Computer models of phase diagrams for ceramic systems.

**TiO₂-SiO₂-Al₂O₃** and **ZrO₂-SiO₂-Al₂O₃**

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**Abstract**

The computer models and the analysis of structure for phase diagrams of ternary systems **TiO₂-SiO₂-Al₂O₃** and **ZrO₂-SiO₂-Al₂O₃** were performed. The calculation possibility of the crystallization paths and the diagrams of vertical and horizontal mass balances are demonstrated.

Keywords: computer model, phase diagrams, ceramic systems.

**1. Introduction**

Along with the experimental and thermodynamic investigation methods of phase diagrams of ceramic systems [1-6], one of the most effective methods to analyze them is to develop the 3D computer models, based on the description of phase regions boundaries [7-8].

The phase regions boundaries are reproduced and 3D models of phase diagrams are constructed on the basis of the scheme of mono- and invariant equilibria, which is compiled from data about the structure of binary systems and the proceeding invariant reactions. The elaborated models permit to calculate the isothermal sections and isopleths and to obtain the data about the crystallization stages for any part of phase diagrams.

We considered the phase diagrams of systems of **TiO₂-SiO₂-Al₂O₃** and **ZrO₂-SiO₂-Al₂O₃**, as an example.

**2. Model of TiO₂-SiO₂-Al₂O₃ T-x-y diagram**

The phase diagram of system **TiO₂-SiO₂-Al₂O₃** (A-B-C) is characterized by the presence of immiscibility surface from the side of binary system SiO₂-TiO₂ and two congruently melting compounds: R₃ = 3Al₂O₃ and R₄ = Al₂O₃·TiO₂ – from two other binary systems. The ternary system has one eutectic (Lₑ→TiO₂+SiO₂+R₃) and two quasiperitectic (Lₑ→SiO₂+R₄→R₃+R₄, Lₑ→TiO₂+SiO₂+R₃) invariant transformations.

Using the coordinates of binary and ternary points as an initial data [1,9], the model of phase diagram containing an immiscibility surface was assembled (i), 5 liquidus surfaces (q₁, q₂, q₃, q₄, q₅), 17 ruled surfaces (3i+14q²), 3 horizontal complexes at temperatures of invariant points (h₁q₀, h₁q₂) and 2 vertical planes, which are the degenerated ruled surfaces on the borders of the two-phase regions B+R2 and R1+R2 (Fig. 1).

The phase diagram includes 8 two-phase regions (L₁+L₂, L₁+L₃, L₁+B, L₁+C, L₁+R₁, L₁+R₂, B+R₂, R₁+R₂) and 11 three-phase regions (L₁+L₃+L₄, L₁+L₃+L₄+R₂, L₁+R₁+R₂, B+R₁+R₂, L₁+C+R₁, L₁+C+R₂, L₁+R₁+R₂, A+B+R₂, B+R₁+R₂, C+R₁+R₂, B+R₂+R₁), as well as two horizontal planes of four-phase regrouping of masses: L₁+C→R₁+R₂+R₄ and L₁+C→R₂+R₄.

The melt composition moves along the ray R₂G to the liquidus line c_BaQ₁, while passing through two-phase region L₁+R₁. Then mass center G falls into three-phase region L₁+C+R₁ and shifts along the monovariant liquidus line c_BaQ₂. After, it changes along liquidus line Q₁Q₂ at the intersection of three-phase region L₁+R₁+R₂ and two simplexes R₁Q₁ and R₂Q₂ of the horizontal complexes at the temperatures of the invariant points Q₁ and Q₂. Phase L is absent at the temperature below the plane Q₂ and the composition falls in the solid three-phase region B+R₁+R₂.

Crystallization stages are confirmed by the diagrams of vertical mass balances (Fig. 2. b), which allow to analyze the crystallization stages in the entire temperature range for the selected mass center. Given mass center G intersects the liquidus surface q₂, and falls into the two-phase region L₁+R₁, where the reaction of primary crystallization L₁→R₁ takes place. Then the melt crosses the ruled surface q₃, on the border of three-phase region L₁+C+R₁ with the proceeding of monovariant eutectic reaction L₁+C→R₁.

Further, the melt puts on the horizontal complex at the temperature of ternary quasiperitectic point Q₃, where the four-
Fig. 1. XY projection (a) and 3D model (b) of TiO$_2$-SiO$_2$-Al$_2$O$_3$ (A-B-C) T-x-y diagram
1. ábra TiO$_2$-SiO$_2$-Al$_2$O$_3$ (A-B-C) T-x-y diagram XY projekciója (a) és 3D modellje (b)

Fig. 2. Crystallization path (a) and diagrams of mass balances:
vertical – for the composition G (b) and horizontal (d,e) - for two isotherms of isopleth
M(0.194; 0.806; 0)-N(0.194; 0; 0.806)
2. ábra Az M(0.194; 0.806; 0)-N(0.194; 0; 0.806) csomótörés két éstromra vonatkozó
(a) kristályképződés út; (b) függőleges irányú tömeggyengés diagram a G jelű összetételre;
(d,e) vízszintes irányú tömeggyengés diagram a G jelű összetételre
Phase regrouping of masses $L^{01}+C \rightarrow R^{01}_1 + R^{01}_2$ takes place. As the result the crystal C is fully expended during this reaction, but the crystals $R_1$ and $R_2$ are increased (therefore the crystal C is not included in the final set of micro-constituents).

Then there is the postperitectic secondary (eutectic) crystallization $L^{n} \rightarrow R^{1n}_1 + R^{2n}_2$ in the three-phase regions $L + R_1 + R_2$. When mass center gets to the horizontal complex $h_{Q_3}$ at the temperature of ternary quasiperitectic point $Q_3$, the invariant quasiperitectic reaction $L^{Q_2} + R_1 \rightarrow B^{Q_2} + R_2^{Q_2}$ ends with the deficit of melt and below there are only crystals B, $R_1$ and $R_2$. As a result this field is characterized by the following set of micro-constituents: $R_1^{1n}$, $R_1^{Q_1}$, $R_2^{Q_1}$, $R_1^{1n}$, $R_2^{n}$, $B^{Q_2}$, $R_2^{Q_2}$.

The diagrams of horizontal mass balances at temperatures 1730° (Fig. 2.d) and 1570° (Fig. 2.e) were calculated on the isopleth M(0.194; 0.806; 0)-N(0.194; 0; 0.806) passing through the composition G (Fig. 2.c). Additionally, the isothermal sections were calculated at the same temperatures (Fig. 3).

3. Model for phase diagram of system $\text{ZrO}_2$-$\text{SiO}_2$-$\text{Al}_2\text{O}_3$

The phase diagram of the system $\text{ZrO}_2$-$\text{SiO}_2$-$\text{Al}_2\text{O}_3$ (A-B-C) has an immiscibility surface [1,10]. Compound $R_2 = \text{ZrO}_2 \times \text{SiO}_2$ decomposes without melt in the binary system $\text{ZrO}_2$-$\text{SiO}_2$ and the congruently melting compound $3\text{Al}_2\text{O}_3 \times 2\text{SiO}_2$ exists in...
the binary system Al2O3-SiO2 [1]. There is a maximum point e_x on monovariant liquidus line QE1, which is the eutectic of quasi-binary section R1-R2.

There are the contradictions in the experimental data concerning the liquidus structure of system ZrO2-SiO2-Al2O3. Authors of [1, 11] suggest the existence of four liquidus surfaces (excluding phase ZrO2+SiO2) and two invariant eutectic points. Authors of [2] show a fragment of phase diagram near the component SiO2 with the liquidus field corresponding to points. Authors of [2] show a fragment of phase diagram near the component SiO2 with the liquidus field corresponding to points.

Because of the compound ZrO2+SiO2 exists at the temperature higher than the invariant points, then it must correspond to the liquidus field, so we used variant [2] for the phase diagram assembling.

The model of phase diagram (Fig. 4) contains the immiscibility surface (i), 5 liquidus surfaces (q_A, q_B, q_C, q_R1, q_R2), 19 ruled surfaces (3r+16qr), 4 horizontal complexes at the temperaturesemax on monovariant liquidus line QE1, which is the eutectic of phase regions (L1+L2+A, L+A+B, L+A+C, L+A+R1, L+A+R2, L+B+R1, L+B+R2, L+C+R1, L+R1+R2, A+C+R1, A+R1+R2, B+R1+R2). A similar investigation for system TiO2-SiO2-Al2O3 can be used for the prediction of geometrical structure of ceramic systems as well as can create a theoretical basis for the comprehensive investigation of the phase diagrams.

4. Summary

Computer models of phase diagrams can produce the information about processes taking place in the investigated ceramic systems as well as can create a theoretical basis for experimental work. A detailed analysis of the structure of phase diagrams for systems TiO2-SiO2-Al2O3 and ZrO2-SiO2-Al2O3 can be used for the prediction of geometrical structure and the development of computer model of phase diagram for the quaternary system TiO2-ZrO2-SiO2-Al2O3 which is applied in membrane technologies [12].

The comprehensive investigation of the phase diagrams of ceramic systems involves the analysis of crystallization processes in any part of the diagram. Forecast of microstructural constituents for the concentration fields of different dimensions (obtained by the projecting of all elements of the phase diagram into the Gibbs triangle) helps to plan and to reduce the volume of experimental study [13-16].

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References


Ref:


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