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Jaromír DRÁPALA[1], Zuzana MORÁVKOVÁ[2], Ivona SVOBODOVÁ[3]

COMPUTER SIMULATION OF CRYSTALLIZATION IN TERNARY SYSTEMS OF THE EUTECTIC AND PERITECTIC TYPES

SIMULACE KRYSTALIZACE V TERNÁRNÍCH SYSTÉMECH EUTEKTICKÉHO A PERITEKTICKÉHO TYPU

[1] *Prof. Ing., CSc., Vysoká škola báňská – Technical University of Ostrava, Department of Non-ferrous metals, Refining and Recycling, Av. 17. listopadu 15, 708 33 Ostrava-Poruba, Czech Republic, e-mail: Jaromir.Drapala@vsb.cz*

[2] *Mgr. Ph.D., Vysoká škola báňská – Technical University of Ostrava, Department of Mathematics and Descriptive Geometry, Av. 17. listopadu 15, 708 33 Ostrava-Poruba, Czech Republic*

[3] *Mgr., Vysoká škola báňská – Technical University of Ostrava, Department of Mathematics and Descriptive Geometry, Av. 17. listopadu 15, 708 33 Ostrava-Poruba, Czech Republic*

Abstract

Modelling of liquidus, solidus and solvus equilibrium areas in ternary systems using polynomials. Examples of calculation of the liquidus, solidus and solvus areas equations in the systems with the ternary eutectic reaction $L = \alpha + \beta + \gamma$ (Class I), the ternary peritectic reaction $L + \alpha + \beta = \gamma$ (Class III) and the ternary peritectic reaction of type $L + \alpha = \beta + \gamma$ (Class II). The ways of distribution coefficients determination under equilibrium conditions of crystallization in ternary alloys are described. The calculation program was elaborated in the system Matlab and it has the user friendly interface.

Abstrakt

Plochy likvidu, solidu a solvu jsou v ternárních systémech modelovány pomocí kvadratických ploch. V článku jsou popsány příklady výpočtu ploch likvidu, solidu a solvu v systémech s ternární eutektickou reakcí $L = \alpha+\beta+\gamma$ (typ I), ternární peritektickou reakcí $L + \alpha+\beta = \gamma$ (typ III) a ternární univariantní peritektickou reakcí typu $L + \alpha = \beta + \gamma$ (typ II). Dále je popsán způsob určování rovnovážných rozdělovacích koeficientů v ternárních slitinách. Celá problematika byla zpracována a naprogramována v systému Matlab a výsledkem je výpočetní program s uživatelsky přátelským prostředím, jehož ukázky jsou v článku uvedeny.

Key words: Ternary system, distribution coefficient, mathematical modelling, eutectic ternary system, peritectic ternary systems.

1. Introduction

Distribution of elements between two or three different phases in a ternary system is an essential specification characterizing isothermal-isobaric phase equilibrium in the given heterogeneous system. The phase data present the equilibrium composition of co-existing phases. They are usually displayed in the graphic form as equilibrium binary or ternary diagrams, i.e. sets of the curves $T(x)$, dependence of the temperature on the equilibrium composition of the system phases [1,2,3] or numerically by the coordinates of the points $[T, x]$ for which the system is in equilibrium. In this second case it is suitable to keep at disposal a mathematical calculus enabling a qualified interpolation among these points.

Kuchař et al. [4,5] elaborated a method for the solidus and liquidus curves in binary systems according to which these curves are expressed by the second degree polynomials. A method of modelling was proposed for ternary systems of an ideal and/or quasi-ideal types or types with a minimum and/or maximum on the solidus and liquidus surfaces and presented e.g. in [6,7]. The present work submits a proposal of modelling of ternary systems of eutectic or peritectic types.

2. Mathematical model

The equilibrium areas in the ternary system *A-B-C* can be described by the surfaces of liquidus, solidus and solvus. The polynomial surface of second degree is used

$$t = k_1x^2 + k_2y^2 + k_3xy + k_4x + k_5y + k_6 \tag{1}$$

where x is the concentration of the component B

y is the concentration of the component C

t is the temperature

The question is: How to describe the surfaces if the projection to composition triangle is only known? Some points are known very well: the components corners, points of ternary and binary eutectics or peritectic reactions. Let n be the number of points through which the surface comes exactly. It is easy to see that $0 \leq n \leq 6$. The linear system with 6-n parameters is solved and n coefficients k are found. Some points designate the character of the surface, their weight is 0% - 99%. The least square method is used to calculate 6-n coefficients k.

Fig. 3 shows a space model of the ternary system *A-B-C*, where each of the binary systems *A-B*, *B-C*, *A-C* is of the eutectic type. Now let us describe the way of constructing a line surface. Let suppose two curves (for example the curve e_1E and a_1a in Fig. 3). Next we find the couple of equilibrium points for every temperature (for example the eutectic binary e_1 and ternary eutectic E in Fig. 3). The line surface is created by the set of lines (tie-lines) passing through every couples of equilibrium points.The equilibrium area disjoins the phase areas by the quadratic and line surfaces. Every area corresponds to one phase. Fig. 1 shows the isothermal view with tie-lines and the vertical view is depicted in Fig. 2.

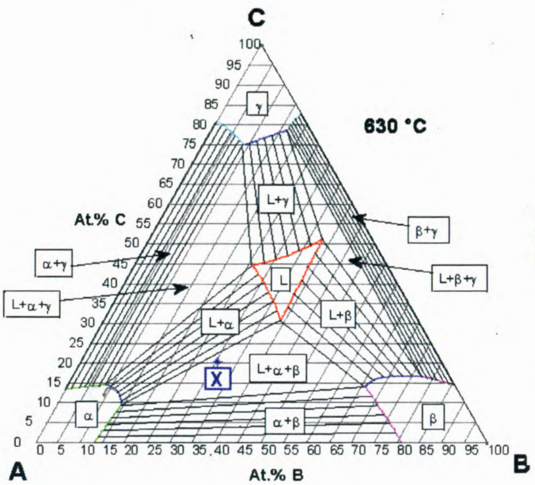

Fig. 1 Isothermal view with tie-lines (ternary eutectic system)

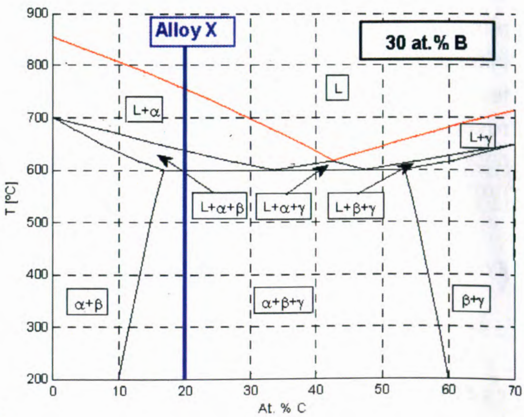

Fig. 2 Vertical section in ternary eutectic system for B = 30%

3. Classes of the ternary systems ternary systems of the eutectic and peritectic types

Let T_A, T_B, T_C be the melting temperatures of the components *A, B, C*. Let T_{ABC} be the temperatures of the ternary eutectic or peritectic reaction (the points *E* or *P* in Figs. 3–6). Let T_{AB} (or T_{BC}, T_{CA}) be the temperatures of eutectic or peritectic reaction of the binary system *A-B* (or *B-C, C-A*), the points e_1 or p_1 (or e_2 or p_2, e_3 or p_3) in Figs. 3–6.

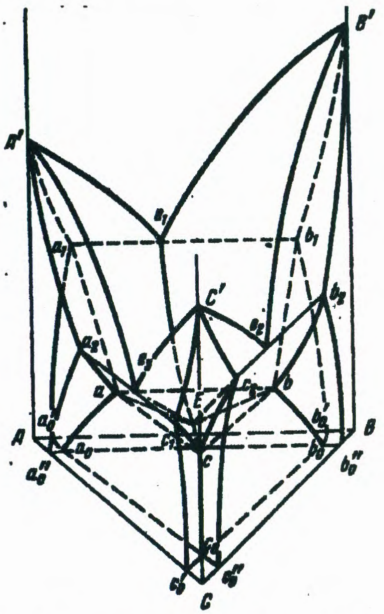

Fig. 3 Ternary eutectic system - Class I

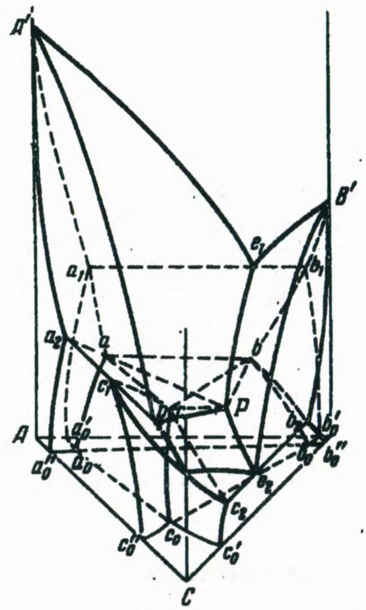

Fig. 4 Ternary peritectic system - Class IIa

Ternary eutectic system – Class I $L \leftrightarrow \alpha + \beta + \gamma$ **(see Fig. 3)**

The system containing a ternary eutectic reaction and in which the three binary systems are of the eutectic type.

$$T_{ABC} < T_{AB}\ ,\ T_{ABC} < T_{BC}\ ,\ T_{ABC} < T_{CA}$$

and

$T_A > T_{AB}$, $T_B > T_{AB}$ eutectic; $T_B > T_{BC}$, $T_C > T_{BC}$ eutectic; $T_C > T_{CA}$, $T_A > T_{CA}$ eutectic

For example: The eutectic valleys run from the binary eutectic points e_1, e_2 and e_3 to meet in the ternary eutectic point *E*.

Ternary peritectic system – Class IIa $L + \alpha \leftrightarrow \beta + \gamma$ **(see Fig. 4)**

The system containing a ternary peritectic reaction and in which two binary systems are of the eutectic type and one is of peritectic type.

$$T_{ABC} < T_{AB}\ ,\ T_{ABC} > T_{BC}\ ,\ T_{ABC} < T_{CA}$$

and $T_A > T_{AB} < T_B$ eutectic; $T_B > T_{BC} < T_C$ eutectic; $T_C < T_{CA} < T_A$ peritectic.

For example: The valleys run from the binary eutectic points e_1 and from the binary peritectic point p_2 to meet in the ternary peritectic point P and after run to the point of the binary eutectic e_2.

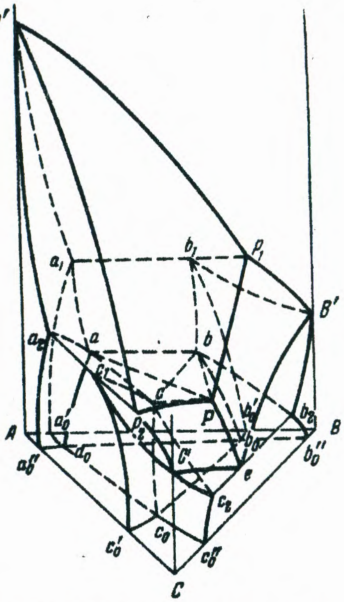

Fig. 5 Ternary peritectic system - Class IIb

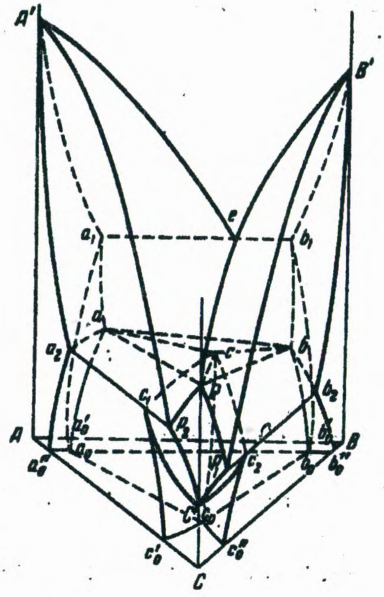

Fig. 6 Ternary peritectic system - Class III

Ternary peritectic system – Class IIb $L + \alpha \leftrightarrow \beta + \gamma$ (see Fig. 5)

The system containing a ternary peritectic reaction and in which one binary system is of the eutectic type and two are of the peritectic type.

$T_{AB} > T_{ABC}$, $T_{CA} > T_{ABC}$ and $T_{ABC} > T_{BC}$

$T_A > T_{AB} > T_B$ peritectic; $T_B > T_{BC}$, $T_C > T_{BC}$ eutectic; $T_A > T_{CA} > T_C$ peritectic

For example: The peritectic valleys run from the binary peritectic points p_1 and p_2 to meet in the ternary peritectic point P and after run to the point of the binary eutectic e.

Ternary peritectic system – Class III $L + \alpha + \beta \leftrightarrow \gamma$ (see Fig. 6)

The system containing a ternary peritectic reaction and in which one binary system is of the eutectic type and two are of the peritectic type.

$T_{AB} > T_{ABC}$ and $T_{ABC} > T_{BC}$, $T_{ABC} > T_{CA}$

$T_A > T_{AB}$, $T_B > T_{AB}$ eutectic; $T_B > T_{BC} > T_C$ peritectic; $T_A > T_{CA} > T_C$ peritectic

For example: The eutectic valley runs from the binary eutectic point e to the ternary peritectic point P and after valleys run to the points of binary peritectic p_1 and/or p_2.

4. Computer program in the system Matlab

The computer program was written in the system Matlab with user friendly interface (Figures 7,8.). Users can create a new data file or read the data from an existing file. The input data for every quadratic surface (liquidus, solidus, solvus) are signed in accordance with Figures 3-6. The program compiles the input data and computes the coefficients $k_1 \div k_6$ (1) of surfaces and their domains in the composition triangle. The Matlab type cell array is used to save all data and continues by further procedures.

The program can calculate

- three binary diagrams
- 3D view of the ternary system
- isothermal sections for selected temperatures (Fig. 9)
- polythermal vertical sections (Fig. 2)
- isothermal sections with tie-lines for the certain temperature (Figs. 1, 10)
- tables with equilibrium distribution coefficients (Tables 2, 3)

Output data: Graphs and tables are exported to external files.

The program is set not only for research, but also for students, so it is necessary to have an interactive user interface.

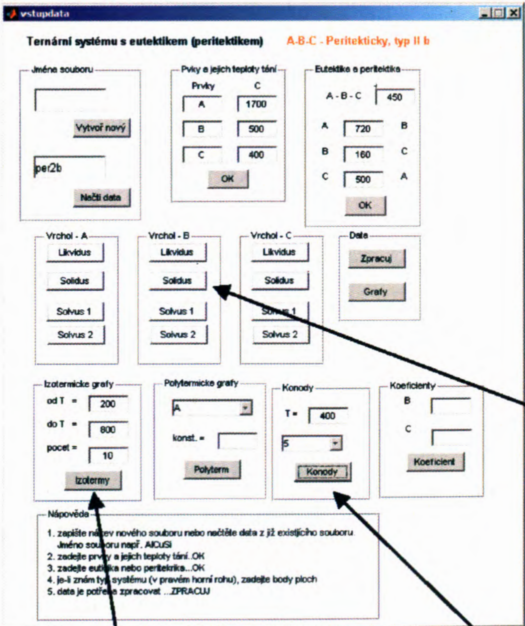

Fig. 7 User interface

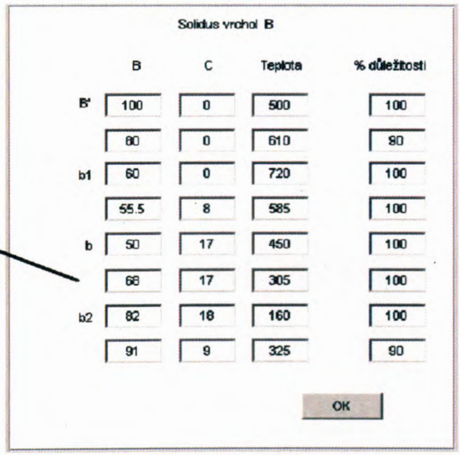

Fig. 8 Window for input data

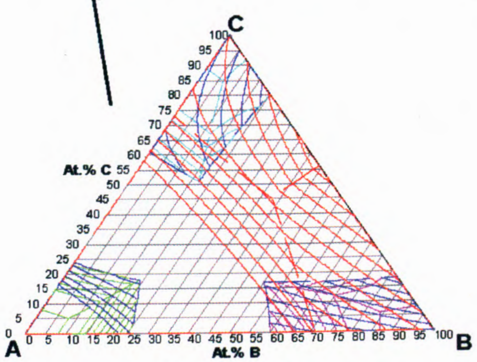

Fig. 9 Isotherms for $T = 200°C \div 800°C$ (peritectic ternary system – Class IIb)

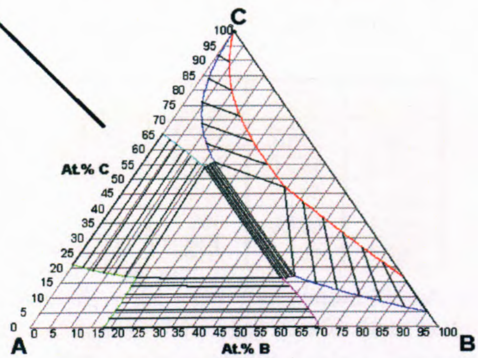

Fig. 10 Isothermal section with tie-lines for $T = 400°C$ (peritectic ternary system – Class IIb)

5. Equilibrium distribution coefficients in ternary systems

The distribution coefficients define the equilibrium between the present phases at the certain temperature T as a ratio of the concentration of the element in the first and second phases – see Fig. 11. We can observe the behaviour of all the present elements in the ternary system, i.e. B, C as well as A. In ternary systems we can find four variants:

1. Equilibrium between the liquid L and the solid phase α, β or γ - equations (2) to (4)
2. Equilibrium between the liquid L and the solid phases α and β or α and γ or β and γ - equations (2) to (4)
3. Equilibrium between two solid phases α and β or α and γ or β and γ - equations (5) to (7)
4. Equilibrium between three solid phases α and β and γ - equations (5) to (7).

For the equilibrium distribution coefficients in ternary systems the following holds:

$$k_{o\,\alpha B}^{A-B-C} = \frac{x_{S\alpha B}}{x_{LB}}; \quad k_{o\,\alpha C}^{A-B-C} = \frac{x_{S\alpha C}}{x_{LC}}; \quad k_{o\alpha A}^{A-B-C} = \frac{x_{S\alpha A}}{x_{LA}}; \quad T = konst. \tag{2}$$

$$k_{o\,\beta B}^{A-B-C} = \frac{x_{S\beta B}}{x_{LB}}; \quad k_{o\,\beta C}^{A-B-C} = \frac{x_{S\beta C}}{x_{LC}}; \quad k_{o\beta A}^{A-B-C} = \frac{x_{S\beta A}}{x_{LA}}; \quad T = konst. \tag{3}$$

$$k_{o\,\gamma B}^{A-B-C} = \frac{x_{S\gamma B}}{x_{LB}}; \quad k_{o\,\beta C}^{A-B-C} = \frac{x_{S\gamma C}}{x_{LC}}; \quad k_{o\beta A}^{A-B-C} = \frac{x_{S\gamma A}}{x_{LA}}; \quad T = konst. \tag{4}$$

$$k_{\alpha-\beta B}^{A-B-C} = \frac{x_{\alpha B}}{x_{\beta B}}; \quad k_{\alpha-\beta C}^{A-B-C} = \frac{x_{\alpha C}}{x_{\beta C}}; \quad k_{\alpha-\beta A}^{A-B-C} = \frac{x_{\alpha A}}{x_{\beta A}}; \quad T = konst. \tag{5}$$

$$k_{\alpha-\gamma B}^{A-B-C} = \frac{x_{\alpha B}}{x_{\gamma B}}; \quad k_{\alpha-\gamma C}^{A-B-C} = \frac{x_{\alpha C}}{x_{\gamma C}}; \quad k_{\alpha-\gamma A}^{A-B-C} = \frac{x_{\alpha A}}{x_{\gamma A}}; \quad T = konst. \tag{6}$$

$$k_{\beta-\gamma B}^{A-B-C} = \frac{x_{\beta B}}{x_{\gamma B}}; \quad k_{\beta-\gamma C}^{A-B-C} = \frac{x_{\beta C}}{x_{\gamma C}}; \quad k_{\beta-\gamma A}^{A-B-C} = \frac{x_{\beta A}}{x_{\gamma A}}; \quad T = konst. \tag{7}$$

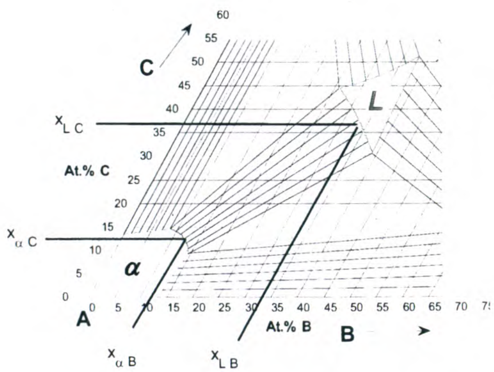

Fig. 11 The equilibrium coefficients for B and C elements in the A–B–C ternary system at high contents of A

$$k_{o\,\alpha B}^{A-B-C} = \frac{x_{\alpha B}}{x_{LB}}; \qquad k_{o\,\alpha C}^{A-B-C} = \frac{x_{\alpha C}}{x_{LC}}$$

Table 1 Distribution of the elements *B* and *C* during equilibrium crystallization of the alloy **X** 50 at.% *A*, 30 at.% *B*, 20 at.% *C*. Eutectic ternary system, ternary eutectic temperature 600°C. Alloy **X** - see Figs. 1, 2

T[°C]	x_{LB}	x_{LC}	$x_{\alpha B}$	$x_{\alpha C}$	$x_{\beta B}$	$x_{\beta C}$	$x_{\gamma B}$	$x_{\gamma C}$
1000	30	20	0	0	0	0	0	0
938.66	30	20	0	0	0	0	0	0
877.33	30	20	0	0	0	0	0	0
815.99	30	20	0	0	0	0	0	0
754.66	30	20	0	0	0	0	0	0
754.66	30	20	8.13	5.12	0	0	0	0
725.52	32.78	21.89	9.37	5.95	0	0	0	0
696.39	35.44	23.75	10.79	6.75	0	0	0	0
667.26	37.88	25.74	12.59	7.32	0	0	0	0
638.12	40.09	27.86	14.46	8.09	67.62	12.38	0	0
628.59	38.77	31.13	14.57	9.58	65.72	14.28	0	0
619.06	37.48	34.22	14.69	11.19	63.81	16.19	0	0
609.53	36.23	37.18	14.84	12.97	61.91	18.09	0	0
600	35	40	15	15	60	20	0	0
600	0	0	15	15	60	20	15	70
500	0	0	13.91	13.88	66.88	16.56	13.75	72.5
400	0	0	12.72	12.69	72	14	12.5	75
300	0	0	11.43	11.41	76.27	11.87	11.25	77.5
200	0	0	10	10	80	10	10	80

Table 2 Equilibrium distribution coefficients of *A*, *B* and *C* elements between α-phase and liquid *L* (first stage of the crystallization) and between α and β and liquid *L* (second stage) for the alloy **X** with 50 at.% *A*, 30 at.% *B*, 20 at.% *C*

T [°C]	$k_{o\,\alpha B}^{A-B-C}$	$k_{o\,\alpha C}^{A-B-C}$	$k_{o\alpha A}^{A-B-C}$
754.66	0.271	0.256	1.735
725.52	0.286	0.272	1.868
696.39	0.304	0.284	2.021
667.26	0.332	0.284	2.201
754.66	0.271	0.256	1.735

T [°C]	$k_{o\,\alpha B}^{A-B-C}$	$k_{o\,\alpha C}^{A-B-C}$	$k_{o\alpha A}^{A-B-C}$	$k_{o\,\beta B}^{A-B-C}$	$k_{o\,\beta C}^{A-B-C}$	$k_{o\beta A}^{A-B-C}$	$k_{o\,\alpha-\beta B}^{A-B-C}$	$k_{o\,\alpha-\beta C}^{A-B-C}$	$k_{o\alpha-\beta A}^{A-B-C}$
638.12	0.361	0.290	2.417	1.687	0.444	0.624	0.214	0.653	3.873
628.59	0.376	0.308	2.520	1.695	0.459	0.664	0.222	0.671	3.793
619.06	0.392	0.327	2.619	1.703	0.473	0.707	0.230	0.691	3.706
609.53	0.410	0.349	2.715	1.709	0.487	0.752	0.240	0.717	3.610
638.12	0.361	0.290	2.417	1.687	0.444	0.624	0.214	0.653	3.873

Table 3 Equilibrium distribution coefficients of *A*, *B* and *C* elements between α and β and γ phases (fourth stage of the crystallization) below the ternary eutectic temperature 600°C for the alloy **X** with 50 at.% *A*, 30 at.% *B*, 20 at.% *C*

T [°C]	$k_{o\,\alpha-\beta B}^{A-B-C}$	$k_{o\,\alpha-\beta C}^{A-B-C}$	$k_{o\alpha-\beta A}^{A-B-C}$	$k_{o\,\alpha-\gamma B}^{A-B-C}$	$k_{o\,\alpha-\gamma C}^{A-B-C}$	$k_{o\alpha-\gamma A}^{A-B-C}$	$k_{o\,\beta-\gamma B}^{A-B-C}$	$k_{o\,\beta-\gamma C}^{A-B-C}$	$k_{o\beta-\gamma A}^{A-B-C}$
600	0.250	0.750	3.500	1.000	0.214	4.667	4.000	0.286	1.333
500	0.208	0.838	4.361	1.012	0.191	5.252	4.864	0.228	1.204
400	0.177	0.906	5.328	1.018	0.169	5.967	5.760	0.187	1.120
300	0.150	0.961	6.506	1.016	0.147	6.859	6.780	0.153	1.054
200	0.125	1.000	8.000	1.000	0.125	8.000	8.000	0.125	1.000

The changes of concentrations of the *B* and *C* elements in the individual phases (liquid, α, β and γ phases) under the conditions of the equilibrium crystallization of the alloy X with 50 at.% *A*, 30 at.% *B*, 20 at.% *C* (see Figs. 1, 2) in the eutectic ternary system are presented in Table 1. The values of equilibrium distribution coefficients of the individual elements in dependence on the temperature and phase constitution are seen in Tables 2 and 3.

The equilibrium distribution coefficients in ternary systems generally enable to:

- carry out an objective control of crystallization processes in the refining and cast metallurgy;
- carry out controlled micro-alloying and doping of the elements during the growth of crystals and commercial alloys thus increasing the physical-metallurgical properties;
- predict the distribution capacity and enrichment of admixtures with $k_o > 1$ in the dendrite arms, build up admixtures with $k_o < 1$ in the spaces between the dendrites, in the mother liquid during dendritic segregation which mostly accompanies the actual solidification of substances;
- predict the distribution of the elements between the individual phases in the region of liquid-solid transformation and in the region where three phases (liquid and α and β phases or α and β and γ phases) exist.

6. Conclusion

In this paper the new computer model for simulation of equilibrium ternary system with the ternary eutectic or peritectic reaction is presented. The computer program was written in the system Matlab with user friendly interface. The input data for every surface (liquidus, solidus, solvus) are inserted by the interactive way, which is easy for users. The program can calculate the individual binary diagrams, 3D view of whole ternary system, isothermal sections, polythermal vertical sections, tie-lines for the individual temperatures and tables with equilibrium distribution coefficients for the specific alloy. At present, the calculation can only be applied for equilibrium conditions of solidification.

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