 14 \times 3 + 5 \times 4 = 90,$$

including 28 unruled ones.

After contours of all surfaces have been written with a help of the monovariant states scheme, it is possible to begin the design of the first variant of the PD computer model if to enter point's coordinates and to join them by straight lines. It is obviously that such primitive model cannot be designed without violating the known "extension rule" (for instance, [14]) about the extension of boundaries between one- and two-phase regions in binary systems and ternary systems sections. However, further the model will be improved as new experimental or agreed with thermodynamical calculations information becomes available. Such violating will be corrected with refinement of lines and surfaces curvature. The achievement of a final goal means that the perfect model, which adequacy represents properties of the investigated or calculated system, has been created.

Phase regions

According to the monovariant states scheme (Fig. 3), 90 surfaces of the phase diagram are borders of $s \times 2 + b \times 2 + c = 5{\times}2 + 9{\times}2 + 5{=}33$ phase regions, including in $s = 5$ regions L + J and J, in $b =$ nine regions L + I + J and I + J, $c =$ five regions I + J + K. As seen from foregoing reasoning, the content designation of points and joining them lines makes possible to have got compact (Fig. 3) but informative description of the PD, which is a great useful for understanding of its geometrical construction and for the computer model creation.

Analogous content designation may be applied to the PD surfaces too. For instance, they may be named as *q*—liquidus, *s*—solidus, *t*—transus, *v*—solvus, *h*—horizontal simplexes. As liquidus (for instance, $\mathrm{e_{AC}E}$), solidus (for instance, $\mathrm{A_CA_E}$), solvus (for instance, $\mathrm{A_EA^0_E}$) contours curves are directing lines of ruled surfaces then ruled surfaces they self may be named by the same letters *q*, *s*, *v*, but with the upper index *r* (**r**uled surface). As a pair of transus surfaces consists of one surface of liquidus type and one surface of solidus type then corresponding to them ruled surfaces, borders of three-phase transformation J → J1 + N, are designated likely as q^{rJ}, s^{rJ}, where J is a polymorphous modification at higher temperature then J1. As a result, thanks to that formalizing destination of surfaces it is possible to describe in a compact form borders of phase regions and to divide the 3D representation of the *T–x–y* diagram into its constituent ("exploded" [6]) phase regions.

Thus, the monovariant states scheme, on the one hand, takes possible to describe in compact and informative form the topology of a known PD, and on the other hand, to decode and to understand the construction of the PD if only its liquidus and possible mono- and invariant transformations are expected.

Computer model and its applied possibilities

PD computer model, done on any stage of its investigation beginning from its primitive sample and ending by perfect thermodynamically agreed model, must be able except visualization function to solve applied tasks with accuracy which is depended on the accuracy of the model itself, naturally.

Decoding of isothermal sections and isopleths

As the PD is intended at first to visualize, then, obviously, the computer model must be able to design any isopleths and isothermal sections. However, it cannot only construct sections but decode all curves and phase regions. For instance, every picture of isopleth and isothermal section is accompanied by two tables. The first table contains all intercrossing surfaces and enumerated section lines and the second one has a list of all intercrossing phase regions and contours of bordering section lines. It is prime important in those cases when section curves pass close together (Fig. 4b). Tables of isopleths have in addition temperature values near every point of the section.

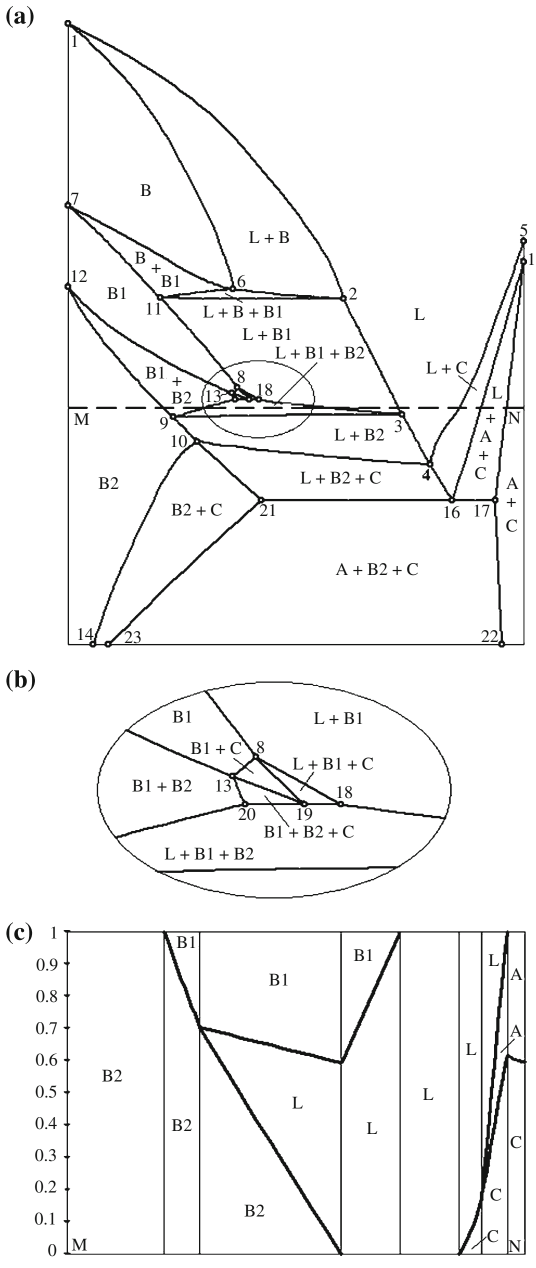

Fig. 4 Isopleth M(0, 1, 0)N(0.45, 0, 0.55) (**a**, **b**) and its horizontal mass balances diagram at $T = 375$ °C (**c**)

Two types of mass balances diagrams

Software intended for T–x–y computer models design includes algorithms for not only mass balances calculations [15, 16], but visualization of calculations results. "A phase-fraction diagram versus temperature diagram" [17] or diagrams for phase evolution during cooling of alloys [18] or so called "structural diagrams" [19, 20] are usually applied for visualization of phase or structural concentration calculations. Diagrams of this sort named as "mass balances diagrams" are constructed by the considered software in two variants.

First, any isopleth MN can be provided with a horizontal mass balances diagram (HMBD) at any given temperature T (Fig. 4c) [19, 20]. In that case, the rectangle of an arbitrary height, equaled to 1, is designed on the line MN. Then the rectangle base is marked by points where the isotherm T intersects the section MN lines. Then the rectangle itself is divided into fragments and every of them corresponds to the intercrossed at given temperature phase region. Lines which represent changing character of mass (mole) fraction of every coexisting phase are drawn inside every fragment. For instance, as it seen (Fig.4c) the homogeneous region B2 is changed by the solid solutions B1 + B2 region from left to right or from M to N during which the concentration of B1 is growing. Further, the B2 concentration in the three-phase region L + B1 + B2 falls to zero and then B1 crystals disappear inside the two-phase region B1 + B2, too. There are the primary crystallization C, eutectic A + C and coexisting of two solid phases A + C at little decreasing of C concentration in the right part of the HMBD.

The second variant of mass balances diagrams has been devised to show crystallization calculation results for the given alloy G (Fig. 5). Such sort diagrams as vertical mass balances diagrams (VMBD) are used to demonstrate how phase concentration is changing at cooling in the point G. Temperature intervals of every crystallization stage and surfaces intercrossed by the perpendicular in the point G are written on the right side of the VMBD. Lines which correspond to concentrations change of alloy and crystallizing phases are drawing. As it seen on this diagram, for instance, two-phase region B1 + B2 is formed after the primary crystallizations of B, the polymorphous transformation and the primary crystallization of B1. Joint crystallization of crystals B1 and B2 is restarted at temperatures below 378°. Then the primary crystallization of B2 takes place again. It is changed by the eutectic B2 + C crystallization. The process is finished by crystallization of two B2 + C and then by three A + B2 + C condensed phases. Numerical results are written simultaneously in a table form.

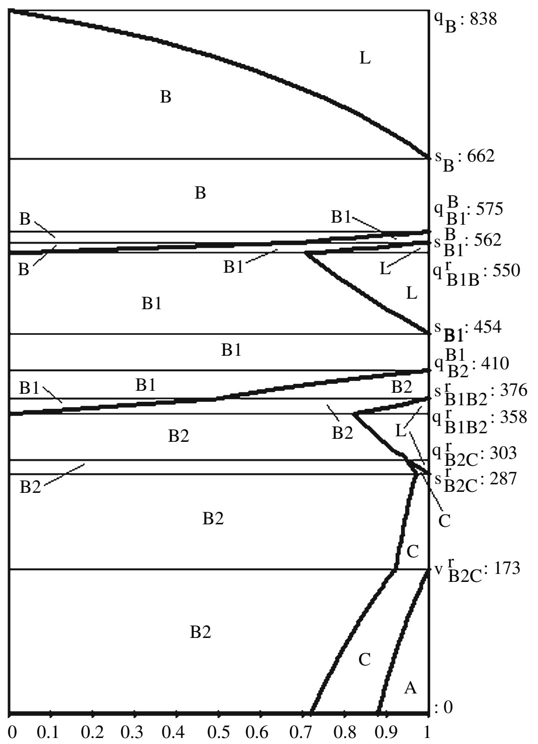

Fig. 5 Vertical mass balances diagram in the point G(0.15, 0.68, 0.17)

Conclusions

- The PD computer model is necessary at all stages of system investigation and the investigation cannot be considered as completed without the PD computer model.
- To understand the PD geometrical construction, to correctly interpret experimental data and to be ready to create computer model it is convenient to use mono-variant states schemes (of three-phase regions).
- This kind of schemes helps to understand PD geometrical construction, to determine types and numbers of its surfaces and phase regions, or, on the other hand, to accumulate in compact form information about its geometrical construction.
- Computer model independently of accuracy and availability of experimental information is able to fulfill functions of visualization, decoding of sections and representation of mass balances calculations results.

References

1. Kosyakov VI. Relationships between the topological features of a liquidus surface for ternary systems. Dokl Chem. 2000;374:199–202.
2. Kosyakov VI, Shestakov VA, Grachev EV. Enumeration of melting diagrams of three-component systems with stoichiometric compounds. Rus J Inorg Chem. 2010;55:611–9.
3. Miura S. Geometrical approach to reaction schemes of multi-component phase diagrams. J Phase Equilib Diffus. 2006;27:34–46.
4. Szczygiel I, Matraszek A, Znamierowska T. Phase equilibria in the Ce_2O_3–K_2O-P_2O_5 system. J Therm Anal Calorim. 2008; 3:671–6.
5. Netriová Z, Boca M, Danielik V, Eva Miksíková E. Phase diagram of the system KF–K_2TaF_7–Ta_2O_5. J Therm Anal Calorim. 2009;95:111–5.
6. Dinsdale A, Watson A, Kroupa A, Vrestal J, Zemanova A, Vizdal J. Atlas of phase diagrams for lead-free soldering. Brno: Vydavatelstvi KNIHAR; 2008.
7. Wenda E, Bielanski A. The phase diagram of V_2O_5-MoO_3-Ag_2O system. Part V. Phase diagram of the ternary system. J Therm Anal Calorim. 2008;93:973–6.
8. Cheynet B, Bonnet C, Stankov M. GEMINI-DiagPlot: 2D & 3D ternary phase diagrams. CALPHAD. 2009;33:312–6.
9. Khaldoyanidi KA. Phase diagrams of heterogeneous systems with transformations. Novosibirsk: SB RAS; 2004.
10. Connell RG. A tutorial on flow diagrams: a tool for developing the structure of multicomponent phase diagrams. J Phase Equilib. 1994;15:6–19.
11. Lutsyk VI, Vorob'eva VP, Nasrulin ER. T-x-y diagrams with primary crystallization fields of low-temperature modifications. Crystallogr Rep. 2009;54:1289–99.
12. Palatnik LS, Landau AI. Phase equilibria in multicomponent systems. New York: Winston Inc.; 1964.
13. Prince A. Alloy phase equilibria. Amsterdam: Elsevier; 1966.
14. Pelton AD, Thompson WT. Phase diagrams. Prog Solid State Chem. 1976;10:119–55.
15. Lutsyk VI, Vorob'eva VP. Parametric and matrix algorithms for calculating heterogeneous states in systems with an incongruently melting binary compound. Rus J Phys Chem. 2006;80:1848–54.
16. Lutsyk VI, Vorob'eva VP. Heterogeneous design: concentration fields determination with the unique crystallization schemes and microstructures. MRS Proc. 2003;755:227–33.
17. Kattner U. The thermodynamic modeling of multicomponent phase equilibria. JOM. 1997;49:14–9.
18. Avraham S, Maoz Y, Bamberger M. Application of the CALPHAD approach to Mg-alloys design. CALPHAD. 2007;31:515–21.
19. Lutsyk VI, Vorob'eva VP. Heterogeneous design: structural diagrams of ternary systems. MRS Proc. 2004;804:321–6.
20. Lutsyk VI, Vorob'eva VP. Phase and structural diagrams for inorganic materials microstructures design. ECS Proc. 2004; 11:204–213.