3D Computer Models of the Ag–Sb–Sn and MgO–Al$_2$O$_3$–SiO$_2$

$T-x-y$ Diagrams

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Three-dimensional (3D) computer models of Ag–Sb–Sn and MgO–Al$_2$O$_3$–SiO$_2$ systems $T-x-y$ diagrams have been designed. For the metal system two versions of 3D model of its phase diagram have been constructed according to the contradictions in the temperature intervals of the compound Sb$_2$Sn$_3$ stability. Possibilities of the analysis of the stages of crystallization and prediction of microstructural constituents with the aid of the calculation of vertical mass balance diagrams are demonstrated on the basis of the 3D computer model for the oxide system.

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1. Introduction

The study of the Ag–Sb–Sn system is connected with the creation of the lead-free solders. The MgO-SiO$_2$-Al$_2$O$_3$ system has wide practical application in the technology of the ceramic and glass-ceramic materials creation. It is used during the study and the description of the forsterite, periclase, spinel, corundum and mullite refractory materials. Its compounds, such as forsterite, periclase, spinel, corundum and mullite refractory materials. Its compounds, such as forsterite, periclase, spinel, corundum and mullite refractory materials.

Thermodynamic investigation methods of the metallic and ceramic systems are usually aimed to the solution of the applied problems, connected with the calculation of the thermodynamic and thermophysical properties [5–8]. But they do not give the possibility to restore the geometric structure of phase diagrams in total, whereas the assembling of 3D models from the phase regions makes it possible to obtain the complete model of phase diagram and to use it as a material-scientist tool for obtaining the data about the crystallization stages and the forming of microstructure constituents [9].

The universal description of all phase transformations within the ternary system can be obtained by its $T-x-y$ diagram 3D computer model [10, 11]. All available data are analyzed before the model construction. Usually this information is limited by binary systems, $x-y$ liquidus projection, table of phase’s compositions, involved in the invariant reactions, by several isothermal sections and isopleths [5, 6, 12–14]. Then a scheme of the uni- and invariant states is constructed. This modernized Shell’ scheme is the excellent tool for “the conclusion” of the description of the $T-x-y$ diagram geometric structure in the tabular, and then in the 3D form. The 3D scheme of uni- and invariant states is the base of the $T-x-y$ diagram, which contains only three-phase regions (ruled surfaces) and isothermal (horizontal) planes, correspond-
Obviously, the 3D model is designed in two versions, too. The first one corresponds to [12–14], where the allotropy transformation passes as the eutectoid reaction E, and the 3D model consists of 99 surfaces and 62 phase regions (Fig. 3a). In another version with two eutectoid reactions E1 and E2, constructed according to [5, 17], the 3D model consists of 109 surfaces and 66 phase regions. Consequently, the conditions for the compound Sb$_2$Sn$_3$ existence require additional experimental study.

Fig. 1. Variants of the T−x diagrams for the system Sb–Sn: [12] (a), [5] (b).

Fig. 2. Variants of the uni- and invariant states scheme according to versions of the binary system Sb–Sn: (a) Fig. 1a, (b) Fig. 1b.

The obtained 3D model makes it possible to analyze the T−x−y diagram in the three-dimensional form or with the aid of any section. For instance, the model isothermal section at 250°C (Fig. 3d) shows that Sb$_2$Sn$_3$ liquidus curve is missed in the analogous section in [12] and this curve is in the same section in [13], but the L + b−SbSn phase region is indicated instead of the L + Sn$_3$Sb$_2$ region.

Fig. 3. 3D model of the Ag–Sb–Sn T−x−y diagram (a), its liquidus x−y projection (b), isothermal section at T = 250°C: [12] (c), 3D model (d).

3. 3D model of the MgO–SiO$_2$–Al$_2$O$_3$ T−x−y diagram

The MgO–SiO$_2$–Al$_2$O$_3$ (A−B−C) T−x−y diagram has complicated geometrical construction. It includes four binary $R_1 = 2$MgO·SiO$_2$, $R_2 = $MgO·SiO$_2$, $R_5 = 3$Al$_2$O$_3$·2SiO$_2$, $R_1 = $MgO·Al$_2$O$_3$ and two ternary $R_5 = 4$MgO·5Al$_2$O$_3$·2SiO$_2$, $R_6 = 2$MgO·2Al$_2$O$_3$·5SiO$_2$ compounds; it is characterized by 11 invariant transformations: one peritectic $L_p + R_3 + R_4 \rightarrow R_5$, five quasi-peritectic $L_{Q1} + R_4 \rightarrow R_4 + R_6$, $L_{Q2} + R_5 \rightarrow R_4 + R_6$, $L_{Q3} + R_3 \rightarrow R_5 + R_6$, $L_{Q4} + C \rightarrow R_3 + R_4$, $L_{Q5} + R_3 \rightarrow B_1 + R_6$, three eutectic $L_{E1} \rightarrow A + R_1 + R_4$, $L_{E2} \rightarrow R_1 + R_2 + R_6$, $L_{E3} \rightarrow B_1 + R_2 + R_6$, two metatectic $B \rightarrow LV + B_1 + R_2$ and $B \rightarrow LV + B_1 + R_3$, corresponding to transfers from the high-temperature polymorphous modification of silica (B — cristobalite) to low-temperature one ($B_1$ — the tridymite) in the presence of liquid and compounds $R_2$ and $R_3$ [18, 19]. There is the immiscibility region of two melts beginning from the binary system MgO–SiO$_2$. Design of the 3D model took into account also three Van Rein’ points in liquidus univariant curves $e_1 \in Q_1Q_1$, $e_2 \in e_2e_3$ and $e_3 \in Q_3Q_5$. 

Fig. 3. 3D model of the Ag–Sb–Sn T−x−y diagram (a), its liquidus x−y projection (b), isothermal section at T = 250°C: [12] (c), 3D model (d).
The MgO–SiO$_2$–Al$_2$O$_3$ $T$–$x$–$y$ diagram 3D model is formed by ten liquidus surfaces $q$, corresponding to primary crystallization of initial components MgO–A, Al$_2$O$_3$ = C, two SiO$_2$ polymorphous modifications ($B$ — cristobalite and $B_1$ — the tridymite) and six compounds $R1$–$R6$. It includes also the liquid immiscibility surface $i$, 75 ruled surfaces as borders of two- and three-phase regions, 11 horizontal complexes at invariant points temperature; it contains 21 two-phase and 30 three-phase regions (Fig. 4a). According to experimental data points $V_1$ and $V_2$ have the same temperature and the liquidus univariant curve $V_1 V_2$ is located horizontally. Therefore the univariant peritectic reaction $L + B_1 + R2 \rightarrow L V_2 + B_1 + R3$, are degenerated into the triangles $B V_1 R2 V_1$ and $B V_2 R3 V_2$, with the superposition of the four points $B V_1, B_{1V1}, B_{V2}, B_{1V2}$ in the point $B V$. In this case the phase region $L + B_1 + B_2$ is degenerated into the plane $V_1 V_2 B V$ and the univariant peritectic reaction $L^p + B \rightarrow B_1^p$, corresponding to it, occurs at constant temperature.

Projections of all geometric elements of the $T$–$x$–$y$ diagram divide its concentration complex into 100 two-dimensional, 170 one-dimensional and 71 zero-dimensional concentration fields. In this case it is revealed that many concentration fields with the coinciding concentration fields, located under the liquid immiscibility regions and the cristobalite liquidus surface. This is connected with the fact that the products of reactions taking place in the phase regions $L + L_1, L_1 + L_1 + B, L + B$ are expanded in the earlier stages of crystallization and do not influence the total set of microstructure elements. It is also confirmed by the vertical mass balance diagrams (Fig. 4b).

Let us consider the mass center $G$ (0.085, 0.808, 0.107) in the cristobalite liquidus field. It intersects 5 phase regions: $L + B, L + B + B_1$ (degenerated into the plane), $L + B_1, L + B_1 + R6, B_1 + R2 + R6$ with reactions as following: primary crystallization $L^1 \rightarrow B^1$; univariant peritectic reaction $L^p + B \rightarrow B_1^p$; post-peritectic primary crystallization $L^{p^1} \rightarrow B_{1p^1}$; post-peritectic secondary eutectic reaction $L^{p^2} + B_1^{p^2} \rightarrow B_{1p^2}$; invariant eutectic reaction $L^{E3} \rightarrow B_{1E3}^{E3} + R_2^{E3} + R_6^{E3}$ (Fig. 4b). Since the crystals $B$ fully disappear as a result of reaction $L^p + B \rightarrow B_1^p$, they are not included in the set of micro-constituents. So the field in consideration is characterized by the following micro-constituents: $B_1^p, B_{1p^1}, B_{1p^2}, R_6^{E3}, R_2^{E3}, R_{1E3}^{E3}$.  

4. Conclusion

1. 3D computer models are the convenient tool for verification of data, represented in the different publications. Two variants of 3D model of the Ag–Sb–Sn $T$–$x$–$y$ diagram have been constructed in accordance to two versions of existence/decomposition of the Sb$_2$Sn$_3$ compound. Furthermore, some inaccuracies in the isothermal section at 250 °C are discovered with their aid.

Fig. 4. $x$–$y$ projection of the MgO–SiO$_2$–Al$_2$O$_3$ $T$–$x$–$y$ diagram (a), the vertical mass balance diagram for the mass center $G$ (0.085, 0.808, 0.107) (b).

2. The 3D computer model of the MgO–SiO$_2$–Al$_2$O$_3$ $T$–$x$–$y$ diagram takes into account all topological features of its structure: cupola and immiscibility regions, Van Reim’s points ($e_1, e_2, e_3$), allotropy of SiO$_2$, formation of six intermediate compounds. The model is used as a tool for study of crystallization schemes and microstructure prediction. It is established on its basis that the concentration fields in the boundaries of phase regions with the liquid immiscibility do not possess the unique sets of microstructure elements and their characteristics coincide with the concentration fields, located under the cristobalite liquidus.

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