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Automating the process of calculating the singular points and modeling the phase diagrams of multicomponent oxide systems

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To automate the processes of calculating elements of state diagrams of multicomponent eutectic type oxide systems and simulate them, a calculation algorithm and an application package using function libraries has been developed. On the example of binary and ternary systems $FeO–Cr_2O_3–SiO_2$, $BeO–MgO–TiO_2$, $BeO–MgO–ZrO_2$, $Ca_3(PO_4)_2–CaF_2$, their functionality was tested. The experimental verification of the compositions of singular points (binary and triple eutectics and van Rijn points) and melting temperatures in them by high temperature microscope *in situ* has shown good correlation between the experimental and calculated data.

Keywords: automation of calculations, multicomponent systems, van Rijn melting point, eutectic, modeling of state diagrams.

Для автоматизации процессов расчета элементов диаграмм состояния многокомпонентных систем оксидов эвтектического типа и их моделирования разработан алгоритм расчета и пакет прикладных программ с использованием библиотек функций. На примере бинарных и тройных систем $FeO–Cr_2O_3–SiO_2$, $BeO–MgO–TiO_2$, $BeO–MgO–ZrO_2$, $Ca_3(PO_4)_2–CaF_2$ проведена проверка их работоспособности. Проведенная экспериментальная проверка температур плавления и составов особых точек — бинарных и тройных эвтектик и точек Ван-Рейна методом высокотемпературной микроскопии *in situ* показала хорошее соответствие экспериментальных и расчетных данных.

Автоматизація процесу розрахунку особливих точок і моделювання діаграм стану багатокомпонентних систем оксидів. *С.П.Кривільова, О.Ю.Заковоротний, В.Ф.Моісеєв, Н.Г.Пономарьова, О.М.Рассоха, О.І.Зінченко.*

Для автоматизації процесів розрахунку елементів діаграм стану багатокомпонентних систем оксидів евтектичного типу та їх моделювання розроблено алгоритм розрахунку і пакет прикладних програм з використанням бібліотек функцій. На прикладі бінарних і потрійних систем $FeO–Cr_2O_3–SiO_2$, $BeO–MgO–TiO$, $BeO–MgO–ZrO_2$, $Ca_3(PO_4)_2–CaF_2$ проведено перевірку їх працездатності. Проведена експериментальна перевірка температур плавлення і складів особливих точок — бінарних і потрійних евтектик і точок Ван-Рейна методом високотемпературної мікроскопії *in situ* показала гарну відповідність експериментальних і розрахункових даних.

1. Introduction

The development of the scientific basis for creating new functional materials is inextricably linked with the creation of efficient and cost-effective methods for constructing phase diagrams of multicomponent oxide systems of which they are composed.

Experimental studies of specific points and the construction of state diagrams are

achieved through considerable material costs. These costs increase manifold as the number of components increases. Therefore, the automation of calculations and modeling of state diagrams is acquiring an increasingly large scale.

Phase equilibria and microstructure are analyzed on the basis of a combination of thermochemical calculations and experimental measurements (based on the necessary thermodynamic parameters). Computational methods enable to bring to the construction of state diagrams the achievements of computer technology and success in the study of components' thermodynamic and physical properties. But with the increase in the number of components, the thermodynamic model of the system becomes more complex. Theoretically powerful software tools can calculate a system with any number of components. In practice, their use is limited due to the insufficient knowledge of the thermodynamic properties of many compounds and the lack of data on the structure of state diagrams of a significant number of ternary and more complex systems.

The modeling of state diagrams' elements is based on the values extracted from special databases. Existing programs for calculating (for example, ThermoCalc) are not only very expensive, but also highly specialized, and therefore in most cases are either unavailable or unsuitable for the tasks [1, 2]. The nature of the phase equilibria in the state diagrams depends on the nature of the equilibrium phases and the conditions of the phase transformations. The current state of materials science of oxide systems does not yet allow one to unequivocally calculate phase diagrams: there is no unified theory of phase transformations and the ability to control the phase state. Therefore, thermodynamic methods are mainly used for calculating state diagrams, which is associated with a large amount of computation. Even the widely used experimental planning methods do not allow to significantly reduce the amount of calculations and experimental studies to obtain data on thermodynamic properties of compounds.

However, computational methods are unsuitable for a quantitative description of the formation process of the phase composition and the structure of multicomponent oxide systems of a given composition with equilibrium and non-equilibrium cooling conditions. With their help, it is impossible to determine changes in chemical compositions and relative amounts of equilibrium phases and structural components during phase transformations depending on the composition of the material and temperature. It is also impossible to calculate the critical points of phase transitions, to estimate the volume velocity and the duration of phase transformations depending on the composition and rate of cooling.

The aim of this work is to automate the process of calculating the singular points of multicomponent oxide systems of the eutectic type and to model their state diagrams.

To achieve this goal it is necessary to solve the following tasks:

Develop calculation algorithms and an application package, based on a modular principle with the application of functions library, for calculating the singular points of multicomponent oxide systems.

Conduct a performance check of the developed algorithms and programs on the example of specific binary and ternary systems: $FeO–Cr_2O_3–SiO_2$, $BeO–MgO–TiO_2$, $BeO–MgO–ZrO_2$, $Ca_3(PO_4)_2–CaF_2$.

Conduct experimental verification of the data obtained (compositions of special points and melting points in them) on the preparations of the calculated compositions using high temperature microscopy *in situ*.

2. Experimental

The calculation of the liquidus curves for eutectic systems without solid solutions with a significant concentration of the second and subsequent components is approximately carried out on the assumption that an ideal solution is formed in the liquid state [4, 5, 7]. The basis of the algorithm is the principle of calculating the eutectic, which is the upper limit of the subsolidus state, as the intersection point of the liquidus curves of the corresponding components using the methods of classical chemical thermodynamics with applying the Schroeder-Le Chatelier and Epstein-Howland's equations.

For N-component systems ($N > 2$), the condition $T_{melting(1)} = T_{melting(2)} = ... = T_{melting(N)}$, is satisfied at the eutectic point, and $x_1 + x_2 + ... + x_N = 1$, where $T_{melting(i)}$ is the melting temperature of the i-th component; x_i is the concentration of the i-th component in molar fractions. The task is reduced to solving a system of N-transcendental equations with N-unknowns, which are the concentrations of the components 1, 2, ...N at the eutectic point:

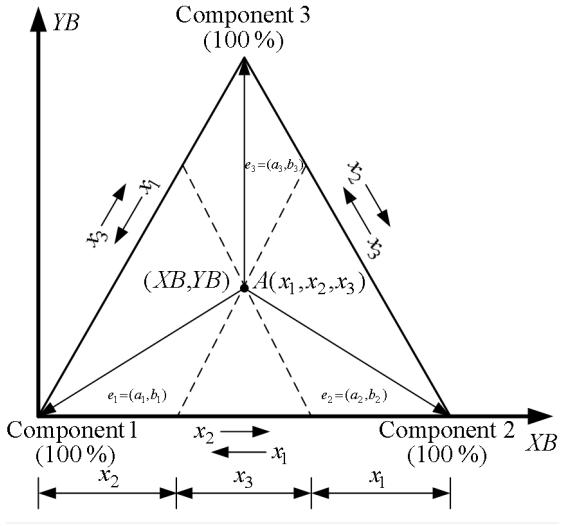


Fig. 1. The position of the singular points on phase diagram of the Fe_2O_3–Cr_2O_3–SiO_2 system.

$$\begin{cases} \dfrac{T_{melting(1)}}{1-\dfrac{R}{\Delta S_1^{melting}}\cdot \ln x_1} = \dfrac{T_{melting(2)}}{1-\dfrac{R}{\Delta S_2^{melting}}\cdot \ln x_2}; \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ x_1 + x_2 + \ldots + x_{N-1} + x_N = 1; \\ \dfrac{T_{melting(N-1)}}{1-\dfrac{R}{\Delta S_{N-1}^{melting}}\cdot \ln x_{N-1}} = \dfrac{T_{melting}(N)}{1-\dfrac{R}{\Delta S_N^{melting}}\cdot \ln x_N} \end{cases},$$

where $\Delta S_j^{melting}$ is the entropy of the melting of the i-th component; R — is the universal gas constant.

An iterative Seidel method, characterized by a small approximation error and high convergence, was used as a solution method. The system of N-equations with N-unknowns is represented as follows:

$$\begin{cases} x(1) = \varphi_1(x(2),\ldots x(N)); \\ x(2) = \varphi_2(x(1),\ldots x(N)); \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ x(N) = \varphi_N(x(1),\ldots x(N-1)). \end{cases}$$

Given a certain initial approximation to the solution of this system $x_1^0, x_2^0, x_N^0 = 1$ and substituting in the equation $x(1) = \varphi_1(x(2), \ldots, x(N))$, we calculate the new value x_1^1. Using the newly calculated value x_1^1 and the initial value x_1^0, we calculate from the equation $x(2) = \varphi_2(x(1), \ldots, x(N))$ a new value $x(2)$: $x_2^{(1)}$. Finally, using the newly calculated values $x_N^{(1)}$, we find the new value of $x(N)$. This ends the first iteration. Replacing the original value $x_1^0, x_2^0, \ldots, x_N^0$ by $x_1^{(1)}, x_2^{(1)}, \ldots, x_N^{(1)}$, we calculate the next approximation with any necessary accuracy. The convergence of the met hod depends on the vector of initial approximations. If it is far from the solution, then there may be an overflow of order or non-divergence for a given number of iterations.

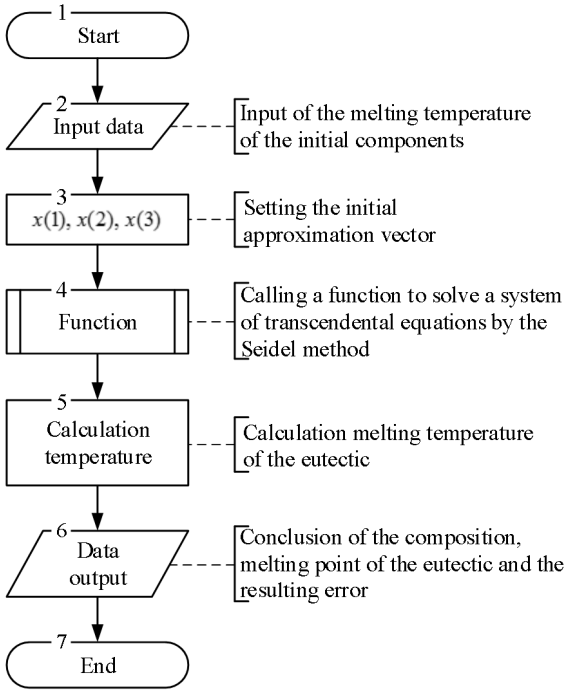


Fig. 2. Algorithm for calculating the composition and melting point of a triple eutectic for a three-component system Fe_2O_3–Cr_2O_3–SiO_2.

When determining the composition and melting point of a triple eutectic, calculations are performed in a uniform — barycentric coordinate system wherein the position of any point A in the P-dimensional space is determined by $(P + 1)$ coordinates that are not in the same hyperplane. For the formation of graphs, a transformation from the barycentric to the Cartesian coordinate system is carried out (see Fig. 1). This is done as follows: using the coordinates of point $A(x_1, x_2, \ldots, x_N)$, as well as the vectors $e_1 = (a_1, b_1)$, $e_2 = (a_2, b_2)$, ..., $e_N = (a_N, b_N)$, we find the coordinates XB and YB of point A:

$$XB = x_1a_1 + x_2a_2 + \ldots + x_Na_N;$$
$$YB = x_1b_1 + x_2b_2 + \ldots + x_Nb_N.$$

In such a way we get the projection of the liquidus surface on the concentrations triangle in the case of a three-component

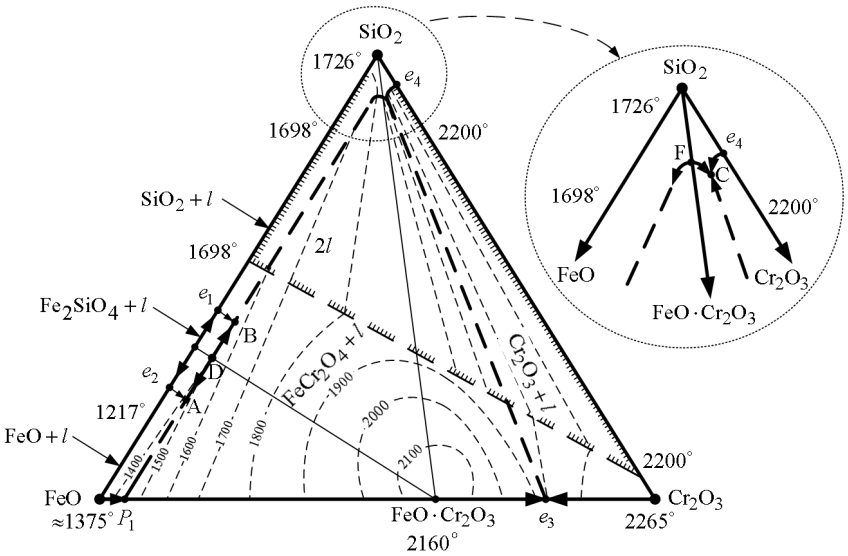


Fig. 3. The position of the singular points on phase diagram of the Fe_2O_3–Cr_2O_3–SiO_2 system.

system or the melting point and composition of the eutectic in the form of a Table with the number of components $N > 3$.

Testing the efficiency of the calculation algorithm was performed on binary and ternary systems FeO–Cr_2O_3–SiO_2, BeO–MgO–TiO_2 and BeO–MgO–ZrO_2, $Ca_3(PO_4)_2$–CaF_2. When studying the FeO–Cr_2O_3–SiO_2 system, the binary eutectic formed by FeO and Fe_2SiO_4, was taken as a conventional "component" with a melting point of 1177°C, a formula number of atoms 3.37 in the formula and the position on the line connecting the composition of the binary eutectic with the opposite phase $FeCr_2O_4$.

In this work CaF_2, $Ca(OH)_2$, H_3PO_4, synthetic wustite ($Fe_{0.95}O$), α–Cr_2O_3, quartz (more than 99.5 % SiO_2), zirconium dioxide of the ZRO-1 brand, and peroxide MgO were used. Binary compounds were synthesized in the solid phase, preparations — by firing tableted mixtures three times. For sintering the samples, a high-temperature chamber furnace with Si–C heaters, with air atmosphere, as well as an electric furnace with cryptol resistance and a quartz capsule with periclase filling were used. The calculations were carried out according to known methods and the developed algorithms [4, 5] using the refined thermodynamic constants of substances [8] as the initial data.

Experimental verification of calculated data — compositions of binary and ternary eutectics, van Rein points, and melting temperatures in them was carried out on preparations of calculated compositions by high temperature microscopy *in situ* on flat-polished plates with a thickness of 0.3 mm, as well as on crushed products with direct observation in a microscope with a special attachment — a silicon camera of the Mikhailov-Shatsky system.

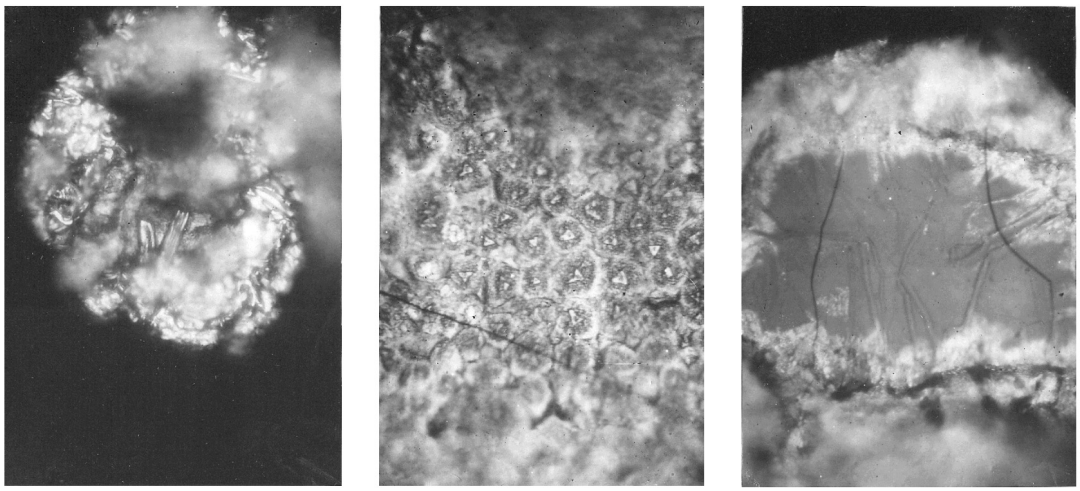
3. Results and discussion

The conducted numerical experiments confirmed the efficiency of the algorithm and programs for solving the tasks. The results obtained allow us to determine the melting points and compositions of the van Rein and eutectic melting points, the course of the liquidus curves and isotherms, the ratio between the components, solubility and other properties with any given accuracy for multicomponent refractory oxide systems.

Thus, for the system of $Ca_3(PO_4)_2$–CaF_2, which is almost ideal eutectic, with one double compound $Ca_5(PO_4)_3F$ [3, 10, 11] when calculating by the proposed algorithm with the use of refined thermodynamic constants of substances [4] the following calculation results were obtained: binary eutectic compositions — 0.415 mol. shares of $Ca_3(PO_4)_2$ and 0.585 mol. the proportion of $Ca_5(PO_4)_3F$, melting point — 1634°C, 0.980 mol.d. $Ca_5(PO_4)_3F$ and 0.02 mol.d. CaF_2, melting point 1408°C. The experimental verification of the calculated data produced on the preparations of the calculated compositions by the method of high-temperature microscopy (accuracy ±10°) showed good agreement between the experimental and the calculated data.

Table. The results of the calculation of singular points of the system Fe_2O_3–Cr_2O_3–SiO_2

Point	Melting point: calculated, °C	Molar composition, %						The melting point of the experimentalny, °C
		FeO	Cr_2O_3	SiO_2	FeO	Cr_2O_3	SiO_2	
A_{eut}	1168	72.0	1,25	36,75	74.20	2.70	23.10	1100
B_{eut}	1146	55.5	1.10	43.30	59.00	2.50	38.50	1106
C_{eut}	1500	1.20	1.20	97.60	1.40	2.90	95.70	>1430
$D_{V\text{-}R}$	1215	66.4	0.80	32.80	69.50	1.80	28.70	1175
$F_{V\text{-}R}$	1527 christobalite 1355 quartz	1.6	1.10	97.30	1.50	1.50	2.50	– 1370



a) b) c)

Fig. 4. Microstructures of the ternary eutectic of the composition SiO_2–$FeCr_2O_4$–$FeSiO_4$, a — 1060°C, reflected light, × 512, b — 1095°C, reflected light, × 640, c — 1075°C, reflected light, × 400.

For three-component systems BeO–MgO–TiO_2 and BeO–MgO–ZrO_2 [6], which are almost ideal eutectic, without formation of any double or ternary compounds, but with limited solid solutions in the regions adjacent to the BeO angle in the BeO–MgO–TiO_2 system and to the BeO–ZrO_2 side in the BeO–MgO–ZrO_2 system when calculating by the proposed algorithm (see Fig. 2), the following data were obtained: the eutectic melting points are 1665°C for the eutectic of 10.4BeO + 5.1MgO + 3.2ZrO_2 and 1790°C for the eutectic of 10.4BeO + 5.1MgO + 1.1TiO_2 against 1669°C (5BeO + 4MgO + 3ZrO_2) and 1801°C (10BeO + 5MgO + 1.1TiO_2), determined experimentally.

The system Fe_2O_3–Cr_2O_3–SiO_2 was studied by computational methods with experimental control of specific points. Table1 shows the compositions of the most important eutectic points and melting points of the Van Rhein system Fe_2O_3–Cr_2O_3–SiO_2, the location of which is shown in Fig. 3 on the projection of the surface of its liquidus. It was found that the lower limit of melt appearance in the system is the temperature of 1175°C. For the chromite — quartz crossing point, the temperature of 1370°C was obtained, which, being non-equilibrium, is important for applications in engineering and geochemistry. The melting microstructures of the triple eutectic of the composition SiO_2–$FeCr_2O_4$–$FeSiO_4$ are shown in Fig. 4. From the data obtained (see Table) it follows that they are in good agreement with the calculated data. The results obtained make it possible to better orientate in issues of high-temperature engineering and the geochemistry of chromites (when considering chromites inclusions in olivinite and similar rocks) [10, 11].

6. Conclusions

To calculate the singular points of multicomponent oxide systems in the present work, an algorithm for calculating and an application package using libraries of functions was developed.

Using the example of specific binary and ternary systems: $FeO–Cr_2O_3–SiO_2$, $BeO–MgO–TiO_2$, $BeO–MgO–ZrO_2$, $Ca_3(PO_4)_2–CaF_2$ their functionality was tested.

Experimental verification of the melting points and compositions of the singular points using high temperature microscopy *in situ* showed good agreement between experimental and calculated data.

Automating the process of calculating the singular points of multicomponent oxide systems simplifies modeling of their projections of liquidus surfaces — a heterogeneous design base that enables to create new materials with desired properties including functional polymer composites for medical purposes, based on phase diagrams by selecting combinations of elements of a multicomponent heterogeneous mixture.

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