T-x-y-z phase diagrams assembling: Na_2MoO_4-Na_2CrO_4-Na_2WO_4-Na_2SO_4, Fe-Ni-Co-Cu, Pb-Cd-Bi-Sn, Fe-Ni-Co-FeS-NiS-CoS

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Abstract

The T-x-y-z diagrams of quaternary Na_2MoO_4-Na_2CrO_4-Na_2WO_4-Na_2SO_4, Fe-Ni-Co-Cu, Pb-Cd-Bi-Sn systems and their four-dimension (4D) computer models are considered. Geometric constructions of these diagrams are described by special di-, uni- and invariant states schemes. Assumed liquidus of the Fe-Ni-Co-FeS-NiS-CoS subsystem T-x-y-z diagram on the basis of the data about the structure of the border systems is predicted and the 4D computer model is designed. The possibilities of calculating of three- (3D) and two-dimensional (2D) iso- and polythermal sections are shown.

Keywords: Phase diagrams, three-dimension visualization, computer simulation, iron, nickel, cobalt, copper, sulfides.

Introduction

Software for the T-x-y diagrams visualization, which combines thermodynamic calculations with 3D images, is well-known (TermoCalc, ChemSage, FACTSage, MTDATA, PanEngine, PANDAT). As far as the visualization of 4-component systems is concerned, there is no information about the programs for the graphic simulation of T-x-y-z diagrams as yet. It occurs, that for understanding of the structure of the diagram being investigated the PD model (not only quaternary, but also ternary) or its fragments is necessary to mount from the wire or the plasticine [**1**]. The new approach to the assembling of phase diagrams from the phase regions and their boundaries is used for the construction of the T-x-y and T-x-y-z diagrams 3D and 4D computer models.

4D computer models of T-x-y-z diagrams

Space 3D (4D) models of phase diagrams are designed beginning from the primary crystallization and to sub solidus. Data for (hyper) surfaces can be obtained both directly from the experiment and, in the case of the absence of the same, by the construction of some virtual temporary (hyper) surfaces, which then can be corrected in accordance with the newly incoming information about the curvature of bounding lines and surfaces, bringing the diagram prototype closer to more advanced model of the real system [**2, 3**].

The prototype is designed with a help of the Sheil phase reactions scheme in the extended form as the scheme of (di- for 4D models), uni- and invariant states [**4**]. It makes it possible to determine quantity and type of all (hyper) surfaces and phase regions and it is constructed in the tabular, and then in the graphic form; therefore it becomes the basis for the geometric construction of the real diagram 3D (4D) model.

If the necessary results of experiment in the low-temperature regions absent, all geometric elements of phase diagram "are derived" from the (di-), uni- and invariant states scheme too. Subsequently, with the appearance of necessary data, they are corrected. It is assumed with this type of "conclusions" for possible surfaces and phase regions that solid solutions in the ranges of low temperatures (especially near the absolute zero temperatures) do not have a right to exist [**5**].

First of all, the 3D model in any stage, from the prototype to the final model of the real system, is a good "visualizer". It makes it possible to observe the T-x-y diagram in axonometric (T-x-y) or concentration (x-y) projections, to produce any isothermal section or isopleth. In this form it is a good tool for to researcher in order "to gather" the model of phase diagram and to understand its structure, revolving exploded view or cutting with any arbitrarily assigned planes. The visualization of 4D geometric objects is reduced to the sequential projection with reduction in the regularity, i.e., by the construction of 3D sections and their 2D sections. The obtained computer model is intended not only for the visualization, since it is possible to obtain from it the images of any isothermal sections and isopleths, or to represent the graphic model, divided

into the phase regions ("exploded", as in [**1**]), but for the calculations of mass balances in the process of the melt solidification at any temperature.

Na_2MoO_4-Na_2CrO_4-Na_2WO_4-Na_2SO_4

The prediction of the Na_2MoO_4-Na_2CrO_4-Na_2WO_4-Na_2SO_4 system construction is complicated by the ambiguous description both of binary and ternary systems, forming it. Thus, according to one data it is assumed that the Na_2MoO_4-Na_2WO_4 system can be eutectic, and on others it is characterized by the continuous rows of solid solutions with minimum [**6**].

Analogously binary systems Na_2MoO_4-Na_2SO_4 and Na_2SO_4-Na_2WO_4 [**6**] are described as the containing continuous rows of solid solutions with the minimum, and from other side the formation of compounds ($3Na_2MoO_4{\cdot}Na_2SO_4$, $Na_2MoO_4{\cdot}Na_2SO_4$ or $2Na_2WO_4{\cdot}Na_2SO_4$, $Na_2WO_4{\cdot}Na_2SO_4$), two eutectic and one peritectic is assumed in each of them. Binary systems Na_2MoO_4-Na_2CrO_4, Na_2CrO_4-Na_2WO_4, Na_2CrO_4-Na_2SO_4 [**6**] are characterized only by continuous rows of solid solutions with minimum.

Because of the ambiguous description of the binary systems the liquidus of the Na_2MoO_4-Na_2SO_4-Na_2WO_4 system is described as one surface with the minimum, located nearer to side Na_2MoO_4-Na_2WO_4, in other case it is assumed the presence of two surfaces of liquidus without invariant points [**6, 7**].

The versions of systems Na_2MoO_4-Na_2WO_4, Na_2MoO_4-Na_2SO_4, Na_2SO_4-Na_2WO_4 and Na_2MoO_4-Na_2SO_4-Na_2WO_4, characterizing by the continuous rows of solid solutions as most typical for this type of systems were selected to design the 3D computer models. Thus, it is assumed, that the Na_2MoO_4-Na_2CrO_4-Na_2WO_4-Na_2SO_4 system is also characterized by the continuous rows of solid solutions. The simulation of the liquidus hypersurface took into account the minimum points and the curvature in the boundary binary and ternary systems **(Fig. 1)**.

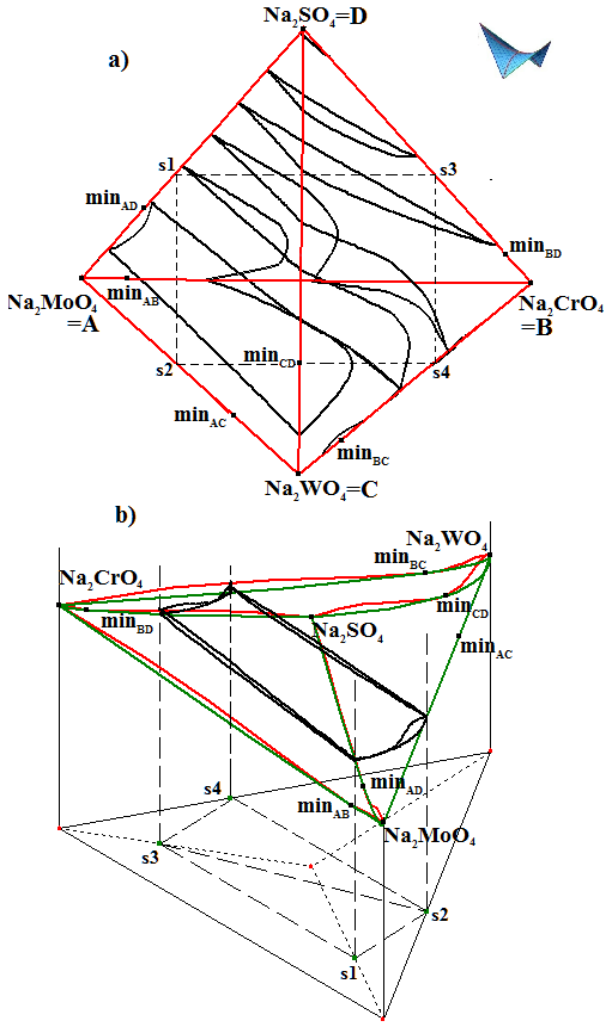


Fig. 1. Concentration projection of the Na_2MoO_4-Na_2CrO_4-Na_2WO_4-Na_2SO_4 liquidus hypersurface with isothermal surfaces (a), 3D isopleth s_1(0.6, 0, 0, 0.4)-s_2(0.6, 0, 0.4, 0)-s_3(0, 0.6, 0, 0.4)-s_4(0, 0.6, 0.4, 0) with the axis of temperatures (b).

Fe-Ni-Co-Cu

Liquidus of all ternary systems, forming the Fe-Ni-Co-Cu=A-B-C-D quaternary system, includes two polymorphous modifications of iron δ-Fe, γ-Fe **(Fig. 2)**. Since the continuous rows of solid solutions are formed in the Fe-Ni=A-B, Fe-Co=A-C, Ni-Co=B-C, Ni-Cu=B-D binary systems (in Fe-Ni and Fe-Co – with the minimum, correspondingly, m_{A1B} or m_{A1C}), that the T-x-y diagram of the Fe-Ni-Co=A-B-C system consists of two primary crystallization surfaces: high-temperature polymorphous modification of iron δ-Fe = A and solid solution of other its modification γ-Fe = A1 with nickel and cobalt.

The T-x-y diagram of the Fe-Ni-Cu=A-B-D system is more complex. The fold $p_{A1D}p_{A1BD}$ and the curve $k_{A1B}k_{A1D}$ correspond to the peritectic L+γ-Fe→Cu (L+A1→B) and metatectic δ-Fe→γ-Fe+L (A→L+A1)

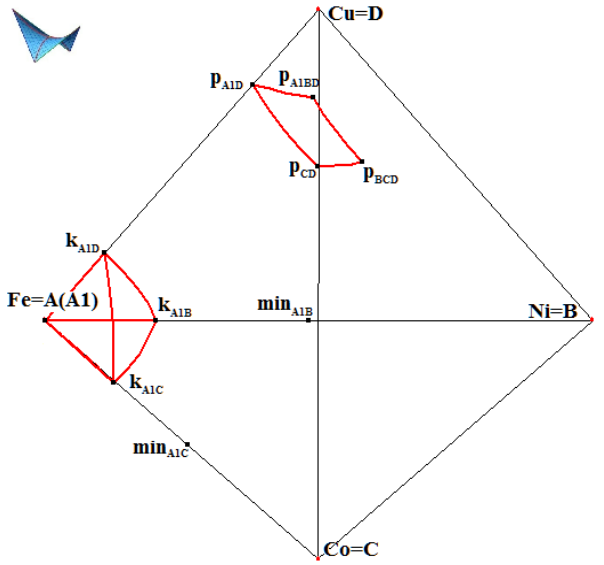


Fig. 2. X-Y-Z projection of liquidus in the 4D computer model of the Fe-Ni-Co-Cu T-x-y-z diagram.

univariant reactions. Three-phase equilibrium L+(ε-Cu)+(γ-Fe) is observed in the temperature interval 1094-1123ºC. Analogous fold $p_{CD}p_{BCD}$ of the Ni-Co-Cu=B-C-D T-x-y diagram corresponds to the univariant peritectic reaction L+Co→Cu (L+C→B). The ternary system Fe-Co-Cu=A-C-D is not also complicated by the complex 4-phase transformations. The metatectic reaction 1501-1499°C: δ-Fe→γ-Fe+L (A→L+A1) proceeds in the high-ferrous region, the region of the copper solution primary crystallization is limited in the high-copper zone of the diagram by the univariant curve: 1112-1094°C: L+γ (Fe,Co)→Cu (L+A1(C)→D).

As a result, the liquidus of the Fe-Ni-Co-Cu=A-B-C-D T-x-y-z diagram consists of two hypersurfaces: high-temperature polymorphous modification of iron δ-Fe = A and solid solution of other its modification γ-Fe = A1 with nickel, cobalt, copper. Second hypersurface has the fold – surface $p_{A1D}p_{A1BD}p_{BCD}p_{CD}$.

One variant for Pb-Cd-Bi-Sn T-x-y-z diagram

History of Pb-Cd-Bi-Sn system study is the obvious example of the need of constructing different computer versions of T-x-y-z diagram for the comparison of different literary opinions about it, agreement and producing the unified approach to planning of experiment for assembling the separate fragments of diagram **(Fig. 3)**. For the first time it was investigated in 1912 [**8**] and became an example of the invariant equilibrium L→Pb+Bi+Cd+Sn [**9**]. Later the incongruent compound Pb_3Bi has been found [**10, 11**], and as it turned out, the primary treatment of phase equilibria [**8**] in the quaternary system is erroneous. Both the invariant eutectic L→Cd+Bi+Sn+Pb_3Bi and the quasi-peritectic L+Pb→Cd+Sn+Pb_3Bi equilibria were observed [**12**] with study of alloys of systems Pb-Bi-Sn, Pb-Bi-Cd and Pb-Bi-Cd-Sn with constant content 40 weight % Bi on the sections $z_{2(Cd)}$=0.22, $z_{4(Sn)}$=0.13 **(Fig. 3b)**, $z_{1(Pb)}$=0.25.

As a result, the primary model of its T-x-y-z diagram with the incongruent compound Pb_3Bi=R is based on the incomplete and contradictory data **(Fig. 3a)** and made it possible to reproduce the sections **(Fig. 3c)**. I can be used to understand the structure of the T-x-y-z diagram and the contradictions, which appear with the interpretation of the different researchers data.

Prediction of the quaternary sulfide subsystem Fe-Ni-Co-FeS-NiS-CoS liquidus reactions and 4D computer model

The phase reactions scheme **(Table 1)** has been written after experimental study of the Fe-Ni-Co ternary system and sulfide subsystems, forming the quaternary subsystem Fe-Ni-Co-FeS-NiS-CoS [**13**]. It helped to predict possible invariant transformations and to outline the contours of liquidus hypersurfaces. Obviously that the assumed liquidus includes the hypersurface, which corresponds to the primary crystallization of the iron high-temperature polymorphous modification δ-Fe=A. It is possible also to assume that, besides it, the liquidus

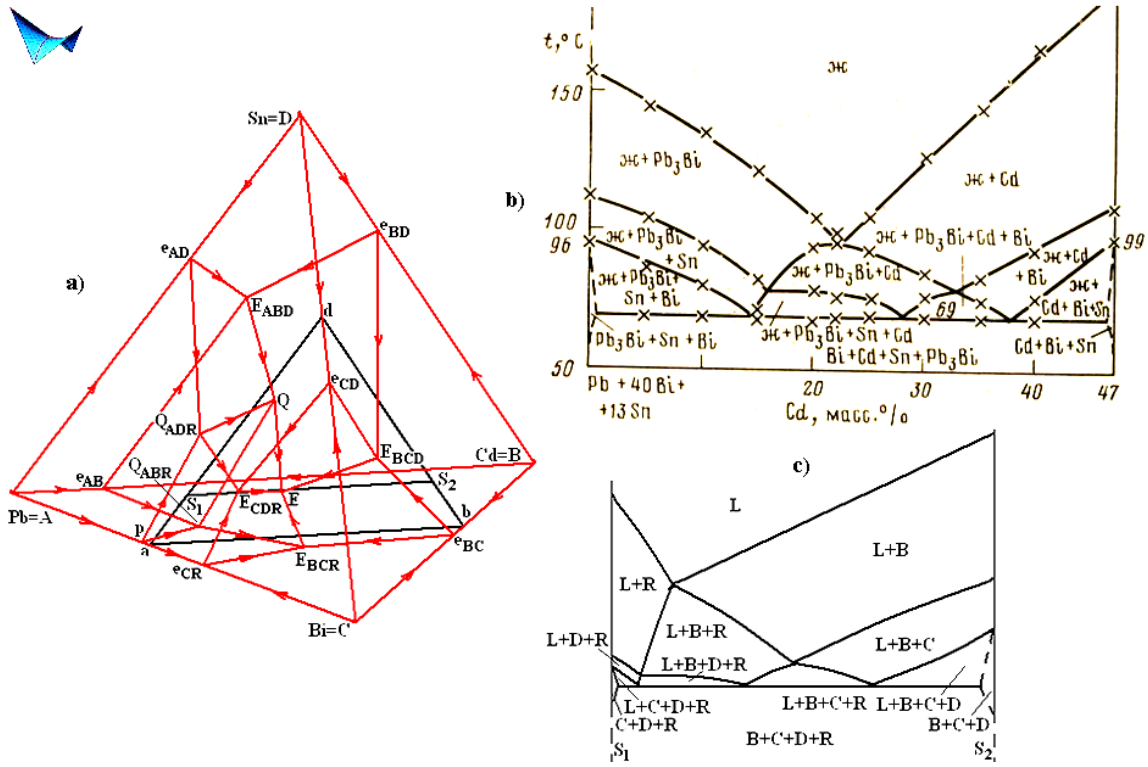


Fig. 3. Projection of liquidus prototype for the system Pb-Cd-Bi-Sn=A-B-C-D with the compound Pb_3Bi=R and invariant eutectic L→Cd+Bi+Sn+Pb_3Bi (ot E: L→B+C+D+R) and quasiperitectic L+Pb→Cd+Sn+Pb_3Bi (or Q: L+A→B+D+R) equilibria (a); variants of the 2D section S_1(0.47, 0, 0.40, 0.13)-S_2(0, 0.47, 0.40, 0.13) of the 3D section $z_{4(Sn)}$=0.13: [12] (b), 4D model (c).

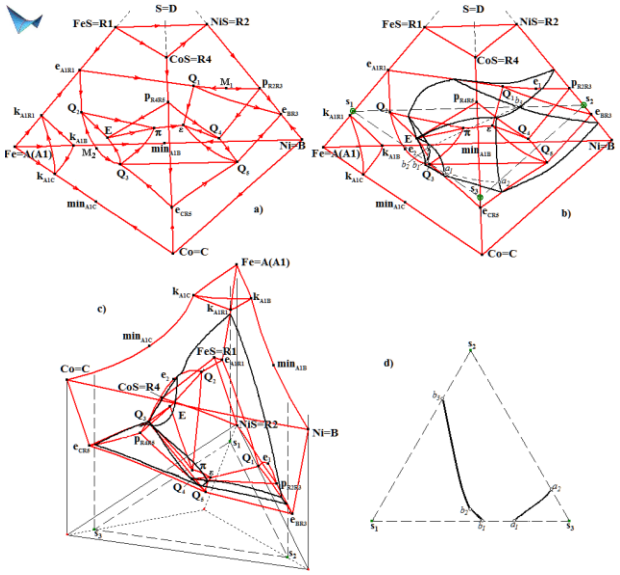


Fig. 4. X-Y-Z projection of liquidus in 4D computer model of the subsystem Fe-Ni-Co-FeS-NiS-CoS T-x-y-z diagram (a); 3D isothermal section (T=500ºC) (b) and 3D isopleth S_1(0.8, 0, 0, 0.2)-S_2(0, 0.8, 0, 0.2)-S_3(0, 0, 0.8, 0.2) (c); the 2D section by the plane $S_1S_2S_3$ of the 3D isothermal section T=500ºC coincides with the 2D section by the plane T=500ºC of the 3D isopleth (d).

is formed by hypersurfaces of the compounds Ni_3S_2 = R3 and Co_4S_3 = R5, and also solid solutions on the basis of two another iron modifications γ-Fe(Ni, Co) = γ(A1, B, C) and α-Fe(Ni, Co)=α(A2, B, C), congruent compounds FeS(NiS, CoS)=R(R1, R2, R4) **(Fig. 4a).** In this case the liquidus must include two points, designating concentrations of liquid, participating in invariant transformations of quasi-peritectic (π) and eutectic (ε) type **(Table 1)**:

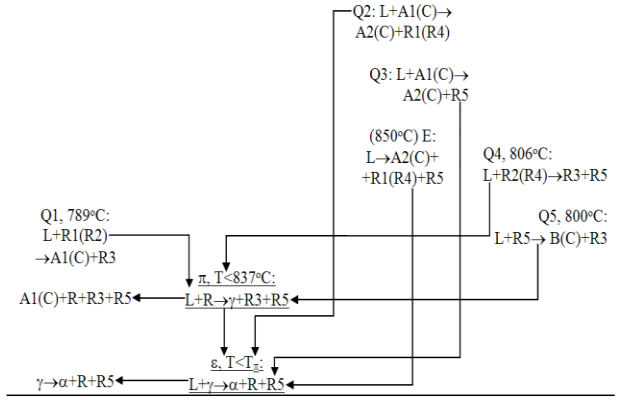
$$\pi: L+\gamma\text{-Fe(Ni,Co)}\rightarrow\alpha\text{-Fe(Ni,Co)}+FeS(NiS,CoS)+Co_4S_3 \text{ or } L+\gamma\rightarrow\alpha+R+R5,$$
$$\varepsilon: L\rightarrow\gamma\text{-Fe(Ni,Co)}+FeS(NiS,CoS)+Ni_3S_2+Co_4S_3 \text{ or } L\rightarrow\gamma+R+R3+R5.$$

Prediction made it possible to compile the plan of experiment, whose results showed that the invariant transformations quasiperitectic π (at T_π<789ºC) and eutectic ε (at T_ε<T_π) in the quaternary subsystem Fe-Ni-Co-FeS-NiS-CoS really exist and two 4-phase regions are located below the π- and ε- temperatures: 1) three rows of continuous solid solutions on the basis of iron allotropy γ-Fe, α-Fe and sulfides (Fe, Ni, Co) coexist with compound Co_4S_3; 2) two rows of continuous solid solutions on the base of γ-Fe and sulfides of all three metals coexist with compounds Ni_3S_2 and Co_4S_3.

The prototype of the T-x-y-z diagram liquidus **(Fig. 4a)** includes 94 hypersurfaces: 6 liquidus, 6 solidus, 2 transus, 70 ruled hypersurfaces (30 with generating line and 40 with generating plane), 10 isothermal hyperplanes of invariant transformations π and ε. We can design any its 3D section: isothermal section **(Fig. 4b)** or isopleths **(Fig. 4c)**. Its section by the arbitrarily assigned plane gives the same 2D section and its curves are the sections of the T-x-y-z diagram hypersurfaces **(Fig. 4d)**. Points (concentrations) of this section are the plan of the experiment. Further the curves of the 2D section are corrected in accordance with the results of this experiment. It significantly helps to perfect the prototype and to reach the 4D model of the real system. As with the work with ternary systems, when the treatment of the experimentally studied of liquidus and solidus surfaces made it possible to reproduce them and further to construct 3D computer model, analogous work must be carried out, also, for the quaternary system. However, in contrast to the ternary systems, when the plan of experiment and the obtained results make it possible to immediately derive isothermal curves on the surfaces, the obtained knowledge about temperatures of beginning and end of primary crystallization, it is insufficient for constructing 3D (or 2D) the isothermal sections in the quaternary systems. In this case the significance of the 4D model is difficultly to overestimate.

Table 1. Assumed phase reactions scheme of liquidus of the subsystem Fe-Ni-Co-FeS-NiS-CoS=A-B-C-R1-R2-R4* (**Fig. 4a**).

Fe-Ni-FeS-NiS= A-B-R1-R2	Fe-Ni-Co-FeS-NiS-CoS= A-B-C-R1-R2-R4	Fe-Co-FeS-CoS= A-C-R1-R4	Ni-Co-NiS-CoS= B-C-R2-R4



* R1(R2), R1(R4), R2(R4)=R; A1(B), A1(C), B(C)=γ; A2(C)=α, R3=Ni_3S_2, R5=Co_4S_3

Results and discussion

3D computer models of T-x-y diagrams are constructed before 4D T-x-y-z diagrams models, then a study and prediction of T-x-y-z diagram possible geometric structure is conducted, on basis of which its prototype is designed. The prototype is converted into the real model when the experimentally obtained coordinates of base points are used and the prototype hypersurfaces curvature is corrected. 4D computer models of T-x-y-z diagrams are capable to design both 3D and 2D isothermal sections and isopleths for the comparison of obtained results with the experimental data. Understanding of T-x-y-z diagrams structure making it possible to predict the form of 2D sections, on the basis of their arrangement in the concentration projection relative to the liquidus elements, which gives the possibility to avoid the errors at their designing.

Conclusion

The procedure of the construction of the 4D computer models of the 4-component systems T-x-y-z diagrams and study of their geometry with the sections of horizontal and vertical hyperplanes is represented.

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