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Solidification Paths within the Ceramic Systems

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Abstract. The aim of this work is to assemble the computer models of phase diagrams (PD) for the typical ternary systems and to examine the processes of crystallization on its base. Spatial schemes of mono- and invariant equilibria have been used for it. Analysis of concentration fields, obtained by the projection of the surfaces on the Gibbs triangle, allows establish the boundaries of phase regions (located above the considered fields), the sequence of phase transformations and microstructural elements for the solidification of the initial melt at equilibrium condition. Concentration fields have been analyzed by means of mass balances for their centers of masses. Based on this technology, the research identifies concentration fields with coinciding sets of phase reactions and microconstituents, and the fields with individual characteristics.

Introduction

Projection of phase regions on the base of T-x-y constitutional diagram divides its concentration area into the unique fields with the individual set of phase reactions and corresponding microstructures. Those fields, which are formed by the 3-phase regions, are additionaly divided by the surfaces of 2-phase reactions on the borders of fragments with the different dynamics for mass increments of material points. Similarly, in the fields with the invariant phase reactions, the fragments are allocated, distinguishing by the combination or the absence of crystals with different dispersity, superabundant after the peritectic reactions. Such 3-fold division of concentration area forms a genotype of multicomponent material. With variability of the concentration fields the nanostructures diversification are correlated too.

T-x-y diagram with incongruently melting compound R=A_3C

The kinematical method is used for the unruled and ruled surfaces simulation. In this case, a diagram surface is presented as the kinematical one, that is, a space curve, given by the interpolation polynomial, moves along the analogously given directing curves [1-4].

Projection of phase regions borders are dividing a simplex of concentration (Fig. 1, to the left) into 37 concentration fields [5-7], two of them are zero-dimensional (Q, E, $Q_e=e_{AB}\cap BR$, $Q_A=AQ\cap BR$, $E_R=RE\cap pQ$), 18 – one-dimensional ($e_{AB}Q_e$, Q_eQ, pE_R, E_RQ, QE, $e_{AC}E$, $e_{BC}E$, A_QA, Q_AQ, BQ_e, BQ, BE, CE, RQ_A, Q_AQ_e, RQ, R_ER, E_RE) and 14 – two-dimensional (1-14).

Phase reactions in this system belong to 5 types: I^1 - primary (bivariant) crystallization $L^1\to I^1$; e(IJ) – secondary (monovariant) eutectical crystallization $L^e\to I^e+J^e$; E – invariant eutectical crystallization $L^E\to B^E+R^E+C^E$; p – monovariant peritectical reaction $L^p+A^p\to R^p$; Q – invariant quasiperitectical regrouping of masses $L^Q+A^Q\to R^Q+B^Q$; $R^{1п}$ – postperitectical primary (bivariant) crystallization $L^{1п}\to R^{1п}$, which begins after («п» - in Russian) the finishing of the monovariant peritectical reaction p; eп(RJ) – postperitectical secondary (monovariant) crystallization $L^{eп}\to R^{eп}+J^{eп}$ (J=B, C), which follows the invariant quasiperitectic reaction Q.

Two zero-dimensional fields (E_R, Q) and 3 one-dimensional ones ($p_{AR}E_R$, E_RQ, BQ) haven't the individual set of the crystallization schemes and are considered as a common concentration fields with the one- or two-dimensional field, which they are neighbored: $E_R\in E_RE$, $Q\in QE$ и $p_{AR}E_R\in 8$, $E_RQ\in 7$, $BQ\in 12$ (Table 1, 2). A sign "∈" means that first field belongs to the second one.

Table 1. Determination of the concentration fields with a unique set of microconstituents

Area 5: R^p, $R^{1п}$, $B^{еп}+R^{еп}$, E_{BCR}	Line $E_RQ \in$ to the field 7: R^1, B^e+R^e, E_{BCR}	Area 7: R^1, B^e+R^e, E_{BCR}
Line RE_R: R^p, $R^{1п}$, E_{BCR}	Point $E_R \in$ to the line E_RE: R^1, E_{BCR}	Line E_RE: R^1, E_{BCR}
Area 6: R^p, $R^{1п}$, $C^{еп}+R^{еп}$, E_{BCR}	Line $p_{AR}E_R \in$ to the field 8: R^1, C^e+R^e, E_{BCR}	Area 8: R^1, C^e+R^e, E_{BCR}

If in the process of comparing of the microstructures of two neighbor 2-dimensional fields, one set of microstructures is present in the more long list of the microconstituents of other field, then a line on their borders, as a one-dimensional field, completely belong to the 2-dimensional field with more short list of microconstituents. Otherwise the microstructure of the compositions on this line is unique.

E.g., the microstructures of the fields 7 (R^1, B^e+R^e, $B^E+C^E+R^E$) and 12 (B^1, B^e+R^e, $B^E+C^E+R^E$) differ by the primary crystals R^1 and B^1, thereby the compositions of the line QE contain a unique in this diagram set of microconstituents (B^e+R^e, $B^E+C^E+R^E$). At the same time the microstructures of the fields 7 (R^1, B^e+R^e, $B^E+C^E+R^E$) and 5 (R^p, $R^{1п}$, $B^{еп}+R^{еп}$, $B^E+C^E+R^E$) differ only by the products of peritectical reaction R^p within the field 5. Consequently, the compositions of the line E_RQ do not have the unique microstructure, and have the same set as field 7 (R^1, B^e+R^e, $B^E+C^E+R^E$).

Table 2. Phase reactions and their products within the concentration fields attached to point E_R

Fields	Surfaces	Phase regions	Phase reactions	Products
E_R (0.455, 0.162, 0.383)	pQ as $q_A \cap q_{R,}$ h_E	L+R B+C+R	$L^1 \to R^1$ $L^E \to B^E+R^E+C^E$	R^1, B^E, C^E, R^E
E_RE (0.295, 0.262, 0.443)	q_R h_E	L+R B+C+R	$L^1 \to R^1$ $L^E \to B^E+C^E+R^E$	R^1 B^E, C^E, R^E
RE_R (0.55, 0.10, 0.35)	q_A q^r_{AR} q^r_{RA} h_E	L+A L+A+R L+R B+C+R	$L^1 \to A^1$ $L^p+A^1 \to R^p$ $L^{1п} \to R^{1п}$ $L^E \to B^E+C^E+R^E$	 R^p $R^{1п}$ B^E, C^E, R^E
$p_{AR}E_R$ (0.505, 0.080, 0.415)	q_R q^r_{RC} h_E	L+R L+C+R B+C+R	$L^1 \to R^1$ $L^e \to C^e+R^e$ $L^E \to B^E+C^E+R^E$	R^1 C^e, R^e B^E, C^E, R^E
E_RQ (0.395, 0.250, 0.355)	q_R q^r_{BC} h_E	L+R L+B+R B+C+R	$L^1 \to R^1$ $L^e \to B^e+R^e$ $L^E \to B^E+C^E+R^E$	R^1 B^e, R^e B^E, C^E, R^E
8 (0.3, 0.2, 0.5)	q_R q^r_{RC} h_E	L+R L+C+R B+C+R	$L^1 \to R^1$ $L^e \to C^e+R^e$ $L^E \to B^E+C^E+R^E$	R^1 C^e, R^e B^E, C^E, R^E
7 (0.3, 0.3, 0.4)	q_R q^r_{BC} h_E	L+R L+B+R B+C+R	$L^1 \to R^1$ $L^e \to B^e+R^e$ $L^E \to B^E+C^E+R^E$	R^1 B^e, R^e B^E, C^E, R^E
6 (0.54, 0.10, 0.36)	q_A q^r_{AR} q^r_{RA} q^r_{RC} h_E	L+B L+A+R L+R L+C+R B+C+R	$L^1 \to A^1$ $L^p+A^1 \to R^p$ $L^{1п} \to R^{1п}$ $L^{еп} \to C^{еп}+R^{еп}$ $L^E \to B^E+C^E+R^E$	A^1 R^p $R^{1п}$ $C^{еп}$, $R^{еп}$ B^E, C^E, R^E
5 (0.48, 0.18, 0.34)	q_A q^r_{AR} q^r_{RA} q^r_{RB} h_E	L+B L+A+R L+R L+B+R B+C+R	$L^1 \to A^1$ $L^p+A^1 \to R^p$ $L^{1п} \to R^{1п}$ $L^{еп} \to B^{еп}+R^{еп}$ $L^E \to B^E+C^E+R^E$	 R^p $R^{1п}$ $B^{еп}$, $R^{еп}$ B^E, C^E, R^E

When all 18 one-dimensional fields were analyzed in this way, it was found that the lines $p_{AR}E_R$, E_RQ and BQ are not the unique ones, and they belong to the fields 8, 7 and 12 properly. Microstructure within the line $p_{AR}E_R$, dividing the fields 6 and 8, coincide with the microstructure within the field 8. Microstructure of line E_RQ, dividing the fields 5 and 7, coincide with the microstructure of field 7. Microstructure of composition E_R, between the fields $p_{AR}E_R$ and E_RE, coincide with the microstructure of field E_RE.

If the comparing of two fragments of one line, divided by the point (one-dimensional field), showed, that a list of the microstructure elements of one fragment is included in the list of other fragment, then a point between them belongs to the fragment with the more short list of microconstituents. Otherwise a microstructure of the compositions of this line is unique. Point Q, which fits the invariant reaction, has no a unique microstructure, and belongs to the line QE.

Point E_R situates on the cross-section of lines $p_{AR}E_R$, E_RQ and RE_R, E_RE. Microstructures of the fragments of the line $p_{AR}Q$ differ by two elements C^e and B^e: $p_{AR}E_R$ (R^1, C^e+R^e, B^E+C^E+R^E) and E_RQ (R^1, B^e+R^e, B^E+C^E+R^E). But the microstructures of the fragments for a line RE differ not only by the existing of element R^p: RE_R ($R^п$, $R^{1п}$, B^E+C^E+R^E) and E_RE (R^1, B^E+C^E+R^E), that confirm the lost of individuality by the point E_R. Its microstructure absolutely coincides with the microstructure of compositions on the line E_RE.

Comparing the microstructures of the next two fields (6 and 8), with the common line $p_{AR}E_R$, showed that one-dimensional field has the same microstructure as the field 8.

Microstructure within the line E_RQ between the fields 5 and 7 coincides with the microstructure of the compositions within the field 7. Elements of microstructure within the field 12 (B^1, B^e+R^e, B^E+C^E+R^E) are implicitly included in the list of elements of the field 13 (B^1, B^e, B^Q+R^Q, $B^{еп}$+$R^{еп}$, B^E+C^E+R^E). Consequently, the dividing them line BQ is not a holder of the unique microstructure, and repeats the list for field 12: B^1, B^e+R^e, B^E+C^E+R^E. Contrary, the microstructures of the fields 7 (R^1, B^e+R^e, B^E+C^E+R^E) и 12 (B^1, B^e+R^e, B^E+C^E+R^E) отличаются первичными кристаллами (R^1 and B^1), hence, the compositions of line QE possess the exclusive set of the microstructure elements: B^e+R^e, B^E+C^E+R^E.

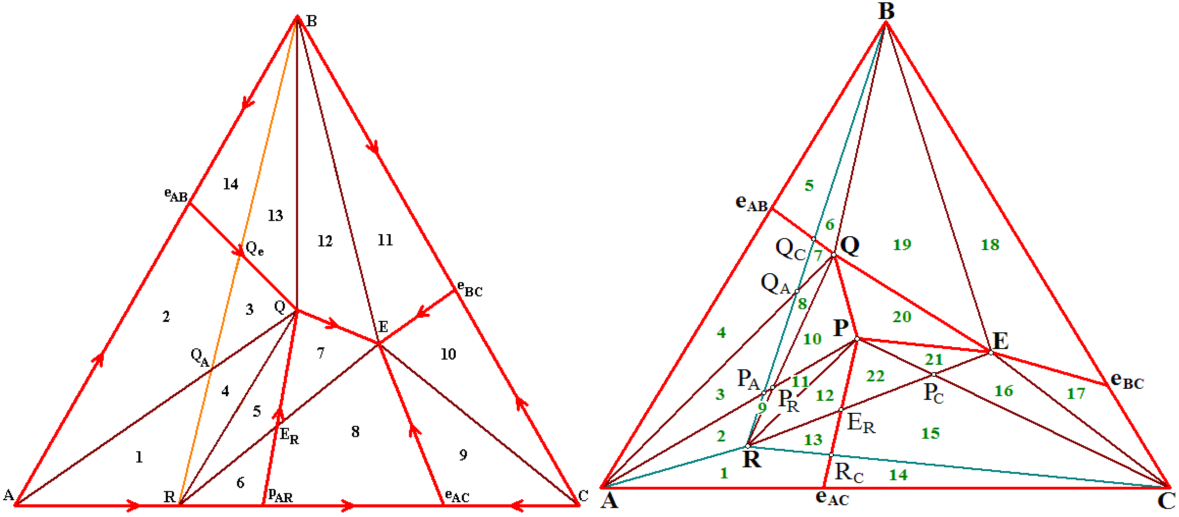

Fig. 1. Concentration fields of the ternary systems with the incongruently melting compounds $R=A_3C$ and $R=A_mB_nC_k$

T-x-y diagram with incongruently melting compound $R=A_mB_nC_k$

Partial investigation of the crystallization schemes in this system (Fig. 1, to the right) were made earlier [5]. May be it wasn't known for the author of [8], where there was written, that the crystallization schemes in this systems are rather sophisticated to analyze them. There are 65 concentration fields here: 11 – zero-dimensional, 32 – one-dimensional and 22 – two-dimensional fields. Besides the 2 4-phase reactions (quasiperitectic and eutectic ones), known for the first system, here there is the third invariant reaction (peritectic): $L^P+A^{1,e}+C^e \rightarrow R^P$.

Reaction $L^p+A^{1,e}\rightarrow R^{p(A)}$ (with the participation of primary and eutectic crystals A) proceeds in the fields 2, 9, 11, RP_A, RP_R, P_RP, P_A, reaction $L^p+A^1\rightarrow R^{p(A)}$ (with participation of only primary crystals A) – in the fields 3, 8, 10, AP_A, P_AQ_A, P_AP_R, P_RQ, P_R, $L^p+C^1\rightarrow R^{p(C)}$ (with the participation of primary crystals C) – within the fielsd 16, 21, EP_C, CP_C, P_CP, P_C, $L^p+C^{1,e}\rightarrow R^{p(C)}$ (with participation of the primary and eutectical crystals C) – in the fields 15, 22, E_RP_C, $L^p+C^e\rightarrow R^{p(C)}$ (with the participation of only eutectical crystals C) – within the fields 12, 13, E_RR_C, E_RR, E_RP, E_R. For the better understanding of the crystallization processes within the two-dimensional field it is convenient to examine the horizontal planes of invariant reactions (the complexes of 4 simplexes) as a degenerated 4-phase region.

Table 3. Microstructure formation within the field 2 with the invariant reactions P & Q

Surface	Region	Reaction	Microconstituents
q_A		$L^1\rightarrow A^1$	A^1
	L+A		
q^r_{AC}		$L^e\rightarrow A^e+C^e$	A^e
	L+A+C		
h^P_{AC}, h^P_{AR}	L+A+C+R	$L^P+A^{1,e}+C^e\rightarrow R^P$	R^P
	L+A+R	$L^p+A^{1,e}\rightarrow R^{p(A)}$	$R^{p(A)}$
h^Q_{AR}, h^Q_{BR}	L+A+B+R	$L^Q+A^{1,e}\rightarrow B^Q+R^Q$	B^Q,R^Q
	A+B+R		A^1, A^e, R^P, $R^{p(A)}$, B^Q, R^Q

CaO-SiO_2-Al_2O_3 system

System CaO-SiO_2-Al_2O_3 (C-A-S) has a great practical importance. When phase regions of C-A-S system were projected to the Gibbs triangle, it has given 117 two-, 163 one- and 45 zero-dimensional concentration fields [9-13]. The crystallization paths and the formation of microconstituents in phases assemblage have been analyzed for the surfaces of CaO, $3CaO\cdot SiO_2$ and $3CaO\cdot Al_2O_3$ primary crystallization. Two-dimensional, one-dimensional and zero-dimensional concentration fields were formed by the surfaces projection on the Gibbs triangle. Some one-dimensional and zero-dimensional concentration fields have no individuality and their microconstituents are the same as within the neighbor zero-dimensional and two-dimensional fields. The crystallization stages for given compositions are illustrated by the vertical and horizontal mass balances. Computer models of phase diagram is mounted of its phase regions with the designation of surfaces: liquidus ones, ruled surfaces, horizontal planes of solidus and the vertical triangulation planes. 3D model of this type permits to analyze the crystallization stages for any composition and to differ the concentration fields with individual set of microconstituents of phases assemblage and the concentration fields with the same crystallization schemes and microconstituents of phases assemblage as within the adjoining field.

Concentration Fields and Crystallization Paths

Analysis of 52 concentration fields (Fig. 2, a), that belong to the primary crystallization of component C(CaO) and neighbor compounds C_3S and C_3A (19 two-, 21 one- and 12 zero-dimensional fields) reveals that there are 18 fields (12 one-dimensional and 6 zero-dimensional) without the unique set of microconstituents (Fig. 2) [13]. At that, only within 2 one- and 1 zero-dimensional fields the crystallization stages and the microconstituents completely coincide with the adjoining fields: $(R_6–3)\in(R_6–3–4)$, $(Q_2–3)\in(Q_2$-$Q_3–4–3)$, $3\in(3–4)$, where sign “∈“ designates the first field belonging to the second one. Other 13 fields (8 one-dimensional and 5 – zero-dimensional) differ from their neighbors by the crossing surfaces and phase regions, but coincide in phase reactions and the set of microconstituents for the phase assemblages: $(p_4$-$4)\in(p_4$-4-Q_3-$e_6)$, $(3$-$4)\in(Q_2$-Q_3-4-$3)$, $(3$-$Q_1)\in(Q_1$-Q_2-$3)$, $(2$-$5)\in(R_1$-1-2-$5)$, $(R_6$-$2)\in(R_6$-1-$2)$, $(5$-$6)\in(R_1$-5-6-$7)$, $(6$-$8)\in(6$-

7-8), (8-9)∈(p_1-7-8-9-e_1), 2∈(1-2), 5∈(R_1-5), 6∈(6-7), 8∈(7-8), 9∈(e_1-9). Two one-dimensional fields (Q_2-9)∈(Q_2-8-9) and (Q_1-Q_2)∈(Q_1-Q_2-8-6) haven't the unique microconstituents, but differ the neighbor two-dimensional fields by the scheme of solidification. These fields belong to the liquidus curves and therefore the reaction of primary crystallization $L^1 \to R_1^1$ is absent.

Let's consider the crystallization stages for two-dimensional field Q_2-8-9 (triangle $R_2R_6R_7$) (Fig. 2a). Mass center G intersects the phase regions L+R_1, L+R_1+R_2, L+R_2+R_6, R_2+R_6+R_7, two planes of four-phase regrouping of phases (at the temperature of invariant points Q_2 and Q_3). The composition of melt changes along the extension of segment R_1-G_1 to liquidus line e_1Q_2 when the point G passes through the region L+CaO. Then mass center G falls into phase regions L+R_1+R_2 and L+R_2+R_6 (with the reaction Q2: $L^{Q2}+R_1 \to R_2^{Q2}+R_6^{Q2}$ between them) and the composition of melt moves along the liquidus curves e_1Q_2 and Q_2Q_3 correspondingly. The crystallization finishes on the subsolidus simplex $R_2R_6R_7$ at the temperature of point Q_3.

On the diagram of vertical materials balance (Fig. 2b) we can deduce the stages of phase transformations: $L^1 \to R_1^1$, $L^{e1} \to R_1^{R2}+R_2^{R1}$, $L^{Q2}+R_1 \to R_2^{Q2}+R_6^{Q2}$, $L^{\text{eп}} \to R_2^{R6,\text{eп}}+R_6^{R2,\text{eп}}$, $L^{Q3}+R_6 \to R_2^{Q3}+R_7^{Q3}$ with the forming of microconstituents R_2^{R1}, R_2^{Q2}, R_6^{Q2}, $R_2^{R6,\text{eп}}$, $R_6^{R2,\text{eп}}$, R_2^{Q3}, R_7^{Q3}. Since the solidification finishes on the simplex $R_2R_6R_7$, then the crystals R_1^1 and R_1^{R2} are absent as the microconstituents (they are expended during quasiperitectic reaction Q_2).

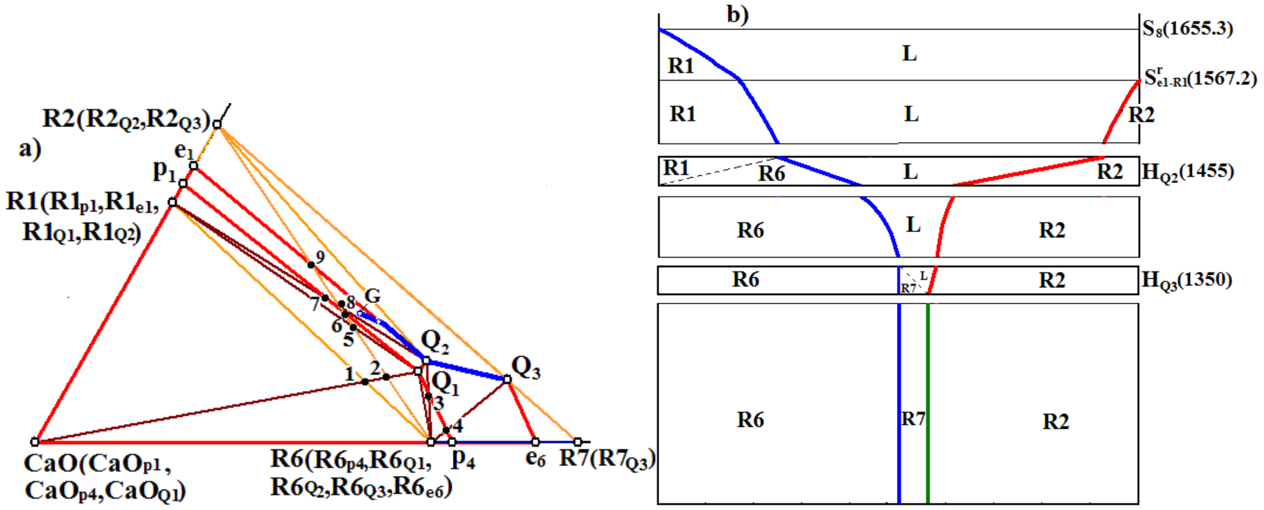

Fig. 2. Crystallization path (a) and mass balances (b) for composition G
(compounds legends: R1 – C_3S, R2 – C_2S, R6 – C_3A, R7 – $C_{12}A_7$)

Summary

Computer model of PD gives the possibility to analyze the crystallization stages for any composition and to find the concentration fields both with individual set of microstructure elements and the fields at which the crystallization scheme and microconstituents of phases assemblage coincide with those in the adjoining fields. It is used as an important tool to investigate multicomponent system, to correct its constitutional diagram, to design the miscrostructures of heterogeneous material, to decipher the genotype of heterogeneous material [14]. One more reason for the microstructures variety is the competition of crystals with different dispersity, when a field of invariant reaction is divided into the fragments with the tiny eutectical crystals, with more large primary crystals and with the both type of these crystals.

The obtained model of phase diagram CaO-Al_2O_3-SiO_2 is used as a template for the simulation of systems CaO-Al_2O_3-Fe_2O_3, CaO-SiO_2-Fe_2O_3, Al_2O_3-Fe_2O_3-SiO_2. The detail analysis of concentration fields of these ternary systems is a base for investigation of quaternary system CaO-Al_2O_3-Fe_2O_3-SiO_2, which has a great importance in the theory and practice for obtaining of Portland cement [15-16] including ferric oxide Fe_2O_3.

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