Para-equilibrium phase diagrams

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ABSTRACT

If an initially homogeneous system at high temperature is rapidly cooled, a temporary para-equilibrium state may result in which rapidly diffusing elements have reached equilibrium but more slowly diffusing elements have remained essentially immobile. The best known example occurs when homogeneous austenite is quenched. A para-equilibrium phase assemblage may be calculated thermodynamically by Gibbs free energy minimization under the constraint that the ratios of the slowly diffusing elements are the same in all phases. Several examples of calculated para-equilibrium phase diagram sections are presented and the application of the Phase Rule is discussed. Although the rules governing the geometry of these diagrams may appear at first to be somewhat different from those for full equilibrium phase diagrams, it is shown that in fact they obey exactly the same rules with the following provision. Since the molar ratios of non-diffusing elements are the same in all phases at para-equilibrium, these ratios act, as far as the geometry of the diagram is concerned, like "potential" variables (such as T, pressure or chemical potentials) rather than like "normal" composition variables which need not be the same in all phases. A general algorithm to calculate para-equilibrium phase diagrams is presented. In the limit, if a para-equilibrium calculation is performed under the constraint that no elements diffuse, then the resultant phase diagram shows the single phase with the minimum Gibbs free energy at any point on the diagram; such calculations are of interest in physical vapor deposition when deposition is so rapid that phase separation does not occur.

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1. Introduction

In certain solid systems, some elements diffuse much faster than others. Hence, if an initially homogeneous single-phase system at high temperature is rapidly cooled and then held at a lower temperature, a temporary para-equilibrium state may result in which the rapidly diffusing elements have reached equilibrium but the more slowly diffusing elements have remained essentially immobile [1–3]. The best known and most industrially important example occurs when homogeneous austenite is quenched and annealed; interstitial elements such as C and N are much more mobile than the metallic elements. Of course, in reality some diffusion of the metallic elements will always occur [2], so that para-equilibrium is a limiting state which is never fully realized but may, nevertheless, be reasonably closely approached in many cases.

The present article discusses the thermodynamic calculation of para-equilibrium and para-equilibrium phase diagrams and the geometrical rules governing the latter (that is, the application of the Phase Rule to para-equilibrium phase diagrams).

The FactSage 6.4 thermodynamic software [4] calculates the conditions for full thermodynamic equilibrium (sometimes called ortho-equilibrium) by Gibbs free energy minimization, taking data from databases which contain optimized thermodynamic model parameters giving the Gibbs free energy of all phases as functions of temperature and composition. These model parameters have been obtained by critical evaluation of literature data. The FactSage thermodynamic software can calculate and plot equilibrium phase diagrams through the repeated systematic application of the Gibbs free energy minimization algorithm.

At para-equilibrium, the ratios of the slowly diffusing elements are the same in all phases and are equal to their ratios in the initial single-phase high-temperature alloy. Hence, the calculation of para-equilibrium simply involves modifying the Gibbs free energy minimization algorithm by the addition of this constraint. This will be discussed in detail in Section 5. Para-equilibrium phase diagram sections can subsequently be calculated by exactly the same procedure as is used to calculate full equilibrium phase diagrams as will be discussed in Section 4.

In the limit, if a para-equilibrium calculation is performed under the constraint that no elements diffuse, then the ratios of all elements remain the same as in the initial homogeneous high-temperature state. Hence, such a calculation will simply yield the

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single homogeneous phase with the minimum Gibbs free energy at the temperature and overall composition of the calculation. Such calculations are of practical interest in physical vapor deposition (PVD) when deposition from the vapor phase is so rapid that phase separation does not occur, resulting in a single-phase solid deposit. The calculation of minimum Gibbs free energy phase diagrams will be discussed in Section 3.

In the following section, the application of the Phase rule to para-equilibrium phase diagrams is discussed.

2. The geometry of para-equilibrium phase diagram sections

All figures shown in this article were calculated with the Fact-Sage 6.4 software [4], with thermodynamic data taken from the FactSage FSstel steel database. In all calculations the formation of graphite has been suppressed.

In the (Fe + Cr + C) system at elevated temperatures the range of homogeneous austenite (FCC) extends from pure Fe to approximately 8 mol% C and 15 mol% Cr as can be seen in the (full ortho-equilibrium) isothermal phase diagram section at 1140 °C in figure 1. Alloys with compositions within this range when cooled rapidly and then held at a lower temperature may exhibit a temporary para-equilibrium state. A vertical section of the same (full ortho-equilibrium) (Fe + Cr + C) phase diagram section is shown in figure 2 where the molar ratio C/(Fe + Cr) is plotted versus temperature, T, at a constant molar metal ratio Cr/(Fe + Cr) = 0.04. (On figures 1 and 2 and other figures, $M_{23}C_6$, M_7C_3 and Cementite are solutions of Fe and Cr carbides.)

Before discussing the geometry of para-equilibrium phase diagrams, we should recall the Law of Adjoining Phase Regions (LAPR) [5–7] which applies to all single-valued phase diagram sections: "As a phase boundary line is crossed, one and only one phase either appears or disappears." (In phase diagrams involving axes other than temperature and composition, such as pressure, volume and chemical potential, it is possible to define the axes in such a way that the diagram is not single-valued in every region. In this case the LAPR does not apply in these regions [6,7]. However, diagrams with temperature and composition as axes are always single-valued and the LAPR always applies.) An examination of figures 1 and 2 will show that the LAPR applies to every phase boundary. Although the isothermal lines abc and def in figure 2 might, at first, appear to be exceptions to the rule, these lines are not simple phase boundaries but are, rather, infinitely narrow four-phase fields with coincident upper and lower phase boundaries. For
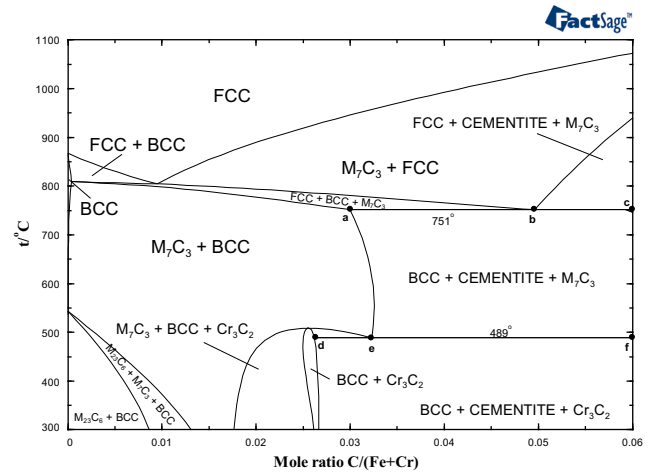
example, the line abc is an infinitely narrow (FCC + BCC + M_7C_3 + Cementite) field where the four phases co-exist. Hence, the LAPR applies. The Phase Rule, at constant total pressure, may be written:

$$F = C - P + 1, \tag{1}$$

where C = number of components, P = number of phases and F = number of degrees of freedom (variance). In the three-component (Fe + Cr + C) system when four phases are at equilibrium, $F = 0$.

Hence, the line abc represents an invariant equilibrium which occurs at only one temperature.

Since a para-equilibrium calculation simply involves an additional constraint, the LAPR also applies to para-equilibrium phase diagram sections.

In figure 3 is shown the para-equilibrium phase diagram for exactly the same section as in figure 2, calculated for the case where C is the only diffusing element. Since the molar ratio Cr/(Fe + Cr) = 0.04 is now constant and the same in every phase, the diagram in this particular example resembles a full (ortho) equilibrium T-composition phase diagram of a two-component system, the "components" being $Fe_{0.96}Cr_{0.04}$ and C. The three-phase (FCC + BCC + Cementite) region bcd now appears as an isothermal invariant, similar to a binary eutectoid.
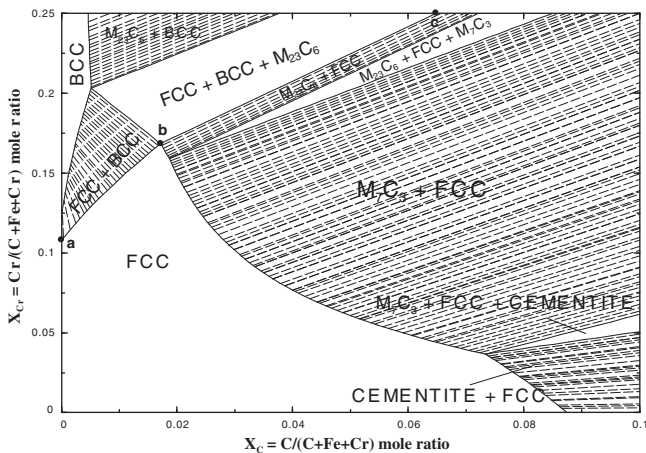

FIGURE 2. Full equilibrium phase diagram section of the (Fe + Cr + C) system. Molar ratio C/(Fe + Cr) versus T at constant mole ratio Cr/(Fe + Cr) = 0.04. (Formation of graphite suppressed.)

FIGURE 1. Full equilibrium phase diagram section of the (Fe + Cr + C) system showing tie-lines. Mole fraction X_C versus mole fraction X_{Cr} at constant T = 1140 °C. (Formation of graphite suppressed.)
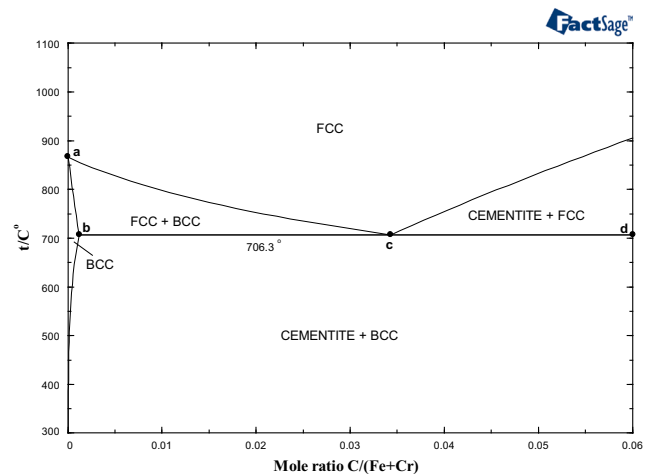

FIGURE 3. Para-equilibrium phase diagram section of the (Fe + Cr + C) system when C is the only diffusing element. Plot of mole ratio C/(Fe + Cr) versus T at constant mole ratio Cr/(Fe + Cr) = 0.04. (Formation of graphite suppressed.)