COMPUTED PHASE EQUILIBRIA IN IRON-BASE TERNARY ALLOYS

by

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To My Guru

CERTIFICATE

This is to certify that the thesis entitled *COMPUTED PHASE EQUILIBRIA IN IRON-BASE TERNARY ALLOYS* by K.C. Hari Kumar submitted to the Indian Institute of Technology Delhi, for the award of the degree of Doctor of Philosophy in Applied Mechanics is a bona fide research work carried out by him under my supervision and guidance. The thesis work, in my opinion, has reached the standard fulfilling the requirements for the Doctor of Philosophy Degree. The research report and results presented in this thesis have not been submitted in part or in full to any other university or institute for the award of any degree or diploma.

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K. C. H. Kumar.
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ABSTRACT

The binary phase diagrams of iron can be classified into four categories according to the type of γ-field formed. These are:

(1) open γ-field type (e.g., Fe-Ni),

(2) expanded γ-field type (e.g., Fe-C),

(3) closed γ-field (γ-loop) type (e.g., Fe-W), and

(4) restricted γ-field type (e.g., Fe-Nb).

This classification of the binary phase diagrams leads to ten different ternary combinations such as (1)-(1), (1)-(2), (2)-(2), (3)-(4), etc., the corresponding examples being Fe-Mn-Ni, C-Fe-Ni, Au-Cu-Fe, Cr-Fe-Ta, etc.

This thesis mainly deals with the computation of BCC(α)-FCC(γ) equilibrium in a large number of iron-rich alloys using thermodynamic descriptions. The motivation for this work is two-fold. One is the fact that experimental information about the BCC-FCC equilibrium in many ternary and other higher order iron alloys is either lacking or obsolete. The other is the industrial importance of the computed information, especially its application in the heat treatment and alloy development processes. The thesis also contains two chapters that deal with full thermodynamic treatments of Fe-V and Al-C-Fe.

Chapter 1 is an introductory chapter. It deals with the classification of binary phase diagrams and their ternary combinations. The aim and scope of the thesis are outlined. Typical examples of uses of phase diagrams are given. The general approach of the ensuing chapters is also outlined.

Chapter 2 is a review of the developments in the thermodynamic aspects of phase equilibria. Fundamental principles such as Gibbs phase rule, common tangent construction, relationship between Gibbs energy-composition curves and phase diagrams etc. are briefly dealt with. A review of various solution models, different formats for representing excess

Gibbs energy and their interrelationships etc. are presented. Models for special physical effects such as ferromagnetic ordering are reviewed. Different approximation techniques such as Muggianu and Toop extrapolation methods and their geometrical representations are discussed. Various first principle estimations of quantities used in the calculation of phase diagrams are reviewed.

Chapter 3 presents a discussion of the thermodynamic models used in the present calculations. The models discussed include: (i) a single lattice random solution model for substitutional solid solutions and the liquid phase, (ii) the sublattice model for interstitial solid solutions and intermetallic phases, and (iii) the model for magnetic ordering.

Chapter 4 presents the computational principles and numerical techniques used in this work. Flow charts for the computer programs developed for the calculation of the phase diagrams and for the optimization of the thermodynamic model parameters are presented.

In **Chapter 5** the computed BCC-FCC equilibria for ternary systems containing two ferrite stabilizing elements are presented. The database presented can be used for computing the BCC-FCC equilibria in all the 105 (3)-(3) combinations. Isothermal sections are given for following systems of the (3)-(3) combination: Al-Cr-Fe, Cr-Fe-Mo, Cr-Fe-Si, Cr-Fe-Ti, Cr-Fe-V, Cr-Fe-W, Fe-Mo-Si, and Fe-Ti-V. It is found that in the chromium containing systems, the solubility limit in the austenite of the other ferrite stabilizer passes through a maximum. In many other cases the phase boundaries are linear and are represented by equations for the best-fitting straight lines. The set of (3)-(4) type combinations computed are: Al-Fe-Nb, Fe-Mo-Nb, Fe-Nb-Si, Fe-Nb-Ti, Fe-Nb-W, Fe-Mo-Ta, Fe-Ta-Ti, Fe-Ta-W, Cr-Fe-Nb, and Cr-Fe-Ta. Here, the noteworthy feature is the appearance of three-phase equilibria between BCC, FCC and the Laves phase(λ). It is found that in the Cr-Fe-Nb and Cr-Fe-Ta systems the coalescence of the two phase fields ($\alpha+\gamma$) and ($\alpha+\lambda$) leads to the occurrence of two critical lines corresponding to the formation and disappearance of the two three-phase fields.

The computed isothermal sections for Fe-Nb-Ta, which is a (4)-(4) combination is also presented.

Chapter 6 deals with the BCC-FCC equilibria in ternary systems containing two austenite stabilizers. Combinations covered are (1)-(1), (2)-(2) and (1)-(2) types, comprising 9 systems. The following three (1)-(1) types are computed: Co-Fe-Mn, Co-Fe-Ni, and Fe-Mn-Ni. The unique nature of Co-containing systems is explained on the basis of the peculiarities observed in the Fe-Co binary phase diagram. The Au-Cu-Fe is an example of the (2)-(2) combination. The Au-Co-Fe, C-Fe-Ni, Co-Cu-Fe, Cu-Fe-Mn, Cu-Fe-Ni systems represent (1)-(2) combination.

In **Chapter 7**, the BCC-FCC equilibria in ternary systems containing one austenite and one ferrite stabilizer are presented. This covers combinations (1)-(3), (1)-(4), (2)-(3), and (2)-(4). The (1)-(3) systems covered are Al-Fe-Mn, Al-Fe-Ni, Co-Cr-Fe, Co-Fe-Ti, Cr-Fe-Mn, Cr-Fe-Ni, Fe-Mn-Ti, Fe-Mo-Ni, Fe-Ni-Si, Fe-Ni-Ti, and Fe-Ni-W. Typical effects of combining an austenite stabilizer with a ferrite stabilizer are discussed. The Co-Fe-Ta and Co-Fe-Nb are presented as examples of (1)-(4) combination. The Cr-Cu-Fe and C-Fe-W are (2)-(3) combinations. Two examples are given for the (2)-(4) combination: Au-Fe-Nb and Cu-Fe-Nb.

Chapter 8 deals with a full thermodynamic reassessment of the Fe-V system. Recent experimental thermochemical data for the various phases and the phase diagram data are used to optimize the thermodynamic parameters. Calculations of the liquid-BCC equilibrium, γ-loop, and the σ regions are carried out. A computed phase diagram of the Fe-V system is presented.

Chapter 9 presents a comprehensive thermodynamic assessment of the ternary system Al-C-Fe. The binary and ternary interaction parameters and the Gibbs energies of formation of Al_4C_3 and the ternary compound $Fe_3AlC_{0.565}(\kappa)$ are obtained by optimization of the most recent thermochemical and phase diagram data. A liquidus projection and a

reaction scheme covering the entire composition range are presented. Isothermal sections covering a wide temperature range are computed. The calculated four-phase invariant reaction temperatures and the coexisting compositions are listed.

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