Concentration fields of the ternary systems and trajectory of phases in T-x-y Diagrams

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Abstract. The possibility of computer models of T-x-y diagrams for analysis two-, one- and zero-dimensional concentration fields are demonstrated using T-x-y diagram of systems CaO-SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} and MgO-SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}. The characteristics of processes proceeding in the concentration fields can be analyzed with the help of diagrams of vertical mass balances, which show the increase or decrease of phases portions for each phase region. Calculation of crystallization paths was made.

1. Introduction
Construction of computer models of ternary systems significantly extends the possibilities of their investigation [1] by the calculation of crystallization paths and the analysis of concentration fields in order to obtain the information about the crystallization stages and the microconstituents. The schema of mono- and invariant equilibria is created on a basis of the data for invariant processes in the binary and ternary systems taking into account the existence and type of binary and ternary compounds. At the first stage of construction of 3D model for T-x-y diagrams, the invariant horizontal complexes at the temperatures of invariant points are reconstructed. Then they are completed by the ruled and unruled surfaces, and the phase regions are formed [2-4]. At the description of surfaces having a complex geometric structure (e.g. the large quantity of points on surface’s contour, the presence of extremes or the gap of smoothness) we used the kinematic method based on the description of surfaces by means of the directing and forming curves [2-3, 5].

Systems CaO-SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} and MgO-SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} having a great practical importance are the objects of investigation. These systems are used at the description of properties of building materials [6-7] as well as at the characterization of geological objects [8-9].

2. Model of T-x-y diagrams of system CaO-SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}
The complexity of elaboration of T-x-y diagram model for system CaO-SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} is associated with the ambiguous descriptions for binary systems, as well as the liquidus surfaces. There are different descriptions of types binary and ternary points, the character of binary compounds. The model of T-x-y diagram is based on the experimental data from [11]. It includes 16 liquidus surfaces and liquid immiscibility surface (fig. 1a), 128 ruled surfaces, 16 horizontal complexes at the temperatures of invariant points, 33 two-phase regions and 46 three-phase regions [4, 11-13].
Notations: incongruently melting compounds $R_1 - 3\text{CaO-SiO}_2$, $R_3 - 3\text{CaO-2SiO}_2$, $R_5 - 3\text{CaO-Al}_2\text{O}_3$, $R_{10} - \text{CaO-6Al}_2\text{O}_5$; and congruently melting compounds $R_2 - 2\text{CaO-SiO}_2$, $R_4 - \text{CaO-SiO}_2$, $R_7 - 3\text{Al}_2\text{O}_3-2\text{SiO}_2$, $R_{11} - \text{CaO-2Al}_2\text{O}_3$, $R_{12} - \text{CaO-Al}_2\text{O}_3-2\text{SiO}_2$.

The most complex geometrical structure have the liquidus surfaces corresponding to the contours $Q_1 Q_2 (Q_5, Q_7), E_1 (E_4, E_5) E_2 Q_9, E_3 (E_6, E_7) E_4 Q_6 (Q_7, Q_8)$ and $E_8 Q_9$. Such surfaces are constructed from several fragments with regards to the smoothness on boundaries of fragments [3, 5].

Let's consider the analysis technology of concentration fields using liquidus field $\text{Al}_2\text{O}_3 (\text{Al}_2\text{O}_3 p_5 Q_7 Q_9) Q_7 e_5$ as an example. At the projection of considered fragment of phase diagram is divided into 46 concentration fields, including 12 two-dimensional, 23 one-dimensional and 11 zero-dimensional fields (fig. 2a). The diagrams of vertical mass balance have been calculated for each concentration field. They permit to obtain the lists of intersected phase regions and the crystallization stages: $Q_7-5\in Q_4-5, 6\in Q_8-6-7$, $Q_8-8\in Q_8-7-8$.

Using the diagram of vertical mass balance we can consider in more detail the concentration fields having same microconstituents, but different by crystallization stages, e.g. for fields $Q_8-8$ and $Q_8-7-8$. The mass center $G_1(0.105; 0.375; 0.52)$ given in two-dimensional field $Q_7-8$ intersects four-phase region $L+C, L+C+R_5, L+R_5+R_{12}, B+R_5+R_{12}$ and two horizontal complexes at the temperatures of invariant points ($Q_8$ and $E_5$) (fig. 2b).

**Figure 1.** XY projection of liquidus surfaces (a), isolines and 3D models of liquidus surfaces $R_{11}$ (b-c) and $R_{12}$ (d-e).
As can be seen from the diagram of vertical mass balance, there are the increasing of phase portion C and decreasing of phase L in two-phase regions L+C. So, the reaction of primary crystallization takes place \( \text{L}^1 \rightarrow \text{C}^5 \). Further, the mass center falls into three-phase L+C+R5, with the increasing of phases C and R5, while the phase L continues to decrease. It corresponds the monovariant eutectic reaction \( \text{L}^3 \rightarrow \text{C}^5(\text{R}5)+\text{R}5^5(\text{C}) \). Next, the invariant quasi-peritectic reaction \( \text{L}^{Q8}+\text{C}^{Q8} \rightarrow \text{R}5^{Q8}+\text{R}12^{Q8} \) takes place on the horizontal complexed at point \( Q_8 \). As a result of this reaction the crystals C is fully expended. In similar way, the postperitectic secondary eutectic reaction \( \text{L}^{ep}\rightarrow \text{R}5^{ep}(\text{R}12)+\text{R}12^{ep}(\text{R}5) \) occurs in the three-phase region L+R5+R12. The phase L is fully disappeared as the result of invariant eutectic reaction \( \text{L}^{E5}\rightarrow \text{C}^{E5}+\text{R}5^{E5}+\text{R}12^{E5} \) on the plane at the temperature of ternary eutectic points \( E5 \). Below the horizontal complex, the composition gets to the solid-phase region B+R5+R12. Since the crystals phase.

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**Figure 2.** Fragment of projection of T-x-y diagram with dividing of liquidus field Al2O3 on the concentration field (a), diagrams of vertical mass balance for compositions G1 (b) and G2 (c), crystallization path for G1 (d).
С1 and С2 are fully expended at the invariant quasi-peritectic reaction, therefore they are not included in the final set of microconstituents. Thus two-dimensional field Q8-7-8 is characterized by the following set of microconstituents: R5е5(C), R5 Q8, R12 Q8, R5е5(R12), R12е5(R3), B E5, S5 E5, R12 E5. As the field Q8-8 is a part of monovariant liquidus line э5Q8, then it hasn’t the reaction of primary crystallization L1→C1. The mass center G3(0.092; 0.376; 0.532) for this field at once gets into three-phase region L+C+R5 (fig. 2c). So, one-dimensional field Q8-8 has shorter crystallization scheme, but coincides with adjacent two-dimensional field Q8-7-8 by set of microconstituents.

Figure 2d show the crystallization path for mass center G1 given in considered two-dimensional field Q8-7-8. The melt G1 moves along the segment C-G1 to the liquidus line э5Q8 at the passing through two-phase region L+C. Next it falls into three-phase region L+C+R5 and the composition of melt moves along the fragment of liquidus line э5Q8 to point Q5. Then melt shifts along the monovariant liquidus line Q5E5 to point E5 at the going through three-phase region L+R5+R12. The reaction L5→B5+R5 E5+R12 E5 is finished on horizontal complex B5R5R12 and below there are only solid crystals B, R5, R12.

3. Model of T-x-y diagrams of system MgO-SiO2-Al2O3

The system MgO-SiO2-Al2O3 has a more simple geometric structure. It includes three binary congruently melting compounds (R1=2MgO·SiO2, R2=3Al2O3·2SiO2, R3=MgO·Al2O3), one binary (R4=MgO·SiO2) and two ternary (R5=4MgO·5Al2O3·2SiO2, R6=2MgO·2Al2O3·5SiO2) incongruently melting compounds. Systems MgO-SiO2-Al2O3 is characterized by 11 invariant transformations: three eutectic 3 eutectic (E1-3), one peritectic (P), five quasiperitectic (Q1-5) transformations and 2 four-phase regroupings of phases with polymorphous modification of silicon oxide (cristobalite and tridymite) (fig. 3).
Ternary points $U_1$ and $U_2$ arrange at the same temperature, and the points $B_1U_1$, $B_2U_1$, $B_1U_2$, $B_2U_2$ coincident into one point on the prism edge. Therefore, the horizontal planes corresponding the four-phase phase re-groupings of phases $L_{U1}+B_1
rightarrow R_3+B_2$ and $L_{U2}+B_2
rightarrow R_1+B_2$ have degenerated structure $U_1$-$R_2$-$U_1$-$B_1$($U_2$-$B_2$) and $U_2$-$R_3$-$U_2$-$B_1$($U_2$-$B_2$), correspondingly. Phase region $L+B_1+B_2$ degenerate into the plane and the corresponding monovariant peritectic reaction $L^1+B_1
rightarrow B_2^p$ occurs at one temperature.

Projection T-x-y diagram is divided into 100 two-dimensional, 170 one-dimensional and 71 zero-dimensional concentration fields. At that four field coincide by crystallization stages and microconstituents: $B$-$3$($B$-$3$-$4$); $B$-$1$($e_2$-$n$-$k$-$1$-$B$-$U_1$); $k$-$nk$; $1$-$B$-$1$. Additionally 11 concentration fields differ by crystallization stages, by coincide microconstituents ($B$-$m$-$1$,$e_2$-$U_1$,$n$-$k$,$m$-$1$,$k$-$1$ (inside immiscibility surface), $k$-$1$ (on the contour of immiscibility surface))$e_2$-$n$-$k$-$1$-$B$-$U_1$; $U_2$-$3$($B$-$U_2$-$3$,$e_3$-$4$($B$-$e_1$-$4$,$4$-$B$-$4$,$3$-$B$-$3$,$U_1$-$B$-$U_1$).

A large quantity of concentration fields with coinciding microconstituents due to the presence of phase regions with liquids immiscibility and two polymorphous modifications of component SiO$_2$. Processes occurring in the phase regions $L_1+L_1$, $L_1+L_1+B_1$, $L+B_1$ not influence on the final set of microconstituents, because the products of reactions for these fields fully expended. Let’s consider two-dimensional field $B$-$U_1$-$2$ as an example. The mass center G (0.1; 0.8; 0.1) given in this field intersects five phase regions $L+B_1$, $L+B_1+B_2$, $L+B_2$, $L+B_2+R_2$, $B_2+R_2+R_6$ (fig. 5b) with the following phase reactions $L^1
rightarrow B_1^1$, $L^p
rightarrow B_1^p$, $L^{ep}
rightarrow B_2^{R2, ep}$, $B_2^{R2, ep}$, $L^{E3}
rightarrow B_2^{E3}$, $B_2^{E3}+R_3^{E3}+R_6^{E3}$ ($^1$ – primary crystallization; $^p$ – monovariant peritectic reaction; $^{ep}$ – postperitectic primary crystallization; $^{E3}$ – invariant eutectic crystallization).

The crystals $B_1$ are fully disappeared as the result of postperitectic primary reaction $L^{ep}
rightarrow B_2^{p}$ and they are not included in the set of microconstituents. Thus, the field $B$-$U_1$-$2$ is characterized by the following microconstituents: $B_2^{p}$, $B_2^{p}$, $B_2^{E3}$, $R_2^{B2, ep}$, $B_2^{E3}$, $R_2^{E3}$, $R_6^{E3}$.
4. Summary

Analysis of two, one and zero-dimensional concentration fields for obtaining the data for the crystallization stages and microconstituents are shown based on the computer models [14] of systems CaO-SiO$_2$-Al$_2$O$_3$ and MgO-SiO$_2$-Al$_2$O$_3$.

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