

CRYSTALLOGRAPHIC  
SOFTWARECompetition of Primary and Eutectic Crystals in Invariant  
and Univariant Reactions

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**Abstract**—The concept of disperse tie-line is introduced to study the competitive participation of eutectic (small) and primary (large) crystals in phase transitions. The problem of partition of the concentration space, in which the reaction  $L + I = J + K$  occurs, into three parts, first of which contains (along with other elements of heterogeneous material microstructure) only large crystals  $I^l$ ; the second part contains only small crystals  $I^s$ ; and the third part contains a mixture of small and large crystals,  $I^s + I^l$ , is considered. As a result of the competitive participation of eutectic and primary crystals in the peritectic stage of a univariant three-phase reaction, the concentration space is divided into two fragments that differ in the presence (or absence) of small eutectic crystals.

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## INTRODUCTION

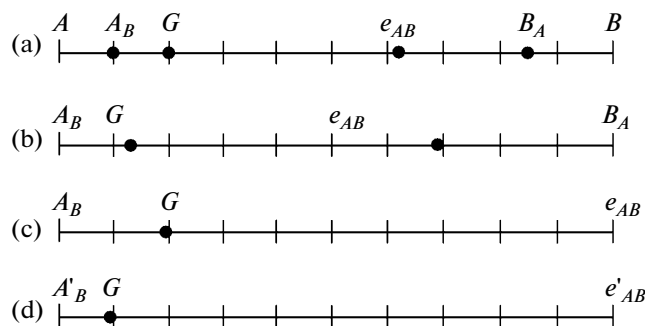
The development of methods of computer design of phase diagrams not only extends the possibilities of their visualization, but also allows researchers to study different topological types of phase diagrams by constructing horizontal and vertical cross sections, calculating conjugate compositions and mechanisms of crystallization, studying transformations of three-phase transition type, etc. Along with the development of thermodynamic-simulation methods, it is necessary to develop working computer models of spatial diagrams, which make it possible to deal with specific physicochemical systems at all stages of their study, including the analysis of crystallization processes.

CONCENTRATION, PHASE (AGGREGATE),  
STRUCTURAL, AND DISPERSE TIE-LINES  
OF BINARY SYSTEMS

Different tie-lines are used in the consideration of the phase transitions that occur in a system characterized by certain external thermodynamic parameters (temperature, pressure, component concentration) (Fig. 1). In a binary system  $A$ – $B$  the concentration tie-line  $AB$  describes any compositions from 0 to 100% of component  $B$ ; the phase tie-line  $A_B B_A$  corresponds to heterogeneous states from two phases,  $A$  and  $B$ ; the structural tie-line  $A_B e_{AB}$  presents a heterogeneous mixture of primary crystals of a solid solution of  $A$  and eutectics  $e_{AB}$  from two solid solutions ( $A + B$ ); and the aggregate tie-line corresponds to the coexistence of phases in different aggregate states, e.g., liquid and solid solutions  $L + A$  [1, 2].

To analyze the competition of large primary  $I^l$  and small eutectic  $I^s$  crystals in invariant (i) mass regrouping  $L + I = J + K$  [3, 4] in the absence of diffusion processes, it is expedient to introduce the concept of disperse tie-line (Fig. 1d), which makes it possible to present compositions with different  $I^l/I^s$  ratios in the  $I$ – $J$  system.

For example, let us find the coordinates of center of mass  $G(0.8; 0.2)$  in the  $A_B(0.9; 0.1)$ – $e_{AB}(0.38; 0.62)$  subsystem. To this end, we will write the matrix expression  $\begin{pmatrix} g_1 \\ g_2 \end{pmatrix} = \begin{pmatrix} a_{B1} & e_1 \\ a_{B2} & e_2 \end{pmatrix} \begin{pmatrix} g'_1 \\ g'_2 \end{pmatrix}$  and substitute the coordinates of the points  $G$ ,  $A_B$ , and  $e_{AB}$  into it:



**Fig. 1.** Types of tie-lines: (a) concentration tie-line  $AB$ , (b) phase tie-line  $A_B B_A$ , (c) structural tie-line  $A_B e_{AB}$ , and (d) disperse tie-line  $A'_B e'_{AB}$ .

$$\begin{pmatrix} 0.8 \\ 0.2 \end{pmatrix} = \begin{pmatrix} 0.9 & 0.32 \\ 0.1 & 0.68 \end{pmatrix} \begin{pmatrix} g_1' \\ g_2' \end{pmatrix}.$$

The coordinates  $g_1' = 0.807692$  and  $g_2' = 0.192308$  indicate the fractions of primary crystals and liquid of eutectic type, i.e.,  $g_1' = A^1$  and  $g_2' = L$ .

Let us consider the  $A_B - e'_{AB}$  subsystem. To make the masses of the points  $A_B'$  and  $e'_{AB}$  equal to unity, it is necessary to locate masses of 10/9 and 100/38, respectively, at these points. Let us find the masses of point  $G''$  in the subsystem under consideration:

$$\begin{pmatrix} 0.807692 \\ 0.192308 \end{pmatrix} = \begin{pmatrix} 10/9 & 0 \\ 0 & 100/38 \end{pmatrix} \begin{pmatrix} m_{g_1''} \\ m_{g_2''} \end{pmatrix},$$

hence,

$$\begin{cases} m_{g_1''} = 0.72692 \\ m_{g_2''} = 0.073077 \end{cases}.$$

Then, we find its coordinates:

$$\begin{cases} g_1'' = \frac{m_{g_1''}}{m_{g_1''} + m_{g_2''}} = 0.90865 \\ g_2'' = \frac{m_{g_2''}}{m_{g_1''} + m_{g_2''}} = 0.09135 \end{cases}.$$

The coordinates  $g_1''$  and  $g_2''$  express the fraction of large  $A^1$  and small  $A^e$  crystals; i.e.,  $g_1'' = A^1 = 0.90865$  and  $g_2'' = A^e = 0.09135$ . Knowing the values of  $A^1$  and  $A^e$ , we can determine the proportionality factor between them:  $k = A^1/A^e = 0.90865/0.09135 = 9.947$ .

Furthermore, we will consider the inverse problem. Let the numbers of primary and eutectic crystals in the binary system  $A(a_1; a_2) - B(b_1; b_2)$  be related as follows:

$A^1 = kA^e$  or  $A^e = \frac{A^1}{k}$ . For center of mass  $G(g_1; g_2)$ , we can write the matrix expression for determining the masses  $A^1$  and  $L$  in the first crystallization stage:

$$\begin{pmatrix} g_1 \\ g_2 \end{pmatrix} = \begin{pmatrix} a_{B1} & e_1 \\ a_{B2} & e_2 \end{pmatrix} \begin{pmatrix} A^1 \\ L \end{pmatrix};$$

this expression yields

$$g = a_{B1}A^1 + e_1L = a_{B1}A^1 + e_1(1 - A^1)$$

$$\text{and } g_2 = a_{B2}A^1 + e_2L = a_{B2}A^1 + e_2(1 - A^1).$$

Let us now write the matrix expression for determining the masses  $A = A^1 + A^e$  and  $B$  in the second crystallization stage for the same center of mass,

$$\begin{pmatrix} g_1 \\ g_2 \end{pmatrix} = \begin{pmatrix} a_{B1} & b_1 \\ a_{B2} & b_2 \end{pmatrix} \begin{pmatrix} A^1 + A^e \\ B \end{pmatrix},$$

and derive expressions for  $g_1$  and  $g_2$  from it:

$$g_1 = a_{B1}(A^1 + A^e) + b_1B \quad \text{and} \quad g_2 = a_{B2}(A^1 + A^e) + b_2B.$$

Since  $b_1 = 0$ ,  $b_2 = 1$ , and  $A^e = \frac{A^1}{k}$ , we have  $g_1 =$

$a_{B1}\left(A^1 + \frac{A^1}{k}\right)$ . The coordinates of center of mass  $G(g_1; g_2)$  in the first and second crystallization stages are identical; therefore, the expressions for determining the first coordinate in the first and second crystallization stages can be equated:

$$a_{B1}A^1 + e_1(1 - A^1) = a_{B1}\left(A^1 + \frac{A^1}{k}\right).$$

We will use this equation to express  $A^1 = \frac{ke_1}{a_{B1} + ke_1}$  and substitute it into  $g_1$ . Let us write the expression for determining the coordinates of center of mass  $G$ :

$$g_1 = \frac{(1+k)a_{B1}e_1}{a_{B1} + ke_1} \quad \text{and} \quad g_2 = 1 - g_1.$$

Then, we find the coordinates of center of mass  $G$  at the previously found factor  $k = 9.947$ . The substitution of  $k$  into  $g_1$  yields

$$g_1 = \frac{(1+9.947) \cdot 0.9 \cdot 0.38}{0.9 + 9.947 \cdot 0.38} = 0.8$$

$$\text{and } g_2 = 1 - g_1 = 0.2.$$

As a result, it is shown that the disperse tie-line for center of mass  $G$  makes it possible to determine the ratio in which large ( $A^1$ ) and small ( $A^e$ ) crystals compete and, vice versa, with the proportionality factor  $k$  between  $A^1$  and  $A^e$  known, one can determine the coordinates of  $G$ .

#### COMPETITION OF EQUALLY DISPERSE CRYSTALS $A^1$ AND $A^e$ IN THE REACTION $L + A = I + J$

We consider an  $A-B-C$  system with incongruently melting compound  $R = A_mC$  [5]. Let us assume that the solid phases  $R$ ,  $A$ ,  $B$ , and  $C$  have a constant composition and that the contour of liquidus surfaces is set by straight lines (Fig. 2a) [6]. The composition of the binary eutectics  $e_{AB}$  is as follows: 38%  $A$  and 62%  $B$ .

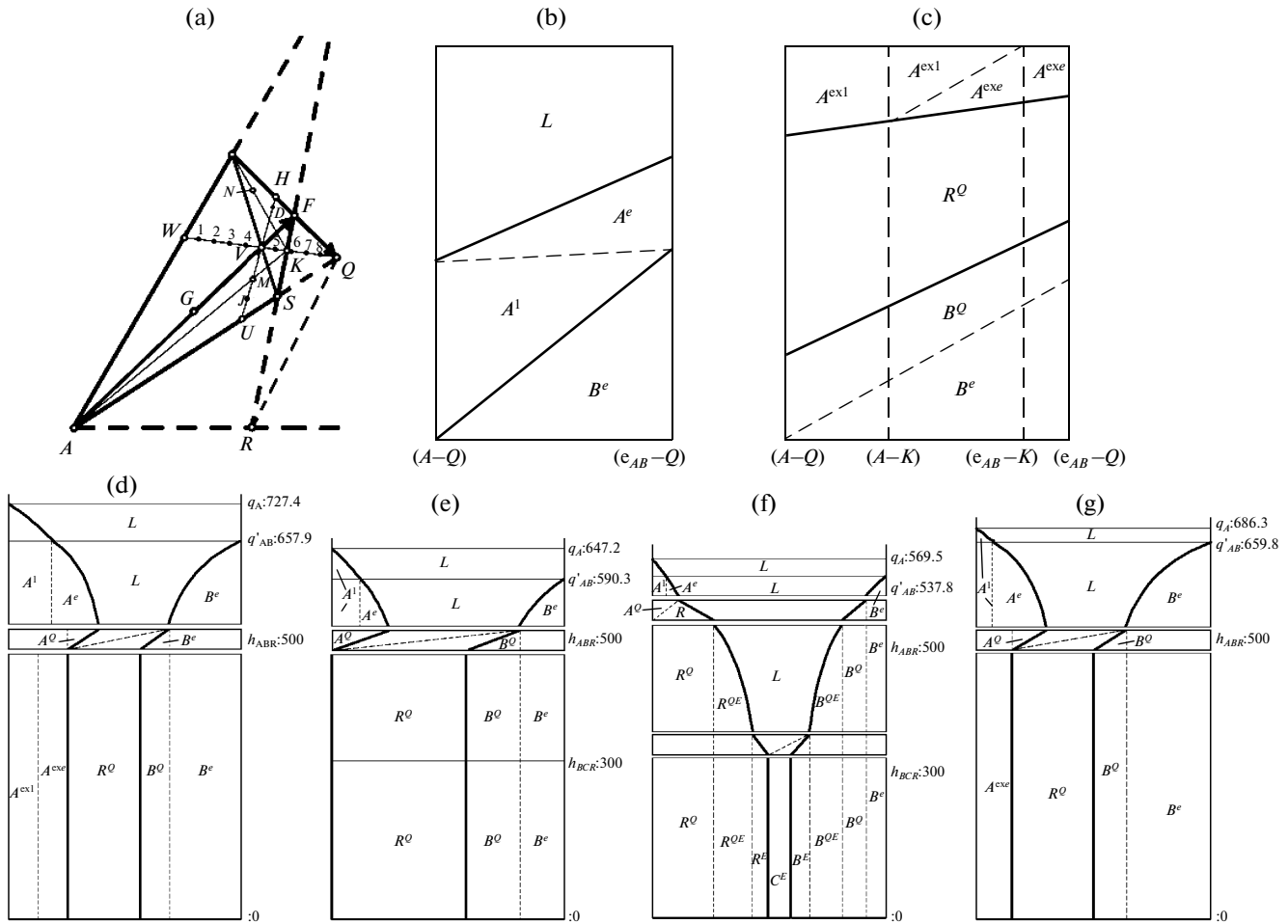
Let us determine the coordinates of center of mass  $W$ , in which the fraction of primary crystals  $A^1$  is equal to the fraction of eutectic crystals  $A^e$ , in the  $A-B$  system. After the primary crystallization we have

$$\begin{pmatrix} w_1 \\ w_2 \end{pmatrix} = \begin{pmatrix} a_1 & e_1 \\ a_2 & e_2 \end{pmatrix} \begin{pmatrix} A^1 \\ L \end{pmatrix} = \begin{pmatrix} 1 & 0.38 \\ 0 & 0.62 \end{pmatrix} \begin{pmatrix} A^1 \\ L \end{pmatrix},$$

$$w_1 = A^1 + e_1L = A^1 + 0.38(1 - A^1),$$

$$\text{and } w_2 = e_1L = 0.38(1 - A^1).$$

Similarly, after the second (invariant) stage, we obtain



**Fig. 2.** (a) Concentration field  $Ae_{AB}Q$  with competition of crystals  $A^e$  and  $A^1$  in the reaction  $L + A = B + R$  and the material balances on the isopleth  $UH$  at (b)  $T_Q + \delta$  and (c)  $T_Q - \delta$  and for centers of mass (d) 3, (e) K, (f) 7, and (g) N (the isothermal mass regroupings  $L + A = B + R$  and  $L = B + R + C$  are shown by rectangles).

$$\begin{pmatrix} w_1 \\ w_2 \end{pmatrix} = \begin{pmatrix} a_1 & b_1 \\ a_2 & b_2 \end{pmatrix} \begin{pmatrix} A^1 + A^e \\ B \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} A^1 + A^e \\ B \end{pmatrix};$$

i.e.,  $w_1 = A^1 + A^e$ ,  $w_2 = B$ . According to the condition,  $A^1 = A^e$ ; hence,  $w_1 = 2A^1$ . Having equated  $w_1$  for the first and second stages,  $A^1 + 0.38(1 - A^1) = 2A^1$ , we obtain  $A^1 = A^e = 0.27535$ ,  $w_1 = 2A^1 = 0.5507$ ,  $w_2 = 1 - w_1 = 0.4493$ .

Considering centers of mass 1–8, V, and K, in which  $A^1 = A^e = 1$ , on the isopleth  $WQ$  (Fig. 2a) and assuming the ratio  $A^{Q1}/A^{Qe} = 1$  to be constant for participation of A in the reaction  $L + A^Q = B^Q + R^Q$  at the quasi-peritectic temperature  $Q$ , we will calculate the fractions of excess (ex) primary  $A^{ex1}$  and eutectic  $A^{ex2}$  crystals (Table 1).

The  $Ae_{AB}FS$  field is divided by the  $Ke_{AB}$  (see the material balance for center of mass N, Table 1) and KA (see the material balance for center of mass M, Table 1) lines into three fragments, i.e.,  $e_{AB}FK$ ,  $Ae_{AB}K$ ,

and  $ASK$ . The microstructure of the upper fragment  $e_{AB}FK$  includes the matrix  $M = R^Q + B^Q + B^e$  and crystals  $A^e$ , while the microstructure of the lower fragment  $ASK$  includes the matrix  $M$  and crystals  $A^1$ . The microstructure of the intermediate fragment  $Ae_{AB}K$  includes both types of crystals A:  $M + A^1 + A^e$ .

The equality  $A^1 = A^e = A^Q = A^{ex}$  is fulfilled for center of mass V. The condition  $A^1 = A^e$  is satisfied for all centers of mass on the isopleth  $WQ$  (Fig. 2a). The conditions  $A^e = A^Q$  and  $A^1 = A^Q$  are fulfilled on the isopleths  $AF$  and  $e_{AB}S$ . They suggest absolute priorities of only eutectic or only primary crystals in the reaction  $L + A^Q = B^Q + R^Q$  and lead to field partition into two fragments, i.e.,  $Ae_{AB}F (M + A^1 + A^e)$ ,  $AFS (M + A^1)$  or  $Ae_{AB}S (M + A^1 + A^e)$ ,  $e_{AB}FS (M + A^e)$ .

The condition  $A^Q = A^{ex}$  is of particular importance. It corresponds to the isopleth  $BV$  with centers of mass D, M, and J (Fig. 2a; Table 1), which intersects the isopleths  $e_{AB}K$  and  $AK$  at the points  $e_{AB}-K$  and

**Table 1.** Diffusionless material balances (Fig. 2) after the reactions  $L \rightarrow A^1$ ,  $L \rightarrow A^e + B^e$ , and  $L + A^Q = B^Q + R^Q (A^{Q1}/A^{Qe} = 1)$ 

Center of mass	$A^1$	$A^e$	$A^Q (A^{Q1} + A^{Qe})$	$A^{Q1}$	$A^{Qe}$	$A^{ex} (A^{ex1} + A^{exe})$	$A^{ex1}$	$A^{exe}$
3	0.193	0.193	0.131	0.0655	0.0655	0.255	0.1275	0.1275
$V$	0.169	0.169	0.169	0.0845	0.0845	0.169	0.0845	0.0845
5	0.138	0.138	0.218	0.069	0.069	0.058	0.029	0.029
$K$	0.123	0.123	0.246	0.123	0.123	0	0	0
7	0.056	0.056	0.112	0.056	0.056			
$J$	0.418	0.026	0.222	0.196	0.026	0.222	0.222	0
$M$	0.295	0.095	0.195	0.1	0.095	0.195	0.195	0
$D$	0.046	0.238	0.142	0.046	0.096	0.142	0	0.42
$N$	0.089	0.233	0.132	0.089	0.043	0.19	0	0.19

$A-K$ . The fragment  $UH \equiv (A - Q)(e_{AB}Q)$  of the isopleth  $BV$  contains constructed horizontal (isothermal) material balances before and after the reaction  $L + A^Q = B^Q + R^Q$  (Fig. 2b, 2c), on which the fraction of crystals  $A$  was divided into  $A^e$  and  $A^1$  and the fraction  $A^{ex}$  was divided into  $A^{exe}$  and  $A^{ex1}$  in the interval  $(e_{AB}-K)(A-K)$ .

In the interval  $KQ$  of the isopleth  $WQ$ , the excess melt is involved in the reaction  $L \rightarrow B^{QE} + R^{QE}$ ,  $L = R^E + B^E + C^E$  (see the material balance for center of mass 7, Fig. 2f). To verify the results obtained, we will construct the vertical diagrams of material balances (Fig. 2d–2g) for the centers of mass at the points 3,  $K$ , 7, and  $N$ .

#### COMPETITION OF MULTIDISPERSE CRYSTALS $A^1$ AND $A^E$ AT A CHANGE FROM THE UNIVARIANT EUTECTIC REACTION $L = A + B$ TO THE PERITECTIC REACTION $L + B = A$

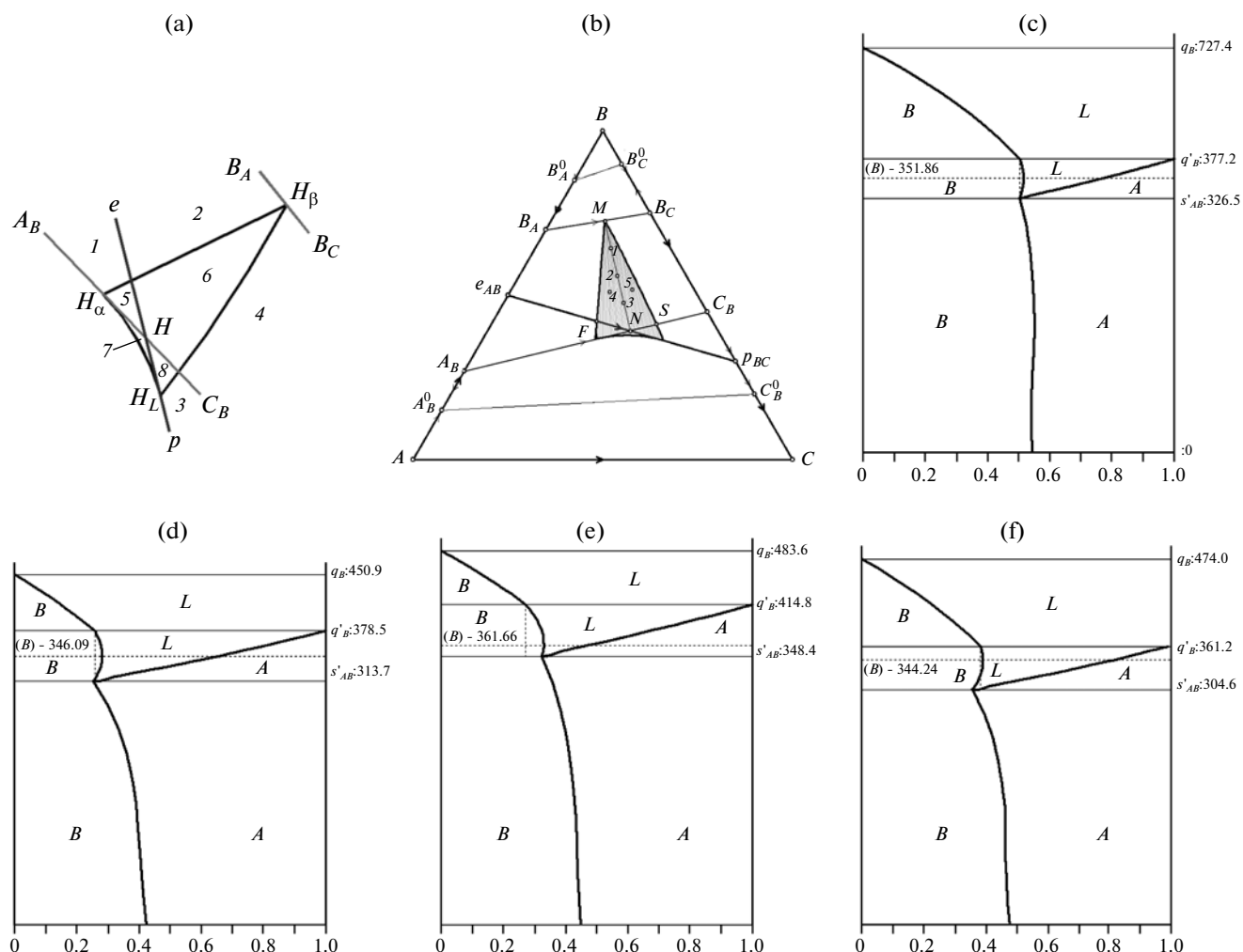
Let us consider the projection of a three-phase region  $L + \alpha + \beta$  with partition into concentration fields 1–8 (Fig. 3a). A unique microstructure corresponds to each field (see Table 2, where  $\alpha^1$  and  $\beta^1$  are primary crystals,  $\alpha^e$  and  $\beta^e$  are eutectic crystals,  $\alpha^p$  are

**Table 2.** Versions of microstructures formed at a change in the reaction type from  $L \rightarrow \alpha + \beta$  to  $L + \beta \rightarrow \alpha$  (Fig. 3a)

Concentration field	Microstructure	Concentration field	Microstructure
1	$\alpha^1 + \alpha^e + \beta^e$	5	$\alpha^1 + \alpha^e + \alpha^p + \beta^{exe}$
2	$\alpha^e + \beta^1 + \beta^e$	6	$\alpha^e + \alpha^p + \beta^{ex1} + \beta^{exe}$
3	$\alpha^p$	7	$\alpha^1 + \alpha^e + \alpha^p$
4	$\alpha^p + \beta^1$	8	$\alpha^e + \alpha^p$

peritectic crystals, and  $\beta^{ex1}$  and  $\beta^{exe}$  are excess crystals after the reaction  $L + \beta \rightarrow \alpha$  [7]).

In concentration field 6 (Fig. 3a), the microstructure contains both  $\beta^{ex1}$  and  $\beta^{exe}$ . In reality, when analyzing the region  $FMSN$  using material balances, one can divide it by the straight line  $MN$  into two fields, i.e.,  $FMN$  with the microstructure  $\beta^1 + \beta^{exe} + \alpha^e + \alpha^p$  and  $NMS$  with  $\beta^1 + \alpha^e + \alpha^p$ . Let us consider the vertical diagrams of material balances for centers of mass 2–5 (Figs. 3c–3f). For center of mass 2 (Fig. 3c), we have the following pattern: large crystals  $\beta^1$  arise in the temperature range of 727–377°C (reaction  $L \rightarrow \beta$ ), growth of small crystals  $\beta^e$  (reaction  $L \rightarrow \beta$ ) begins in the range of 377–352°C, the reaction changes type ( $L + \beta \rightarrow \alpha$ ) at  $T = 352^\circ\text{C}$ , and the concentration of small crystals  $\beta^e$  decreases to zero with a further decrease in temperature to 326°C. A similar situation is observed for centers of mass 1 and 3 (Fig. 3d) and for any point lying on  $MN$ . The pattern changes for centers of mass 4 and 5, which are located in concentration fields  $FMN$  and  $NMS$ , respectively. The vertical diagram of material balance for center of mass 4 (Fig. 3e) demonstrates the following: large crystals  $\beta^1$  (reaction  $L \rightarrow \beta$ ) are formed in the temperature range of 484–415°C, small crystals  $\beta^e$  arise in the range 415–362°C, the reaction changes type ( $L + \beta \rightarrow \alpha$ ) at  $T = 362^\circ\text{C}$ , and the concentration of small crystals  $\beta^e$  decreases with a further decrease in temperature to 348°C. Eutectic crystals  $\beta^e$  are not spent completely and some part of excess crystals  $\beta^{exe}$  remain. For center of mass 5 (Fig. 3f), small crystals  $\beta^{exe}$  disappear completely and large crystals  $\beta^1$  disappear partially in the temperature range from 304°C (change in the reaction type) to 384°C. Thus, we can conclude that concentration field 6 ( $FMSN$ ) (Figs. 3a, 3b) is divided into two parts, i.e.,  $FMN$  (with excess crystals  $\beta^{exe}$  and  $NMS$  (without them).



**Fig. 3.** (a) Projection  $L + \alpha + \beta$  divided into concentration fields 1–8; (b) parts of field 6 ( $MFNS$ ):  $FMN$  ( $\beta^1 + \beta^{\text{exe}} + \alpha^e + \alpha^p$ ) and  $NMS$  ( $\beta^1 + \alpha^e + \alpha^p$ ) (crystals  $\beta^1$  are not involved in the reaction  $L + \beta \rightarrow \alpha$ ); and (c–f) the material balances at points (c) 2, (d) 3, (e) 4, and (f) 5.

## CONCLUSIONS

It was proposed to use the concept of disperse tie-line to analyze the competition between primary ( $I^1$ ) and eutectic ( $I^e$ ) crystals in the invariant mass regrouping  $L + I = J + K$ . Algorithms for calculating the material balances and concentration boundaries of the alternative microstructures formed in three-phase regions were described. A microstructural analysis was performed for the change in the type of univariant reaction from  $L \rightarrow \alpha + \beta$  to  $L + \beta \rightarrow \alpha$  in the three-phase region.

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