IOP Conference Series: Materials
Science and Engineering

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To cite this article: V I Lutsyk *et al* 2011 *IOP Conf. Ser.: Mater. Sci. Eng.* **18** 162021

Precision of the eutectic points determination by the isopleths

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Abstract. An imitation of quaternary eutectic point searching techniques by means of two-dimensional sections set construction (tie-lines method) was made, using the model of T-x-y-z diagram of eutectic type without solid-phases solubility as an example. The errors, appearing in sections graphics of experimentally studied systems, are analyzed.

1. Introduction

Computer models of T-x-y-z diagrams make possible to clearly illustrate its geometrical structure both in the concentration projection and in the projections with consideration of temperature axis, as well as to realize different vertical and horizontal sections [1]. The understanding of investigated T-x-y-z diagrams structures regularity permits to predict the view of two-dimensional sections reasoning from their arrangement in the concentration projection relative to liquidus elements and to avoid the errors at the sections construction [2].

Let's carry out a tie-lines method for the search of invariant point coordinates using model of T-x-y-z diagram of eutectic type without solid-phases solubility as an example.

2. Model of T-x-y-z diagram of eutectic type without the solubility in solid phases

Given diagram contains (table 1, figure 1a) 4 liquidus hypersurfaces Q_I, 24 ruled hypersurfaces (12 hypersurfaces with one-dimensional forming segment Q^r_{IJ} and 12 hypersurfaces with two-dimensional forming simplex Q^r_{IJK}) and horizontal hyperplane H_ε at the quaternary eutectic temperature T_ε [3]. Four two-phase regions (L+A, L+B, L+C, L+D), six three-phase regions (L+A+B, L+A+C, L+A+D, L+B+C, L+B+D, L+C+D) and five four-phase regions (L+A+B+ , L+A+B+D, L+A+C+D, L+B+ +D, A+B+C+D) are arranged between hypersurfaces.

The kinematical method of hyper-surfaces description is used for the simulation of diagram computer model [1, 4]. In this schematic case the initial data are only the coordinates of unary, binary, ternary and quaternary points.

Table 1. Contours of liquidus (Q_I) and ruled hypersurfaces (Q^r_{IJ} and Q^r_{IJK}).

Name	Contour	Name	Contour
Q_A	$Ae_{AB}e_{AC}e_{AD}E_{ABC}E_{ABD}E_{ACD}\varepsilon$	Q^r_{DC}	$E_{B\ D}e_{\ D}E_{ACD}\varepsilon D_\varepsilon D_{EACD}D_{EB\ D}D_{e\ D}$
Q_B	$Be_{AB}e_{BC}e_{BD}E_{ABC}E_{ABD}E_{BCD}\varepsilon$	Q^r_{ABD}	$E_{ABD}\varepsilon A_\varepsilon B_\varepsilon B_{EABD}A_{EABD}$
Q_C	$Ce_{AC}e_{BC}e_{CD}E_{ABC}E_{ACD}E_{BCD}\varepsilon$	Q^r_{ADB}	$E_{ABD}\varepsilon A_\varepsilon D_\varepsilon D_{EABD}A_{EABD}$
Q_D	$De_{AD}e_{BD}e_{CD}E_{ABD}E_{ACD}E_{BCD}\varepsilon$	Q^r_{BDA}	$E_{ABD}\varepsilon B_\varepsilon D_\varepsilon D_{EABD}B_{EABD}$
Q^r_{AB}	$E_{ABD}e_{AB}E_{ABC}\varepsilon A_\varepsilon A_{EAB}\ A_{EABD}A_{eAB}$	Q^r_{ACD}	$E_{ACD}\varepsilon A_\varepsilon C_\varepsilon C_{EACD}A_{EACD}$
Q^r_{A}	$E_{ABC}e_{A}\ E_{A\ D}\varepsilon A_\varepsilon A_{EA\ D}A_{EABC}A_{eA}$	Q^r_{ADC}	$E_{ACD}\varepsilon A_\varepsilon D_\varepsilon D_{EACD}A_{EACD}$

Q^r_{AD}	$E_{ABD}e_{AD}E_{ACD}\varepsilon A_\varepsilon A_{EACD}A_{EABD}A_{eAD}$	Q^r_{CDA}	$E_{ACD}\varepsilon C_\varepsilon D_\varepsilon D_{EACD}C_{EACD}$
Q^r_{BA}	$E_{ABD}e_{AB}E_{ABC}\varepsilon B_\varepsilon B_{EAB}\ B_{EABD}B_{eAB}$	Q^r_{ABC}	$E_{ABC}\varepsilon A_\varepsilon B_\varepsilon B_{EABC}A_{EABC}$
Q^r_{B}	$E_{BCD}e_{B}\ E_{ABC}\varepsilon B_\varepsilon B_{EABC}B_{EBCD}B_{eB}$	Q^r_{ACB}	$E_{ABC}\varepsilon A_\varepsilon C_\varepsilon C_{EABC}A_{EABC}$
Q^r_{BD}	$E_{ABD}e_{BD}E_{B\ D}\varepsilon B_\varepsilon B_{EB\ D}B_{EABD}B_{eBD}$	Q^r_{BCA}	$E_{ABC}\varepsilon B_\varepsilon C_\varepsilon C_{EABC}B_{EABC}$
$Q^r_{\ A}$	$E_{ABC}e_{A}\ E_{A\ D}\varepsilon C_\varepsilon C_{EA\ D}C_{EABC}C_{eA}$	Q^r_{BCD}	$E_{BCD}\varepsilon B_\varepsilon C_\varepsilon C_{EBCD}B_{EBCD}$
$Q^r_{\ B}$	$E_{BCD}e_{B}\ E_{ABC}\varepsilon C_\varepsilon C_{EAB}\ C_{EBCD}C_{eB}$	Q^r_{BDC}	$E_{BCD}\varepsilon B_\varepsilon D_\varepsilon D_{EBCD}B_{EBCD}$
$Q^r_{\ D}$	$E_{B\ D}e_{\ D}E_{ACD}\varepsilon\ _{\varepsilon\ \ EACD\ \ EB\ D\ \ e\ D}$	Q^r_{CDB}	$E_{BCD}\varepsilon C_\varepsilon D_{\varepsilon EBCD}C_{EBCD}$
Q^r_{DA}	$E_{ABD}e_{AD}E_{ACD}\varepsilon D_\varepsilon D_{EACD}D_{EABD}D_{eAD}$	H_ε	$A_\varepsilon B_\varepsilon C_\varepsilon D_\varepsilon\varepsilon$
Q^r_{DB}	$E_{ABD}e_{BD}E_{B\ D}\varepsilon D_\varepsilon D_{EB\ D}D_{EABD}D_{eBD}$		

3. Tie-lines method imitation

The three-dimensional vertical section mnk parallel to the tetrahedron side BCD and situated as hypoeutectic is considered in "traditional" tie-lines method [5-7] for the determination of quaternary eutectic point ε coordinates (figure 1b). Then the two-dimensional vertical section gf is constructed parallel to the edge nk on plane mnk. This section contains the point (r) on common forming simplex $_{\varepsilon}\ _{\varepsilon}\varepsilon$ of the ruled hypersurfaces Q^r_{ABC} and Q^r_{ABD}, which belongs to the horizontal hyperplane at the quaternary eutectic temperature (T_ε). On the next step the section mh, passing through the top m and obtained point r, is simulated. This section mh intersects the tie-line $A_\varepsilon\varepsilon$ (in point r_ε), belonging at the same time to the ruled hypersurfaces Q^r_{AB} and the horizontal hyperplane H_ε. The last section Ap passes through the tetrahedron top A and point r_ε and includes the required point ε.

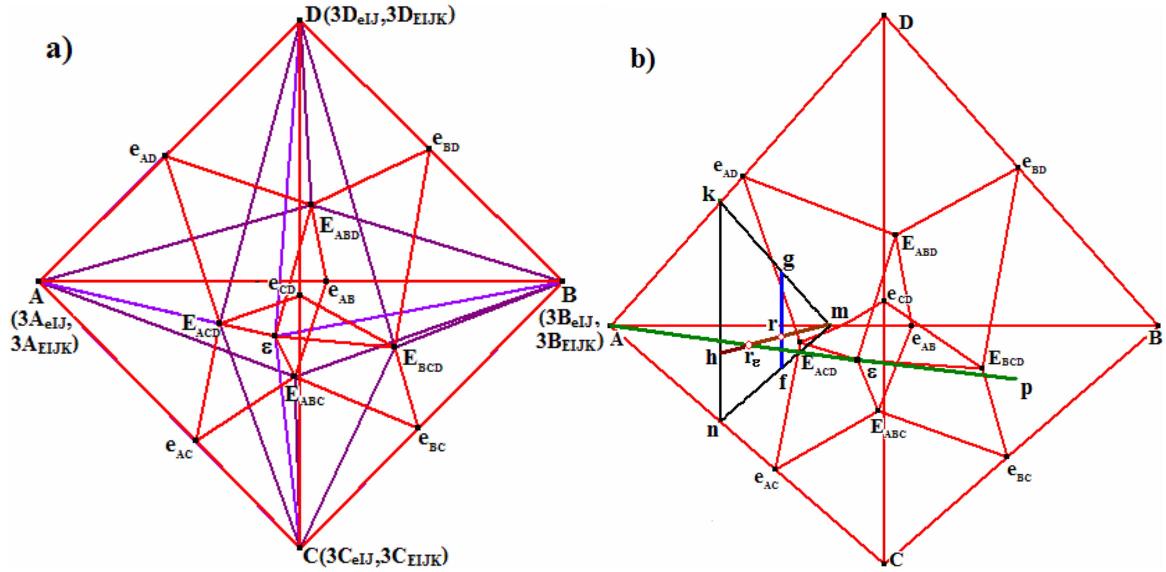

Figure 1. T-x-y-z diagram model in XYZ projection (a) and a scheme for sections construction (b).

We put forward a new approach, when the construction of three-dimensional vertical section is not required; in so doing the first two sections (gf and mh) can't belong to one plane (figure 2a). In the first stage the two-dimensional vertical section is given within the projection of a liquidus hypersurface. For example, the section s1(0.6; 0.25; 0.15; 0) - s2(0.6; 0.25; 0; 0.15) intersects the liquidus hypersurface Q_A (line 1-2), ruled hypersurfaces Q^r_{AB} (3-4), Q^r_{ABC} (5-6), Q^r_{ABD} (6-7) and horizontal hyperplane at T_ε (8-6-9) (figure 2b). The section point 6≡r is shared by the common two-dimensional forming simplex $A_\varepsilon B_\varepsilon\varepsilon$ of two ruled hypersurfaces Q^r_{ABC} and Q^r_{ABD} at T_ε. Taking the segment s1s2 length equal to unit, we obtain that the section base is divided into the parts with the lengths 0.673 and 0.327 at the projecting of point r on the section base (figure 2b). The coordinates of point r can be calculated using the matrix transformation [8]:

$$\begin{pmatrix} r_1 \\ r_2 \\ r_3 \\ r_4 \end{pmatrix} = \begin{pmatrix} s1_1 & s2_1 \\ s1_2 & s2_2 \\ s1_3 & s2_3 \\ s1_4 & s2_4 \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} \rightarrow \begin{pmatrix} r_1 \\ r_2 \\ r_3 \\ r_4 \end{pmatrix} = \begin{pmatrix} 0.6 & 0.6 \\ 0.25 & 0.25 \\ 0.15 & 0 \\ 0 & 0.15 \end{pmatrix} \begin{pmatrix} 0.673 \\ 0.327 \end{pmatrix} \rightarrow \begin{matrix} r_1 = 0.6, \\ r_2 = 0.25, \\ r_3 = 0.101, \\ r_4 = 0.049. \end{matrix}$$

In the second stage one more two-dimensional vertical section passing through the obtained point r and the arbitrary point s3(0.6; 0.4; 0; 0) of tetrahedron edge AB is constructed to the intersection with tetrahedron face ACD in the point s4 (figure 2a). The coordinates $s4_1$, $s4_3$ and $s4_4$ (as s4∈ACD, then $s4_2$=0) are received as a common solution of the plane ACD equation and the segment s3r equation. The plane equation was taken in the form: $s4_1+s4_3+s4_4-1=0$. The segment equation in parametric view is given as follows:

$$\begin{cases} s4_1 = s3_1 + t(r_1 - s3_1) \\ s4_3 = s3_3 + t(r_3 - s3_3) \\ s4_4 = s3_4 + t(r_4 - s3_4) \end{cases} \rightarrow \begin{cases} s4_1 = 0.6 \\ s4_3 = 0.101 \cdot t \\ s4_4 = 0.049 \cdot t \end{cases}$$

The obtained values $s4_1$, $s4_3$ and $s4_4$ are substituted in the plane's equation and the parameter t can be found: 0.6·t+0.101·t+0.049·t=1→t=2.667. The substitution of parameter t in the equation of segment s3r gives:
$$\begin{cases} s4_1 = 0.6 \\ s4_3 = 0.101 \cdot 2.667 = 0.2694. \\ s4_4 = 0.049 \cdot 2.667 = 0.1306 \end{cases}$$

So the point s4 has the coordinates (0.6; 0; 0.2694; 0.1306). The section s_3s_4 intersects the liquidus hypersurface Q_A (line 1-2), ruled hypersurfaces Q^r_{AB} (3-4), Q^r_A (4-5), Q^r_{ACD} (4-6) and horizontal hyperplane at the temperature of quaternary eutectic $A_\varepsilon\varepsilon$ (7-4-8) with the common point 4≡r_ε (figure 2c). Then we define that the point r_ε divides the segment s_3s_4 into the parts with lengths 0.78 and 0.22. The coordinates of point r_ε can be calculated as:

$$\begin{pmatrix} r_{\varepsilon1} \\ r_{\varepsilon2} \\ r_{\varepsilon3} \\ r_{\varepsilon4} \end{pmatrix} = \begin{pmatrix} s3_1 & s4_1 \\ s3_2 & s4_2 \\ s3_3 & s4_3 \\ s3_4 & s4_4 \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} \rightarrow \begin{pmatrix} r_{\varepsilon1} \\ r_{\varepsilon2} \\ r_{\varepsilon3} \\ r_{\varepsilon4} \end{pmatrix} = \begin{pmatrix} 0.6 & 0.6 \\ 0.4 & 0 \\ 0 & 0.2694 \\ 0 & 0.1306 \end{pmatrix} \begin{pmatrix} 0.22 \\ 0.78 \end{pmatrix} \rightarrow \begin{matrix} r_{\varepsilon1} = 0.6, \\ r_{\varepsilon2} = 0.088, \\ r_{\varepsilon3} = 0.2101, \\ r_{\varepsilon4} = 0.1019. \end{matrix}$$

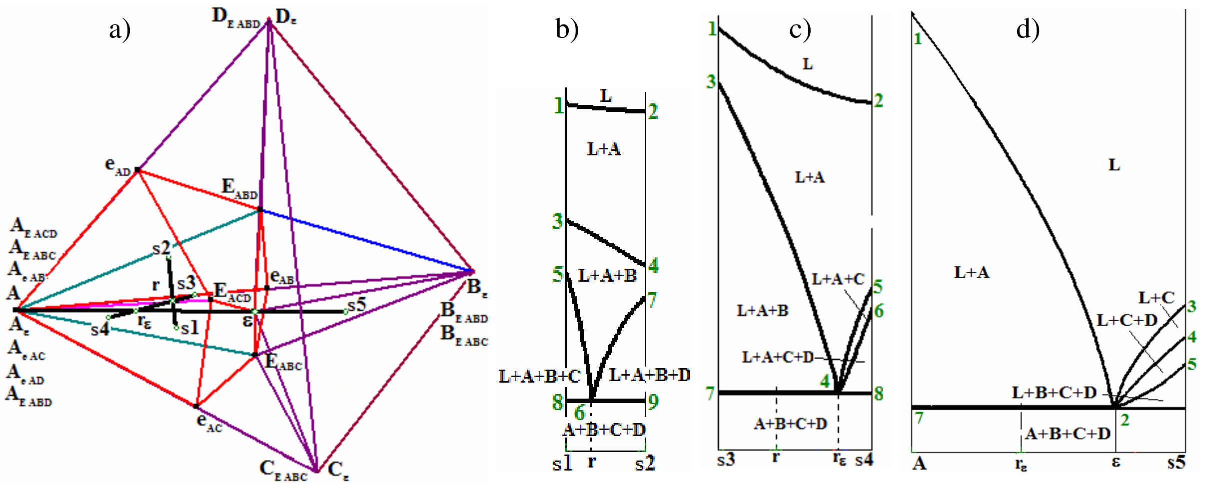

Figure 2. Sections s1s2 (b), s3s4 (c), As5 (d) and their position ( ).

In the third stage the new section are constructed along a ray Ar_ε till the intersection with the face BCD in the point s5 (figure 2a). The simultaneous solution of plane BCD and segment Ar_ε equations gives the coordinates $s5_2$, $s5_3$ and $s5_4$ ($s5_1$=0 because s5∈BCD). The plane equation takes view: $s5_2+s5_3+s5_4-1=0$. The equation of segment is given as:

$$\begin{cases} s5_2 = A_2 + t(r_{\varepsilon 2} - s5_2) \\ s5_3 = A_3 + t(r_{\varepsilon 3} - s5_3) \\ s5_4 = A_4 + t(r_{\varepsilon 4} - s5_4) \end{cases} \to \begin{cases} p_2 = 0.088 \cdot t \\ p_3 = 0.2101 \cdot t \cdot \\ p_4 = 0.1019 \cdot t \end{cases}$$

The obtained coordinates $s5_2$, $s5_3$ and $s5_4$ are substituted into the plane equation: 0.088·t+0.2101·t+0.1019·t=1 →t=0.25. Then the substitution of parameter t in the equation of segment gives the coordinates of point s5 (0; 0.22; 0.5252; 0.2548). The section s5 intersects the Q_A (1-2), Q_C (2-3), Q^r_{CD} (2-4), Q^r_{CDB} (2-5) and H_ε (figure 2d). The section point 2 is the required point of quaternary eutectic ε. It divides the section base into parts with length 0.74 and 0.26. Its coordinates are calculated as follows:

$$\begin{pmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \\ \varepsilon_4 \end{pmatrix} = \begin{pmatrix} A_1 & s5_1 \\ A_2 & s5_2 \\ A_3 & s5_3 \\ A_4 & s5_4 \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} \to \begin{pmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \\ \varepsilon_4 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 0.22 \\ 0 & 0.5252 \\ 0 & 0.2548 \end{pmatrix} \begin{pmatrix} 0.26 \\ 0.74 \end{pmatrix} \to \begin{matrix} \varepsilon_1 = 0.26, \\ \varepsilon_2 = 0.1628, \\ \varepsilon_3 = 0.3886, \\ \varepsilon_4 = 0.1886. \end{matrix}$$

Two ternary eutectics position may be used as the first section base for the optimal scheme of tie-lines method.

4. The errors in the graphics of T-x-y-z diagrams sections

The section view can be suggested from its arrangement relative to the diagrams elements in tetrahedron. This permits to avoid the errors at the experimental data interpretation. For example, incorrect section is presented in [9]: one section top arranges as a point s1∈ C (within the simplex E_{ABC}B) (figure 2a), but the other section top situates behind the line AE_{ABD} (within the simplex E_{ABD}D). As a result this section is to intersect two ruled hypersurfaces with one-dimensional forming simplex (Q^r_{AB}, Q^r_{AD}) and three ruled hypersurfaces with two-dimensional forming simplex (Q^r_{ABC}, Q^r_{ABD}, Q^r_{ADB}). Nevertheless, the authors interpret this section as a section of s1s2 type (figure 2b). So, section view follows from the section arrangement.

Li,Ba,Mg,Zr//F is a system with the problems in graphics too [10]. Nobody tried to search a ternary eutectic on the section, connecting a binary eutectic with the third compound, but according to this idea a quaternary eutectic was in the process of inquiring in the system Li,Ba,Mg,Zr//F. At first the ternary eutectic Li,Ba,Mg//F coordinates was changed for 52.8% LiF, 21.7% BaF_2, 25.5% MgF_2, 927K. Then a quaternary eutectic was searched on the section joining the ternary eutectic Li,Ba,Mg//F and ZrF_4 top of tetrahedron. Really the invariant point wasn't found there [10].

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