第15卷 第2,3期　　广东有色金属学报　　Vol. 15, No. 2,3
2005年9月　　JOURNAL OF GUANGDONG NON-FERROUS METALS　　Sep 2005

Article ID: 1003−7837(2005)02,03−0174−05

Contradictions between 3-phase region eutectical and peritectical fragments borders determination methods in monographs by A. Prince and D. Petrov

Lutsyk V. I., Vorob'eva V. P., Zyryanov A. M.

(Buryat Scientific Center, Russian Academy of Sciences, Ulan-Ude 670047, Russia)

CLC number: TG113　　**Document code:** A

Phase diagrams are very effective instrument for elaboration of new materials. Computer technologies give a possibility with their help to design microstructure of multicomponent heterogeneous materials[1]. The phase regions dividing into thermodynamically unstable fragments at projection of phase diagram geometrical elements to the concentration simplex direction correspond to them. In this case it is necessary to test some theoretical views about a phase diagrams construction. For instance, it turns out that the problem received a big resonance to grow qualitative monocrystals of congruent solid solutions has not strengthened by the correct description of the 2-phase region saddle borders [2].

Another very important problem is a distinction between interpretations of the T-x-y diagrams 3-phase regions fragmentation, which is depend on one of solid phases sign amount increment, in monographs by A. Prince [3] and D. Petrov [4]. The gist of distinctions is revealed with a help of the diagram with one binary eutectic solubility gap as an example. Both authors cite the state diagram figure described by G. Mazing [5, P. 110, Figure 112] and devote much attention to investigations of conditions for changing of the eutectic transformation to peritectic one (Figure 1). This figure depicts seven isothermal cross-sections of the 3-phase region at temperatures $T_1 \div T_7$. At T_4 the tie line a_4e_4 is the tangent to the curve aa_7, at T_5 the line a_5e_5 coincides with the tangent to the curve ee_7, and at some temperature $T_6<T_i<T_5$ the tangent to bb_7 is parallel to the tie line a_ie_i. Both A. Prince and D. Petrov consent that at cooling from T_e to T_7 the 3-phase transformation is turned from eutectic type near the binary eutectic into the peritectic one but they diversity in modes to correct define the 3-phase transformation type change temperature.

D. Petrov uses the tangents rule, applies its modifications named as the common tangents rule and finds 3 contradictions in the citing figure of the 3-phase region:

(1) The transfer from the eutectic transformation $L \to \alpha + \beta$ to the peritectic one $L + \beta \to \alpha$ must be at such temperature when the tangent to the curve ee_7 of the liquid phase L concentration change coincides with the tangent to the line aa_7 of the solid phase (concentration change. These tangents on the diagram in consider are drawn at different temperatures.

(2) The tangents rule is not fulfilled for the second peritectic reaction $L + \alpha \to \beta$, while it is obviously

Received date: 2005−08−29

that such reaction must be going with that alloys which fall from the 3-phase region $L+\alpha+\beta$ to the 2-phase region $L+\beta$.

(3) The line $e_7a_7(b_7)$ has not become the tangent to the solidus and solvus intersection curve in its critical point $a_7(b_7)$ when the 3-phase transformation finishes and the tie triangle degenerates into the line.

Because of this, D. Petrov insists on the necessity of the agreed alignment of 3-phase region border directing curves.

Prince solves these contradictions and admits free configurations of both the gap on the liquidus surface and the intersection curve of solubility and solidus surfaces. He uses the Hillert's criterion[6] to construct generating lines of the 2-phase reaction surface, which divides the 3-phase region to fragments with different increment signs of one of solid phases amount. Given the liquid initial concentration G values g_1, g_2, g_3 are expressed as dependences on concentrations (α_i, β_i, L_i) and amounts (m_j, $j=\alpha$, β, L) of coexisting phases:

$$g_i=\frac{m_\alpha\alpha_i+m_\beta\beta_i+m_L L_i}{m_\alpha+m_\beta+m_L},\ i=1\cdots\cdots3. \tag{1}$$

The little change of the temperature to ΔT produces little changes both concentration and amounts of every phase but not of the initial mixture concentration, therefore $\Delta g_i=0$ and the differentiation of the expression (1) gives:

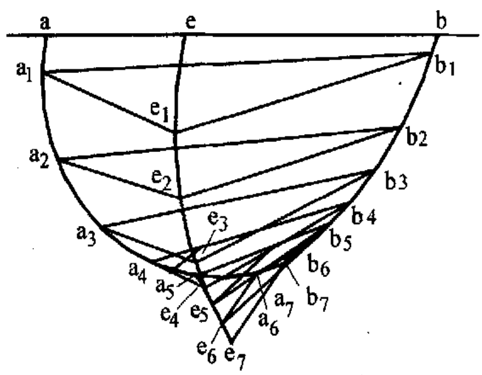

Fig. 1 3-phase region in the system with a binary eutectical solubility gap

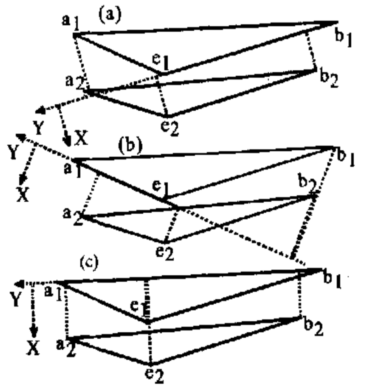

Fig. 2 Increments Δm_α(a), Δm_β(b) and Δm_L(c) signs definition schemes in $\Delta a_1 e_1 b_1$

$$\Delta g_i=\frac{\Delta(m_\alpha\alpha_i+m_\beta\beta_i+m_L L_i)(m_\alpha+m_\beta+m_L)-\Delta(m_\alpha+m_\beta+m_L)(m_\alpha X_A^\alpha+m_\beta X_A^\beta+m_L X_A^L)}{(m_\alpha+m_\beta+m_L)^2}=0 \tag{2}$$

As $m_\alpha+m_\beta+m_L\neq0$ and $\Delta(m_\alpha+m_\beta+m_L)=0$ then the expression (2) is become more simple:

$$m_\alpha\Delta\alpha_i+\alpha_i\Delta m_\alpha+m_\beta\Delta\beta_i+\beta_i\Delta m_\beta+m_L\Delta L_i+L_i\Delta m_L=0 \tag{3}$$

To find the increment sign Δm_α of the α phase, M. Hillert proposes such coordinates system: the axis Y passé across points β and L (b_1 and e_1 in the Figure 2,a) and the orthogonal to it axis X is oriented in opposite to the point α (from a_1) direction. Then in (3)

$$\beta_i=L_i>\alpha_i \tag{4}$$

and, with account $\Delta m_\beta+\Delta m_L=-\Delta m_\alpha$, the expression (3) is transformed to

$$m_\alpha\Delta\alpha_i+m_\beta\Delta\beta_i+m_L\Delta L_i+\Delta m_\alpha\alpha_i+\beta_i(\Delta m_\beta+\Delta m_L)=m_\alpha\Delta\alpha_i+m_\beta\Delta\beta_i+m_L\Delta L_i+\Delta m_\alpha(\alpha_i-\beta_i)=0$$

and further to

$$\Delta m_\alpha(\beta_i-\alpha_i)=m_\alpha\Delta\alpha_i+m_\beta\Delta\beta_i+m_L\Delta L_i. \tag{5}$$

As according to the condition (4) $\beta_i>\alpha_i$, then the value Δm_α- the direction of the phase α amount change at the mixture cooling to ΔT—has the same sign as the expression $m_\alpha \Delta\alpha_i + m_\beta \Delta\beta_i + m_L \Delta L_i$.

Analogously, such coordinate system to estimate the phase β amount increment is choosing to the condition $\alpha_i = L_i > \beta_i$ is fulfilled. The axis Y connects points α and L (a_1 and e_1) and the axis X is drawing oppositely to the point β (from b_1 in the Figure 2, b). The expression (3) is transformed to

$$\Delta m_\beta (\alpha_i - \beta_i) = m_\alpha \Delta\alpha_i + m_\beta \Delta\beta_i + m_L \Delta L_i. \quad (6)$$

The sign of Δm_L is defined with a help a new coordinate system. The axis Y coincides with the line $\alpha\beta$ ($a_1 e_1$) and the axis X direction is opposite to the point L (from e_1 in the Figure 2, c). Then $\alpha_i = \beta_i > L_i$ and it is possible to estimate with a help of the equation (3) the sign of Δm_L:

$$\Delta m_L (\alpha_i \Delta L_i) = m_\alpha \Delta\alpha_i + m_\beta \Delta\beta_i + m_L \Delta L_i.$$

Thus the change in the amount of α, β and liquid phases has the same sign as the expression $m_\alpha \Delta\alpha_i + m_\beta \Delta\beta_i + m_L \Delta L_i$, when the coordinate system is suitably chosen. Three cases are possible:

(1) $\Delta m_\alpha > 0$, $\Delta m_\beta > 0$ and $\Delta m_L < 0$. Eutectic reaction, $L \to \alpha + \beta$.

(2) $\Delta m_\alpha > 0$, $\Delta m_\beta < 0$ and $\Delta m_L < 0$. Peritectic reaction, $L + \beta \to \alpha$.

(3) $\Delta m_\alpha < 0$, $\Delta m_\beta > 0$ and $\Delta m_L < 0$. Peritectic reaction, $L + \alpha \to \beta$.

Hence, the phase reaction type depends on relative amounts of phases α, β and L (m_α, m_β, m_L) or on the initial liquid concentration. And it is right because, for instance, the sign of Δm_α in (5) depends on α, β and L concentrations change. If $\Delta\beta_i < 0$ then the expression $m_\alpha \Delta\alpha_i + m_\beta \Delta\beta_i + m_L \Delta L_i$ becomes negative when the amount m_β of the phase β becomes reasonably large. Thus it is possible that some mixtures take part in the eutectic reaction and some mixtures participate in the peritectic reaction inside the same 3-phase triangle.

Changing of phases concentrations in the 3-phase region in considering at cooling from the temperature T_1 to the temperature T_2 is determined by positions of points a_2, b_2, e_2 relatively the tie triangle $a_1 b_1 e_1$ sides (Figure 2). As deviations of points a_2, e_2 and the difference of points b_1 and b_2 deviations from the line $a_1 e_1$ are positive then the increment Δm_β is positive too (Figure 2, b). It means that the β phase amount is growing at cooling from the temperature T_1 to T_2. Deviations of points b_2, e_2 and difference of deviations of a_1 и a_2 from the line $e_1 b_1$ are positive too and then $\Delta m_\alpha > 0$ (Figure 2, a). From this figure we notice also that the liquid amount is decreasing at cooling and $\Delta m_L < 0$, if to look deviations of points a_2, b_2 and the difference ($e_2 - e_1$) from the line $a_1 b_1$. Finally, as $\Delta m_\alpha > 0$, $\Delta m_\beta > 0$ and $\Delta m_L < 0$, then the reaction at T_1 for any liquid inside the triangle $a_1 e_1 b_1$ is eutectic: $L \to \alpha + \beta$. The eutectic reaction will be made at lower temperatures not all concentrations $G \in \Delta\alpha\beta L$.

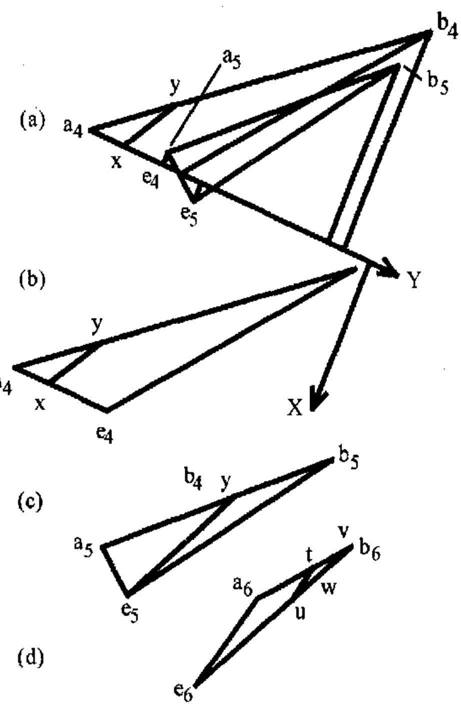

Fig. 3 Determination of the Δm_β sign change conditions at T_4 (a) and the line corresponding to conditions $\Delta m_\beta = 0$ (xy, e_5y, tu) and $\Delta m_\alpha = 0$ (vw) in tie triangles at T_4 (b), T_5 (c) and T_6 (d)

For instance, the tie triangle $a_5 e_5 b_5$ tops situate relatively $a_4 e_4 b_4$ so, that $\Delta m_\alpha > 0$, $\Delta m_L < 0$, but Δm_β may be either positive or negative. This can be verified by consideration of points a_5, e_5 positions and the difference ($b_4 - b_5$) relatively the line $a_4 e_4$ (Figure 3, a). The increment $\Delta\alpha_i < 0$, but $\Delta\beta_i > 0$ and $\Delta L_i > 0$.

Since, according to (6), Δm_β and the expression $m_\alpha \Delta\alpha_i + m_\beta \Delta m\beta_i + m_L \Delta L_i$ have the same sign, then the Δm_β sign depends on the negative member $m_\alpha \Delta\alpha_i$ value in comparison with the positive member $m_\beta \Delta\beta_i + m_L \Delta L_i$. Hence, there will be a border line across $\Delta a_4 e_4 b_4$ separating those alloys undergoing at T_4 a peritectic reaction from alloys with the eutectic type phase reaction (Figure 3(a)). This border line corresponds to the transfer from the reaction $L+\beta \rightarrow \alpha$ to $L \rightarrow \alpha+\beta$. The β phase along the line does not participate in the reaction and alloys with compositions along this line take part in the 2-phase transformation $L \rightarrow \alpha$ at T_4. Along the border line $\Delta m_\alpha = 0$ and its equation coefficients are values $\Delta\alpha_i$, $\Delta\beta_i$ and ΔL_i:

$$\Delta m_\beta = m_\alpha \Delta\alpha_i + m_\beta \Delta\beta_i + m_L \Delta L_i = 0.$$

As $m_\alpha = 1-(m_\beta + m_L)$, then the equation of the border line in the $\Delta a_4 e_4 b_4$ is:

$$\Delta\alpha_i + m_\beta(\Delta\beta_i - \Delta\alpha_i) + m_L(\Delta L_i - \Delta\alpha_i) = 0. \quad (7)$$

In (7) at $m_\beta = 0, m_L = \Delta\alpha_i/(\Delta\alpha_i - \Delta L_i)$ and at $m_L = 0$, $m_\beta = \Delta\alpha_i/(\Delta\alpha_i - \Delta\beta_i)$. The condition $m_\beta = 0$ corresponds to the point x position in the side $a_4 e_4$ of the triangle $a_4 e_4 b_4$ and the condition $m_L = 0$ is consistent with the point $y \in a_4 b_4$. The 3-phase reaction at T_4 in the region $a_4$xy is peritectic: $L+\beta \rightarrow \alpha$ (Figure 3(b)), it is eutectic: $L \rightarrow \alpha+\beta$ in the region xy$b_4 e_4$ and it becomes the 2-phase one: $L \rightarrow \alpha$ along the line xy.

If this were so that the triangle $a_5 e_5 b_5$ (at the temperature T_5) is infinitely near the triangle $a_4 e_4 b_4$, then the peritectical reaction region is limited by the point a_4 only. In fact, the transfer from the eutectic reaction to the peritectical one ($L+\beta \rightarrow \alpha$) begins in the top a_4, when the tangent to the curve of the α phase ($a_1 a_7$) coincides with the direction of the tie line $L\alpha$($e_4 a_4$). Further consideration of 3-phase triangles at lower temperatures will show that the peritectic region extends from the corner α to β and L corners. The tangent to the liquid phase curve $e_1 e_7$ near the top e_5 coincides with the tie line $L\alpha$ ($e_5 a_5$) in the triangle $a_5 e_5 b_5$. Because of this, the border between the peritectic and eutectic regions passes across the point a_5 (Figure 3(c)).

At further cooling such state is reached when the tangent to the curve of the phase β ($b_1 b_7$) is parallel to the tie line $L\alpha$. It takes a place on the Figure 1 at some temperature $T_6 < T_i < T_5$ between isotherms $a_5 e_5 b_5$ and $a_6 e_6 b_6$. The second peritectic region appears at T_i near the corner β of the 3-phase triangle. The region of the second peritectic reaction at T_6 moves to the $\Delta a_6 e_6 b_6$ field and alloys $G \in \Delta a_6 e_6 b_6$ undergo the following phase reactions: (1) peritectic $L+\beta \rightarrow \alpha$ in $a_6 e_6$ut; (2) 2-phase $L \rightarrow \alpha$ along the line tu; (3) eutectic $L \rightarrow \alpha+\beta$ in tuwv; (4) 2-phase $L \rightarrow \beta$ along the line vw; (5) peritectic $L+\alpha \rightarrow \beta$ in $b_6$vw.

The line tu corresponds to the 2-phase reaction $L \rightarrow \alpha$ (рис. 3,d) and the condition $\Delta m_\beta = 0$ described by the equation (6). The 2-phase reaction $L \rightarrow \beta$, the condition $\Delta m_\alpha = 0$ and the equation (5) given by deviations of points a_6, a_7(b_7) and e_7 from the line $b_6 e_6$ ($\Delta\alpha_i > 0$, $\Delta\beta_i < 0$, $\Delta L_i > 0$) correspond to the line vw.

As a result, the 3-phase reaction has initially the eutectic type for all mixtures of 3-phase region emperature reaches T_4 and the tie line $a_4 e_4$ becomes the tangent to the curve aa_7. Beginning with this temperature and down to the 3-phase reaction ending on the tie line $e_7 a_7$(b_7) the phase reaction type depends on the liquid concentration inside some triangles sequence. It stays eutectic or becomes peritectic: $L+\beta \rightarrow \alpha$ or $L+\alpha \rightarrow \beta$. By this means, according to A. Prince:

(1) The 3-phase transformation type change temperature is not constant for the given 3-phase region.

(2) It is possible that the tie triangle has two fragments with negative increments of different solid phase's amounts. Both these fragments are separated from the eutectic fragment by two curves of 2-phase reactions.

(3) As the analysis of (5) and (6) formulas, determining the solid phase amount change sign or a 3-phase transformation type, indicates the tangents rule is correct only at conditions $\Delta\alpha_i = \Delta\beta_i = 0$ that is for fixed concentrations of solid phases.

The problem to define conditions of 3-phase transformations (eutectic-peritectic, eutonic-peritonic, eutectoid-peritectoid) type change is interest and stays actual for diagrams of other topological types too [7,8].

References

[1] Lutsyk V I. Heterogeneous Design: Phase Diagram-Microstructure-Materials Genotype //Phase Diagrams in Materials Science, MSI GmbH (2004). P304
www. matport. com/publishing/pdms/index. shtml.

[2] Fedorov P P, Buchinskaya I I. , Stasyuk V A. , Bondareva O S. Saddle-Type Points on Liquidus Surfaces of Solid Solutions in Systems PbF_2-CdF_2-RF_3 (R - Rare-earth Elements) //Russian J. of Inorgan. Chem. , 1996, V. 41, No 3, P 464.

[3] Prince A. Alloy Phase Equilibria. Elsevier Publ. Comp. Amsterdam-London-N. Y. 1966.

[4] Petrov D A. Binary and Ternary Systems. M. : Metallurgy, 1986.

[5] Mazing G. Ternare Systeme. Leipzig. 1933.

[6] Hillert M. Criterion for Peritectic and Eutectic Reactions //J. of the Iron and Steel Institute. 1958. Vol. 189. P. 224; 1960. Vol. 195. P201.

[7] Khaldoyanidi K. A. Peritectic and Eutectic Equilibria Mutual Transformations Simulation in Binary and Ternary Systems //Russian J. of Phys. Chem. 2000. V. 47, No 10. P1761.

[8] Vorob'eva V. P. , LutsykV. I. Microstructure Design in Systems with Replacing the Eutectic Type Reaction by Peritectic //Abstracts of the XV International Conference "Chemical Thermodynamics in Russia". Moscow, 2005. Vol. II. P183.