New Phase Regions of Ir-Ru-Ti System with Eutectic-Peritectic Transformation

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Abstract. Special surfaces, corresponding to phase transformation type changing, have been found and designed within six three-phase regions of the system Ti-Ir-Ru with a help of 3D computer model of its T-x-y diagram.

1. Introduction

Three-phase transformation type changing in systems Ti-C-V, V-Zr-Cr, Mo-Zr-Cr, W-Zr-Cr, Mo-Zr-V, Nb-Ni-V, Zr-Ru-Ir, Ti-Ir-Ru have been found experimentally [1]. For instance, changing of the eutectic reaction L→ε+Ru (ε=$TiIr_3$) for the peritectic one L+ε→Ru has been known in A-B-C=Ti-Ir-Ru system [2], where R1=TiIr=δ=R, R2=TiRu=δ=R (R1 and R2 form continuous row of solid solution), R3=$TiIr_3$=ε, R4=Ti_3Ir=γ.

A method to construct the borders of the T-x-y diagram three-phase region fragments with the opposite signs of a solid phase mass increment in the process of the melt solidification has been offered in [3]. A ternary system A-B-C, bounded by eutectic system A-B, peritectic system B-C and A-C system with the continuous series of solid solutions, was used as a model for the computational experiment. An equation for a straight line of compositions with the zero increment of the solid phase β mass within the tie-triangle Lαβ had been derived. A concentration field of the three-phase region L+α+β was considered as seven domains with the different microstructure sets. The described algorithms permits: 1) to calculate the temperature of the three-phase transformation type changing; 2) to get at any temperature the straight line joining all compositions with the zero value of the solid phase mass increment that divides eutectic and peritectic fragments; 3) to divide the concentration projection of three-phase region into three domains with eutectic, peritectic and mixed type of reaction and to divide the three-phase region into the fragments with the eutectic or peritectic type of equilibrium. The method gave a possibility to settle contradictions between three-phase region eutectic and peritectic fragments borders determination methods [4]. According to the well-known tangents rule, temperature of three-phase transformation type changing is constant. However this rule is correct only for fixed compositions of the solid phases [5].

As it was found, a special surface appears within phase region in a case of 3-phase transformation type changing (figure 1) [6]. Moreover every three-phase region has always (theoretically) three this kind of surfaces. But a real three-phase region can have one, two, all three surfaces or no surfaces within its ruled borders (in agreement with its structure). For instance, the specific features of the melt crystallization with transition from syntectic equilibrium to monotectic one have been considered, and surfaces with a sign change of the mass increment within a three-phase region have been constructed and confirmed by the mass balances [7]. Phase region L1+L2+δ with two liquids L1 and L2 has two specific surfaces, which divide the region into three fragments: monotectic L1→L2+δ and L2→L1+δ fragments and a syntectic L1+L2→δ one between them (figure 2).

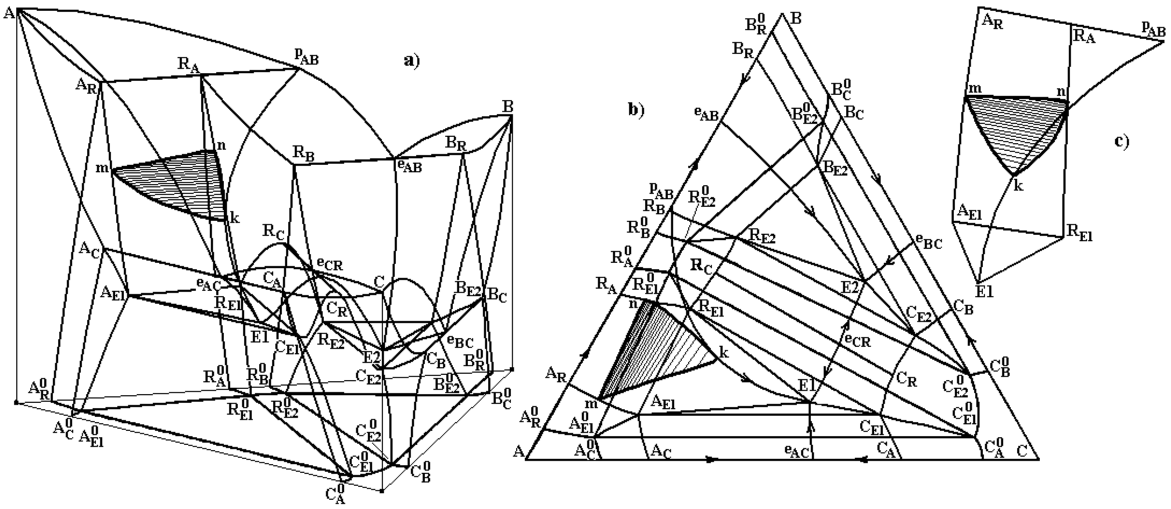


Figure 1. T-x-y diagram with a binary incongruent compound R (a, b) and surface mnk of three-phase transformation type changing from L+A→R for L→A+R (c).

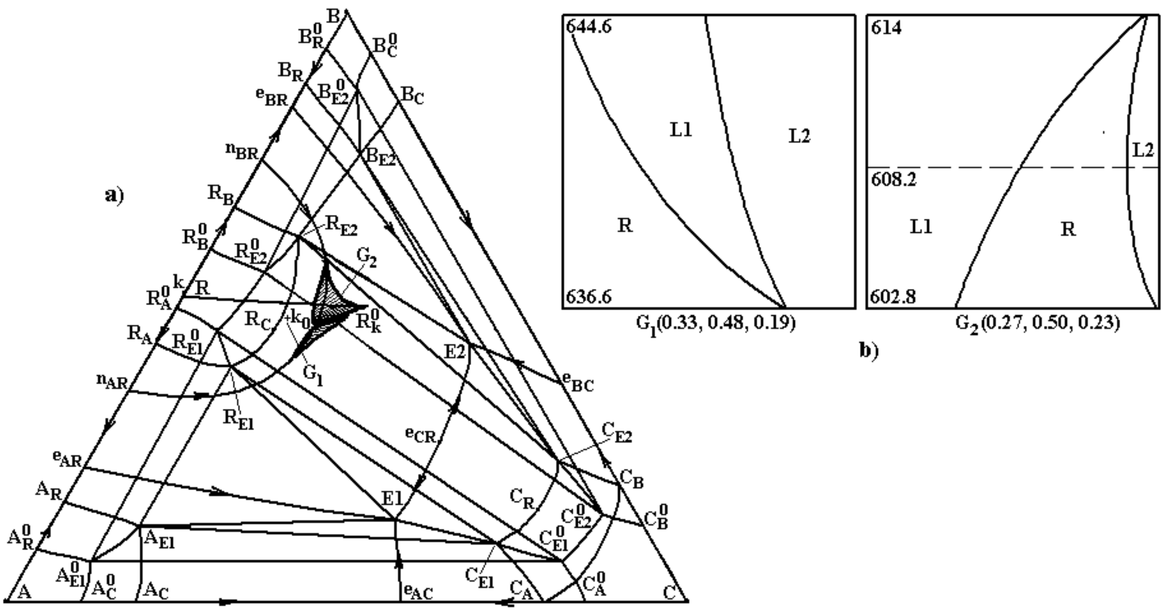
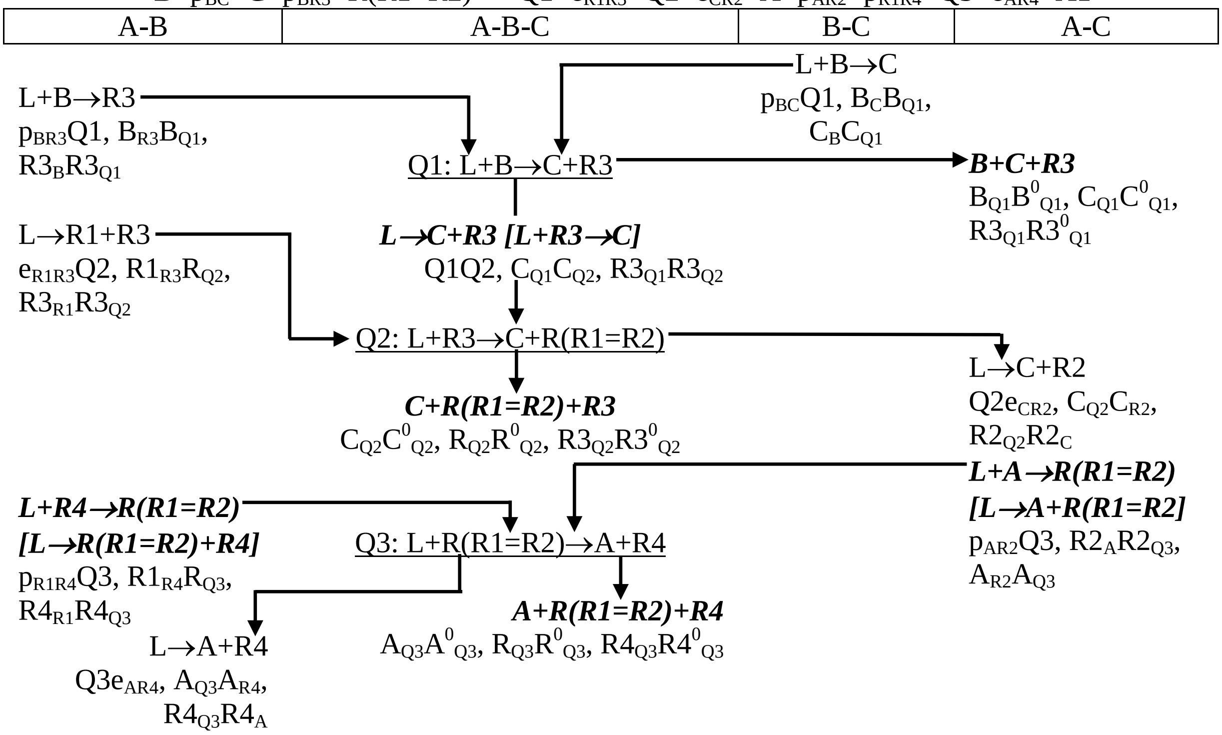


Figure 2. Univariant syntectic transformation (a) and its changing for monotectic one at 608.2 (b).

The geometrical sense of such surfaces is the ruled nature with a horizontal (isotherm) originating line. Their physical sense consists in the next: a three-phase transformation (for instance, L→α+β) on this originating line becomes temporally two-phase one (for instance, L→α) in a presence of third phase (β). Increment of phase mass (Δm_β), which is passive in this moment, changes sign, that is $\Delta m_\beta=0$ at $\Delta m_L<0$ and $\Delta m_\alpha>0$. So, this surface may be designated as "two-phase reaction surface". To find conditions when this surface appears in a three-phase region and to design it, is much more conveniently by means of 3D computer model of T-x-y diagram [8].

Table 1. 2D scheme* of uni- and invariant states with temperature row
$B>p_{BC}>C>p_{BR3}>R(R1=R2)$**$>Q1>e_{R1R3}>Q2>e_{CR2}>A>p_{AR2}>p_{R1R4}>Q3>e_{AR4}>A1$



* three-phase regions with phase transformation type changing are bold and italic
** binary compounds R1 and R2 in the ternary system form solid solution R=R1(R2), and this phase participates in the second-order phase transition R=R'

2. T-x-y diagram 3D computer model of Ti-Ir-Ru

To design computer model the scheme of uni- and invariant states in 2D (Table 1) and 3D (figure 5,a) variants is used [9]. It is a traditional Scheil reaction scheme, but with trajectories of phases, which participate in three-phase reactions. Such kind of scheme makes a reaction scheme more informative one and helps to understand T-x-y diagram construction and to be ready to create its computer model. There are other ideas to make the reaction scheme more informative. For instance, it is assumed that in ternary systems with second-order transitions corresponding to them univariant ones are degenerated to infinitely narrow phase fields [10]. This assumption means that second-order transition can be formally treated like first-order transition and is described by the Scheil scheme.

Firstly 3 planes for 3 invariant (Q1-Q3) reactions and 33 ruled surfaces for 11 univariant reactions (including 8 transformations with alloy L and three ones without L) are constructed (figure 5,a). They are boundaries of 8 type L+I+J and 3 type I+J+K three-phase regions. Then unruled surfaces are constructed: 6 liquidus and 6 solidus surfaces (Figure 3). Eight three-phase regions type L+I+J have neighbors of 8 two-phase regions type I+J. Eight pairs of solvus surfaces serve side borders of I+J regions (Figure 3,a). Except them 2 transus surfaces are in the T-x-y diagram. Two polymorphous modifications of titanium (A and A1, Ti=A) are between them. So, the T-x-y diagram consists of 75 surfaces (6 liquidus, 6 solidus, 16 solvus, 2 transus, 33 ruled surfaces, 12 planes (every of 3 complexes of invariant reactions is divided into 4 simplexes) and 32 phase regions (6 L+I and 6 I, where I=A, B, C, R, R3, R4; 8 L+I+J and 8 I+J, A+A1, 3 I+J+K). (Additional 2 surfaces correspond to second-order phase transition and are boundaries of the region R+R').

3. Three-phase regions with changing of phase transformation type

Computer model of T-x-y diagram gives additional information about processes of phase transformation type changing. Regions with liquid phase, L+γ+δ & L+Ti+δ (L+R4+R & L+A+R), have the only surface of two-phase reaction. Sub-solidus region Ir+Ru+ε (B+C+R3) is divided by three surfaces of two-phase reaction into four fragments. Three surfaces of two-phase reaction ($\Delta m_{Ru}=0$, $\Delta m_{\delta}=0$ and $\Delta m_{\varepsilon}=0$) within the region Ru+δ+ε (C+R+R3) form six fragments; eutectoid reactions are fulfilled in three of them and peritectoid ones are carried out between them (Figure 5,b). Reaction γ+Ti→δ (A+R4→R) is changing for γ→Ti+δ (R4→A+R).

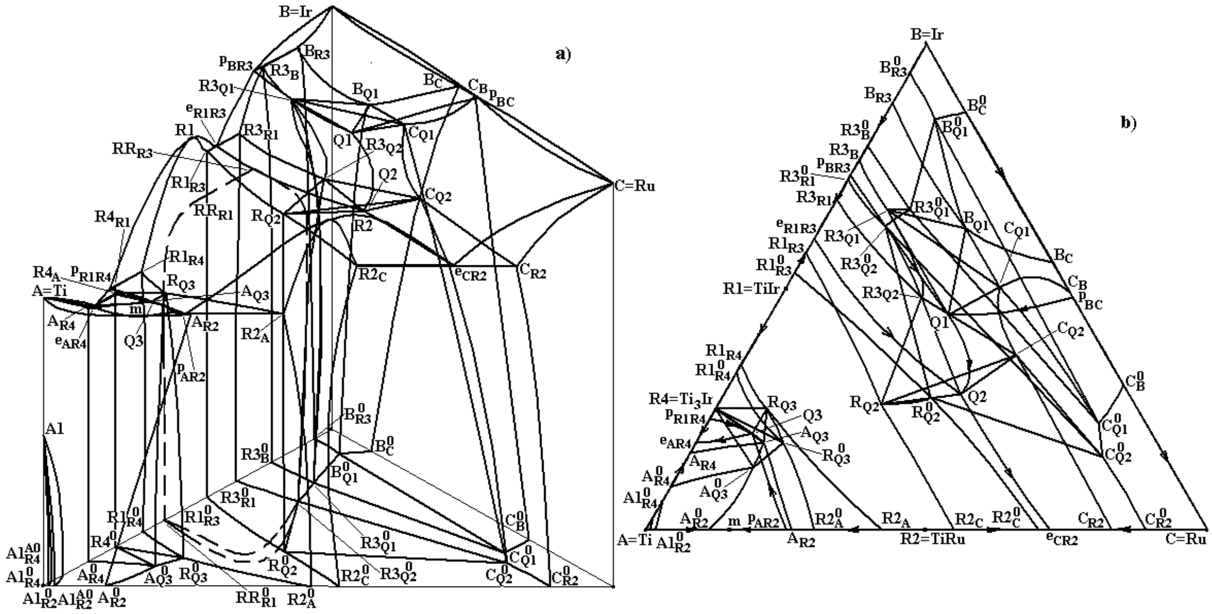


Figure 3. T-x-y diagram Ti-Ir-Ru=A-B-C computer model (a) and its x-y projection (b) (second-order phase transition R=R' is shown by dashed lines).

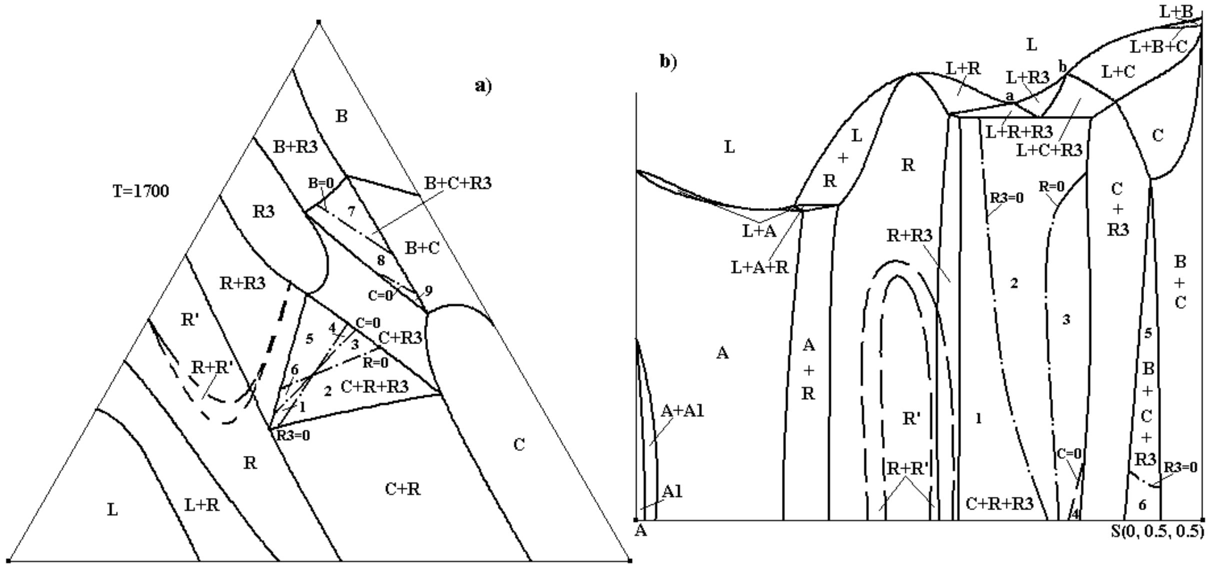


Figure 4. Isotherm T=1700°C (a) & isopleth A-S(0, 0.5, 0.5) (b) (second-order phase transition R=R' is shown by dashed lines; sections of surfaces for two-phase reactions are shown by dash-dotted lines; curve ab presences in this isopleths in [1], but is missed in [2]) mass increments for phases within region C+R+R3 – 1(R=C+R3), 2(R+R3=C), 3(R3=C+R), 4(C+R3=R), 5(C=R+R3), 6(C+R=R3) (a) and 1(R=C+R3), 2(R+R3=C), 3(R3=C+R), 4(C+R3=R) (b) & within region B+C+R3 – 7(C=B+R3), 8(B+C=R3), 9(B=C+R3) (a) and 5(B=C+R3), 6(B+R3=C) (b).

One can see tracks of sections of two-phase reaction surfaces in isotherm sections and isopleths (Figure 4). They divide sections of three-phase regions in fragments with different signs of mass increments of coexisting phases. For instance, sections of three surfaces Δm_C=0, Δm_R=0, Δm_{R3}=0 divide a section of the region C+R+R3 into six fragments at 1700^{o}C (Figure 4,a). Tracks of two surfaces Δm_B=0 and Δm_C=0 are in a section of the region B+C+R3 at the same temperature only, third surface Δm_{R3}=0 is below. Tracks of sections of three surfaces Δm_C=0, Δm_R=0, Δm_{R3}=0 within the region C+R+R3 and one surface Δm_{R3}=0 within the region B+C+R3 are in the isopleth A-S (figure 4,b). Track of the surface Δm_{R3}=0 section within the region L+C+R3 is not seen in this isopleth.

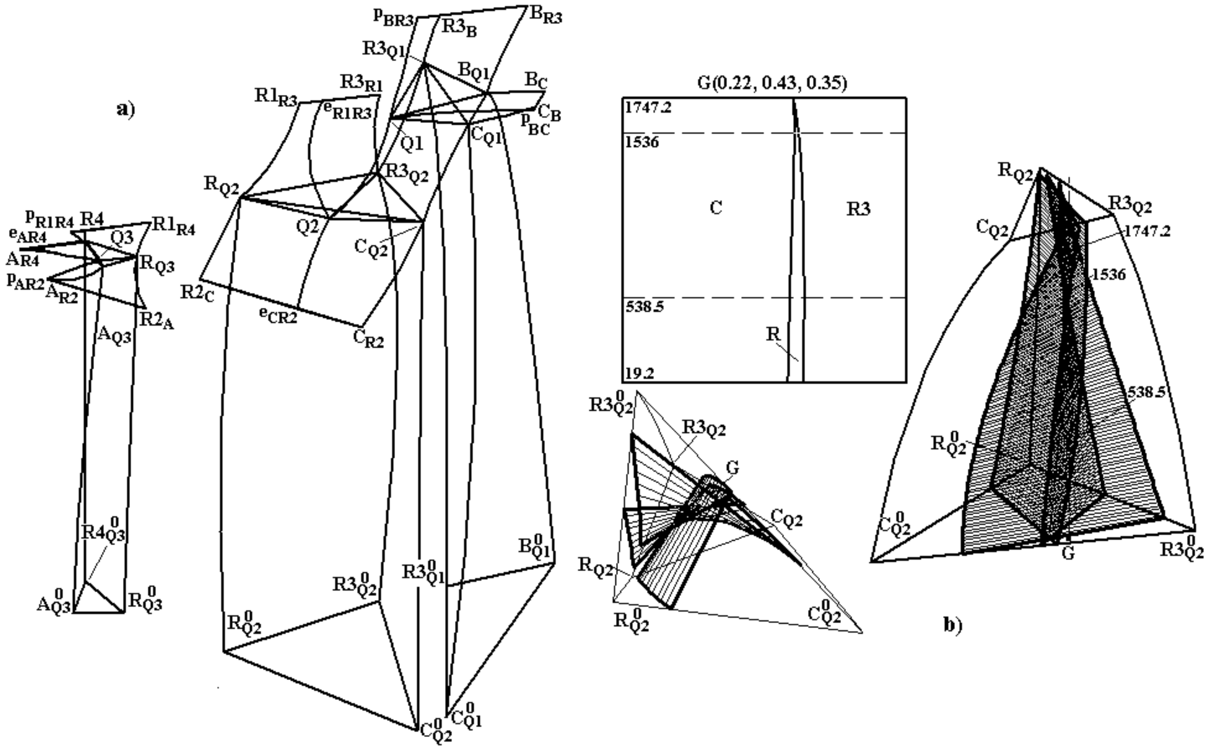


Figure 5. 3D scheme of uni- and invariant states - a). Changing of reaction R3→C+R for C+R3→R (Δm_C=0, Δm_{R3}<0, Δm_R>0), and then for C→R+R3 (Δm_{R3}=0, Δm_C<0, Δm_R>0) in the alloy G - b).

4. Temperature-concentration condition for the reaction type changing within the three-phase and four-phase regions

Geometrically a task for 3-phase region A+B+N is formulated as follows: on the side borders of this region there are 3 ruled surfaces with the 3 generating lines aa, bb, nn and 3 originating horizontal segments. Any horizontal section of the region is a tie triangle: $A_1B_1N_1$ at T_1 and $A_2B_2N_2$ at T_2.

For a mass centre G condition $G\in A_1B_1N_1$ and $G\in A_2B_2N_2$ equals to:

$$\begin{pmatrix} g_1 \\ g_2 \\ g_3 \end{pmatrix} = \begin{pmatrix} A_{11} & B_{11} & L_{11} \\ A_{12} & B_{12} & L_{12} \\ A_{13} & B_{13} & L_{13} \end{pmatrix} \begin{pmatrix} m_{A1} \\ m_{B1} \\ m_{N1} \end{pmatrix} = \begin{pmatrix} A_{21} & B_{21} & N_{21} \\ A_{22} & B_{22} & N_{22} \\ A_{23} & B_{23} & N_{23} \end{pmatrix} \begin{pmatrix} m_{A2} \\ m_{B2} \\ m_{N2} \end{pmatrix}, \qquad (1)$$

where (g_1, g_2, g_3), (A_{11}, A_{12}, A_{13}), (B_{11}, B_{12}, B_{13}), (N_{11}, N_{12}, N_{13}), (A_{21}, A_{22}, A_{23}), (B_{21}, B_{22}, B_{23}), (N_{21}, N_{22}, N_{23}) – mass-centric coordinates of the points, (m_{A1}, m_{B1}, m_{N1}) и (m_{A2}, m_{B2}, m_{N2}) – portions of 3 phases in the same mass centre G: $m_{A1}+m_{B1}+m_{N1}=1$ at T_1 and $m_{A2}+m_{B2}+m_{N2}=1$ at T_2.

If in an alloy G a sign of mass increment is changing for a phase B at temperature T_1, then a condition $\Delta m_B=m_{B1}-m_{B2}=0$ by means of the expression:

$$m_{B1}=[(A_{11}-N_{11})(g_2-N_{12})-(A_{12}-N_{12})(g_1-N_{11})]/\delta_1, \qquad (2)$$

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$$m_{B2}=[(A_{21}-N_{21})(g_2-N_{22})-(A_{22}-N_{22})(g_1-N_{21})]/\delta_{12}, \qquad (3)$$

leads to an equation $k_1g_1+k_2g_2+k_3=0,$ (4)

where $\delta_1=(A_{11}-N_{11})(B_{12}-N_{12})-(A_{12}-N_{12})(B_{11}-N_{11})$, $\delta_2=(A_{21}-N_{21})(B_{22}-N_{22})-(A_{22}-N_{22})(B_{21}-N_{21})$, $k_1=(B_{12}-N_{12})/\delta_1-(B_{22}-N_{22})/\delta_2$, $k_2=(B_{21}-N_{21})/\delta_2-(B_{11}-N_{11})/\delta_1$, $k_3=(N_{12}B_{11}-N_{11}B_{12})/\delta_1+(N_{21}B_{22}-N_{22}B_{21})/\delta_2$.

Equation (4) describes a horizontal segment RS of the reaction $N\to A$ at T_1. Segments RS at different temperatures form a ruled surface $\Delta m_B=0$. Analogous equations describe the families of segments $\Delta m_A=0$, $\Delta m_N=0$, that form the ruled surfaces for the reactions $N\to B$ and $A\to B$.

In the quaternary system the change of reaction is possible for 3 phases and for 4 phases. These processes are described by the hypersurfaces of the same ruled nature, which are formed by the horizontal simplexes of 2 types: a segment or a triangle.

An equation of mass balances for 3 phases, similar to (1) for the phases N+A+B, describes a horizontal generating segment for a ruled hypersurface of 2-phase reaction in 3-phase region.

Mass balance equation for 4 co-existing phases N+A+B+C of alloy G at T_1 and $T_2=T_1-dT$ within the isothermal tetrahedra $N_1A_1B_1C_1$, $N_2A_2B_2C_2$ is similar to (1) also. Two equations, like (2) and (3) for phase A, e.g., with the increment of its mass sign $\Delta m_A=m_{A1}-m_{A2}=0$ is equivalent to the horizontal (atT_{is}) originating plane (triangle) of the ruled hypersurface $\Delta m_A=0$ for the interaction of 3 phases N, B, C with the indifferent behavior of phase A.

Conclusions

1) It was found with a help of the uni- and invariant states scheme that the T-x-y diagram of the system Ti-Ir-Ru consists of 75 surfaces and 32 phase regions.

2) Its 3D computer model has been designed.

3) Existence of two-phase reaction $L\to C$ ($\Delta m_{R3}=0$) surface within the region L+C+R3 and a changing of eutectic reaction $L\to C+R3$ for peritectic one $L+R3\to C$ had been confirmed with a help of 3D computer model.

4) Two-phase surfaces $\Delta m_A=0$ and $\Delta m_{R4}=0$ in another two regions with liquid (L+A+R, L+R+R4) and in three regions in sub-solidus have been discovered: surface $\Delta m_A=0$ in the region A+R+R4, three surfaces in the region B+C+R3 and three surfaces in the region C+R+R3. The region B+C+R3 is divided into four fragments, the region C+R+R3 to six fragments.

5) It was found with a help of 3D computer model that the phase region L+ε on the isopleth (Ru/Ir=1/1)–Ti had been lost when experts loaded it into the data base MSIT [11].

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