Liquid immiscibility gap technology within the ternary systems

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T-x-y diagrams with liquid immiscibility is employed widely for the solution of problem associated with a refractory compounds obtaining (borides, silicides and intermetallides). Besides the well-known flax method with only one solvent, the immiscibility gap method for the metallic systems was offered in the third millennium [1-2]. In this method the synthesis and crystallization of compounds have place on the border of two solvents. As this technology includes many unknown details, computer models of phase diagrams will be a useful tool for its understanding.

1. Immiscibility gap method.

The experiments that were carried out indicate the possibility of obtaining various compounds and crystal forms by this method, as well as the existence of various processes in immiscible systems whose analysis presents great interest [1-2]. The new method uses the ratio of densities of components in immiscible systems to perform processes of interdiffusion and convection for realization of chemical reactions on the immiscibility boundary and subsequent crystallization of the generated compounds. The method has a number of advantages in comparison with usual solution melt method. The interdiffusion and convection promote a fuller contact of reacting components on the immiscibility boundary of melts. This leads to a more complete yield of synthesis.

The new method allows one to obtain various shapes of crystals (isomeric, lamellar, needle), while the solution-melt method obtains crystals of one shape (for example, plates of TiB_2) [1-2]. It is possible to produce nanoparticles (or particles of size close to them) (for example, needles of TiB_2 in system Ca/Ce) under appropriate conditions and initial sizes and shape of reacting particles in certain systems. The interdiffusion and convection can facilitate production of various solid solutions and also can contribute to production of new compounds from initial reacting components with sharply distinguished densities, since in the usual solution-melt method such components settle above and below the melt and cannot react.

It is necessary to emphasize that synthesis and crystallization of compounds in immiscible systems is a rather new method, which is necessary to research and develop further. Generic aspects of the new method concern the boundary temperature and concentration immiscibility conditions of melts of elements, the presence of an immiscibility region bounded by a binodal, and the relation of densities of initial reacting components, utilization of mixed solvents, and existence of an immiscibility boundary. As nobody yet used the ternary systems for this new method of syntheses, the simulation of some T-x-y diagrams was made.

2. T-x-y diagrams with liquid immiscibility.

Phase diagrams with immiscibility can be calculated and investigated using both thermodynamic methods [3-5] and mathematic ones. The elaboration of the algorithms and attendant software based on a mathematical description of phase diagrams surfaces makes alloy to obtain the space model of T-x-y diagrams and its investigation to do. In this case the set of initial experimental data concerning the type of interaction taking place in the system and the data about surfaces contour are used. The hypothetic data can be applied at the deficiency of such initial information. The kinematical method of T-x-y diagrams surfaces description is chosen as the most efficient method [6-7].

Computer templates is convenient to use for the simulation of phase diagrams with immiscibility surfaces having a great quantity of topological modifications produced by different

arrangements and intersections of monovariant lines and immiscibility surfaces [8-9], and at the degenerations of solidus and solvus surfaces [10].

Let's consider the models of T-x-y diagrams with mono- and invariant monotectic equilibrium and monovariant syntectic equilibria as an example.

2.1. Monovariant monotectic equilibrium.

T-x-y diagram with monovariant monotectic equilibrium without solid phase solubility is formed by by surface of liquid immiscibility (i: $mknk^0$), 3 liquidus surfaces (Q_A: $Amk^0ne_{AB}Ee_{AC}$, Q_B: $Be_{AB}Ee_{BC}$, Q_C: $Ce_{AC}Ee_{BC}$), 9 ruled surfaces (i^r: $mnkk^0$, i^r_m: $A_mmk^0A_{ko}$, i^r_n: $A_mnk^0A_{ko}$, Q^r_{AB}: $A_Be_{AB}EA_E$, Q^r_{BA}: $B_Ae_{AB}EB_E$, Q^r_{AC}: $A_Ce_{AC}EA_E$, Q^r_{CA}: $C_{CA}e_{AC}EC_E$, Q^r_{BC}: $B_Ce_{BC}EB_E$, Q^r_{CB}: $C_Be_{BC}EC_E$) and horizontal complex at invariant eutectic point E (H_E: $A_EB_EC_EE$) (Fig. 1a) [8]. The coordinates of initial components (A, B, C), binary eutectic points (e_{AB}, e_{AC}, e_{BC}), a ternary eutectic point (E), points on the contour of immiscibility cupola (k, k^0, m, n) and appropriate points on the edges of prizm (I_{eIJ}, I_E, $I_{m(n)}$, I_{k0} (I=A,B,C)) are given as an initial data at phase diagram model.

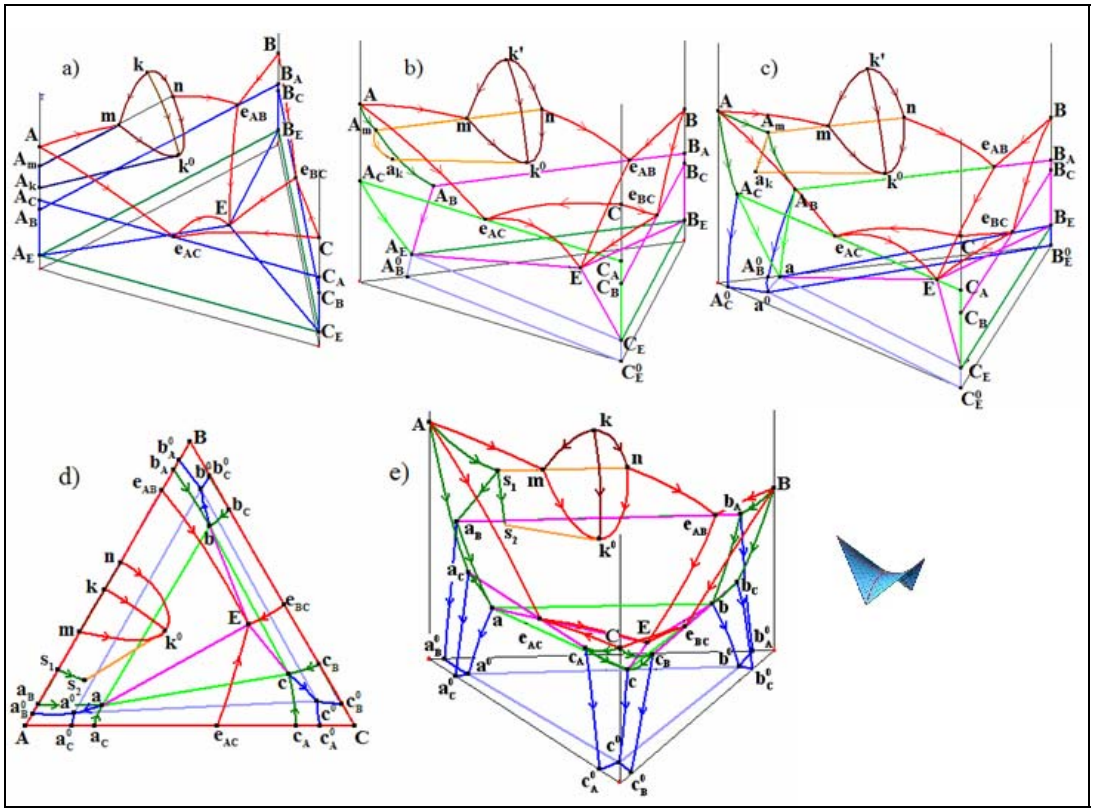

Fig. 1. Model of phase diagram with monovariant monotectic equilibrium without (a) and with solid-phase solubility in one (b-c) and three (d-e) components

The use of given computer model we can consider step by step the appearance of solid phase solubility at one (Fig. 1b-c), two and three components (Fig. 1d-e). Fig. 1b-c presents the appearance of solid phase solubility in component A in binary system AB (Fig. 1b) and both binary system A-B and A-C (Fig. 1c). In first case we can see the line of solidus (AA_m, A_mA_B, A_BA_E, A_CA_E, A_mA_k - pseudo-fold) and solvus ($A_EA^0_B$), but second case visualizes the surfaces of solidus ($AA_CaA_BA_m$ with fold A_mA_k) and solvus ($A_Baa^0A^0_B$, $A_Caa^0A^0_C$). Simulation of solidus and solvus surfaces at all three compounds gives the complete T-x-y diagram with solid phases (Fig. 1d-e). As models come to be more complex the coordinates of points on the contour of solidus and solvus surfaces are added as initial data of model.

2.2. Invariant monotectic equilibrium.

T-x-y diagram with invariant monotectic equilibrium and solid phases solubility includes surface of liquid immiscibility (i: mMk^0Qnk), 4 liquidus surfaces (Q_A: $AmMe_{AC}$, Q_{A1}: $ne_{AB}EQ$, Q_B: $Be_{AB}Ee_{BC}$, Q_C: $Ce_{AC}Ee_{BC}$), 4 solidus surfaces (S_A: $Am_Ba_Qa_C$, S_{A1}: $m_Ba_Ba_Ea_Q$, S_B: $Bb_Ab_Eb_C$, S_C: $Cc_Ac_Qc_Ec_B$), 6 solvus surfaces (V_{AB}: $a_Ba_Ea^0{}_Ea^0{}_B$, V_{AC}: $a_Ca_Qa_Ea^0{}_Ea^0{}_C$, V_{BA}: $b_Ab_Eb^0{}_Eb^0{}_A$, V_{BC}: $b_Cb_Eb^0{}_Eb^0{}_C$, V_{CA}: $c_Ac_Qc_Ec^0{}_Ec^0{}_A$, V_{CV}: $c_Bc_Ec^0{}_Ec^0{}_B$), 21 ruled surfaces ($6i^r+8Q^r+4S^r+3V^r$) and 2 horizontal complex at invariant points E and M(Q). The peculiarity of phase diagram is the surface of liquid immiscibility containing two maximum points (k, k^0) on the borders of edge kk^0 and two minimum points (M, Q) at the same temperature. Solidus surface $Cc_Ac_Qc_Ec_B$ includes the fold $c_{k0}c_Q$ and the adjoining solvus $c_Ac_Qc_Ec^0{}_Ec^0{}_A$ has five points on counter.

The use of computer model permits to find the error in the visualization of phase diagrams with liquid immiscibility gap [11]. In [9] the solvus surfaces have orthogonal position of some lines on the contours (Fig. 2c-d – solvus lines $C_AC^0{}_A$, $C_BC^0{}_B$ and $C_EC^0{}_E$ are projected into the points $C_A(C^0{}_A)$, $C_B(C^0{}_B)$ и $C_E(C^0{}_E)$). At that the projections of solvus surfaces with five points have not closed contour: line $C_A(C^0{}_A)$- $C_E(C^0{}_E)$ is absent (Fig. 2d).

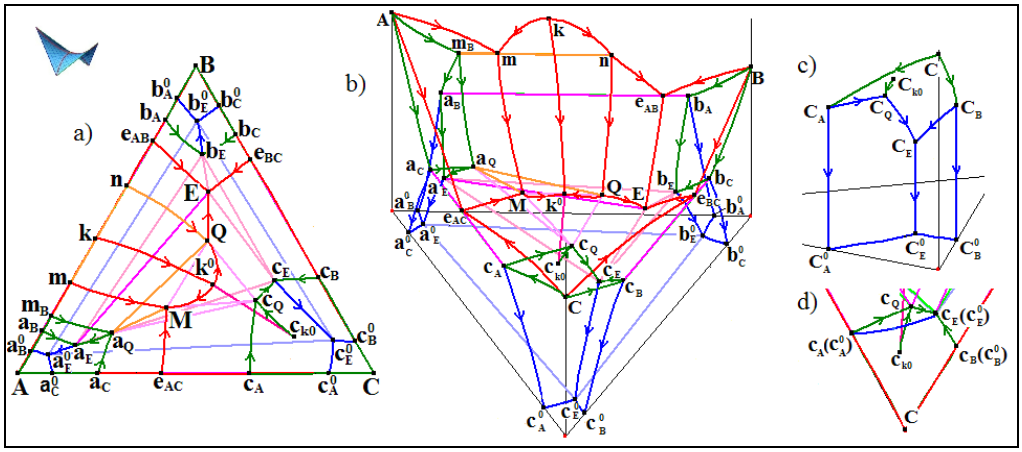

Fig. 2. XY projection (a) and 3D model (b) of phase diagram with invariant monotectic equilibrium; fragment with orthogonal position of lines on the contours of solvus surfaces (c-d)

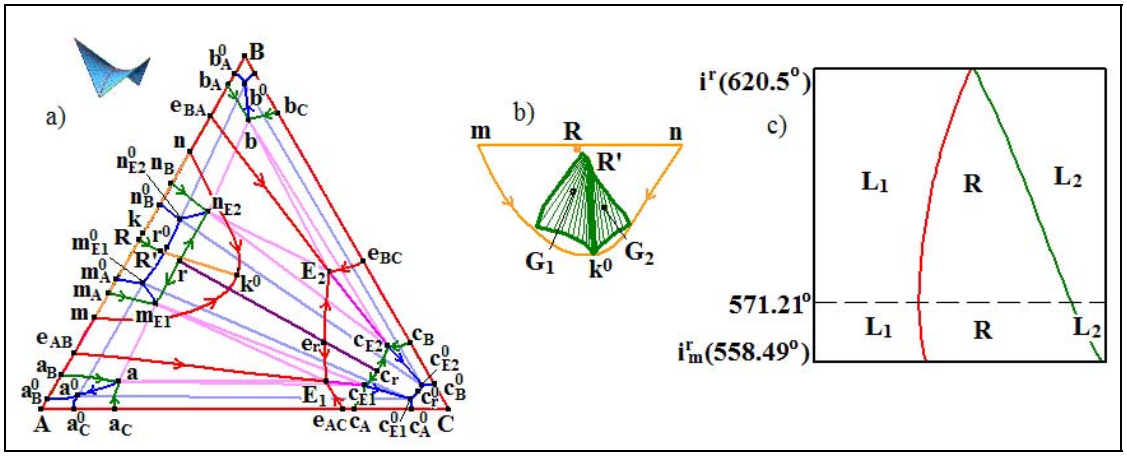

Fig. 3. XY projection of phase diagram with monovariant syntectic equilibrium (a), surfaces of two-phase reaction for phase region L_1+L_2+R (b) and the material balances for points G_1 (c)

2.3. Monovariant syntectic equilibrium.

T-x-y diagram with monovariant syntectic equilibrium has intermediate compound R in the AB binary system (Fig. 3a-b) and forms a surface of liquid immiscibility, 4 liquidus surfaces, 4 solidus surfaces, 10 solvus surfaces, 24 ruled surfaces ($3i^r+10Q^r+5S^r+6V^r$) and 2 horizontal planes at temperatures of the ternary eutectics (E_1 and E_2). The solidus surface $S_R(m_ARn_Bn_{E2}rm_{E1})$ has the fold RR' (the point R' is located at a temperature corresponding to the lower point k^0 of the liquid immiscibility surface) and maximum point r. The surfaces of liquid $Q_R(e_{AB}mk^0ne_{BA}E_2e_rE_1)$ and solidus $S_C(Cc_Ac_{E1}c_rc_{E2}c_B)$ contain maximum points e_r and c_r.

A transition of syntectic equilibrium $L_1+L_2\rightleftarrows R$ in monotectic one ($L_1\rightleftarrows L_2+R$ or $L_2\rightleftarrows L_1+R$) occurs in the phase region L_1+L_2+R [7-8]. In this case two surfaces with three-phase reaction type change having a common tie-line k^0R' are appeared (Fig. 3b-c). One, two or three surfaces of two-phase reaction can appear at the deformation of phase region L_1+L_2+R in such way that the line RR' is beyond the contour of line mk^0n in projection [7]. Usually this surface forms in the area of lines RR' and mk^0n intersection. More powerful transformation gives else two surfaces of two-phase reaction adjoining to tie-line $R'k^0$.

Using the mathematical methods of phase diagrams elements descriptions at the computer software allow to simulate all geometrical structure of diagram on a basis of minimum initial information. At that the effectiveness of corresponding physics-chemical systems study is increased: the visualization of diagram geometrical model and its sections has been possible, the founding of information about the results of initial components interaction for the work content reduction of new materials creation has become available. Such software makes possible to solve the problem of heterogeneous materials computer simulation.

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