SPECIFICATION OF THE CONFIGURATION OF TWO-PHASE REGIONS IN EQUILIBRIUM PHASE DIAGRAMS

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Abstract

The purpose of the present study is to obtain more specific information on the configuration of two-phase regions in binary equilibrium phase diagrams. Applying thoroughly Gibbs’s phase rule, we have found out that this rule is not obeyed with conventional configuration of closed two–phase (\(\alpha + \gamma\)) regions in diagrams of binary systems based on iron: Fe – Al, Fe – Si, Fe – Cr, Fe – V, Fe – W, etc. We speak about the coexistence region of the \(\alpha\)-phase (ferrite) and \(\gamma\)-phase (austenite) close to the iron ordinate to which one-phase \(\alpha\)- and \(\gamma\)-regions are adjacent. By means of Gibbs’s phase rule it is shown that in diagrams of binary systems based on iron with elements stabilizing the \(\alpha\)-phase having the bcc – structure, two-phase \(\alpha + \gamma\) regions must consist of two parts with the contiguity point at the maximum content of the second element. In the work cases when Gibbs’s phase rule is not obeyed in binary phase diagrams (Cu – Fe, Al – Si, Cu – Co, etc.) with reversing solidus are considered and examples of changing the configuration of the two-phase regions ensuring the compliance with this rule are given. Thus in the diagram of the Cu – Fe system instead of one so called reversing solidus there must be : the coexistence region of two liquids (L 1 + L2); monotectic transition (L1 \(\rightarrow\) \(\gamma\) + L2) at \(\approx\) 1400 ºC; one conventional solidus, separating the \(\gamma\)-region from the \(\gamma\) + L1 - region, and the second solidus between the \(\gamma\)- and \(\gamma\) + L - regions which is really reversing.

1. INTRODUCTION

Two-phase regions, confined by one-phase regions, are present in many phase diagrams based on iron: Fe-Al, Fe-Cr, Fe-Si, Fe-V, Fe-W and others [1 – 3]. We speak about the coexistence region of the \(\alpha\)-phase (ferrite) and \(\gamma\)-phase (austenite) close to the Fe ordinate, to which one-phase \(\alpha\)- and \(\gamma\)-regions are adjacent. Because of high temperatures and subsequent phase transitions it is very difficult to determine experimentally the configuration and the boundaries of these regions.

The purpose of the present theoretical research is to define more accurately the configuration of two-phase regions in the equilibrium phase diagram applying Gibbs’s phase rule.

2. THEORY

For the two-phase (\(\alpha + \gamma\)) equilibrium in the binary \(A - B\) system, number of degrees of freedom (or alternatives), with no account taken of the pressure, is equal to \(C = K - F + 1 = 2 - 2 + 1 = 1\). This means that the equilibrium under examination must be definitely specified by one freely selected variable. As a rule, temperature is such variable. In Fig. 1 it is evident that at any temperature within \(t_{\alpha}\) and \(t_{\gamma}\), where the (\(\alpha + \gamma\)) two-phase region is present, compositions of the coexisting phases are defined really unambiguously. However, phase compositions, to say more correctly the content of one element in any of them (the content of the other one is determined by the difference from 100 %), are other rightful variables.
Let us choose the $\alpha$-phase composition equal to $\alpha_1$. Now as it is seen in Fig. 1, in the curve, representing the composition of the $\alpha$-phase, equilibrium to the $\gamma$-phase, there are two points of such composition: 3 and $3'$. In the point $3$ the $\alpha$-phase is equilibrium to the $\gamma$-phase in the point $4$ at a different temperature as compared to the $\alpha$-phase in the point $3'$ to the $\gamma$-phase in the point $4'$.

Exactly the same situation arises if we choose the $\alpha$-phase composition equal to $\alpha_2$. In this case there are two such compositions in the points $5$ and $5'$, the first being equilibrium to the $\gamma$-phase, represented by the point $6$, and the second by the point $6'$. One may also choose the $\gamma$-phase composition as one acceptable degree of freedom. It is not difficult to receive evidence that also in this case instead of one pair of equilibrium $\alpha$- and $\gamma$-phases there are always two such pairs.

Fig. 1. Section of the phase diagram of the $A-B$ system with conventional configuration of the $(\alpha+\gamma)$ two-phase region

Fig. 2. Section of the phase diagram of the $A-B$ system with the proposed configuration of the $(\alpha+\gamma)$ two-phase region ensuring Gibbs’s phase rule observance

It is obvious that situation arises which is impossible according to Gibbs’s phase rule. This situation is similar to that, investigated by A.A. Bochvar in diagrams of binary $A-B$ continuous liquid and solid solutions, where alloys based on both components exhibit liquidus and solidus temperature increase or decrease. It is found that contact of liquidus and solidus lines is the only way to ensure the phase rule observance. As a result, an extreme temperature point (maximum or minimum) emerges, in which solid and liquid phase compositions coincide [4, p. 153 – 154]. $A-B$ binary system disintegrates into two independent $A-M$ and $M-B$ systems, where $M$ is the solid solution composition, corresponding to the temperature maximum or minimum. This composition behaves like an independent element [5, p. 120 – 121].

The statement that in some ternary diagrams at the crystallization of solid solutions to observe Gibbs’s phase rule liquidus and solidus surfaces must contact each other is used in paper [6], in which the configuration of the Cu–Ni–Mn phase diagram has been defined more accurately.

In the case discussed in the present research, with regard to the $A-B$ system diagram, to observe Gibbs’s phase rule, boundary lines between phase regions $(\gamma) - (\alpha+\gamma)$ and $(\alpha+\gamma) - (\alpha)$ must have a contact point at the maximum $B$ element content in the $\gamma$-region as it is demonstrated in Fig. 2. One can see that
now there are two ($\alpha + \gamma$) regions with the common $V_{\text{MAX}}$ point at the $t_0$ temperature. The alloy with this composition and at this temperature nominally is able to change its structure at infinitely small composition changes similar to the structure change of the pure $A$ element as a result of the slightest deviation from the temperature of the $\alpha \leftrightarrow \gamma$ phase equilibrium. In other words, behavior of the alloy with the $V_{\text{MAX}}$ composition at the $t_0$ temperature is similar to the pure element behavior as it is emphasized in paper [5].

It is not difficult to receive evidence that, with the proposed configuration of the $\gamma$ and ($\alpha + \gamma$) phase regions in Fig. 2, Gibbs’s phase rule is observed when temperature as well as composition of any phase are chosen as the only degree of freedom.

The form of the regions of the ($\alpha + \gamma$) two-phase equilibrium represented in Fig. 2 is typical of the majority of binary systems with the presence of iron. The exception is the Fe–Cr system, in which the ($\alpha + \gamma$) two-phase region has a minimum. The drawing of this section of the Fe–Cr diagram is given in Fig. 3, a.

Based on the above stated considerations, it is easy to conclude that in the right-hand section of the ($\alpha + \gamma$) two-phase region (beyond the minimum) Gibbs’s phase rule is not observed either, if any composition of the $\alpha$- or $\gamma$- phase is taken for the only degree of freedom. Changing the configuration of the ($\alpha + \gamma$) two-phase equilibrium region, as it is demonstrated in Fig. 3, b, enables to observe Gibbs’s phase rule undoubtedly.

The considered cases, when Gibbs’s phase rule is not obeyed, and examples of changing the configuration of the two-phase regions, ensuring the compliance with this rule, enabled us to formulate the following statement: “A line in a phase diagram displaying a constant content of any element in the alloy located in a two–phase region may enter this region from adjacent one-phase region, i.e. may cross the boundary between these regions only once; way out for the mentioned line from the two–phase region must be either into another one–phase region or through three–phase and more complicated transformations in case of multi-component systems.”

This statement is not observed in the equilibrium phase diagram of the Co–Cu system (Fig. 4), where there is so called reversing solidus separating the $\alpha$- region from the ($\alpha + L$) region. This solidus in the Co–Cu system begins at the melting temperature of Co, reaches the 18 % Cu point and finishes at 1112 °C in the 12 % mol Cu point. As a result, the line-ordinate displaying the specified 15 % mol Cu composition crosses
twice the boundary of the \((L + \alpha)\) region with the \(\alpha\) region – at 1400 and 1180 °C. Thus, it appears that the \(\alpha\) solid solution of this composition can be in equilibrium with the \(L\) liquid of two different compositions. According to the phase rule, only one liquid phase composition must correspond to the given \(\alpha\) phase composition.

![Phase diagram of the Co-Cu system](image1)

**Fig. 4.** Phase diagram of the Co-Cu system

The revealed misunderstanding can be eliminated, if we assume (Fig. 5) that there is a non-blending region in the liquid state in the Co-Cu system, and the monotectic reaction \((L_1 \rightarrow \alpha + L_2)\) at ~ 1320 °C takes place resulting in the formation of the \(\alpha\) phase with the 18 % mol Cu content. In earlier researches such transition was demonstrated in this diagram.

![The proposed version of the phase diagram of the Co–Cu system with monotectic equilibrium](image2)

**Fig. 5.** The proposed version of the phase diagram of the Co–Cu system with monotectic equilibrium

In Fig. 5 there are two soliduses. One is the boundary between the \(\alpha\) and \((\gamma+\alpha+L_1)\) – regions, and indicates, like in the majority of cases, the increase of the Cu content up to 18 % mol at the temperature decrease to 1320 °C, i.e. this is a conventional solidus. The other solidus, separating the \(\alpha\) and \((\alpha+L_2)\) – regions, indicates on the contrary the decrease of the Cu content from 18 % to ~ 12 % mol at the temperature decrease from 1320 °C to 1112 °C. Exactly that very solidus and the lines similar to it should be named *reversing.*
3. CONCLUSION

Applying Gibbs’s phase rule, it is shown that in phase diagrams of binary iron based systems with elements, stabilizing the $\alpha$-phase with the bcc structure, two-phase ($\alpha + \gamma$) regions must consist of two sections with the contact point at the maximum content of the second element. In the phase diagrams of the Co-Cu and Fe–Cu systems instead of one so called reversing solidus there must be the coexistence region of two ($L_1 + L_2$) liquids, the monotectic ($L_1 \to \alpha(\gamma)+L_2$) transition, one conventional solidus, separating the ($\alpha\gamma$ - region from the ($\gamma + L_1$) - region and the second solidus between the ($\alpha\gamma$ - and ($\alpha(\gamma)+L_2$) – regions, which is really reversing.

LITERATURE REFERENCES