PHASE EQUILIBRIA AND ELASTIC MODULI OF RAPIDLY SOLIDIFIED Fe-Cr-Mo-B AND Fe-Cr-Ni-B ALLOYS

by

Li-Mei PAN

A Thesis Submitted to the University of Surrey for the Degree of Doctor of Philosophy

April 1992
A study was carried out on rapidly solidified Iron-Transition Metal-Boron alloys (Fe-TM-B, TM = Cr, Mo, Ni) in order to understand the effect of microstructure on the elastic properties of the materials. The thermodynamic principles governing phase equilibria in alloy systems are presented and phase diagram calculation techniques introduced. A brief review of rapid solidification technology is given, followed by thermodynamic modelling of phase formation in gas atomised powders. The elastic behaviour of metallic alloys and mathematical modelling of their elastic modulus are discussed.

Thermodynamic characterisations of the relevant phase diagrams in the Fe-TM-B systems are presented together with critical assessments of previous work in these system. A thermodynamic database is established and used in designing test alloy compositions. The criteria are defined, and subsequent calculations made, for the selection of a series of model alloys based in the Fe-Cr-B, Fe-Cr-Ni-B, and Fe-Cr-Mo-B systems.

Phase formation in the gas atomised powders of the designed alloys are predicted as a function of powder diameter, using a combined thermodynamic and kinetic approach, and the undercooling and critical powder size necessary for producing the desired amorphous or supersaturated solid solutions calculated. The elastic properties of the alloys are estimated in terms of microstructural parameters using Eshelby's Equivalent Inclusion model. These predictions helped reveal the microstructural evolution in rapidly solidified alloys and understand the relations between microstructure and the properties, in particular the elastic properties of the materials. The calculations were made by taking advantage of both computerised software available, and that developed by the present author.

Metallographic and mechanical examination results of the designed test alloys are discussed and analysed with respect to the theoretical calculation results. The effect of a number of variables, in particular the microstructure, on the elastic properties of the alloys is analysed, and the routes for achieving alloys with optimum microstructure and elastic properties recommended.
I would like to acknowledge my gratitude to Professor Peter Miodownik and Dr. Nigel Saunders for their continuous supervision and encouragement throughout the period of my PhD work. I would also like to thank Dr. Panos Tsakiropoulos for his valuable guidance and our many useful discussions.

I also wish to acknowledge Rolls-Royce plc Derby, U.K. for providing the financial support for the research project, as well as the Vice-Chancellors’ Committee for granting me an Overseas Research Student Award to cover part of the PhD tuition fee.

I am grateful to The National Physical Laboratory, Division of Materials Metrology, for the provision of the MTDATA source code, and I would like to express my appreciation to Mr. Hugh Davies, Mrs. Susan Hodson, and Dr. Alan Dinsdale for their assistance which made it possible for me to create an application package in connection with the MTDATA software.

My thanks go to the people of the Materials Science and Engineering Department, in particular to those of the Departmental Laboratory and Microstructural Studies Unit for their help in the metallography, mechanical testing and electron microscopy work. I should especially acknowledge Dr. Chaitanya Baliga for fruitful discussions during our project work and for providing microanalysis and many other results.

Finally my special thanks are due to my parents who have always been there with their love and endless support whenever I needed it.

Li-Mei Pan
SYNOPSIS

ACKNOWLEDGEMENT

CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF FLOWCHART

CHAPTER I INTRODUCTION

CHAPTER II LITERATURE SURVEY

2.1 Introduction to Literature Survey

2.2 Phase Equilibria in Alloy Systems

2.2.1 Thermodynamic Characterisations of Phase Equilibria

2.2.2 Computerised Calculations of Phase Diagrams

2.2.3 Thermodynamic Models (i): Substitutional Model

2.2.4 Thermodynamic Models (ii): Sublattice Model

2.2.5 Energy Contribution Due to Magnetic Ordering

2.3 Rapid Solidification Process

2.3.1 Review of Rapid Solidification Technology

2.3.2 Microstructural and Constitutional Effects of Rapid Solidification

2.4 Phase Transformations in Rapid Solidification Process

2.4.1 Thermodynamic Aspects of Solidification

2.4.2 Metastable Phase Equilibrium

2.4.3 The Driving Force for Solidification

2.4.4 The Kinetics of Phase Transformations

2.4.5 Classic Nucleation Theory
4.4 Thermodynamic and Thermophysical Data Used in Solidification Calculations
  4.4.1 Thermodynamic Database for the Alloy Systems
  4.4.2 Thermophysical Data

CHAPTER V MATHEMATICAL MODELLING OF ELASTIC MODULI USING
ESHELBY'S EQUIVALENT INCLUSION METHOD
  5.1 Introduction
  5.2 Calculation Procedures of Eshelby Method
    5.2.1 Input of Elastic Stiffness Tensor
    5.2.2 Calculation of Eshelby's Tensor
    5.2.3 Calculation of Composite Compliance Tensor
  5.3 Computer Programming for the Modulus Prediction
  5.4 Modelling of Elastic Properties Using Eshelby Method
    5.4.1 Estimation of Young's Modulus of Boride
    5.4.2 Determination of Young's Modulus of Fe-Based Matrix
  5.5 Prediction of Young's Moduli of Designed Test Alloys

CHAPTER VI TEST ALLOY DESIGN
  6.1 Introduction
  6.2 General Selection Criteria for Test Alloys
  6.3 Selection Criteria for Test Alloy Compositions in Specific Systems
    6.3.1 Test Alloys in the Fe-Cr-B System
    6.3.2 Test Alloys in the Fe-Cr-Ni-B System
    6.3.3 Test Alloys in the Fe-Cr-Mo-B System
  6.4 The Calculation Procedures
    6.4.1 Calculations for Fe-Cr-B Alloys
    6.4.2 Calculations for Fe-Cr-Ni-B Alloys
    6.4.3 Calculations for Fe-Cr-Mo-B Alloys
  6.5 Volume Fraction of Borides in Designed Alloys
    6.5.1 Theoretical Density of Matrix and Borides
    6.5.2 Calculation of Volume Fraction of Borides
  6.6 Summary
CHAPTER VII EXPERIMENTAL PROCEDURES

7.1 Production and Processing of Test Alloys

7.1.1 Production of Test Alloys

7.1.2 Liquidus and Solidus of Designed Model Alloys

7.1.3 Processing of Test Alloys

7.1.4 Analysed Compositions of Test Alloys

7.2 Heat Treatment

7.3 Hardness Measurement

7.4 Tensile Testing

7.4.1 Testing Conditions

7.4.2 Elasticity of Model Alloys

7.4.3 Other Tensile Properties

7.4.4 Accuracy of Tensile Measurement

7.5 Metallographic Examination

7.5.1 Sample Preparation

7.5.2 Examination of Microstructure

7.5.3 Measurement of Volume Fraction of Borides

7.6 Examination of Porosity in Consolidated Alloys

7.6.1 Examination of Porosity via Density Measurement

7.6.2 Examination of Porosity via Metallography

CHAPTER VIII RESULTS AND DISCUSSION

8.1 Introduction

8.2 Phase Equilibria in Designed Test Alloys

8.2.1 Calculated Phase Compositions in Test Alloys

8.2.2 Discussion on Phase Equilibria in the Fe_{70}Cr_{18}Mo_{2}B_{10} Alloy

8.2.3 Discussion on Phase Equilibria in Designed Fe-TM-B Alloys

8.3 Predicted Phase Formation in Gas Atomised Powders and Discussion

8.4 Microstructure of Consolidated Alloys

8.4.1 Observed Microstructure

8.4.2 Volume Fractions of Borides

8.4.3 Porosity in Consolidated Alloys

8.5 Tensile Test Results

8.6 Analysis of Effect of Consolidation Conditions on Mechanical Properties
8.6.1 Effect of Hipping Temperature 185
8.6.2 Effect of Consolidation Route 185
8.7 Correlation of Hardness with Elastic Modulus 187
  8.7.1 Hardness of Consolidated Alloys 187
  8.7.2 Hardness of Alloys after Heat Treatment 187
  8.7.3 Analysis of Modulus with Respect to Observed Hardness 189
8.8 Predicted Young's Moduli of the Fe-TM-B Alloys 191
8.9 Discussion on the Effect of Phase and Microstructure Variables on Alloy Modulus 192
  8.9.1 Effect of Matrix Composition 192
  8.9.2 Effect of Nature of Matrix 194
  8.9.3 Effect of Boride Type 197
  8.9.4 Effect of Boride Amount 198
  8.9.5 Effect of Porosity 199
8.10 Optimisation of Alloy Compositions 201
8.11 Summary 204

CHAPTER IX CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK 205
  9.1 Conclusions 205
  9.2 Suggestions for Further Work 206

REFERENCES 207

APPENDIX I Thermodynamic Parameters for the Fe-Cr-Mo-Ni-B System 218

APPENDIX II The Micro File APP.101 231

APPENDIX III The Nucleation Subroutine ITR101 233

APPENDIX IV The Programme for Eshelby Calculation 247

APPENDIX V Derivation of Tensor A and B in the Mean Stress Equation 255
CHAPTER I INTRODUCTION
Table 1.1 Young's modulus data of chromium carbon steels from the literature.

CHAPTER II LITERATURE SURVEY
Table 2.1 General formula for Eshelby's tensor $S_{ijkl}$.
Table 2.2 Comparison between effect of matrix and inclusion on Young's modulus of a composite according to Eshelby's model.

CHAPTER III PHASE DIAGRAM ASSESSMENTS
Table 3.1 Overview of phase diagram assessments on the Fe-Cr-Mo-B and Fe-Cr-Ni-B systems.
Table 3.2 Enthalpies of formation for Fe- borides.
Table 3.3 Melting points for the Fe- borides.
Table 3.4 Invariant reaction data on the calculated Fe-B phase diagram.
Table 3.5 Enthalpies of formation of Cr- borides.
Table 3.6 Invariant reaction data on the calculated Cr-B phase diagram.
Table 3.7 Invariant reactions for the calculated Mo-B phase diagram.
Table 3.8 Gibbs energy of formation of Mo-B compounds.
Table 3.9 Comparison of enthalpy of formation of Ni$_2$B and NiB from the present work with literature [82Sat].
Table 3.10 Invariant reaction data on the calculated Ni-B phase diagram.
Table 3.11 Summary of the calculated and the experimental data on the three phase equilibrium in the Fe-Cr-B system.
Table 3.12 Summary of ternary reaction data on the calculated Fe-Cr-B liquidus projection plot.
Table 3.13 Comparison between the calculated and experimental data on the three-phase equilibrium in the Fe-Ni-B system at 800°C.
Table 3.14  Mole fractions and compositions of the phases in equilibrium at 1000°C of the alloy Fe_{70}Cr_{18}Mo_{2}B_{10}.

CHAPTER IV  THEORETICAL PREDICTION OF PHASE FORMATION
Table 4.1  Thermophysical properties of gases used in the atomisation. Data for an estimated effective temperature of 400 to 500 K are taken from Handbook of Chemistry and Physics [82Wea].

CHAPTER VI  TEST ALLOY DESIGN
Table 6.1  Designed alloy compositions.

CHAPTER VII  EXPERIMENTAL PROCEDURES
Table 7.1  Calculated liquidus and solidus of the test alloys.
Table 7.2  HPGA processing conditions for a typical model alloy.
Table 7.3  Hipping conditions for Osprey powders of Fe_{70}Cr_{18}Mo_{2}B_{10}.
Table 7.4  Correspondence of the two sets of alloy codes and their nominal compositions. (Compositions are given in both at% and wt%.)
Table 7.5  Analysed compositions of consolidated alloys.
Table 7.6  Sample preparation route for metallography study.
Table 7.7  Details of Vilellas Reagent.

CHAPTER VIII  RESULTS AND DISCUSSION
Table 8.1  Calculated proportions and compositions of equilibrium phases for the model alloys at 1000°C.
Table 8.2  Comparison between the calculated ratios of the metallic components and EDX analysis results [89Kim, 91Bal] of matrix and borides for an Fe_{70}Cr_{18}Mo_{2}B_{10} alloy produced via different processing routes.
Table 8.3  Comparison between the calculated ratios of the metallic components and EDX analysis results [91Bal] of matrix and borides in the designed Fe-Cr-B test alloys (RCX440→RCX443).
Table 8.4  Comparison between the calculated ratios of the metallic components and EDX analysis results [91Bal] of matrix and borides in the designed Fe-Cr-Ni-B test alloys (RCX470 and RCX472).
Table 8.5  Comparison between the calculated ratios of the metallic components and EDX
analysis results [91Bal] of matrix and borides in the designed Fe-Cr-Mo-B test alloys (RCX477 and RCX478).

Table 8.6 Predicted critical nucleation temperatures and undercoolings for the competing phases at various powder diameters of the designed Fe-TM-B alloys atomised in nitrogen. a: SU1→SU4; b: RR and SU7→SU8; c: SU5→SU6.

Table 8.7 Measured volume fraction of borides in the test alloys.

Table 8.8 Measured level of porosity in the test alloys.

Table 8.9 Measured density of the test alloys with the estimated level of porosity.

Table 8.10 Tensile data.
   a Tensile data for extruded Fe-Cr-B alloys.
   b Tensile data for Fe_{70}Cr_{18}Mo_{2}B_{10} alloys.
   c Tensile data for carburised Fe_{70}Cr_{18}Mo_{2}B_{10} alloys.
   d Tensile data for extruded Fe-Cr-Mo-B alloys.
   e Tensile data for extruded Fe-Cr-Ni-B alloys.

Table 8.11 Measured hardness of the test alloys as extruded and after various heat treatment.

Table 8.12 Predicted Young's moduli of the designed alloys using Eshelby method.

Table 8.12a Modification of Young's modulus by deducting the effect of porosity based on Eshelby method.

Table 8.13 Designed alloy compositions with the matrix structure at room temperature, boride type and amounts. Alloy compositions are given in both atomic and weight percentages.

Table 8.14 Calculated proportions and compositions of equilibrium phases for the proposed optimum alloys at 1000°C.

Table 8.15 Calculated liquidus and solidus of the proposed optimum alloys.

Table 8.16 Predicted range of Young's modulus for the proposed optimum alloys.
LIST OF FIGURES

CHAPTER II  LITERATURE SURVEY

Figure 2.1  Schematic diagram of high pressure gas atomiser layout [86Ric].
Figure 2.2  Schematic illustrations of Chill Block Melt Spinning technique [85Lie, 87Ana].
Figure 2.3  Driving force of solidification.
Figure 2.4  Transformations from initial to final state through an activated state of higher free energy [86Por].
Figure 2.5  Eshelby's Equivalent Inclusion Method.
Figure 2.6  A plot of the effective composite modulus obtained using Eshelby method with the mean field approach for composites with inclusions of different aspect ratios.
Figure 2.7  Magnetostriction effect [91Mio].
   a) Effect of chromium on elastic modulus;
   b) Modulus effect versus magneto-damping.

CHAPTER III  PHASE DIAGRAM ASSESSMENTS

Figure 3.1  The Fe-Cr phase diagram from Andersson and Sundman [87And].
Figure 3.2  The Fe-Mo phase diagram from Fernandez Guillermert [84Fer].
Figure 3.3  The Fe-Ni phase diagram from Xing et al [85Xin].
Figure 3.4  The Cr-Mo phase diagram from Frisk and Gustafson [88Fri].
Figure 3.5  The Cr-Ni phase diagram from Chart [90Cha].
Figure 3.6  The Mo-Ni phase diagram from Frisk [90Fri].
Figure 3.7  The Fe-B phase diagram from assessment by Chart [80Cha].
Figure 3.8  Calculated phase diagram of Fe-B system with experimentally determined phase boundaries superimposed.
Figure 3.9  Calculated Fe-rich corner of the Fe-B phase diagram with experimentally determined phase boundaries superimposed.
Figure 3.10  Calculated excess enthalpy of liquid of the Fe-B with experimental data [75Esi] for comparison.
LIST OF FIGURES

Figure 3.11 The Cr-B phase diagram from the assessment of Liao and Spear [86Lia].
Figure 3.12 Calculated phase diagram of the Cr-B system with experimentally determined phase boundaries superimposed.
Figure 3.13 The Mo-B phase diagram from the assessment of Spear and Liao [88Spe].
Figure 3.14 Calculated phase diagram of the Mo-B system with experimentally determined phase boundary data superimposed.
Figure 3.15 Comparison between the calculated and observed Mo-solvus.
Figure 3.16 Comparison between the calculated and the experimentally measured [77Sto] activity data of boron in Mo-B alloys. a) at 1790 K; b) at 2073 K.
Figure 3.17 Calculated phase diagram of Ni-B binary system with experimentally measured phase boundaries superimposed.
Figure 3.18 Summary of the experimental information [66Kan, 70Che, 73Bor, 76Gor, 83Gia] on the three-phase field of the Fe-Cr-B isothermal section.
Figure 3.19 Calculated isothermal section of the Fe-Cr-B system at 900°C from the present work, with experimental data from [70Che] for comparison.
Figure 3.20 Calculated isothermal section of the Fe-Cr-B system at 700°C from the present work, with experimental data from [70Che] for comparison.
Figure 3.21 Calculated liquidus projection of the Fe-Cr-B system from the present work.
Figure 3.22 Experimentally determined isothermal section of the Fe-Mo-B system at 1000°C from Gladysheevski [66Gla].
Figure 3.23 Experimentally determined isothermal section of the Fe-Mo-B system at 1050°C from Haschke [66Has].
Figure 3.24 Calculated isothermal section of the Fe-Mo-B system at 1000°C from the present work.
Figure 3.25 Calculated isothermal section of the Fe-Mo-B system at 1050°C from the present work.
Figure 3.26 Experimentally determined isothermal section of the Cr-Mo-B system at 1400°C from Kuz’ma et al [69Kuz].
Figure 3.27 Experimentally determined isothermal section of the Cr-Mo-B system at 1000°C from Kolomytsev et al [69Kol].
Figure 3.28 Calculated isothermal section of the Cr-Mo-B system at 1400°C from the present work.
Figure 3.29 Experimentally determined isothermal section of the Fe-Ni-B system at 800°C from Kuz’ma et al [68Kuz].
LIST OF FIGURES

Figure 3.30 Experimentally determined isothermal section of the Fe-Ni-B system at 800°C by Stadelmaier and Pollock [69Sta].

Figure 3.31 Calculated isothermal section of the Fe-Ni-B system at 800°C from the present work.

Figure 3.32 Experimentally determined isothermal section of the Cr-Ni-B system at 800°C by Chepiga et al [72Che].

Figure 3.33 Experimentally determined isothermal section of the Cr-Ni-B system at 1000°C by Lugscheider et al [74Lug].

Figure 3.34 Calculated isothermal section of the Cr-Ni-B system at 1000°C from the present work.

Figure 3.35 Comparison of the alloy partitioning in the phase $M_3B_2$ between the calculated results from this work and the experimental data from Takagi et al [86Tak].
   a) B contents; b) Cr contents; c) Mo contents; d) Fe contents in $M_3B_2$ as a function of Mo/B atomic ratio.

Figure 3.36 Calculated phase mole fraction versus temperature for the alloy Fe$_{70}$Cr$_{18}$Mo$_2$B$_{10}$.

CHAPTER V MATHEMATICAL MODELLING OF ELASTIC PROPERTIES

Figure 5.1 Comparison of the estimated Young's modulus of boride with the literature [66Ame].

Figure 5.2 Young's moduli of Cr carbon steels vs. volume percentage of carbide, compared with Eshelby curves.
   a) full scale; b) expanded scale for 0→25 vol% of carbide.

Figure 5.3 Modified Young's moduli of Cr carbon steels by deducting the effect of Cr, vs. volume percentage of carbide, compared with Eshelby curves.
   a) full scale; b) expanded scale for 0→25 vol% of carbide.

CHAPTER VI TEST ALLOY DESIGN

Figure 6.1 Calculated isothermal section of the Fe-Cr-B system at 1000°C.

Figure 6.2 Composition matrix of the designed alloys (SU1→SU4) in relation to the tie lines of the equilibrium between the boride and the solid solution matrix phase on the isothermal section of the Fe-Cr-B system at 1000°C.

Figure 6.3 Mole fraction of equilibrium phases as a function of temperature for the proposed test alloy SU5: Fe$_{55}$Cr$_{24}$Ni$_{11}$B$_{10}$.

Figure 6.4 Mole fraction of equilibrium phases as a function of temperature for the proposed...
test alloy SU6: Fe_{63}Cr_{18}Ni_{14}B_{5}.

Figure 6.5 Tie triangle of the three phase equilibrium between fcc, M_{2}B_{orth}, and M_{3}B_{2} of the original alloy Fe_{70}Cr_{18}Mo_{2}B_{10} (RR).

Figure 6.6 Mole fraction of equilibrium phases as a function of temperature for the proposed test alloy SU7: Fe_{73}Cr_{12}Mo_{6}B_{10}.

Figure 6.7 Mole fraction of equilibrium phases as a function of temperature for the proposed test alloy SU8: Fe_{81}Cr_{9}Mo_{4}B_{6}.

CHAPTER VII EXPERIMENTAL PROCEDURES

Figure 7.1 An example of HPGA particle size distribution [91Bal].

Figure 7.2 Tensile test piece used in the present investigation.

CHAPTER VIII RESULTS AND DISCUSSION

Figure 8.1 Variation of critical nucleation temperatures for the competing phases with the size of atomised powders. Powder diameter d: \( \mu m \); Alloy code: RR.

Figure 8.2 Variation of critical nucleation temperatures for the competing phases in the atomised powders. Powder diameter: \( \mu m \).

a) Alloy code: SU5, M_{23}B_{6} observed;
b) Alloy code: SU6, M_{23}B_{6} not observed.

Figure 8.3 Microphotographs showing the microstructure of model alloys processed via HPGA followed by extrusion or hipping.
a) RCX440; b) RCX441; c) RCX442; d) RCX443; e) RCX445; f) HIP9;
g) RCX470; h) RCX472; i) RCX477; j) RCX478

Figure 8.4 Summary of tensile data (UTS, VPN and Young’s modulus vs. elongation), [91Mio].

Figure 8.5 Hardness of consolidated alloys (HIPped, RCX442, and RCX445) as received and after heat treatment.

Figure 8.6 Comparison of mechanical properties between model alloys with a ferritic and a transformed austenitic matrix.

Figure 8.7 Comparison of mechanical properties (before and after oil quench) between alloys designed with a ferritic and a transformed austenitic matrix.

Figure 8.8 Comparison of mechanical properties between model alloys designed with an austenitic matrix at room temperature and a martensitic matrix.

Figure 8.9 Comparison of tensile properties between alloys with Cr- and Mo- borides.
Figure 8.10  Comparison between Eshelby curves and tensile test results of model alloys with various boride content. The estimated Young's modulus range was taken for the matrix (160–215 GPa) and the borides (420±40 GPa).

Figure 8.11  Eshelby curves with Young's modulus modified by deducting the deterioration due to the porosity present in the test alloys.
CHAPTER IV  THEORETICAL PREDICTION OF PHASE FORMATION

Chart 4.1  Flowchart of the nucleation programme for solidification studies.

CHAPTER V  MATHEMATICAL MODELLING OF ELASTIC PROPERTIES

Chart 5.1  Flowchart of the programme for the effective modulus of composites.
Rapid Solidification Powder Technology has been used to achieve superior mechanical properties, and corrosion resistance in the conventional iron-base alloys modified with appropriate amount of boron [83Ray, 85Hah, 87Hah]. The addition of boron was intended to provide a fine dispersion of refractory metal borides in the matrix of the rapidly solidified alloys after suitable heat treatment, and the enhanced properties of the alloy were attributed to the chemically homogeneous, ultra-fine microcrystalline structure obtained after consolidation and subsequent heat treatment. The boride particles help in retaining an ultra-fine recrystallised matrix grain structure, and contribute to the microstructural stability and enhanced mechanical strength at high temperatures compared to the commercial steels with similar composition.

Ray et al [83Ray] demonstrated the effect of introducing specific amount of boron (boron content: 0.45 to 4 wt% B depending on the alloy system) in conventional precipitation hardening stainless steels, Fe-Al-B alloys, and high speed tool steels produced via rapid solidification powder metallurgy technology. The alloys were processed by chill block melt spinning to form rapidly solidified ribbons with a microstructure of either amorphous or supersaturated bcc or fcc solid solution phases. The ribbons were then crushed into fine powders, followed by hot extrusion to produce bulk material. During consolidation at elevated temperature and subsequent heat treatment, the amorphous and metastable phases broke down into a fine dispersion of stable particles (~30 vol%), embedded in a ductile iron-based metallic matrix. The resulting in situ composites exhibited high strength, excellent thermal stability, superior corrosion and oxidation resistance, which encouraged further intensive development works being carried out on more alloys of this class.
Hahn et al [85Hah] showed the results of one of the conventional Precipitation Hardening ferro alloys modified with boron (2.1 wt\%B) and processed via rapid solidification technology. Significantly higher tensile strength, especially at elevated temperatures, were obtained via generation of an ultra fine grained microstructure stabilised by boride phases. Following this work, Hahn et al [87Hah] further improved yield strength and ductility at elevated temperatures using rapid solidification technology in the Precipitation Hardening ferro alloys modified by appropriate amount of Ti as well as boron in stoichiometric proportions to allow a preferential formation of stable titanium diborides.

The latter work demonstrated that metallic glasses containing a critical combination of refractory transition metal solutes provide high strength with acceptable ductility and high thermal stability, due to the multi-phase microstructure formed at high temperature during consolidation, whereas conventional metallic glasses undergo transition at relatively low temperatures into brittle microstructure consisting of a very large proportion of intermetallic phases.

It was therefore felt worthwhile considering exploiting the potential of rapid solidification powder metallurgy technology in some other iron-based, transition metals and boron-containing alloys. Among this range of alloys, the Fe-TM-B system (TM = Cr, Mo, Ni) has been chosen to be examined for applications where a combination of high strength and acceptable modulus at elevated temperatures is required. A high specific modulus was particularly emphasised in the development of this new alloy in order to meet the requirement of future advanced aero-engines. In addition, high yield strength and maximum elastic stress were desirable with regard to solving some design problems.

Initial investigations were conducted on a Fe_{70}Cr_{18}Mo_{2}B_{10} (the composition Fe_{70}Cr_{18}Mo_{2}B_{10} will be from now on referred to as 'the base composition') alloy [88Raw]. The alloy was first manufactured by chill block melt spinning in air, and amorphous ribbons of 30 to 80 \( \mu \)m in thickness were produced. The amorphous ribbons were subsequently pulverised under Ar atmosphere in a hammer mill to produce powders of \(<150 \mu m\) in size. The pulverised powders were finally consolidated into a bar by hot extrusion, at a ratio of 10:1, after soaking for 2 hours at 950°C. This work achieved some promising results in particular in high Young's modulus (from 255 up to 270 GPa), high hardness (HV 690) and improved fatigue properties [88Raw].
INTRODUCTION

The improvement in Young's modulus is remarkable considering modulus values for ordinary steels. A literature search for available Young's modulus data of chromium carbon steels was conducted and the measured Young's modulus data from various sources are listed in Table 1.1. The mole fraction of carbide (based on Fe₃C) are converted from carbon content (wt% C) in the alloys by a factor of 4. The table also gives a modified modulus for each alloy after excluding the effect of Cr by a factor of +0.5 for 1 wt%Cr, a value given by Leslie [72Les]. It can be seen from these data that the Young's modulus of steels are not very high by carbide strengthening. The borides in the initial test alloy seem to have an important effect on the elastic modulus.

The extruded microstructure were examined [89Kim] using a combination of electron microscopy and X-ray diffraction methods, and were found to have a structure consisting of a homogeneous distribution of ~30 vol% of Cr-rich boride particles and Mo-rich particles, embedded in an α'-Fe lath martensite matrix. The larger Cr-rich boride particles (~6 μm in size) were found to have an orthorhombic M₂B structure whereas the smaller Mo-rich (~2 μm in size) were of unknown origin. It was not clear as to why the matrix was martensite after consolidation, considering the amount of Cr and Mo in the alloy which should be expected to stabilise the α-Fe structure.

In order to maximise the potential of rapid solidification technology in alloys of this class, it is essential to obtain a detailed understanding of phase formation and microstructure evolution during the processing of the materials. This requires detailed information on phase equilibria in the relevant alloy systems, and an effective way to obtain this information is computerised phase diagram assessments based on fundamental thermodynamic principles. The thermodynamic database established as a result of the phase diagram assessments in turn provides the essential data, which is often lacking, for solidification studies in the rapid solidification process.

Another objective of this project is to understand how the mechanical properties, especially the elastic modulus of these alloys, are affected by their microstructure parameters, in order to produce a new generation of turbine engine materials with high elastic modulus, sufficient yield strength, and adequate ductility. An appropriate model is needed to relate the mechanical properties of materials with their microstructure morphology parameters. The intention is not only to predict the properties of the materials from their microstructure parameters, but also to design alloys with the microstructure which provides the optimum mechanical properties.
<table>
<thead>
<tr>
<th>Data Source</th>
<th>Alloy No.</th>
<th>E,Observed 'Fe-Cr-C' (wt%)</th>
<th>Cr (wt%)</th>
<th>Carbide (mol%)</th>
<th>E,Modified 'Fe-C'</th>
</tr>
</thead>
<tbody>
<tr>
<td>[78ASM]</td>
<td>1</td>
<td>207</td>
<td>0</td>
<td>15</td>
<td>207</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>210</td>
<td>1</td>
<td>5</td>
<td>209.5</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>188</td>
<td>9</td>
<td>1</td>
<td>183.5</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>220</td>
<td>2.25</td>
<td>7</td>
<td>219</td>
</tr>
<tr>
<td>[83Smi]</td>
<td>10</td>
<td>210</td>
<td>0</td>
<td>11</td>
<td>210</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>202</td>
<td>0</td>
<td>11</td>
<td>202</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>215</td>
<td>13</td>
<td>3</td>
<td>208.5</td>
</tr>
<tr>
<td>[43Sea]</td>
<td>19</td>
<td>221</td>
<td>13</td>
<td>5</td>
<td>214.5</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>193</td>
<td>0</td>
<td>3</td>
<td>193</td>
</tr>
<tr>
<td></td>
<td>21</td>
<td>202</td>
<td>0</td>
<td>7</td>
<td>202</td>
</tr>
<tr>
<td></td>
<td>22</td>
<td>203</td>
<td>0</td>
<td>12</td>
<td>203</td>
</tr>
<tr>
<td></td>
<td>23</td>
<td>179</td>
<td>0</td>
<td>0</td>
<td>179</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>190</td>
<td>18</td>
<td>2</td>
<td>181</td>
</tr>
<tr>
<td>[47Jon]</td>
<td>26</td>
<td>202</td>
<td>1.5</td>
<td>15</td>
<td>201</td>
</tr>
<tr>
<td></td>
<td>27</td>
<td>210</td>
<td>1.5</td>
<td>15</td>
<td>209</td>
</tr>
<tr>
<td></td>
<td>28</td>
<td>213</td>
<td>1.5</td>
<td>15</td>
<td>212</td>
</tr>
<tr>
<td></td>
<td>29</td>
<td>204</td>
<td>0</td>
<td>5</td>
<td>204</td>
</tr>
<tr>
<td>[47Rob]</td>
<td>30</td>
<td>204</td>
<td>0</td>
<td>1</td>
<td>204</td>
</tr>
<tr>
<td></td>
<td>31</td>
<td>214</td>
<td>0</td>
<td>5</td>
<td>214</td>
</tr>
<tr>
<td></td>
<td>32</td>
<td>212</td>
<td>7.7</td>
<td>7</td>
<td>208</td>
</tr>
<tr>
<td></td>
<td>33</td>
<td>219</td>
<td>12.2</td>
<td>6</td>
<td>213</td>
</tr>
<tr>
<td></td>
<td>34</td>
<td>188</td>
<td>29</td>
<td>0.4</td>
<td>173</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>204</td>
<td>0.5</td>
<td>4</td>
<td>204</td>
</tr>
<tr>
<td>[78ASM]</td>
<td>36</td>
<td>193</td>
<td>1</td>
<td>30</td>
<td>192.5</td>
</tr>
<tr>
<td>[72Les]</td>
<td>37</td>
<td>208</td>
<td>0</td>
<td>0</td>
<td>208</td>
</tr>
<tr>
<td></td>
<td>38</td>
<td>211</td>
<td>6</td>
<td>0</td>
<td>208</td>
</tr>
</tbody>
</table>
INTRODUCTION

The thesis, therefore, contains five major parts due to the nature of the objectives described above. The literature survey covers the theoretical background of phase equilibrium calculations followed by the modelling of phase formation in rapid solidification process. A survey is made for the rapid solidification processing technology. The analytical models developed for the elastic modulus of metal matrix composites are critically reviewed and the selection of Eshelby's approach is explained. The effect of constituent parameters on the elastic properties of materials according to the model is discussed. A substantial part of the thesis is devoted to phase diagram characterisations for the Fe-Cr, Mo, Ni-B systems, following a relevant literature review on each alloy system. The third part deals with calculation procedures in the prediction of phase formation in high pressure gas atomised powders (high pressure gas atomisation chosen as an alternative route to chill block melt spinning for bulk production), and in mathematical modelling of elastic moduli of alloys with an in situ composite structure. The fourth part consists of a detailed account of selection procedures for model alloys, in addition to the experimental procedures for the processing and testing of the designed alloys. The final part of the thesis presents the calculated and experimental results, followed by discussion of results from which the conclusions are drawn.
2.1 Introduction to Literature Survey

The objective of the present work is to study the effect of alloying and microstructural parameters on the elastic properties of the iron based boron-containing alloys processed via rapid solidification technology. The literature survey will first cover the thermodynamic principles in characterisations of phase equilibria and various models used in the thermodynamic descriptions of phases. A review of phase diagram and thermodynamic data available for each alloy system characterised in this work will be given, under the relevant alloy system, in the following chapter for the presentational convenience of comparisons to be made between the assessed phase diagrams and the literature. A brief review on the rapid solidification technology currently employed will be given, followed by the benefits of the process on the microstructure and properties of alloys. Phase formation or suppression in rapidly solidified alloys will be discussed on the basis of thermodynamic and nucleation theory. The analytical models developed for the elastic properties of metal matrix composites will be examined, and the Eshelby's equivalent inclusion method proposed for the present study will be described in detail. The effect of various microstructural parameters on the elastic properties of alloys will be discussed based on the Eshelby's approach.

2.2 Phase Equilibria in Alloy Systems

2.2.1 Thermodynamic Characterisations of Phase Equilibria

The thermodynamic principles that govern the phase equilibria in alloy systems are attributed
to the pioneering work of Willard Gibbs. The Gibbs free energy ($G$), under isobaric conditions, is defined in terms of enthalpy ($H$), entropy ($S$) and temperature ($T$): $G = H - TS$. This equation may be used to determine the stable phases co-existing in a system of specified composition and temperature. The most stable phase or a combination of phases is the one that possesses the lowest Gibbs free energy. Phase equilibria in alloy systems are usually studied under isobaric conditions. Therefore, if the Gibbs free energies of all possible phases in a system may be calculated at a given temperature, pressure being constant, as a function of composition, it is possible to determine the limits of composition over which any phase, or a combination of phases, is stable. After repeating this analysis for a number of temperatures, the phase boundaries of the system may be drawn to produce a temperature-composition diagram [70Rao].

The application of thermodynamics to phase equilibria can provide a useful check on the experimental data, and allow its extension to regions difficult to determine experimentally. The conventional method of analysis to determine phase diagrams, such as chemical, microscopic, thermal, and X-ray analysis, frequently fail to give the exact positions of equilibrium phase boundaries on account of kinetic factors. The determination of a solidus curve by thermal analysis, for example, involves diffusion in the solid state. The composition of the solid phase initially precipitated on cooling from liquid state differs from the final equilibrium composition. The time required to reach equilibrium conditions is difficult to predict and is frequently underestimated by the investigators. This opens to doubt many of the solidus curves in the supposedly 'well established' phase diagrams. It is of interest to investigate the methods for the construction of phase boundaries in the conventional temperature-composition phase diagram with reference to free energy-composition curves at several temperatures, because a phase diagram represents the temperature-composition relations corresponding to the minimum free energy of all possible competing phases. Such methods now provide a means of supplementing the valuable information shown on the conventionally determined phase diagrams.

2.2.2 Computerised Calculations of Phase Diagrams

Calculations of phase diagrams provide a cost-effective way of obtaining phase equilibrium information and have become more and more popular with the availability of computer software and thermodynamic databases for alloy systems of importance. There has been increased collaboration between different centres throughout the world. The CALPHAD organisation
(CALculation of PHAse Diagrams) hosts a conference every year and publishes a journal (CALPHAD) quarterly focusing on the development of ideas, methods and data. Another organisation SGTE (Scientific Group Thermodata Europe) has been set up to provide European industries with a source of reliable thermodynamic data and facilities for their use in equilibrium calculations.

If all of the thermodynamic properties of the phases were known, characterisations of phase diagrams would be quite straightforward. In reality, however, this is not usually the case. Information concerning phase diagram and thermodynamics of the various phases is limited. Critical assessment of the available phase diagram information combined with measured thermodynamic data is used in an optimisation procedure where the best fit possible is obtained between the various experimental properties of the system. A number of thermodynamic quantities, for instance the ideal entropy of mixing and the lattice stabilities of the component elements, are fixed. Others such as the excess Gibbs energies of formation of the compounds and the solution phases are floating parameters. The latter need to be optimised to give the best fit between the calculations and measured thermodynamic properties and phase diagrams.

Computer software provide a convenient tool in constructing the phase diagrams which otherwise would be impossible or time consuming to achieve. The packages available at the present for thermodynamic equilibrium calculations include the THERMO-CALC from the Royal Institute of Technology in Stockholm, Sweden [85And], and MTDATA developed at the National Physical Laboratory, Teddington, U.K. [90Dav]. However, utilising such computer software for the calculations of phase diagrams does not replace the need in understanding the theory of phase diagrams. The fact is that a deeper understanding of the underlying thermodynamic principles is required, in order to judge the correctness of the phase diagrams produced from purely theoretical calculations. For example, if there is limited experimental information, or the information available is widely scattered, there are difficulties in converging calculation and experimental data accurately. In such cases it is necessary to use a combination of scientific judgement together with such programmes to optimise the various parameters. This may involve making judgements such as to the accuracy of various experimental studies, if they differ significantly, or utilising theoretical predictions for the thermodynamic properties. The computer can also produce some new and complicated types of sections or projections of phase diagrams which cannot be interpreted sensibly without a wider knowledge of thermodynamics and phase equilibria.
Phase equilibria in a multi-component system have often been established based on the thermodynamic descriptions of all the constituent sub-systems. This simplification has been proved in practice to be very convenient in modelling multi-component systems without introducing significant error. The excess free energy of mixing of a phase in a ternary system, for example, can be described by summing the constituent binary interactions. Phase diagram calculation in multi-component systems are based on the criteria that:

(a) at equilibrium the total energy of the system as a whole is a minimum, and
(b) the chemical potential of any single component in all co-existing phases is the same.

The free energy of the relevant phases is described as a function of composition and temperature using various mathematical models which are described in the next section.

2.2.3 Thermodynamic Models (i): Substitutional Model

Phases such as liquid and other substitutional solid solutions can be described using a substitutional model [70Kau, 75Cha, 79Ans, 80Hill]. In this model the general equation that describes the free energy of a binary solution phase ($\Delta G^S$) is given by:

$$
\Delta G^S = x_A \Delta G_A^o + x_B \Delta G_B^o + \Delta G_{mix}^x - T\Delta S_{mix}^{ideal}
$$

where $x_A$, $x_B$ is the mole fraction of element A and B respectively. $\Delta G_A^o$, $\Delta G_B^o$ is the free energy of the phase in the pure element, and is termed the lattice stability [67Kau, 70Kau]. $\Delta G_{mix}^x$ is the excess Gibbs free energy of mixing. T is the temperature and $\Delta S_{mix}^{ideal}$ is the ideal entropy of mixing equal to $-R(x_A \ln x_A + x_B \ln x_B)$. $\Delta G_{mix}^{x^{n}}$ can be described using a Redlish-Kister polynomial series such that:

$$
\Delta G_{mix}^{x^{n}} = x_A x_B \left[ \Delta G(A, B; 0) + \Delta G(A, B; 1) (x_A - x_B) + \Delta G(A, B; 2) (x_A - x_B)^2 + \cdots + \Delta G(A, B; n) (x_A - x_B)^n \right]
$$

where $\Delta G(A, B; 0)$, $\Delta G(A, B; 1)$, $\ldots$, $\Delta G(A, B; n)$ are temperature dependent interaction energy parameters. The temperature dependence of Gibbs energy above 298.15 K for most materials,
where contribution to the thermodynamic properties arise from electronic, vibrational and translational degrees of freedom, can be conveniently and accurately represented by an expression of the form:

\[
\Delta G = a + bT + cT \ln(T) + dT^2 + eT^3 + fT^{-1} + gT^7 + hT^{-9}
\]

(2.2.3)

with \( a, b, c, ..., h \) coefficients and \( T \) the temperature. Sometimes it is not possible to represent data over a wide temperature range and it is generally convenient in practice to split the temperature range into two or more intervals, each with a set of these coefficients. The coefficients would normally be chosen such that there was no discontinuity in the Gibbs energy, its first derivative or its second derivative at the change from one temperature range to another [84Din].

Phase equilibria in multi-component alloys can then be predicted using the constituent binary characterisations as a basis. The free energy for a phase in a multi-component system is given by:

\[
\Delta G^\text{S} = \sum_i x_i \Delta G_i^\circ + \Delta G_{\text{mix}}^\text{xs} - T\Delta S_{\text{mix}}^\text{ideal}
\]

(2.2.4)

where \( 'i' \) denotes the components in the system, \( \Delta G_i^\circ \) is the lattice stability of the phase in the pure element \( i \). The excess free energy of mixing \( \Delta G_{\text{mix}}^\text{xs} \) can be described utilising Margules expansion [79Ans, 80Hill] which sums the binary interactions and is given by:

\[
\Delta G_{\text{mix}}^\text{xs} = \sum_{i,j} x_i x_j \sum_k \Delta G(i, j; k) (x_i - x_j)^k
\]

(2.2.5)

in which \( 'i', 'j' \) denotes the components and \( 'k' \) denotes the number of terms taken into account in the Redlich-Kister polynomial series. The ideal entropy is given by:

\[
\Delta S_{\text{mix}}^\text{ideal} = - R \sum_i x_i \ln x_i
\]

(2.2.6)

and here \( 'i' \) again represents the components.

Energies which are specific to higher order interactions can be taken into account. Ternary
interactions are often included where information exists; however it is worth noting that terms of higher order than these are not usually found necessary.

2.2.4 Thermodynamic Models (ii): Sublattice Model

For interstitial and intermetallic phases with broad ranges of homogeneity, the sublattice model is now often used [70Hil, 81Sun]. This is suitable for describing phases where the difference in size, charge or electronegativity causes a deviation from random mixing of the atoms. In the model the phase is conceived as being made up of various interlocking sublattices. Each sublattice (i) has a total number of sites (N$_i$) which can be occupied by various elements or species (j). The occupation of the relevant element or species on each sublattice is given by the site fraction, y$_{ij}$ = N$_{ij}$/N$_i$, where N$_{ij}$ is the actual number of sites occupied by the element or species, j, on the sublattice, i.

A non-stoichiometric phase with a number of sublattices (n) can be schematically described by the formulae:

$$(A, B, \ldots)_U (C, D, \ldots)_V (E, F, \ldots)_W \ldots \text{etc}$$

where the element or species A and B occupy the first sublattice, C and D the second, E and F the third and so on. U, V, W ... represent respectively the relevant number of sites for the sublattices and in this work satisfy the relation:

$$U + V + W + \ldots = 1$$

Any number of different atom or species type can occupy each sublattice and there can be many different sublattices.

The Gibbs energy of such a system is equal to:

$$\Delta G_{\text{mix}} = \Delta G^{\text{ref}} + \Delta G^{\text{ID}} + \Delta G^{\text{XS}} \quad \ldots(2.2.7)$$

The term $\Delta G^{\text{ref}}$ defines the reference plane of energy and is associated with the complete
occupation of each sublattice by the element mixing on it as a function of similar complete occupation on the other sublattices. For example, in a two sublattice model (A, B)\text{U}(C, D)\text{v}, \Delta G^{\text{ref}} is given by:

\[ \Delta G^{\text{ref}} = y_A' y_C'' \Delta G(A : C) + y_A' y_D'' \Delta G(A : D) + y_B' y_C'' \Delta G(B : C) + y_B' y_D'' \Delta G(B : D) \] ... (2.2.8)

The free energy terms \(\Delta G(\ldots)\) correspond to the free energy of the phase at the respective points of complete occupation.

The term \(\Delta G^{\text{ID}}\) expresses the Gibbs energy arising from the ideal entropy of mixing of the elements on each separate sublattice. \(\Delta G^{\text{ID}}\) is written as:

\[ \Delta G^{\text{ID}} = RT \sum_i N_i \sum_j y_j^i \ln y_j^i \] ... (2.2.9)

In the sublattice model, \(\Delta G^{\text{XS}}\) takes into account interaction energies between elements or species on a specific sublattice as a function of site occupation of elements in the other sublattices. For example, in the two sublattice model (A, B)\text{U}(C, D)\text{v}, \Delta G^{\text{XS}} is given by:

\[ \Delta G^{\text{XS}} = y_A' y_B' \{ y_C'' \Delta G(A, B : C) + y_D'' \Delta G(A, B : D) \} + y_C'' y_D'' \{ y_A' \Delta G(A : C, D) + y_B' \Delta G(B : C, D) \} \] ... (2.2.10)

By convention a comma separates the elements on the same sublattice whereas a colon separates the elements on the different sublattices.

The interaction coefficients \(\Delta G(i, j : k)\) can vary with composition and can be expressed in terms of a Redlish-Kister polynomial. For example, if the expansion is limited to a quadratic form the interaction coefficient \(\Delta G(A, B : C)\) can be expressed as

\[ \Delta G(A, B : C) = \Delta G(A, B : C; 0) + (y_A' - y_B') \Delta G(A, B : C; 1) + (y_A' - y_B')^2 \Delta G(A, B : C; 2) \] ... (2.2.11)

For higher order systems, where more than two atoms or species can occupy a sublattice, the
total energy of the phase is obtained by summating the energies of binary interactions using a
Redlish-Kister polynomial as described in section 2.2.3.

When intermetallic phases in a binary system have strictly limited solubility, they can be treated
as stoichiometric compounds. In such cases the free energy of the phase, which has a fixed
composition, is given as a function only of temperature, and is equal to the formation energy of
the compound referred to the constituent elements in their standard states. For stoichiometric
compounds the extension into the ternary and higher order systems is usually done by limiting
the occupation of one of the sublattices to an individual atom or species and varying the
occupation on the other sublattice. For example, in a M₂B compound where M represents
transition metals and B is boron, boron completely occupies a sublattice where \( N^1 = 0.333 \) while
the transition metals mix on the opposite sublattice where \( N^1 = 0.667 \). The compound is then
called a 'line' compound with a strict stoichiometry associated with the boron concentration but
with additional energies associated with the mixing of the transition metals.

2.2.5 Energy Contribution Due to Magnetic Ordering

In systems containing ferromagnetic elements such as iron, there is a magnetic energy
contribution to the free energy that needs to be taken into account in treating phase equilibria.
This magnetic energy term denoted \( \Delta G_{\text{m}}^{\text{mo}} \) is related to the crystal structure, the Bohr-magnetron
number ' \( \beta \) ', and the critical temperature of magnetic ordering ' \( T_C \) ' (Curie or the Neel
temperature) by the following equation:

\[
\Delta G_{\text{m}}^{\text{mo}} = RT \ln (\beta + 1) f(\tau) \tag{2.2.12}
\]

where \( \tau \) is defined as \( T/T_C \) and \( f(\tau) \) is obtained from the polynomial expressions of Hillert and
Jarl [78Hi1]. Data for \( T_C \), \( \beta \), and expressions for \( f(\tau) \) of each magnetic phase are given in the
appendix. In applying Equation (2.2.12) the composition dependence of the quantities \( T_C \) and
\( \beta \) has also to be considered, and this is accounted for by a Redlish-Kister polynomial which sums
binary interaction parameters in the same fashion as for the free energy term (refer to Section
2.2.3):

\[
T_C = x_A T_C(A) + x_B T_C(B) + x_A x_B \left( T_C(A, B; 0) + T_C(A, B; 1) (x_A - x_B) + \right)
\]
Notations in the above equation follow those explained before (Section 2.2.3) and the formula for \( \beta \) is obtained by replacing \( T_C \) with \( \beta \).

With the free energies of all the phases described using the equations shown above, a computer programme is used to calculate the phase equilibria which gives the lowest free energy for the system at any combination of temperature and composition. The main computer programme used here is THERMO-CALC, which was developed by the Division of Physical Metallurgy, Royal Institute of Technology, Stockholm, Sweden (see Section 2.2.2).

2.3 Rapid Solidification Process

2.3.1 Review of Rapid Solidification Technology

Rapid Solidification is often associated with cooling rates in excess of \( 10^3 \) K sec\(^{-1} \), compared to the cooling rate of a few K sec\(^{-1} \) in commercial sized ingots. Solidification speed is controlled by the latent heat it releases and the efficiency the heat can be removed by the environment through its surface. One way to speed up the process is, therefore, to create small dimension of the elementary volume so that the latent heat is extracted effectively via a surrounding fluid or by contact with a conducting chill surface. The maximum contact area between the melt and cooling medium may be effected by either altering the shape of the melt during the processing, or by physically segmenting the initial charge by various means [82Lie].

Numerous processing methods have been developed to achieve the fragmentation of the melt which is the essential requirement for rapid solidification. Jones [91Jon] reviewed the historical development of rapid solidification technologies. Examples include splat quenching, melt-spinning, surface melting and quenching, melt atomisation and solidification, and deposition by sputtering and evaporation. The majority of these process are largely on an experimental and developmental basis. It was, however, not until the development of methods for effective bulk consideration of splat flake and of techniques for high speed continuous casting of ribbon, wire and strip during the seventies, that the technological potential of rapid solidification to form the metastable solid solution [60Dew] from the melt became fully apparent. The most commonly
employed methods at the present for achieving rapid solidification of bulk production are chill block melt spinning (CBMS) and high pressure gas atomisation (HPGA).

Consolidation usually follows rapid solidification and the common consolidation process of rapidly solidified particulates usually involves cold-compacting, followed by hot isostatic pressing (HIP), and/or hot extrusion, forging or rolling. The temperature excursion during the consolidation process and the cooling rate following the consolidation determine the final structure of the bulk material. Metallic glass or super-saturated solid solution phase will decompose if the temperature is sufficiently high.

Rapid solidification production methods have been classified into three categories, according to Jones [82Jon]: (i) spray methods, (ii) chill methods and (iii) melt in situ methods. A brief description of each group will be given below, followed by more details of the two rapid solidification techniques (HPGA and CBMS) used in the present study.

(i) Spray Methods

Here a continuous stream of liquid metal is disintegrated into fine droplets by means of either a liquid (e.g. water), a gas (e.g. helium, argon, or nitrogen), or an electric field. Among the spray methods, high pressure gas atomisation is of particular interest in the present work and therefore described in detail below.

High Pressure Gas Atomisation (HPGA)

The earliest method used for rapid solidification of powders is gas atomisation where a stream of molten metal is atomised by a gas jet or jets. The high pressure gas fragments the melt (as if the melt were atomized) into tiny droplets (a few μm or larger in diameter) which subsequently solidify into solid powders during free flight as a result of convective heat flow or radiation or upon reaching the substrate, as in the case of spray forming.

The layout of the inert gas atomiser used at the University Foundry Laboratory at Surrey is schematically illustrated in Figure 2.1. The design was originally intended to process aluminium alloys, based on a similar atomiser designed at MIT [83Dom1,2], though many modifications have been subsequently introduced to produce finer powder and achieve more efficient atomisation.
The basic operation involves melting the alloy, atomising the melt, and collecting the powders. Up to 4 kg of an alloy can be melted in a crucible by induction heating, and the melt is held at 200-300°C above the liquidus of the alloy for about 30 minutes to ensure homogeneity of the melt. During the atomisation process the melt runs through the nozzle from the base of the crucible where high velocity inert gas (helium, nitrogen, or argon) fragmentes the melt stream into fine droplets. Finally the droplets are solidified, and the powders are separated from the gas at the cyclone with the inert gas directed to the exhaust whilst the powders are collected within the collection box.

Powders provide a convenient form for compaction following solidification. Considerable effort has been extended to prepare rapidly solidified powders which contain fine microstructure, fine
(ii) Chill Methods

These methods involve injecting the melt into a die cavity, or forming a thin section by forging the melt between chill surface, or extruding the melt on a chill surface, or extraction of melt by contact with a rotating disc. The most commonly used chill method to produce long and continuous ribbons is chill block melt spinning, where the molten stream solidifies against a chill surface.

Chill Block Melt Spinning (CBMS)

Chill block melt spinning is a process by which metallic materials may be rapidly and continuously cast from the melt, in the form of thin filament or strip, by the impingement of a stream of melt onto the circumferential surface of a rotating roller. This involves the flow of a molten alloy stream onto a rapidly rotating quenching substrate. A schematic plot for CBMS is shown in Figure 2.2 [85Lie, 87Ana]. The rapidly solidified ribbons will normally be crushed then consolidated, via extrusion or hot isostatic pressing, into bulk form.

Figure 2.2  Schematic illustrations of Chill Block Melt Spinning technique [85Lie, 87Ana].
Melt In Situ Methods

Spray and chill methods involve melting of the complete material prior to rapid solidification processing. An alternative is localised surface melting (depth of 10 to 1000 µm). This method will not be explored further here since it is not applied in the present work.

2.3.2 Microstructural and Constitutional Effects of Rapid Solidification

Rapid Solidification processing of materials results in large departure from equilibrium constitutions which include, according to Jones [82Jon], production of metastable phases, substantial extension of solid solubility, and formation of amorphous phases.

Most of the non-equilibrium crystalline phases occurring in rapidly solidified alloys are intermediate rather than terminal phases. They tend to be disordered and can be related to some iso-structural equilibrium phase. Alloy systems exhibiting few intermetallic phases with terminal phases of limited solid solubility and high critical cooling rates to form glasses are most likely to form non-equilibrium crystalline phases.

Non-equilibrium solid solubility extension can be attained up to various extent, depending on alloy composition as well as the cooling rate. Extensive solid solubility is allowed by the Hume-Rothery rules provided that the constituents do not differ in atomic size by more than 15 percent and are not too different in electronegativity or valence. However complete extension of solid solubility between terminal phases with the same crystal structure and partial extension beyond eutectic compositions have now been observed repeatedly on rapid solidification even when the Hume-Rothery criteria are substantially exceeded.

Amorphous phases are non-crystalline phases which are characterised by a complete lack of long range crystallographic order. In other words, there is no regularity in relative atomic position (no structural periodicity) beyond a distance of a few atomic or molecular diameters. It can be regarded as liquid phase structure supercooled into solid state. Glass formation readily occurs in alloy systems containing transition metals at particular compositions. Essentially a large liquidus depression assures that the viscosity of the melt is sufficiently high in the critical temperature range for the glass transition temperature to be reached before significant
crystallization of the melt can intervene [83Lub].

Prediction of the cooling conditions required to achieve such supercooling without appreciable formation of other equilibrium or non-equilibrium solid phases in general requires a knowledge of the kinetics of formation of these phases. Criteria which successfully define the cooling rate at which extended solid solutions should form in preference to the equilibrium solution phases can be obtained from thermodynamic considerations. A combined thermodynamic and kinetic approach developed for predicting phase formation in high pressure gas atomised powders will be discussed in the following section.

2.4 Phase Transformations in Rapid Solidification Process

2.4.1 Thermodynamic Aspects of Solidification

Classical thermodynamics is concerned primarily with the interdependence of certain well-defined macroscopic concepts (temperature, pressure, entropy, energy, composition, etc) possessed by a closed assembly. The usual thermodynamic equations are valid only for assemblies at equilibrium and for reversible transitions between such equilibrated assemblies. When thermodynamic considerations are applied to irreversible (i.e. 'natural') processes, the equations become inequalities, and are much less useful. For example, the principle of the increase in entropy during an adiabatic irreversible process provides information only about the direction of the change.

However, thermodynamics can be applied to the complicated non-equilibrium process of solidification even though it is at its best only when used to describe a system at equilibrium state. This can be done by assuming constrained equilibrium, in which the thermodynamics is applied locally to individual processes while other process are assumed to occur at negligible rate or not at all. One example is the application of thermodynamics to metastable phase formation.

Baker and Cahn [71Bak] have summarised a number of aspects of thermodynamics of solidification process, including metastable equilibrium, solidification of metastable phases, some thermodynamic aspects of the mathematical analysis of solidification problems, local equilibrium
in particular, and irreversible thermodynamics of interface processes. It has been shown that thermodynamics is useful and rigorous when applied to systems in stable and metastable equilibrium.

An attempt to remedy the inability of thermodynamics to predict precisely what will happen in non-equilibrium systems has led to the development of a theory, although not rigorous, known as ‘irreversible thermodynamics’ [62Gro, 58Den, 61Pri]. This approach proposes relationships between the rates of processes and macroscopic thermodynamic quantities. A combined thermodynamic and kinetic model, similar to the concept of irreversible thermodynamics, was applied in the present work to yield a plausible description of rapid solidification processes. Details of the model are presented in a later section of this chapter.

2.4.2 Metastable Phase Equilibrium

Metastable phase equilibrium obeys the same thermodynamic rules that apply to stable equilibrium [52Hum, 53Hof]. At this equilibrium, the temperature and the chemical potentials of all phases present are equal. The Gibbs phase rule applies if we use the actual number of phases present. Metastable phase diagrams show no unusual features except near limits of metastability where the nucleation barrier ceases to exist. If a phase is stable in one portion of a diagram and becomes metastable in another, no discontinuity is expected in its behaviour as it becomes metastable. For example the metastable extension of the liquidus and the solidus curve below the eutectic should show no break. When the stable phase in an alloy does not form but is replaced by a metastable phase, the resulting metastable equilibrium is thermodynamically indistinguishable from stable equilibrium. Hence we may construct metastable phase diagrams, and the most common of which is the well known Fe-Fe₃C diagram.

The assumption of interface equilibrium is a valuable and realistic one for describing many solidification processes. This assumption appears to have broad applicability to metals and many non-metals for solidification rates encompassed by usual casting and ingot making processes. When the solidification rate becomes sufficiently rapid in metals, significant deviations from interface equilibrium become possible. Thermodynamics cannot predict what these variations will be, but it can still define the domain of possible interface compositions.
2.4.3 The Driving Force for Solidification

Thermodynamics nevertheless can determine the essential driving force for solidification, which is the difference in the Gibbs free energies between the liquid and the solid phase at temperatures away from the equilibrium temperature. This will not be affected by the solidification rate or whether there is metastable phase forming in the solidification process.

The driving force for a solid phase, \( \beta \), to solidify from a liquid of composition \( C_L \), at a temperature below the liquidus, is illustrated as \( \Delta G_{L\rightarrow \beta} \) in Figure 2.3. The chemical potentials of the liquid phase, \( \mu_L^A \) and \( \mu_L^B \), can be used to calculate the driving force:

\[
\Delta G_{L\rightarrow \beta} = \{ (1 - C_\beta) \mu_L^A + C_\beta \mu_L^B \} - \Delta G_\beta
\]  \hspace{1cm} \text{(2.3.1)}

where \( \Delta G_\beta \) is the Gibbs free energy of the solid phase \( \beta \) at composition \( C_\beta \).

![Diagram of Driving force of solidification.](image-url)
2.4.4 The Kinetics of Phase Transformations

Thermodynamics can be used to describe stable or metastable equilibrium, it can therefore be used to calculate the driving force for a transformation, as has been shown in the above section. However, how fast a possible transformation proceeds is described by the kinetics of solidification.

Figure 2.4 shows the free energy of a single atom as it takes part in a phase transformation from an initially metastable state into a state of lower free energy. If $G_1$ and $G_2$ are the free energies of the initial and final state, the driving force for the transformation will be $\Delta G = G_2 - G_1$. However, before the free energy of the atom can decrease from $G_1$ to $G_2$ the atom must pass through a so-called transition or activated state with a free energy $\Delta G^a$ above $G_1$. The energies shown in Figure 2.4 are average energies associated with large numbers of atoms. As a result of passing through the activated state, the system has an energy of activation $\Delta G^a$.

![Figure 2.4](image)

**Figure 2.4** Transformations from initial to final state through an activated state of higher free energy [86Por].
of the random thermal motion of the atoms, the energy of any particular atom will vary with time and occasionally it may be sufficient for the atom to reach the activated state. This process is known as thermal activation [86Por].

A simple kinetic theory (also frequently referred to as the collision theory) dealing with the effect of temperature on the rate of a transformation is due to Arrhenius [1889Arr]. The probability of an atom reaching the activated state is given by \( \exp(-\frac{\Delta G^a}{kT}) \), where \( k \) is Boltzmann's constant \( (R/Na) \) and \( \Delta G^a \) is known as the activation free energy barrier [86Por]. The rate at which a transformation occurs will depend on the frequency with which atoms reach the activated state. Therefore the following equation can be written:

\[
\text{rate} \propto \exp \left( -\frac{\Delta G^a}{kT} \right)
\]

This equation was first derived empirically from the observed temperature dependence of the rate of chemical reactions and is known as the Arrhenius rate equation. It is customary to write the Arrhenius equation in the following format:

\[
k = A \exp \left( -\frac{Q}{RT} \right)
\]

where \( k \) denotes rate of a transformation, \( A \) proportionality constant and \( Q \) activation energy. This equation is of a very general form, and can be successfully applied to a wide range of processes and transformations in metals and alloys [66Mac, 86Por].

The concept of activated atoms and activation energy can be best explained from the Boltzmann's distribution law based on a statistical approach to the problem. The exponential factor \( \exp \left( -\frac{Q}{RT} \right) \) may be taken to represent the fraction of all the atoms which have an energy of activation at least equal to \( Q \) [66Mac].

### 2.4.5 Classical Nucleation Theory

The kinetics of a heterogeneous reaction can usually be described in terms of the separate nucleation and growth of the transformed regions [75Chr]. The classical theory of nucleation by random fluctuations in a metastable assembly is due mainly to Volmer [29Vol, 39Vol] and to
Becker and Doring [35Bec], though many other workers have made significant contributions.

The essential driving force for a phase transformation is the difference in the free energies of the initial and final configurations of the assembly, but when small particles of the new phase are formed, the free energy rises at first. The situation is conventionally described by assigning volume free energies to the bulk phases, and a surface free energy to the interface region. The surface term is dominant for sufficiently small particles of the new phase. A substantial undercooling is necessary to compensate the free energy increase in the case of homogeneous nucleation. In usual commercial practice, sufficient heterogeneous nuclei are present so that supercooling observed before solidification begins is rarely a few degrees centigrade. Therefore large undercoolings are obtained only when no heterogeneous nucleation sites are available. A typical example is high pressure gas atomised powders where the liquid has been divided into tiny droplet virtually free of impurity particles.

Solidification process is both a nucleation and kinetic process. Nucleation serves as two purposes in the solidification process: i) to determine which phase is going to form; ii) to provide sufficient undercooling for the subsequent growth. The kinetics of solidification studies how fast a process occurs and in what mechanism the solid forms. The growth rate of solidification is determined by the movement of the solid/liquid interface, which in turn depends on temperature gradient, cooling rates, interface structure, and composition difference between the solid and the liquid phase. There will be a solute concentration distribution in the solidified solution phase, when the solidification is not an equilibrium one [86Por].

Many theoretical attempts have been made to calculate growth velocity of undercooled melts. The problem is in most cases very complicated and rigorous solutions are only available for simplified cases. Since the nucleation of a phase is a prior requirement for its formation, it is plausible to study phase formation in alloys during rapid solidification by assuming that nucleation predominates the process. A combined nucleation and kinetic approach has been applied to the study of phase formation in the high pressure gas atomised powders [86Sau].

2.4.6 A Combined Thermodynamic and Kinetic Approach

A combined thermodynamic and kinetic approach was put forward by Saunders and Miodownik.
[88Sau2] for predicting glass forming range as well as phase formation and undercooling in rapidly quenched alloys. This approach was extended, in parallel to the present project, by the present author, Saunders and Tsakiropoulos [89Pan] to model more realistically the cooling conditions in a high pressure gas atomiser. The method described below was applied to several binary and ternary Al alloys as well as to alloy systems in the present study.

Critical nucleation is defined to occur at a temperature where the nucleant population per unit volume reaches a critical value, \( N_{\text{crit},d} \), which gives on average one nucleus per powder of diameter, \( d \). This critical population, \( N_{\text{crit},d} \), is given by the following equation:

\[
N_{\text{crit},d} = \frac{1}{(4\pi/3)(d/2)^3} \quad \text{...(2.4.1)}
\]

During the continuous cooling of a gas atomised powder of diameter, \( d \), the number of nuclei formed, \( n \), corresponds to the integration over time, \( t \), of the nucleation rate, \( J(T) \), where \( T \) is the temperature:

\[
\frac{\pi d^3}{6} \int J(T) \, dt = n \quad \text{...(2.4.2)}
\]

The nucleation rate, \( J \), at a given temperature, \( T \), is a function of liquid diffusion coefficient, \( D \), the free energy barrier of nucleation, \( \Delta G^* \), and the temperature as expressed in the following equation for homogeneous nucleation:

\[
J = \frac{D N_V}{a_0^2} \exp \left( - \frac{\Delta G^*}{kT} \right) \quad \text{...(2.4.3)}
\]

where \( N_V \) is the number of atoms per unit volume (Avogadro’s number), \( k \) Boltzmann’s constant and \( a_0 \) an atomic spacing.

The continuous cooling conditions experienced by gas atomised powders can be simulated by introducing a numerical stepping sequence in the computation. The necessary time, \( t \), to extract the superheat from the powder of diameter, \( d \), in order to decrease the temperature by a fixed amount \( \Delta T_{\text{sup}} \) can be calculated using an equation proposed by Clyne et al [84Cly]. The temperature drop, \( \Delta T_{\text{sup}} \), experienced by the powder as a result of the heat extracted from it within a set time span, \( t \), can be derived from the same equation:
In the equation, \( c_L \) is the heat capacity of the liquid. \( \Delta H_f \) is the latent heat of fusion of the alloy, taken as zero as only the initial stages, not the growth, of the liquid \( \rightarrow \) solid transformation are considered here. \( \Delta T_i \) is the time averaged mean value for the melt/environment interface temperature difference taken here as the temperature difference between the powder and the gaseous environment, the gas being at ambient temperature. \( h_i \) is the melt-environment heat transfer coefficient, estimated for the atomising gas with a relative velocity of 1000 m sec\(^{-1}\) using the equation

\[
h_i = \frac{2K}{d} + 0.6 \left( \frac{u}{d} \right)^{1/2} (K^2c)^{1/3} \left( \frac{P}{\mu} \right)^{1/6} \quad \ldots(2.4.5)
\]

The nomenclature of the above equation is given below, where all the thermophysical properties refer to the gas:

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K )</td>
<td>W m(^{-1}) K(^{-1})</td>
<td>Thermal Conductivity</td>
</tr>
<tr>
<td>( c )</td>
<td>J m(^{-3}) K(^{-1})</td>
<td>Specific Heat</td>
</tr>
<tr>
<td>( \rho )</td>
<td>kg m(^{-3})</td>
<td>Density</td>
</tr>
<tr>
<td>( \mu )</td>
<td>Pa s</td>
<td>Viscosity</td>
</tr>
<tr>
<td>( u )</td>
<td>m s(^{-1})</td>
<td>Convective Flow Velocity (Gas/Droplet)</td>
</tr>
<tr>
<td>( d )</td>
<td>m</td>
<td>Droplet Diameter</td>
</tr>
</tbody>
</table>

The values for the thermophysical properties for an estimated effective temperature of \(-500\) K of the gas (helium and nitrogen are among the ones commonly in use) can be obtained from [82Crc]. A value of 1000 m/s was taken to approximate the value of convective flow velocity between the gas and the droplet, \( u \). This approximation will bring a small amount of error into the solidification calculation because the magnitude of \( h_i \) is sensitive to this parameter. However this error is not significant over the powder size range of interest.

By calculating the amount of heat extracted within a set time and the subsequent temperature drop felt by the powder, the total number of nuclei can be computed from an integration of nucleation rate, taken as the isothermal nucleation frequency at the median temperature in the
temperature span, over time. The integration of nucleation over a series of time spans, therefore, will closely reflect the real continuous cooling conditions when the time step size is selected to be very small. An alternative way of simulating the time-temperature history of the atomised powder can be done by choosing the temperature as the stepping variable, calculating the necessary time to extract the super heat, and subsequently accumulating the nucleation population within the various time spans over the series of temperatures.

In the calculation of the nucleation frequency, \( J \), two important quantities have to be defined: \( D \), the liquid diffusion coefficient, and \( \Delta G^* \), the free energy barrier of nucleation. The liquid diffusion coefficient is calculated using different formula depending on whether the alloy is a glass forming or a non-glass forming one. For non-glass forming materials, the diffusion coefficient is calculated from an Arrhenius expression:

\[
D = D_0 \exp \left( -\frac{Q}{RT} \right) \quad \text{(2.4.6)}
\]

It is not easy to get accurate values for \( D_0 \) and \( Q \) required in the diffusion coefficient function. As a general value the self diffusion of Fe was taken, from a paper by Saxton et al [62Sax] which gives expressions for calculating the \( D_0 \) and \( Q \):

\[
D_0 = \frac{C}{\sqrt{M}} \quad \text{(2.4.6a)}
\]

where

\[
C = 7.0 \times 10^{-7} \text{ m}^2 \text{ sec}^{-1} (\text{g.mol})^{1/2}
\]

\( M \): atomic mass of Fe, \( M_{Fe} = 55.85 \)

and

\[
Q = R k T_M \quad \text{(2.4.6b)}
\]

where

\( R \) is gas constant and \( k = 3.0 \),
\( T_M \) is the melting temperature of pure Fe (\( T_M = 1809 \text{ K} \)).

Therefore, for self diffusion of Fe,

\[
D_0 = 9.4 \times 10^{-8} \text{ m}^2 \text{ sec}^{-1};
\]

\( Q = 45.1 \text{ kJ} \).
For glass-forming alloys the Stokes-Einstein formula [75Cot] of the inverse relation between diffusion and viscosity in liquids is applied:

\[ D = \frac{kT}{6\pi\eta r_a} \]  

...(2.4.7)

with \( r_a \) being the radius of the diffusing particle i.e. the atomic spacing \( a_0 \) and \( k \) being Boltzmann's constant. The viscosity \( \eta \) can be approximated between the liquidus temperature \( T_m \) and the glass forming temperature \( T_g \) by a Dolittle expression involving the relative free volume of \( f_T \) [77Ram] such that

\[ \eta = A \exp \left( \frac{B}{f_T} \right) \]  

...(2.4.7a)

and

\[ f_T = C \exp \left( \frac{-E_H}{RT} \right) \]  

...(2.4.7b)

whereas \( E_H \) is the hole formation energy, and \( A, B, \) and \( C \) are constants. For the present work the \( E_H \) value is approximated from \( T_g \) [77Ram]. Assuming at \( T_g, f_T = 0.03, \eta = 10^{12} \text{ N cm}^{-2} \), and giving \( B \) a value of 1, the other constants \( A, C \) can then be evaluated. If \( T_g \) value is not available, crystallisation temperature can be used as a first approximation.

The free energy barrier of nucleation is expressed in the following formula using molar quantities, following the earlier treatment [88Sau1],

\[ \Delta G^* = \left( \frac{16\pi}{3N_V} \right) \left( \frac{\sigma_m^3}{\Delta G_m^2} \right) \]  

...(2.4.8)

where \( \sigma_m \) is the molar liquid/crystal interfacial energy and \( \Delta G_m \) the free energy driving force for the liquid-crystal transformation. The term \( \sigma_m \) is related to the molar heat of fusion such that \( \sigma_m = \alpha \Delta H_m^f \), where \( \alpha \) is a constant. For the purpose of the present work, it is assumed that \( \alpha = 0.45 \), the value suggested by Turnbull [50Tur] for metals. Letting \( \Delta G_m = \Delta H_m^f \Delta T_r \) where \( \Delta T_r = (T_m - T) / T_m \), dividing through by \( kT \) and rearranging gives,

\[ \frac{\Delta G^*}{kT} = \left( \frac{16\pi\alpha^3}{3N_k} \right) \left( \frac{\Delta S_m^f}{\Delta T_r^2T_r} \right) \]  

...(2.4.9)

where \( T_r = T/T_m \). The entropy of fusion becomes, therefore, a very important term in determining relative nucleation frequencies.
2.5 Modelling of Elastic Properties of Metal Matrix Composites

2.5.1 Introduction

In order to optimise the mechanical properties of the alloys of interest in this work attempts have been made to theoretically model how the properties of the materials are influenced by their microstructure. The typical microstructure of the alloys in the present study can be categorised as in situ: metal matrix composites with boride particles dispersed on the Fe-rich solution matrix. The models which have been developed in the past for composite materials, in particular those for short fibre/metal matrix composites, therefore, are explored in the modelling of the present alloy system.

A number of composite models have been developed over the last two decades with the aim of predicting the thermomechanical properties of composites for given data of constituent phases. The analytical models for metal matrix composites, including particulate composites, can be grouped into five basic models, according to Taya and Arsenault [89Tay], ranging from the simplest Law of Mixtures to shear lag, laminated plates, to more rigorous Eshelby's equivalent inclusion method and variational principle models. A summary of the models is given below. The laminated plates model is for very specifically structured composites with continuous fibre unidirectionally aligned, which is not relevant to this study and therefore will not be discussed further here.

2.5.2 The Law of Mixtures

The Law of Mixtures, which was originally proposed by Voigt [1889Voi], approximated the composite shear modulus $\mu_C$ by:

$$\mu_C = \sum_{i=0}^{n} V_i \mu_i$$  ...(2.5.1)

where

$$\sum_{i=0}^{n} V_i = 1$$

Here a composite is considered as having $n$ different reinforcing phases distributed in a matrix.
Each reinforcing element is assumed having a shear modulus $\mu_i$ with volume fraction $V_i$ (where $i = 1, ..., n$), and the corresponding values of the shear modulus and volume fraction for the matrix are $\mu_0$ and $V_0$, respectively.

The basic assumption of the Law of Mixtures is that the externally applied shear strain is equal to the shear strain in all the phases including the matrix. The Law of Mixtures gives an upper bound to the mechanical property values because in reality the strain in the reinforcement and the matrix are not the same. It does, though, predict longitudinal properties of unidirectional continuous fibre composites quite well. In other cases which involve transverse properties or the properties of a short fibre composite, the Law of Mixtures value is well above the measured property.

### 2.5.3 Other Models

**(i) Shear Lag Model**

This model, originally developed by Cox [52Cox], is best suited for aligned short fibre composites where fibres of uniform length and diameters, i.e. constant aspect ratio, are all aligned in the loading direction and distributed uniformly throughout the material. The detailed derivation is summarized by Kelly [73Kel] and the elastic modulus of a composite is given by the following two equations:

When no load transfer at fibre ends,

$$E_C = (1 - V_f) E_M + V_f E_f \left( 1 - \frac{\tanh(\beta l/2)}{\beta l/2} \right) \quad \ldots (2.5.2a)$$

When load is fully transferred through the matrix,

$$E_C = (1 - V_f) E_M + V_f E_f \left( 1 + \frac{(E_M/E_f - 1) \tanh(\beta l/2)}{\beta l/2} \right) \quad \ldots (2.5.2b)$$

where $E_M$, $E_f$ are modulus of matrix and fibres, $V_f$ is volume fraction of fibres and $\beta, l$ constants.

As can be seen from the two equations above, the shear lag model is actually a modified version of the Law of Mixtures.
The Law of Mixtures and the shear lag model have been used extensively because of their simplicity. But the shear lag model tends to give a poorer approximation for stiffness and other mechanical properties than the other more rigorous models such as Eshelby method.

(ii) Self Consistent Scheme

A well-known approximation for effective properties of particulate composites is the so-called Self Consistent Scheme. It is suited for cases where the volume fraction of fibres or particles is large. The self-consistent model has been applied to composites (e.g. [65Hil]) and can be discussed within the framework of Eshelby's fundamental inclusion problem. In most cases, however, any self-consistent model requires rigorous calculations such as the iterative method. The essential problem with this simple method is that it violates the so-called MMM principle explained by Hashin [83Has], and produces unreasonable results; hence it should be considered with caution.

(iii) Variation Principles

Composite models based on Variational Principles are aimed at providing the upper and lower bounds on the thermomechanical properties. For most applications, however, the bounds are not close enough [83Has]. Improved bounds for arbitrary statistically isotropic phase geometry have been derived among which are those by Hashin and Shtrikman [62Has], which were in fact based on Eshelby method.

(iv) Deterministic Continuum Mixture Theory

Toledano and Murakami [87To1] constructed a Deterministic Continuum Mixture Theory by applying the variational principle for periodic particulate composites. The accuracy of the model was tested and the comparison with some available experimental data for harmonic wave propagation made. However, this model does not take into account the effect of any variations of the morphology of microstructure and is not an appropriate approach for the particular microstructure of interest.
2.5.4 Eshelby's Equivalent Inclusion Method

When the aspect ratio of short fibres becomes small, the above methods all tend to give poor estimates. The geometry of such short fibres is three-dimensional therefore requiring a more rigorous mathematical treatment. Eshelby's approach is best suited for such a short fibre system. It provides a rigorous theoretical basis for the model system consisting of aligned ellipsoids randomly dispersed within an isotropic matrix. In the special case of short fibres, it is also applicable to particulate composites.

Eshelby [57Esh] proposed an approach for the determination of the stress-strain field around an inclusion of ellipsoidal shape (Figure 2.5). The problem is simplified by choosing ellipsoid as the shape of the inclusion because: (i) it can be proved that the stress within the inclusion is uniform as long as the inclusion is ellipsoidal in shape; (ii) the general ellipsoid is versatile enough to cover a wide range of three dimensional geometrical cases encountered in usual composite materials, including long fibres, short fibres, spheres, thin plates, etc. Wider use of Eshelby's method in the application on internal stress determination to short fibre metal matrix composites.

![Figure 2.5 Eshelby's Equivalent Inclusion Method.](image)
was encouraged in a recent paper by Withers et al [89Wit], where the Eshelby method was explained in a simple yet systematic format. The matrix notation used here follows that paper in the expressions for the relevant stress equations. For most materials the symmetry of the fourth rank stiffness tensor (C) enables its reduction to a 6x6 matrix and the stress (σ) and strain (ε) tensors to six element row or column vectors. Bold face characters are used to denote tensor quantities and C^{-1} is used to represent the compliance tensor.

According to Eshelby's original idea, surface traction (ε^T) is to be applied in order to fit an ellipsoidal inclusion of certain size into the hole with the same shape but smaller size set in an infinite homogenous material with the same elastic constants of the ellipsoid (Figure 2.5). Equilibrium is reached between the matrix and the inclusion at a constrained strain (ε^C) on removal of the surface traction. The stress-strain relationship can be established for the inclusion by Hooke's Law,

$$\sigma = C_M (\epsilon^C - \epsilon^T)$$  \(\text{...(2.5.3)}\)

Eshelby defined a tensor, S, called Eshelby's tensor, to express the connection between the constrained strain (ε^C) and the transformation strain (ε^T),

$$\epsilon^C = S \epsilon^T$$  \(\text{...(2.5.4)}\)

Eshelby's tensor S is a function of the geometry of the ellipsoidal inclusion and the Poisson's ratio of the matrix. Although the derivation of the S tensor is complicated, its final form is relatively simple. The general formulas for the case of arbitrary aspect ratio p (major to minor axis ratio of the ellipsoid) of the inclusion were given by Brown and Clarke [77Bro]. The detailed expressions for a variety of inclusion shapes are also available from Brown and Clarke [75Bro], and Appendix C in Taya and Arsenault [89Tay]. Table 2.1 lists the expressions of Eshelby's tensor S_{ijkl} for inclusion aspect ratios p = 1 and infinity as well as the general formula for arbitrary value of p.

In the case where the matrix and the inclusion have different elastic constants C_M and C_I respectively, it is always possible to choose a value for the transformation strain (ε^T) in such a way that the resulting constrained strain is the same as in the homogeneous case. As a result, the inhomogeneity and the equivalent inclusion can be interchanged without disturbing the
matrix and the same uniform stress state is attained in the inhomogeneous case as in the equivalent homogeneous case. Another equation can be written in terms of Hooke's Law,

\[
\sigma_i = C_i (\varepsilon^C - \varepsilon^T)
\]
\[
= C_M (\varepsilon^C - \varepsilon^T)
\]

\(\ldots(2.5.5)\)

<table>
<thead>
<tr>
<th>Table 2.1 Eshelby's tensor (S_{ijkl}).</th>
</tr>
</thead>
<tbody>
<tr>
<td>(S_{ijkl})</td>
</tr>
<tr>
<td>(S_{1111} = S_{2222})</td>
</tr>
<tr>
<td>(S_{1122} = S_{2211})</td>
</tr>
<tr>
<td>(S_{1133} = S_{2233})</td>
</tr>
<tr>
<td>(S_{3311} = S_{3322})</td>
</tr>
<tr>
<td>(S_{3333})</td>
</tr>
<tr>
<td>(S_{1212} = S_{1221})</td>
</tr>
<tr>
<td>(S_{1313} = S_{1331})</td>
</tr>
<tr>
<td>(S_{2233} = S_{2323})</td>
</tr>
</tbody>
</table>

where \(Q = 3/(8\pi(1-v))\); \(R = (1-2v)/(8\pi(1-v))\); \(I_a = 2\pi p (p^2 -1)^{3/2} \) \([ p (p^2 -1)^{1/2} - \cosh^{-1} p \] ; \(I_c = 4\pi - 2I_a\); \(T = Q(4\pi - 3I_a)/(3(p^2 -1))\).
When a stress ($\sigma^A$) is applied externally, the change in stress in the homogeneous inclusion within the composite is simply the addition of the applied stress, since both the matrix and the inclusion undergo the extra uniform elastic distortion ($e^A$). Therefore,

$$\sigma_I + \sigma_A = C_M (e^C - e^T) + C_M e^A$$

and

$$\sigma_A = C_M e^A$$

As for the inhomogeneity, despite the fact that the inclusion and the matrix will extend by different amounts, the final total stress state ($\sigma_I + \sigma_A$) of the two composites can be made identical by selecting the appropriate equivalent transformation strain ($e^{T*}$, by now also a function of $e^A$). The new equivalent homogeneous inclusion then has the constrained shape ($e^C + e^A$). Again by Hooke's Law:

for an inhomogeneity,

$$\sigma_I + \sigma_A = C_I (e^C + e^A - e^{T*})$$

for an equivalent inclusion,

$$\sigma_I + \sigma_A = C_M (e^C + e^A - e^T)$$

The above analysis is only valid for an infinite composite containing a single inclusion. Some approximations have been made for the simulation of finite materials. Following the concept of 'image stress' introduced by Eshelby and a 'mean field approach' proposed by Pedersen [78Ped, 79Ped, 83Ped], the internal balance of mean stress ($<\sigma>_M$ and $<\sigma>_I$ for the mean stress of matrix and inclusion respectively) for a finite number of inclusions consisting a volume fraction $f$ can be written as:

$$(1 - f) <\sigma>_M + f <\sigma>_I = 0$$

The general equation for the stress within the inhomogeneous inclusion is then given similar to Equation (2.5.8) by:
for an inhomogeneity,

\[ \sigma_I + \sigma_A = C_I (e^C + e^A + \langle e \rangle_M - e^T) \]

for an equivalent inclusion,

\[ \sigma_I + \sigma_A = C_M (e^C + e^A + \langle e \rangle_M - e^T) \]

Equating the two expressions gives:

\[ e^T = -\frac{[C_M - C_I] \{ S - f(S - I) \} - C_M^{-1} \left[ C_I e^T - (C_I - C_M) e^A \right]}{[C_M - C_I] - C_M^{-1} \{ S - f(S - I) \} - C_M} \] (2.5.10)

where

\[ e^C = S e^T, \quad \langle e \rangle_M = C_M \langle e \rangle_M, \quad \text{and} \quad \sigma^A = C_M e^A \] (2.5.11)

The mean stress can then be written:

\[ \langle \sigma \rangle_M = A e^T + B \sigma^A \] (2.5.12)

The tensors \( A \) and \( B \) are functions only of the elastic constants of the two phases and the inclusion volume and shape. They can be deduced from Equation (2.5.9) bearing in mind the relations given in Equation (2.5.11). The tensor \( B \) is of particular importance in the modulus calculation later, and has been derived by the present author (Appendix V):

\[ B = C_M f \{ S - I \} \left[ (C_M - C_I) \{ S - f(S - I) \} - C_M^{-1} (C_M - C_I) C_M^{-1} \right] \] (2.5.13)

The equivalent transformation strain can be used to calculate the composite's effective stiffness tensor which relate stress average to strain average, defined as:

\[ \sigma^A = C_C e^C \]

Since the elastic constants are the same throughout the equivalent homogeneous composite, the balance of internal stress expressed in Equation (2.5.8) can be related as a balance of elastic strain:
As a result, on integrating the strain over the equivalent homogeneous transformation strain $\mathbf{e}^T$ within the inclusion one retains:

$$\mathbf{e}_C^A = (1 - f) (\mathbf{e}^A + <e>_M) + f (\mathbf{e}^A + <e>_I + \mathbf{e}^T)$$

$$= \mathbf{e}^A + f \mathbf{e}^T$$

Replacing $\mathbf{e}^T$ with the earlier expressions (Equation (2.5.10)) for the equivalent transformation strain, the composite effective compliance can be written as:

$$\mathbf{C}_C^{-1} = \mathbf{C}_M^{-1} - [\mathbf{S} - \mathbf{I}]^{-1} \mathbf{C}_M^{-1} \mathbf{B}$$

Once the compliance tensor for the composite has been calculated, the effective Young's modulus of the composite $E_C$ is derived simply as:

$$E_C = \frac{1}{\mathbf{C}_{C33}^{-1}}$$

The shear modulus of the composite $G_C$, as observed by the present author, can also be conveniently obtained from the calculated compliance:

$$G_C = \frac{1}{\mathbf{C}_{C44}^{-1}}$$

The expression $\mathbf{C}_{Cij}^{-1}$ donates the components on the $i$th row and $j$th column in the composite compliance tensor $\mathbf{C}_C^{-1}$.

2.5.5 Effect of Constituent Parameters According to Eshelby's Model

The Young's modulus of composite materials is affected by the constituent structural parameters to various degrees. Among the parameters the important ones are volume fraction of the second
phase, the Young's modulus of the matrix and the inclusion, the aspect ratio of the inclusion, and the orientation of the inclusion. Figure 2.6 shows typical Young's modulus curves, at a selected value of matrix and inclusion modulus, calculated via Eshelby's method as a function of inclusion volume fraction with a variety of inclusion aspect ratios. These variables will be discussed in more detail below.

(i) Volume Fraction of the Inclusions

It is to be expected that the higher the volume fraction of the inclusion, the higher the elastic modulus of the composite. The increase in composite modulus for inclusion with finite aspect ratio estimated by Eshelby treatment is however not proportional to the volume fraction of the second phase (Figure 2.6). In fact it is always lower than the value given by the Law of Mixtures. On the other hand other mechanical properties such as fracture toughness tend to deteriorate when the percentage of the harder phase is higher than 30%, hence it is not practical to attain high elastic properties purely by including a larger amount of the hard phase.

Figure 2.6  A plot of the effective composite modulus obtained using Eshelby method with the mean field approach for composites with inclusions of different aspect ratios [89Wit].
Elastic Constants of the Matrix and Inclusions

The elastic constants of the matrix and the fibres determine theoretically the lower and upper bounds of the modulus of the composite. At lower volume fractions (e.g. below 30%) of the inclusion, the modulus of the composite is more sensitive to a change in the matrix modulus than the modulus of the inclusion. For example in the Fe-Cr-Mo-B alloy (see Table 2.2), at $E_M = 214$ GPa, $E_I$ estimated as 425 GPa and the boride volume fraction 30%, an increase of 20 GPa in the matrix modulus brings the composite modulus up 18 GPa whereas the same increase in the inclusion yields only an extra 3 GPa, according to Eshelby's model.

Table 2.2 Comparison between effect of matrix and inclusion on Young's modulus of a composite according to Eshelby's model.

<table>
<thead>
<tr>
<th>$E_M + \Delta E_M$, GPa</th>
<th>$E_I + \Delta E_I$, GPa</th>
<th>Boride, vol%</th>
<th>$\Delta E_C$, GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>214+0</td>
<td>425+0</td>
<td>30</td>
<td>0</td>
</tr>
<tr>
<td>214+20</td>
<td>425+0</td>
<td>30</td>
<td>+18</td>
</tr>
<tr>
<td>214+0</td>
<td>425+20</td>
<td>30</td>
<td>+3</td>
</tr>
</tbody>
</table>

Aspect Ratio of the Inclusions

The effect of aspect ratio of the short fibres is reflected through the Eshelby's tensor $S_{ijkl}$. The general formula for computing the tensor are given in Table 2.1 (see the previous section). The value of Eshelby's tensor for two special cases when the aspect ratio is 1, denoting spheres, and for an infinite aspect ratio, representing continuous fibre composite, can be derived from the general format of the Eshelby's tensor formula, as are also given in Table 2.1. At a fixed volume fraction of the inclusions, increasing the aspect ratio of the fibres with aligned orientation improve the composite's elastic modulus (see Figure 2.6).

Orientation effect

The stiffness of a metal matrix composite is strongly dependent on fibre misorientation. The value of the tensor quantity in a misaligned short fibre composite depends on the overall fibre
orientation distribution and can be given by the integration of the stiffness tensor quantity of unidirectionally aligned short fibre composite, with the probability density function of the fibre orientation determined from experiment as a weighting factor. The integration is given in the following function,

$$F'' = F'(\theta, \phi) \ n(\theta, \phi) \ dS$$

$$= \frac{1}{2\pi} \int_0^{2\pi} d\phi \int_0^{\pi/2} n(\theta, \phi) F'(\theta, \phi) \sin\theta \ d\theta$$

... (2.5.19)

in which \(n(\theta, \phi)\) is the probability density function of fibre orientation, determined by experiment, and \(F'(\theta, \phi)\) is a unidirectional aligned short fibre composite tensor quantity F.

The effective Young's modulus of a short-fibre composite is more sensitive to fibre orientation distribution than fibre volume fraction. In the case of spherical inclusions, the modulus is independent of orientation; whereas for randomly orientated fibres, the positive effect of high aspect ratio on the modulus of the composite is almost counteracted by the negative effect of fibre misorientation.

A unidirectional fibre composite is highly anisotropic and therefore has many more stiffness and strength parameters than a particulate composite. Stiffness and strength in the fibre direction are approximately those of the fibre, and thus very high. By contrast stiffness and strength transverse to the fibre direction are close to those of the matrix, similar to those of a particulate composite, and thus much lower. For a random distribution of fibres, the fibre aspect ratio has little influence on the effective elastic constant, and the whole composite becomes isotropic.

### 2.5.6 Effect of Magnetostriction on Elastic Properties

An anomalous elastic modulus in magnetic materials sometimes correlates with the magnetostrictive behaviour, and this effect is therefore discussed here.

Magnetostriction refers to changes in dimensions with state of magnetization. In engineering terms, magnetostriction means the change in length when a demagnetized polycrystalline sample is magnetized. In physical terms, magnetostriction refers to the change in dimensions resulting from the rotation of the saturation magnetization from one crystallographic direction...
Figure 2.7 Magnetostriction effect [91Mio]. a) Effect of chromium on elastic modulus; b) Modulus effect versus magneto-damping.
to another in single crystal. This effect can be expressed as the relation between the elastic constants of a material and the strain dependence of the anisotropy energy.

Magnetic alloys are prone to show anomalous modulus effects which are related to: (i) the magnitude of the magneto-strictive coefficients and (ii) the ease or difficulty of domain movement [65Lub]. The latter in turn is controlled by the pinning of domain walls which is a function of (a) dislocation density and (b) suitable precipitates within the magnetic matrix. In addition the factors which reduce domain movement, and therefore also reduce the anomalous reduction in modulus, often scale with the mechanical hardness of the material, since this is frequently a measure of the density of both precipitates and dislocations. In many alloys, thermal or mechanical treatments that lead to increases in coercity, e.g. by precipitation, also lead to increases in yield stress. In addition, the magnitude of the effect is composition and structure dependant, and can produce unexpectedly large effects.

The modulus of iron chromium alloys containing little or no carbon shows a marked elastic modulus anomaly which is absent in alloys containing higher carbon content. An overview of the possible role of the magneto-electric effects in the Fe-Cr system showed that the magnetostriction and magneto-damping effects are maximum around 10 wt%Cr (Figure 2.7, [91Mio]).
3.1 Introduction

In order to understand phase evolution and microstructure formation during the processing of the alloys, as well as to design a series of test alloys to study the effect of various phase and microstructure on the properties, phase diagram assessments for the Fe-Cr-Mo-Ni-B system have been carried out based on thermodynamic principles. It was expected that well established phase equilibrium information would allow a selection of test alloy compositions, so that the effect of phase variables on the properties of alloys could be evaluated in a cost-effective way by limiting the necessary number of alloys to be examined.

The effects of variables such as type and amount of boride, type and composition of matrix can be manipulated based on the well defined phase diagram information. For example, a composition matrix can be defined in the Fe-Cr-B system with different levels of boron content on the same tie-line between the matrix and the boride. As a result the two test alloys differ only in the amount of borides and its effect on the mechanical properties of the alloy can be isolated. It would be otherwise very difficult to analyse any testing results obtained with different variables present at the same time.

Phase equilibria in a multi-component system can be established based on the thermodynamic descriptions of all the constituent sub-systems. To perform a characterisation for the quaternary alloy system Fe-Cr-Mo-B and Fe-Cr-Ni-B, therefore, it is necessary to obtain thermodynamic descriptions of the binary (Fe-Cr, Fe-Mo, Fe-Ni, Fe-B, Cr-Mo, Cr-Ni, Cr-B, Mo-Ni, Mo-B, and Ni-B) and the ternary (Fe-Cr-Mo, Fe-Cr-B, Fe-Mo-B, Cr-Mo-B, Fe-Cr-Ni, Fe-Ni-B, and Cr-Ni-B) systems.
The phase diagrams which only contain metallic components in the Fe-Cr-Mo-Ni-B system have been previously thermodynamically assessed, and their results adopted in the present work (see Table 3.1). The Fe-Cr system has been evaluated by Andersson and Sundman [87And], and the calculated phase diagram is shown in Figure 3.1; The Fe-Mo system by Fernandez Guillermet [84Fer], the calculated phase diagram shown in Figure 3.2; The Fe-Ni system by Xing, Gohil, Dinsdale and Chart [85Xin] and the calculated phase diagram shown in Figure 3.3; The Cr-Mo system characterised by Frisk and Gustafson [88Fri], the calculated phase diagram shown in Table 3.1: Overview of phase diagram assessments on the Fe-Cr-Mo-B and Fe-Cr-Ni-B systems.

<table>
<thead>
<tr>
<th>SYSTEM</th>
<th>SOURCE &amp; REFERENCE</th>
<th>FIGURE No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-Cr-Mo-B</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe-Cr-Mo</td>
<td>Andersson and Lange [86And]</td>
<td></td>
</tr>
<tr>
<td>Fe-Cr-B</td>
<td>&lt; To be assessed &gt;</td>
<td></td>
</tr>
<tr>
<td>Fe-Cr</td>
<td>Andersson and Sundman [87And]</td>
<td>Figure 3.1</td>
</tr>
<tr>
<td>Fe-B</td>
<td>&lt; To be assessed &gt;</td>
<td></td>
</tr>
<tr>
<td>Cr-B</td>
<td>&lt; To be assessed &gt;</td>
<td></td>
</tr>
<tr>
<td>Fe-Mo-B</td>
<td>&lt; To be assessed &gt;</td>
<td></td>
</tr>
<tr>
<td>Fe-Mo</td>
<td>Fernandez Guillermet [84Fer]</td>
<td>Figure 3.2</td>
</tr>
<tr>
<td>Mo-B</td>
<td>&lt; To be assessed &gt;</td>
<td></td>
</tr>
<tr>
<td>Cr-Mo-B</td>
<td>&lt; To be assessed &gt;</td>
<td></td>
</tr>
<tr>
<td>Cr-Mo</td>
<td>Frisk and Gustafson [88Fri]</td>
<td>Figure 3.4</td>
</tr>
<tr>
<td>Fe-Cr-Ni-B</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe-Cr-Ni</td>
<td>Gustafson [87Gus1,2]</td>
<td></td>
</tr>
<tr>
<td>Fe-Ni-B</td>
<td>&lt; To be assessed &gt;</td>
<td></td>
</tr>
<tr>
<td>Fe-Ni</td>
<td>Xing, Gohil, Dinsdale and Chart [85Xin]</td>
<td>Figure 3.3</td>
</tr>
<tr>
<td>Ni-B</td>
<td>&lt; To be assessed &gt;</td>
<td></td>
</tr>
<tr>
<td>Cr-Ni-B</td>
<td>&lt; To be assessed &gt;</td>
<td></td>
</tr>
<tr>
<td>Cr-Ni</td>
<td>Chart [90Cha]</td>
<td>Figure 3.5</td>
</tr>
</tbody>
</table>
Figure 3.4; The Cr-Ni system by Chart [90Cha], the phase diagram of Cr-Ni system after Chart shown in Figure 3.5; The Mo-Ni system by Frisk [90Fri], and the phase diagram of Mo-Ni system shown in Figure 3.6. The Fe-Cr-Mo ternary system has been characterised thermodynamically and experimentally by Andersson and Lange [86And] and a description of the Fe-Cr-Ni system is available through two reports by Gustafson [87Gus1,2]. The thermodynamic parameters for the relevant systems given by these evaluations are listed in the appendix.

Figure 3.1 The Fe-Cr phase diagram from Andersson and Sundman [87And].
The phase diagrams which need to be assessed, therefore, are the binary systems Fe-B, Cr-B, Mo-B, Ni-B, the ternary system Fe-Cr-B, Fe-Mo-B, Cr-Mo-B, Fe-Ni-B, and Cr-Ni-B (see Table 3.1). A literature search was carried out for all the available experimental phase diagram information and thermodynamic data before assessing each of these diagrams.

Figure 3.2  The Fe-Mo phase diagram from Fernandez Guillermet [84Fer].
Figure 3.3 The Fe-Ni phase diagram from Xing et al [85Xin].
Figure 3.4 The Cr-Mo phase diagram from Frisk and Gustafson [88Fri].
Figure 3.5  The Cr-Ni phase diagram from Chart [90Cha].
Figure 3.6 The Mo-Ni phase diagram from Frisk [90Fri].
3.2 Presentation of Data

The pure element 'G' values are given relative to the enthalpy of selected reference states for the elements at 298.15 K. This state is denoted by the letter 'SER'. The thermodynamic parameters pertaining to the calculation of the phase diagrams are presented in the appendix in the following format:

(i) Elements involved and their stable state reference
(ii) $H_{\text{SER}}$ function for the pure elements

The thermodynamic description of each phase is given as follows:

(i) Phase identification and the polynomial representation adopted
(ii) Number of sublattices and site occupancies associated with each phase
(iii) The elements in the sublattices
(iv) Energy and magnetic parameters for the pure elements
(v) The Redlish-Kister coefficients for the interaction energy and the magnetic interaction parameters associated with each solution phase
(vi) Function $f(t)$ describing magnetic contribution (if any)

The energy parameters are denoted by 'G' and the magnetic parameters by 'β' and 'T_C'. The Redlish-Kister coefficients for the chemical free energy interaction parameters are denoted by the symbol $\Delta G(A, B : C; I)$ where the interacting species A, B, C etc are defined as in the different sublattices separated by a colon ' : ' and the order of the Redlish-Kister coefficient is indicated by the number 'I'.

The Redlish-Kister coefficients for the magnetic parameters $\beta$ and $T_C$ are denoted by the symbols $\beta(A, B : C; I)$ and $T_C(A, B : C; I)$ respectively, A, B, C, etc again indicating the interacting species in the different sublattices as in the case of the chemical interaction energy parameters and I denoting the order of the Redlish-Kister coefficient.
3.3 Characterisations of Binary Systems

3.3.1 The Fe-B System

Literature Review

Experimental work on Fe-B phase diagram has been reviewed by Hansen [58Han], with additional information given by Elliott [65Ell] and Shunk [69Shu]. Chart [80Cha] assessed both the phase diagram, as shown in Figure 3.7, and the experimental thermodynamic data. In

Figure 3.7 The Fe-B phase diagram from assessment by Chart [80Cha].
addition, Kaufman [84Kau] presented a calculated phase diagram based on pair potential calculations and as part of work on Fe-B-C, Ohtani et al [88Oht] presented calculations for the Fe-rich part of the Fe-B phase diagram.

The general features of the phase diagram have been established by thermal and microscopic investigation up to 32.5 at%B by Hannesen [14Han], up to 41 at%B by Tschischewsky [15Tsc], up to 34 at%B by Wever [30Wev] and by X-ray structural as well as thermal and metallographic investigations over the whole concentration range by Portnoi [69Por1]. According to the above studies and the additional work of Sidorenko [77Sid], the phase diagram for this system is characterised by eutectic reactions in Fe-rich and B-rich alloys and two compounds Fe2B and FeB.

Early work on the Fe-rich eutectic suffered because of the purity of the boron that was added to relatively pure iron. Because of this Wever and Muller [30Wev] pointed out that results from low concentration boron alloys should be preferred. However, in spite of possible purity problems, there is general agreement on the temperature and the composition of the eutectic reaction.

It is now established that Fe2B melts peritectically while FeB melts congruently [30Wev, 69Por1, 70Vor, 72Plo]. The higher boride FeBx, where x=20 to 40, reported by Portnoi [69Por1] is taken to be a solid solution of iron in boron as proposed by Chart [80Cha].

There are reports of two further phases FeB2 and Fe3B. Voroshnin [70Vor] reported the existence of FeB2, but this was not observed previously by Portnoi [69Por1], or in later studies by Plotnikova et al [72Plo] and has not been included in the present calculations. Khan et al [82Kha] observed that single phase Fe3B could be produced by quenching liquid Fe76B24 at certain cooling rates and on this basis suggested that Fe3B might exist in thermodynamic equilibrium at high temperature. However, the decomposition of the Fe3B to Fe and Fe2B is well known in crystallisation studies of amorphous alloys [84Ant] and no phase diagram studies were done to confirm their hypothesis.

A large number of studies have been done to determine the solubility of boron in iron using a variety of methods [53Bus, 54Bus, 54Nic, 54McB, 69Luc, 74Bro, 84Bro, 86Cam]. Since the solubilities in question are very low (less than 0.1 at%), chemical analysis of saturated solid solutions was chosen by Nicholson [54Nic] in preference to X-ray diffraction or metallographic
techniques. In the work of McBride et al [54McB], the solid solubility of boron in alpha iron and
gamma iron was determined by equilibrating high purity iron with Fe₂B, and the reaction
isotherms in the Fe-Fe₂B system were studied using metallographic techniques and differential
thermal analysis. Busby et al [53Bus, 54Bus] made use of diffusion and deboronizing methods
while internal friction measurements were employed by Lucci and Venturello [69Luc]. All of
these studies while differing in some details are in broad agreement as to the degree of solubility
of boron in both alpha and gamma iron. However the work by Brodowsky and Wernicke
[84Bro] gives results for the solubility of boron in alpha iron which are an order of magnitude
larger.

Brown et al [74Bro] used the technique of boron autoradiography, which can distinguish between
boron in solution, boron-rich precipitates and boron segregated to grain boundaries, to determine
solubility limits. Cameron and Morral [86Cam] used the same technique as the one by Brown
et al [74Bro] but with a different detector material and analysis method. The solubility results
of the two studies agree fairly well and they indicate that the solubility of boron in iron is lower
than that proposed by the previous studies. However, as the previous work makes use of a wide
variety of experimental techniques which all give broadly the same results, the higher solubilities
[52Nic, 53Bus, 54Bus, 54Nic, 54McB, 69Luc] are preferred here.

There is some ambiguity concerning the site occupation of boron in alpha iron. McBride et al
[54McB] suggested that boron was substitutional on the basis of site effect. This was supported
by the analysis of diffusion data by Busby and Wells [54Bus], and the lattice parameter
measurements by Shevelev [58She]. More recently Lucci and Venturello [71Luc], on the basis
of their own experimental work using internal friction and dilatometry [69Luc] and a review of
the literature, concluded that boron was not interstitial in alpha iron but proposed that its
solubility was associated with defects. The occupancy of boron in gamma iron has not been
experimentally resolved although McBride et al [53McB] and Busby and Wells [54Bus] suggest
that it may be interstitial.

Some thermodynamic measurements have been made for the system. The enthalpy of mixing
of the liquid phase at 1840 K was measured by Esin et al [75Esi], the enthalpies of formation of
the two borides by Sato and Kleppa [82Sat], Gorelkin et al [72Gor], and Omori et al [76Omo,
80Omo], and the enthalpy of fusion of FeB by Sidorenko [71Sid]. Activity coefficients of B in
alpha iron and gamma iron at certain temperatures were measured by Brodowsky [84Bro], with
alpha-gamma transus determined.

The Calculation

The calculated phase diagram together with the experimentally determined phase boundary data is shown in Figure 3.8. Figure 3.9 shows details of the Fe-rich region. The calculated enthalpies of formation as well as enthalpy of fusion are compared with the experimental data for the borides in Table 3.2 and the calculated heat of mixing of the liquid with the results of Esin et al.

Table 3.2 Enthalpy of formation and enthalpy of fusion for Fe-borides.

Standard state: alpha pure iron and rhombohedral boron.

<table>
<thead>
<tr>
<th>Boride</th>
<th>$x_B$</th>
<th>Enthalpy of Formation (kJ/g. atom)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$B</td>
<td>0.333</td>
<td>-24.2</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-22.6</td>
<td>[82Sat]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-22.3</td>
<td>[72Gor]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-33.8</td>
<td>[76,80Omo]</td>
</tr>
<tr>
<td>FeB</td>
<td>0.5</td>
<td>-33.0</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-32.3</td>
<td>[82Sat]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-35.6</td>
<td>[72Gor]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-46.5</td>
<td>[76,80Omo]</td>
</tr>
</tbody>
</table>

Enthalpy of Fusion (kJ/g. atom)

<table>
<thead>
<tr>
<th>Boride</th>
<th>$x_B$</th>
<th>Enthalpy of Fusion (kJ/g. atom)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeB</td>
<td>0.5</td>
<td>30.0</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td></td>
<td>31.6</td>
<td>[71Sid]</td>
</tr>
</tbody>
</table>
[75Esi] in Figure 3.10. The experimentally determined melting temperatures for the two borides together with the calculated values are shown in Table 3.3. A summary of the reaction types, calculated temperatures and compositions of invariant reactions of the system is given in Table 3.4.

Figure 3.8  Calculated phase diagram of Fe-B system with experimentally determined phase boundaries superimposed.
The calculated phase diagram agrees well with the experimental data although some discrepancies arise at very high boron concentrations as the assessed melting point for boron used here differs from that determined by Portnoi et al [69Por1]. At the Fe-rich corner of the phase diagram, the solubility of boron in iron is consistent with the preferred experimental data [52Nic, 53Bus, 54Bus, 54Nic, 54McB, 69Luc].

Figure 3.9 Calculated Fe-rich corner of the Fe-B phase diagram with experimentally determined phase boundaries superimposed.
Figure 3.10  Calculated excess enthalpy of liquid of the Fe-B with experimental data [75Esi] for comparison.
### Table 3.3 Melting points for the Fe-borides.

<table>
<thead>
<tr>
<th>Boride</th>
<th>$x_B$</th>
<th>$T_m$ (°C)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$B</td>
<td>0.333</td>
<td>1386</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1325</td>
<td>[15Tsc]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1389</td>
<td>[14Han]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1360</td>
<td>[30Wev]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1410</td>
<td>[69Por$_1$]</td>
</tr>
<tr>
<td>FeB</td>
<td>0.5</td>
<td>1610</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1540</td>
<td>[14Han]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1550</td>
<td>[30Wev]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1650</td>
<td>[69Por$_1$]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1590</td>
<td>[77Sid]</td>
</tr>
</tbody>
</table>

### Table 3.4 Invariant reaction data on the calculated Fe-B phase diagram.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Compositions (at% B)</th>
<th>Temp. (°C)</th>
<th>Reaction Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>L $\rightarrow$ Fe</td>
<td>0</td>
<td>1538</td>
<td>Melting</td>
</tr>
<tr>
<td>L $\rightarrow$ γ-Fe + Fe$_2$B</td>
<td>16.5 0.11 33.3</td>
<td>1175</td>
<td>Eutectic</td>
</tr>
<tr>
<td>L + FeB $\rightarrow$ Fe$_2$B</td>
<td>32.4 50 33.3</td>
<td>1386</td>
<td>Peritectic</td>
</tr>
<tr>
<td>L $\rightarrow$ FeB</td>
<td>50</td>
<td>1611</td>
<td>Congr.melt</td>
</tr>
<tr>
<td>L $\rightarrow$ FeB + B</td>
<td>63.0 50 100</td>
<td>1492</td>
<td>Eutectic</td>
</tr>
<tr>
<td>γ-Fe + Fe$_2$B $\rightarrow$ α-Fe</td>
<td>0.009 33.3 0.013</td>
<td>912</td>
<td>Peritectoid</td>
</tr>
<tr>
<td>L $\rightarrow$ B</td>
<td>100</td>
<td>2075</td>
<td>Melting</td>
</tr>
</tbody>
</table>
3.3.2 The Cr-B System

Literature Review

Hansen [58Han], Elliott [65Eli], and Shunk [69Shu] compiled early literature reviews on the phase diagram information of the Cr-B system. More recently Hack and Chart [80Hac] and Liao and Spear [86Lia] reviewed the phase diagram and thermodynamic properties of the system. The diagram of Liao and Spear [86Lia], which is very similar to that of Hack and Chart [80Hac], is shown in Figure 3.11. Kaufman et al. [84Kau] performed phase diagram calculations for this system, but their calculated diagram differed in a number of important aspects from the experimental assessment by Liao and Spear [86Lia]. The calculations presented by both Hack and Chart [80Hac] and Liao and Spear [86Lia] indicate that entropies of formation for the Cr-rich

![Figure 3.11](image-url)  
*Figure 3.11*  The Cr-B phase diagram from the assessment of Liao and Spear [86Lia].
PHASE DIAGRAM ASSESSMENTS

borides may be positive, which would be very unusual considering the behaviour of exothermic compounds of this type [87Spe] and the observed behaviour of the isostructural Mo$_2$B phase in the Mo-B system [77Sto].

Most investigations of the phase diagram have been occupied with the intermediate phases. Early works at the turn of the century identified the monoboride CrB [1894Moi, 02Tuc, 06Bin, 07Wed] and two further compounds Cr$_2$B, and Cr$_3$B$_2$ [06Bin]. Additionally the boride phases Cr$_2$B, Cr$_3$B$_4$, and CrB$_2$ were found to exist by Kiessling and Andersson [49Kie, 52Kies, 50And]. Sindeband [49Sin] confirmed the existence of all of these borides with the exception of Cr$_3$B$_2$. Andrieux and Marion [53And] isolated and identified Cr$_4$B, Cr$_2$B, Cr$_5$B$_3$, CrB and Cr$_3$B$_4$. They also investigated a sample of Cr-boride corresponding to composition of Cr$_3$B$_2$ and found that the phase 'Cr$_3$B$_2$', originally identified by Kiessling and Andersson [49Kie, 50And], consisted of a mixture of two borides Cr$_2$B and CrB.

Epel'baum et al [58Epe] made a brief review of the previous work on Cr-borides investigations, and gave tentative boundaries of homogeneity determined by X-ray, chemical analysis and metallographic methods for the following phases in the range of boron content 26 to 75 at%B: Cr$_2$B, Cr$_5$B$_3$, CrB, Cr$_3$B$_4$, and CrB$_2$, which confirmed Kiessling's results as mentioned above. Neither the Cr$_4$B or Cr$_3$B$_2$ phases were detected by them.

In B-rich alloys the CrB$_6$ phase was reported by Ormont [60Orm]. Later work by Serebryakova [67Ser] confirmed that CrB$_6$ phase was stable at between 1000° and 1300°C and decomposed with the formation of CrB$_2$ and partial removal of boron at high temperatures. However, further chemical analysis results indicated that the compound contained a considerable amount of oxygen and that the CrB$_6$ was probably a Cr-oxyboride. Andersson and Lundstrom [68And] reported from X-ray powder data, and the results from a structure determination, that a phase CrB$_4$ existed up to 1600°C, above which temperature it gave a mixture of (CrB$_2$ + boron). They also suggested that this phase was most probably the same as the phase CrB$_6$.

In Cr-rich alloys, some disagreement exists as to whether the Cr$_4$B phase exists. Some studies indicate that it is a stable phase [53And, 53Ber, 58Now, 62Fed], and it was included by Shunk [69Shu] in his assessed diagram. However, detailed later work has failed to find evidence for this phase [58Aro, 69Por, 76Guy], and following Liao and Spear [86Lia] it has not been included in the calculated phase diagram in the present work.
There have been a large number of studies on the determination of melting points of the compounds [52Keif, 53Sch, 54Pos, 57Isk, 57Mar, 58Now, 59Nes, 62Fed, 65Bin, 67Ser, 69Por2], the results of which are very scattered, with measured melting temperature data varying by as much as 500°C. In comparison the results of [52Kief, 53Sch, 54Pos, 57Isk, 67Ser] lie substantially lower than those of [57Mar, 58Now, 59Nes, 62Fed, 65Bin, 69Por2]. As impurities tend to lower the melting points of these phases, the higher values are considered to be more accurate.

There have been only three systematic attempts at determining the liquidus over a wide range of composition [58Now, 62Fed, 69Por2]. The work of Portnoi et al [69Por2] is the most complete determination and is similar in form to that reported by Nowotny et al [58Now], with the exception of the formation of Cr4B. Eutectics were established between Cr and Cr2B and CrB2 and rhombohedral boron and the solid region of the system was investigated using X-ray and single-crystal methods, with five intermediate phases Cr2B, Cr5B3, CrB, Cr3B4 and CrB2 observed. In a later review paper Portnoi [71Por] confirmed that the compound CrB4 formed during the annealing of alloys for 100 hours at 1400°C in vacuum. The work of Fedorov et al [62Fed] concentrated on Cr-rich alloys and reported a second allotrope of chromium as well as a eutectic between Cr4B and Cr2B. The formation of various allotropes of chromium is now considered to be due to impurities such as nitrogen [69Por2], and the eutectic between Cr4B and Cr2B has not been reported in any other work.

Solubility data is limited. Shunk [69Shu] reported that the solubility of B in Cr varied from 0.72 at%B at 1100°C to 0.38 at%B at lower temperatures. A rather consistent value of 0.6 at%B was reported by Borlera [71Bor] for a temperature at about 1527°C. Portnoi [69Por2] gave the maximum solubility of Cr in boron as approximately 2 at%.

Little experimental thermodynamic information is available on the Cr-B system. Brewer and Haraldsen [55Bre] estimated the enthalpy of formation of CrB2 as > -43 kJ.mol⁻¹ by an indirect method, and a later, more detailed study of the thermodynamic properties of CrB2 by Topor and Kleppa [85Top] gave a value of -39.81±1.1 kJ. mol⁻¹. Estimation has been made for Cr-B compounds by Niessen and Boer [81Nie] using the Miedema model [76Mie, 80Mie] and the value for CrB2 is close to that of Topor and Kleppa [85Top].
The Calculation

The calculated phase diagram together with the experimentally determined phase boundary data is shown in Figure 3.12. The calculated enthalpies of formation are given in Table 3.5; the value for the enthalpy of formation of CrB$_2$ is very close to the reported experimental result of Topor and Kleppa [85Top]. A summary of the reaction types, calculated temperatures and compositions of invariant reactions of the system is given in Table 3.6. The calculated diagram, obtained using the thermodynamic parameters given in the appendix, agrees well with the experimentally measured points.

Table 3.5 Enthalpies of formation of Cr- borides.

<table>
<thead>
<tr>
<th>Boride</th>
<th>$x_B$</th>
<th>$\Delta H$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(kJ/g. atom)</td>
</tr>
<tr>
<td>Cr$_2$B</td>
<td>0.333</td>
<td>-37.67</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-35</td>
</tr>
<tr>
<td>Cr$_5$B$_3$</td>
<td>0.375</td>
<td>-40.30</td>
</tr>
<tr>
<td>CrB</td>
<td>0.5</td>
<td>-47.61</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-45</td>
</tr>
<tr>
<td>Cr$_3$B$_4$</td>
<td>0.571</td>
<td>-44.75</td>
</tr>
<tr>
<td>CrB$_2$</td>
<td>0.667</td>
<td>-38.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\geq 42$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-35</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-39.8$\pm$1.1</td>
</tr>
<tr>
<td>CrB$_4$</td>
<td>0.8</td>
<td>-25.0</td>
</tr>
</tbody>
</table>
Figure 3.12  Calculated phase diagram of the Cr-B system with experimentally determined phase boundaries superimposed.
Table 3.6 Invariant reaction data on the calculated Cr-B phase diagram.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Compositions (at% B)</th>
<th>Temp. (°C)</th>
<th>Reaction Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>L → Cr</td>
<td>0</td>
<td>1907</td>
<td>Melting</td>
</tr>
<tr>
<td>L → Cr + Cr₂B</td>
<td>15  0  33.3</td>
<td>1636</td>
<td>Eutectic</td>
</tr>
<tr>
<td>L + Cr₅B₃ → Cr₂B₂</td>
<td>30  37.5  33.3</td>
<td>1870</td>
<td>Peritectic</td>
</tr>
<tr>
<td>L + CrB → Cr₅B₃</td>
<td>35  50  37.5</td>
<td>1900</td>
<td>Peritectic</td>
</tr>
<tr>
<td>L → CrB</td>
<td>50</td>
<td>2100</td>
<td>Congr. melt</td>
</tr>
<tr>
<td>L → CrB + Cr₃B₄</td>
<td>56.6 50  57.1</td>
<td>2080</td>
<td>Eutectic</td>
</tr>
<tr>
<td>L + CrB₂ → Cr₃B₄</td>
<td>55  66.7  57.1</td>
<td>2080</td>
<td>Peritectic</td>
</tr>
<tr>
<td>L → CrB₂</td>
<td>66.7</td>
<td>2156</td>
<td>Congr. melt</td>
</tr>
<tr>
<td>L → CrB₂ + B</td>
<td>85.1 66.7  100</td>
<td>1880</td>
<td>Eutectic</td>
</tr>
<tr>
<td>Cr₂B + B → CrB₄</td>
<td>66.7 100  80</td>
<td>1500</td>
<td>Peritectoid</td>
</tr>
<tr>
<td>L → B</td>
<td>100</td>
<td>2075</td>
<td>Melting</td>
</tr>
</tbody>
</table>

3.3.3 The Mo-B System

Literature Review

The phase diagram of Mo-B system has been assessed by Hansen [58Han] with additional information given by Elliott [65Ell] and Shunk [69Shu]. More recently Spear and Liao [88Spe] assessed both the phase diagram and thermodynamic properties of the system based on available experimental data. The phase diagram from this work [88Spe] is shown in Figure 3.13 and is characterised by a series of intermetallic phases and limited solid solubility of the phases.

Early work by Kiessling [47Kie] established three intermediate phases of the system: Mo₂B, MoB, and Mo₂B₅. According to Kiessling [47Kie] both MoB and Mo₂B were stoichiometric whereas Mo₂B₅ was slightly deficient in boron, existing at about 70 at% B. Bertaut and Blum [51Ber] further reported a diboride MoB₂. Steinitz et al [52Ste], based on X-ray diffraction results,
confirmed the results of Kiessling [47Kie] and reported a homogeneity range for Mo$_2$B$_5$ of 68.2 to 70.0 at%B. They further proposed that (i) a high-temperature modification of MoB (β-MoB) existed, (ii) MoB$_2$ was a high temperature phase, and (iii) a further compound Mo$_3$B$_2$ existed at high temperature between 1850°C and 2070°C. The phase diagram up to 50 at%B was also studied by Gilles and Pollock [53Gil] who confirmed the results of Steinitz et al [52Ste].

On the basis of X-ray, melting point, metallographic and differential thermo-analytical studies, Rudy and Windisch [65Rud] presented a constitution of the phase diagram over the whole range of composition for the system, which forms the basis for the assessed diagram of Spear and Liao [88Spe]. Higher purity materials and more refined investigation techniques were used in this work. In the high temperature regions, their phase diagram differed significantly from the previously reported results in that melting points were significantly higher. Previously reported borides were confirmed in this study except Mo$_3$B$_2$, whose formation in earlier studies [52Ste, 53Gil] was attributed to carbon contamination of the alloys which were contained in graphite.
crucibles. In addition the formation of an MoB$_{12}$ phase by eutectoid reaction at 1807°C was reported.

Portnoi et al [67Por1] constructed a phase diagram for the entire range of concentrations based on thermal, X-ray structural, and metallographic analysis, and basically confirmed the diagram of Rudy and Windisch [65Rud] except that the MoB$_{12}$ phase melted congruently. Recently Storms and Mueller [77Sto] gave phase relationships between 1527°C and 1927°C which were generally consistent with both Rudy and Windisch [65Rud] and Portnoi et al [67Por1] but supported the eutectoid formation of MoB$_{12}$.

Some dispute surrounds the stoichiometry of the most B-rich compound, taken by Rudy et al [63Rud, 65Rud] and Portnoi et al [67Por1] to be MoB$_{12}$. A tetragonal phase, MoB$_4$ was reported by Chretien and Helgorsky [61Chr] but Rudy et al [63Rud, 65Rud] showed that its structure could be related to the hexagonal MoB$_{12}$ which they reported. Later work by Galasso and Pinto [68Gal] showed that the diffraction pattern of the MoB$_{12}$ phase could be reproduced by assuming that it possessed the hexagonal WB$_4$ structure and Lundstrom and Rosenberg [73Lun] fixed its composition at 80 at%B in agreement with the MoB$_4$ stoichiometry. In accordance with later work and following Spear and Liao [88Spe], the most B-rich compound is taken as MoB$_4$ here.

Detailed solubility data on the terminal solid solutions is limited. Zakharov et al [71Zak] reviewed previous determinations of the solubility of boron in molybdenum and results from the different studies varied between 0.177 and 1.75 at%B at the eutectic temperature. From their own study, the maximum solubility was determined as 0.6 at%B at the eutectic temperature and falling to 0.019 at%B at 1200°C.

Experimental work on the thermodynamic properties of the Mo-B the system is limited to the determination of activities in the solid state. Both Gilles and Pollock [54Gil] and Storms and Mueller [77Sto] carried out vapour pressure studies across the whole composition range of Mo-B system, while Baehren and Vollath [69Bae] measured the activity of boron in the Mo+Mo$_2$B two-phase field between 1358 and 1448 K. The activity data for Mo-rich alloys from the various studies was shown by Storm and Mueller [77Sto] to be inter-consistent, however, at higher boron concentrations the work of Gilles and Pollock [54Gil] and Storms and Mueller [77Sto] differ somewhat. By combining the data for Mo-rich alloys the Gibbs energy of formation of Mo$_2$B was estimated to be -46720+5.04T.
The Calculation

The calculated phase diagram together with the experimentally determined phase boundary data is shown in Figure 3.14. Figure 3.15 shows the comparison between the calculated Mo-solvus and that observed experimentally. The agreement with the observed phase diagram is generally good, although the experimental results are quite scattered. The thermodynamic parameters used in the calculations are listed in the appendix. The invariant reactions with concentrations of each corresponding phases in the reactions are listed in Table 3.7 and these results agree well with the assessment of Spear and Liao [88Spe].

The comparison between calculated and experimentally measured activity data of boron at 1790 and 2170 K are shown in Figure 3.16a and b respectively where there is a very good agreement. Table 3.8 gives the derived free energy of formation for the various Mo-borides at 1800°C.

Table 3.7 Invariant reactions for the calculated Mo-B phase diagram.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Compositions (at% B)</th>
<th>Temp. (°C)</th>
<th>Reaction Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>L → Mo</td>
<td>0</td>
<td>2603</td>
<td>Melting</td>
</tr>
<tr>
<td>L → α-Mo + Mo₂B</td>
<td>21.3  2   33.3</td>
<td>2177</td>
<td>Eutectic</td>
</tr>
<tr>
<td>L + MoB → Mo₂B</td>
<td>30.1 50  33</td>
<td>2276</td>
<td>Peritectic</td>
</tr>
<tr>
<td>L → MoB</td>
<td>50</td>
<td>2605</td>
<td>Congr.Melt.</td>
</tr>
<tr>
<td>L + MoB → MoB₂</td>
<td>65.6 50  62</td>
<td>2367</td>
<td>Peritectic</td>
</tr>
<tr>
<td>L + MoB₂ → Mo₂B₅</td>
<td>77.2 62  68</td>
<td>2137</td>
<td>Peritectic</td>
</tr>
<tr>
<td>L → Mo₂B₅ + B</td>
<td>87.1 68 100</td>
<td>1885</td>
<td>Eutectic</td>
</tr>
<tr>
<td>MoB₂ → MoB+Mo₂B₅</td>
<td>62  50  68</td>
<td>1518</td>
<td>Eutectoid</td>
</tr>
<tr>
<td>Mo₂B₅ + B → MoB₄</td>
<td>68 100  80</td>
<td>1600</td>
<td>Peritectoid</td>
</tr>
<tr>
<td>L → B</td>
<td>100</td>
<td>2075</td>
<td>Melting</td>
</tr>
</tbody>
</table>
Figure 3.14  Calculated phase diagram of the Mo-B system with experimentally determined phase boundary data superimposed.
Figure 3.15  Comparison between the calculated and observed Mo-solvus.
Figure 3.16  Comparison between the calculated ( ——— ) and the experimentally measured [77Sto] activity data of boron in Mo-B alloys. a) at 1790 K; b) at 2073 K.
Table 3.8  Gibbs energy of formation of Mo-B compounds.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Comp.</th>
<th>This Work (calc.)</th>
<th>[77Sto] (exp.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo₂B</td>
<td>0.333</td>
<td>-36.3</td>
<td>-37.1</td>
</tr>
<tr>
<td>MoB</td>
<td>0.50</td>
<td>-50.0</td>
<td>-50.1</td>
</tr>
<tr>
<td>MoB₂</td>
<td>0.62</td>
<td>-43.3</td>
<td>-45.2</td>
</tr>
<tr>
<td>Mo₂B₅</td>
<td>0.68</td>
<td>-39.4</td>
<td>-40.7</td>
</tr>
<tr>
<td>MoB₄φ</td>
<td>0.8</td>
<td>-24.4</td>
<td>-25.5</td>
</tr>
</tbody>
</table>

φ  This phase has also been reported as MoB₁₂ but has been taken here as MoB₄ (see discussion in text). Value derived from activity data of [77Sto] assuming x_B=0.8.

3.3.4 The Ni-B System

Literature Review

The Ni-B binary phase diagram has been evaluated by Jansson and Agren [84Jan], Hack and Chart [75Hac], and Kaufman et al [84Kau] and a set of thermodynamic descriptions for the phases was obtained as a result of each evaluation. However these assessments were either incomplete or in disagreement with the experimental phase diagram data to a fairly large extent. The thermodynamic data from these previous calculations are considered inappropriate for some of the phases. A detailed review on the assessments followed by the experimental works on this system will be given below.

Jansson and Agren [84Jan] assessed the Ni-B system for up to 30 at%B composition in conjunction with the thermochemical characterisation of liquid-solid equilibrium in Ni-rich Ni-Si-B alloys. This evaluation was done based on the experimental phase diagram by Schobel and Stadelmaier [65Sch] and high temperature Gibbs energy of formation data of the compounds Ni₃B and Ni₂B from the EMF measurements by Omori and Hashimoto [73Omo]. The evaluated
PHASE DIAGRAM ASSESSMENTS

The phase diagram of [84Jan] agreed with the experimental data in the composition region of below 30 at% B, and with the Gibbs energy of formation for the compound Ni$_2$B and Ni$_3$B, the partial enthalpy of mixing of Ni and B in the Ni-B liquid, and the boron activity in the Ni-rich fcc phase at the lower temperatures. The liquid phase was treated with a sublattice model assuming that boron occupies the interstitial sites on the Ni lattice. This model, however, is not suitable at boron content more than 50% because by then all the interstitial sites on Ni lattice would have been fully occupied.

Hack and Chart [75Hac] performed a critical assessment of thermodynamic data for the whole concentration range of the Ni-B system. A set of provisional data was obtained for the thermodynamic description of the phases. However the number of parameters used for the liquid phase was unnecessarily high (five coefficients in the polynomial expression representing the excess energy of formation), and the entropy of formation of Ni$_2$B was given as positive which is not likely to be true in systems of this class.

Kaufman et al [84Kau] provided a set of thermodynamic data for binary systems of boron with various transition metals including Ni-B by utilising a pair-potential calculation method. However the calculated phase diagram using this data shows considerable discrepancy with the experimentally measured phase boundary data. It was therefore necessary to reassess the phase diagram and the thermodynamic data of the Ni-B system in order to achieve a more accurate result.

Numerous experimental studies of the Ni-B systems have together revealed a general outline of the phase diagram in spite of some controversial points of difference. Earlier experimental works, though far from systematic and comprehensive, on the existence of the compounds and the determination of the phase diagram of the Ni-B system were compiled by Hansen and Anderko [58Han], and supplemented by Elliot [65Ell] and Shunk [69Shu] for some later work.

Phase diagram measurements for the Ni-B system has been performed by Schobel and Stadelmaier [65Sch] for up to 70 at% B from thermal analysis, microscopic and X-ray diffraction results, by Portnoi et al [67Por] for all the composition range based on thermal, metallographic and X-ray diffraction analysis and X-ray spectra analysis results, and Lugscheider et al [74Lug] in their work to establish the ternary Ni-Cr-B system by using X-ray diffraction and metallographic methods. Additional phase boundary data for equilibrium between liquid and
fcc were provided by Ajao and Hamar-Thibault [85Aja] from their examination of the system Ni-Ni$_3$B by differential thermal analysis, X-ray and electron diffractions, scanning and transmission electron microscopy, and for equilibrium between liquid and boron by Storm and Szklarz [87Sto] from their calculations using the measured Ni activity values.

A stable eutectic between fcc and Ni$_3$B was established from these experimental phase diagram examinations. It was reported to occur to a liquid of 17 at.%B at 1093°C with the solubility limit of boron in Ni-fcc as 0.3 at.%B at the eutectic temperature. Portnoi et al [67Por2] and Ajao and Hamar-Thibault [88Aja] provided a slightly higher reaction temperature of 1110°C with liquid concentration of 19 at.%B and 16.2 at.%B and boron solubility limit of 0.135 at.%B and -0.3 at.%B, respectively.

A metastable eutectic between fcc and Ni$_2$B was proposed by Schobel and Stadelmaier [65Sch] and confirmed by Lugscheider et al [74Lug]. The reaction was detected at 986°C and with the liquid at -20 at.%B. The explanation seems to be that Ni$_3$B is a fairly unstable phase and can easily be suppressed at a high cooling rate. However, a study made on the solidification of the Ni-B alloy in particular the crystallography of the Ni-Ni$_3$B eutectic revealed no metastable eutectic between fcc and Ni$_2$B at a cooling speed of 10°C sec$^{-1}$. Instead two or three solid state transformations were observed at 970°C-950°C and 850°C in alloys with < 30 at.%B at slow cooling rate of 5°C min$^{-1}$. The alloys showed significant undercooling but no suppression of Ni$_3$B was reported to occur.

The majority workers [65Sch, 67Por2, 74Lug] have confirmed the existence of Ni$_3$B, Ni$_2$B, o$_{-}$Ni$_4$B$_3$ (orthorhombic), m$_{-}$Ni$_4$B$_3$ (monoclinic), and NiB. Other Ni-borides reported include Ni$_3$B$_2$ [58Han], which was not detected by later workers, and NiB$_{12}$ [67Por2], which was most possibly due to the high content of impurity (Fe, Al, Mg, Cu, C) in the testing materials.

The phase diagram proposed by Schobel and Stadelmaier [65Sch] was strongly supported by the later work by Lugscheider et al [74Lug]. The congruent melting point for Ni$_3$B and Ni$_2$B were indicated as 1166°C and 1125°C respectively. The two borides with crystalline structure of orthorhombic (o$_{-}$Ni$_4$B$_3$) and monoclinic (m$_{-}$Ni$_4$B$_3$) and stoichiometry of around 41.4 at.%B and 43.6 at.%B were characterised in their diagram as congruent compounds with the melting temperature of 1025°C and 1031°C respectively. The monoboride NiB was defined to be in peritectic equilibrium with boron at 1035°C [65Sch, 74Lug].
In the experimental report of Portnoi et al [67Por2], however, the melting points for all the compounds given were much higher than the values supplied by Schobel and Stadelmaier [65Sch] apart from an only slightly higher eutectic temperature of 1110°C between Ni-fcc and Ni3B. The difference in the reported melting temperatures was as large as 500°C. This again suggests a high degree of inaccuracy in the experiments and the work of [67Por2] was in general not given much weighting in the present assessment.

Some thermodynamic data have been obtained for the Ni-B system from various experiments. Sato and Kleppa [82Sat] reported the enthalpy of formation of some transition metal borides including Ni2B and NiB determined by high temperature solution calorimetry with liquid copper as the solvent. The enthalpy of formation of Ni2B and NiB was given as -22.6±1.4 and -20.1±2.8 kJ/g.atm respectively from their measurements at 1385±2 K. The Gibbs energy of formation of Ni3B and Ni2B were determined by Omori and Hashimoto [73Omo] by EMF measurements and fairly large values (-33.2 and -35.7 for the two borides respectively) were found for their enthalpy and entropy results.

The activity of Ni was measured as a function of temperature and composition throughout the Ni-B liquid range by Storma and Szklarz [87Sto] using the Knudsen effusion technique. The experiments resulted the activity functions in the form of log a = A/T + B, where a is the activity, T the temperature, and A, B are the constants whose values were tabulated for different boron concentrations.

The Calculation

The calculation of the Ni-B system has been performed over the whole composition range in order to achieve a systematic account for the thermodynamic description of the liquid. The lattice stability values for the Ni and B elements have been taken from the recommended SGTE database [88STGE].

The liquid phase was treated using the substitutional model assuming that the metallic components mix with boron on the same sublattice. The substitutional solution model has been used by the present author in modelling the other transition metal-boron systems including Fe, Cr, Mo-B systems and was considered as a suitable model to be used for the liquid phase in the Ni-B system. It was possible to simulate the highly stable liquid phase at < 50 at%B by using
two additional composition terms. All the borides were treated as line compounds. The borides above 50 at%B were not considered. The two Ni$_4$B$_3$ borides were represented by a single compound with 43.6 at%B concentration for reasons of simplicity since the melting points of the two are fairly close.

Figure 3.17 Calculated phase diagram of Ni-B binary system with experimentally measured phase boundaries superimposed.

After the thermodynamic parameters for the liquid phase were defined during the initial stage of the assessments, the thermodynamic definitions of the compound phases were almost
complete because their melting points are directly related to the liquid stability. The entropy of the compounds were constrained by the invariant reactions occurring between them and the liquid. The thermodynamics of the Ni-rich fcc solution phase was determined largely by its solubility limit at the eutectic temperature.

The calculation was based mostly on the experimental phase boundary data of Schobel and Stadelmaier [65Sch], but data from other measurements was also taken into account. A very good agreement was found between the calculated phase diagram and most of the experimental measurements especially around the liquidus, the Ni-rich fcc phase and Ni3B eutectic, and the melting points of the Ni-rich borides (see Figure 3.17).

Some disagreement with experimental data was found in the melting point of the Ni4B3 boride. The experimentally determined phase diagrams presented the Ni4B3 phase as a congruent melting compound whereas the calculations showed the phase dissolving in a peritectic reaction before melting. It is quite possible that the two Ni4B3 borides reported in the literature were in fact one incongruent compound considering the consistency in thermodynamics for the rest part of the alloy system.

Enthalpy of formation of Ni2B and NiB from the literature [82Sat] and the values given by the present author are compared in Table 3.9. There was a disagreement between the Gibbs energy

<table>
<thead>
<tr>
<th>Boride</th>
<th>$x_B$</th>
<th>$\Delta H_f$ (kJ/g.at)</th>
<th>Source of Data</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni2B</td>
<td>0.333</td>
<td>-22.6</td>
<td>This work</td>
<td>calculated</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-22.6±1.4</td>
<td>[82Sat]</td>
<td>experimental</td>
</tr>
<tr>
<td>NiB</td>
<td>0.5</td>
<td>-20.1</td>
<td>This work</td>
<td>calculated</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-20.1±2.8</td>
<td>[82Sat]</td>
<td>experimental</td>
</tr>
</tbody>
</table>
PHASE DIAGRAM ASSESSMENTS

of formation at high temperature for the \( \text{Ni}_2\text{B} \) and \( \text{Ni}_3\text{B} \) from the present work and data from Omori et al [73Omo] when the more accurate and more reliable experimental work [82Sat] was favoured. The invariant reactions with concentrations of each corresponding phase in the reactions are listed in Table 3.10.

Table 3.10  Invariant reaction data on the calculated Ni-B phase diagram.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Compositions (at% B)</th>
<th>Temp. (°C)</th>
<th>Reaction Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>L \rightarrow \text{Ni}</td>
<td>0</td>
<td>1455</td>
<td>Melting</td>
</tr>
<tr>
<td>L \rightarrow \gamma\text{-Ni} + \text{Ni}_3\text{B}</td>
<td>15.9 0.42 25.0</td>
<td>1095</td>
<td>Eutectic</td>
</tr>
<tr>
<td>L \rightarrow \text{Ni}_3\text{B}</td>
<td>25.0</td>
<td>1165</td>
<td>Congr.melt</td>
</tr>
<tr>
<td>L \rightarrow \text{Ni}_3\text{B} + \text{Ni}_2\text{B}</td>
<td>32.0 25.0 33.3</td>
<td>1124</td>
<td>Eutectic</td>
</tr>
<tr>
<td>L \rightarrow \text{Ni}_2\text{B}</td>
<td>33.3</td>
<td>1125</td>
<td>Congr.melt</td>
</tr>
<tr>
<td>L + \text{Ni}_2\text{B} \rightarrow \text{Ni}_4\text{B}_3</td>
<td>45.2 33.3 43.6</td>
<td>1027</td>
<td>Peritectic</td>
</tr>
<tr>
<td>L \rightarrow \text{Ni}_4\text{B}_3 + \text{Ni}\text{B}</td>
<td>45.9 43.6 50</td>
<td>1025</td>
<td>Eutectic</td>
</tr>
<tr>
<td>L + \text{B} \rightarrow \text{NiB}</td>
<td>49.1 100 50</td>
<td>1035</td>
<td>Peritectic</td>
</tr>
<tr>
<td>L \rightarrow \text{B}</td>
<td>100</td>
<td>2075</td>
<td>Melting</td>
</tr>
</tbody>
</table>

3.4 Characterisations of Ternary Systems

3.4.1 The Fe-Cr-B System

Literature Review

There have been five experimental determinations of the Fe-Cr-B system [66Kan, 70Che, 73Bor, 76Gor, 83Gia]. All of these studies basically agree that, in the range 0 to 33.3 at%B, both the orthorhombic \( \text{Cr}_2\text{B} \) (hereafter referred to as \( \text{M}_2\text{B}_\text{orth} \)) and the tetragonal \( \text{Fe}_2\text{B} \) (hereafter \( \text{M}_2\text{B}_\text{tetr} \)) have extensive solubility in the ternary and that there is a three-phase equilibrium between the Fe-Cr based solid solution, the \( \text{M}_2\text{B}_\text{orth} \) and the \( \text{M}_2\text{B}_\text{tetr} \) phases. However, there
are quantitative discrepancies between the studies with relation to (i) the compositions of the phases in the three-phase equilibrium, (ii) the formation of Cr-rich boride phases with compositions less than 33.3 at%B.

In relation to the three phase field between M$_2$B$_{\text{orth}}$, M$_2$B$_{\text{tetr}}$, and the Fe-Cr based solid solution, the experimental details are summarised in Figure 3.18 and Table 3.11. The solubility extension of the two boride phases is very similar in the work of Kaneko et al [66Kan] at 700°C, Chepiga and Kuz'ma [70Che] at 700°C and 900°C and Gorbunov and Boduryan [76Gor] at 1100°C, while the work of Gianogli et al [83Gia] gives compositions about 10 at% richer in Cr for both of the boride phases. In comparison to the previous four studies, the results of Borello et al [73Bor] are quite different with respect to the composition difference between the two borides.

![Figure 3.18](image_url)  
Figure 3.18  Summary of the experimental information [66Kan, 70Che, 73Bor, 76Gor, 83Gia] on the three-phase field of the Fe-Cr-B isothermal section.
Table 3.11 Summary of the calculated and the experimental data on the three phase equilibrium in the Fe-Cr-B system.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Composition (at% Cr)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>α(or γ)</td>
<td>M₂B_tetr</td>
</tr>
<tr>
<td>900</td>
<td>2.76</td>
<td>11.7</td>
</tr>
<tr>
<td>700</td>
<td>6.4</td>
<td>7.8</td>
</tr>
<tr>
<td>900</td>
<td>4</td>
<td>10</td>
</tr>
<tr>
<td>1250</td>
<td>9.3</td>
<td>16</td>
</tr>
<tr>
<td>1100</td>
<td>36</td>
<td>11.8</td>
</tr>
<tr>
<td>1100</td>
<td>20</td>
<td>18</td>
</tr>
</tbody>
</table>

The biggest discrepancies concerned with the three-phase field lies in the composition of the Fe-Cr based solid solution. The work of Kaneka et al [66Kan], Chepiga and Kuz'ma [70Che], and Boriello et al [73Bor] indicate that it lies below 10 at%Cr, while Gorbunov and Boduryan [76Gor] and Gianogli et al [83Gia] give 20 at%Cr and 36 at%Cr respectively. It is worth noting that the extent of the γ loop in Fe-Cr is such that if the concentration lies below about 13 at%Cr, it may be the γ phase which is involved in equilibrium, rather than the α phase, if temperatures are above 850°C.

Gorbunov and Boduryan observed the Cr₄B phase in Cr-B, which disagrees with the Cr-B phase diagram assessed both in this present work and in the reviews of Hack and Chart [82Hac] and Liao and Spear [86Lia] where it has been concluded that the phase Cr₄B is in fact a metastable phase. Boriello et al [73Bor] also reported a boride which is very rich in chromium in the Cr-B binary system, but again this has been taken to be metastable.

The Calculation

Thermodynamic calculations of the ternary system Fe-Cr-B have been made for boron contents up to 50 at%B. The calculated isothermal section of the Fe-Cr-B system at 900° and 700°C for boron contents up to 30 at%B are shown in Figure 3.19 and Figure 3.20 respectively, with
Figure 3.19  Calculated isothermal section of the Fe-Cr-B system at 900°C from the present work, with experimental data from [70Che] for comparison.
Figure 3.20  Calculated isothermal section of the Fe-Cr-B system at 700°C from the present work, with experimental data from [70Che] for comparison.
PHASE DIAGRAM ASSESSMENTS

experimental data from Chepiga and Ku'zma [70Che] superimposed for comparison. The calculated compositions of the $M_2B_{\text{orth}}$, $M_2B_{\text{tetr}}$, and $\alpha$ or $\gamma$ (Fe, Cr)- based solid solution phases in the three-phase equilibrium are given in Table 3.11 and compared with experimental data given in the same table. The solubility extension of the higher borides into the ternary is consistent with all the experimental studies, although CrB and FeB are in three-phase equilibrium with $M_2B_{\text{tetr}}$ rather than $M_2B_{\text{orth}}$. The calculated results show that there is little change in the compositions of the three phases in equilibrium at different temperatures.

The results compare favourably with Kaneko et al [66Kan], Chepiga and Kuz'ma [70Che], and Gorbunov and Boduryan [76Gor] for the composition of the borides, and with Kaneko et al [66Kan] and Chepiga and Kuz'ma [70Che] for the composition of the Fe-based solid solution in three-phase equilibrium. As mentioned previously, the solution may be fcc at certain temperatures.

Table 3.12 Summary of ternary reaction data on the calculated Fe-Cr-B liquidus projection plot.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Compositions (at%)</th>
<th>Temp. (°C)</th>
<th>Reaction Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>71.3 12.3 16.4</td>
<td>1091</td>
<td>Eutectic</td>
</tr>
<tr>
<td>U1</td>
<td>65.4 21.4 13.2</td>
<td>1124</td>
<td>Quasi-peritectic</td>
</tr>
<tr>
<td>U2</td>
<td>63.3 14.1 22.6</td>
<td>1244</td>
<td></td>
</tr>
<tr>
<td>U3</td>
<td>62.5 11.2 26.3</td>
<td>1311</td>
<td></td>
</tr>
<tr>
<td>U4</td>
<td>5.2  63.2 31.6</td>
<td>1839</td>
<td></td>
</tr>
</tbody>
</table>

The liquidus surface up to 50 at%B has been calculated using the parameters optimised from the above evaluation and is shown in Figure 3.21. Five ternary reactions are defined during the liquidus calculation (see Table 3.12): a ternary eutectic E at 16.4 at%B, 12.3 at%Cr and 1091°C; four ternary quasi-peritectic reactions with U1 at 13.2 at%B, 21.4 at%Cr and 1124°C, U2 at 22.6 at%B, 14.1 at%Cr and 1244°C, U3 at 26.3 at%B, 11.2 at%Cr and 1311°C, and U4 at 31.6 at%B, 63.2 at%Cr and 1839°C.
Figure 3.21 Calculated liquidus projection of the Fe-Cr-B system from the present work.

3.4.2 The Fe-Mo-B system

Literature Review

There have been two papers on the experimental investigation of the Fe-Mo-B system, one by Gladyshevskii et al [66Gla] and the other by Haschke et al [66Has]. A private communication has also been received from Dr. Rogl [89Rog] concerning the stability of a ternary phase.

Gladyshevskii [66Gla] established the isothermal section of the Mo-Fe-B system at 1000°C based on X-ray examination and microstructural analysis on 74 alloys with composition distributed over the whole composition range. The isotherm is shown in Figure 3.22. In the 0-50 at% B concentration range, five compound phases originating in the binaries were presented: MoB,
Figure 3.22 Experimentally determined isothermal section of the Fe-Mo-B system at 1000°C from Gladyshevski [66Gla].

FeB, Mo$_2$B, Fe$_2$B, and the $\mu$-phase originating from the Fe-Mo system. The solubility of the ternary component in the binary compounds was reported to be very limited and had no effect on the lattice constants. A ternary compound (Mo,Fe)$_3$B$_2$ (U$_3$Si$_2$-type structure) was determined with homogeneity region of 40 at%B, 20-28 at%Fe, 40-32 at%Mo and including the composition Mo$_2$FeB$_2$. The X-ray pattern of the ternary phase was indexed in the tetragonal system with c/a = 0.54. A phase (Mo,Fe)B appearing in the ternary system was also reported described as being the high temperature form of the MoB phase stabilised at lower temperatures by the addition of iron.

Haschke et al [66Has] experimentally determined an isothermal section of the Fe-Mo-B at 1050°C (Figure 3.23) which included an additional ternary compound named Fe$_{13}$Mo$_2$B$_5$ (i.e. M$_3$B).
phase with this structure has been observed in rapidly quenched Fe-B alloys, but is metastable in the equilibrium binary phase diagram. The solubilities of ternary components in the binary compounds of the Mo-B, Fe-B, and Fe-Mo systems were indicated as insignificant in agreement with Gladyshevskii et al [66Gla].

In Fe-rich alloys, the diagrams of Gladyshevskii et al [66Gla] and Haschke et al [66Has] are actually consistent as it has been experimentally determined by Rogl [89Rog] that the Fe$_{13}$Mo$_2$B$_5$ phase is stable just above 1000°C but decomposes by eutectoid reaction to give the phase diagram of Gladyshevskii at about 1000°C. It is noted, however, that in Mo-rich alloys the diagram of Haschke et al [66Has] indicates equilibrium between the Mo$_2$FeB$_2$ phase and Mo (bcc) solid solution, whereas equilibrium between Mo$_2$B and $\mu$-phase was established by Gladyshevskii et al [66Gla].

![Figure 3.23](image_url) Experimentally determined isothermal section of the Fe-Mo-B system at 1050°C from Haschke [66Has].
The Calculation

Calculated isothermal sections of the Fe-Mo-B system at 1000°C and at 1050°C are shown in Figure 3.24 and 3.25. Because of the small solubilities in this system, the phase diagrams are relatively straightforward and the calculated phase diagrams from the present work agree well with the experimental result from [66GlA] at 1000°C and Haschke et al [66Has] at 1050°C.

The compositions of the two metallic components in \(M_3B_2\) phase vary from 40-32.2 at%Mo and 20-27.8 at%Fe according to this calculation, which is in very good agreement with the experimental data of Gladyshevskii [69GlA]. The phase has been modelled assuming three sublattices, one of which is completely occupied by B, another is occupied by Fe, and Fe and Mo are taken to mix on the remaining sublattice. The \(M_3B\) phase is shown in the isothermal section.

**Figure 3.24** Calculated isothermal section of the Fe-Mo-B system at 1000°C from the present work.
Figure 3.25 Calculated isothermal section of the Fe-Mo-B system at 1050°C from the present work.

of the system at 1050°C with metallic compositions at 5.4-6.3 at%Mo and 61.3-60.4 at%Fe. It has been modelled using two-sublattices, one of which is occupied by B and the other on which Fe and Mo mix. With respect to the tie-line direction at Mo-rich corner of the isothermal sections, the calculated results are in agreement with the experimental data from Haschke [66Has].

3.4.3 The Cr-Mo-B System

Literature Review

Kuz'ma et al [69Kuz] investigated the Cr-Mo-B system at 1400°C and 1000°C and an isothermal section at 1400°C was given, as shown in Figure 3.26. It is established that Cr is virtually insoluble in Mo-borides while Mo has a more profound solubility in Cr-borides. The compounds
CrB, Cr₅B₃ and Cr₂B (i.e. M₂B\textsubscript{orth}) were reported to dissolve up to 40, 48, and 6 at\%Mo, respectively. Of the Mo-borides, only Mo₂B dissolved up to 10 at\%Cr, the solubility of Cr in the other Mo-borides being less than 3 at\%Cr. Two ternary compounds were reported: a Cr-rich, L phase with a tetragonal CuAl₂ structure, and (Mo,Cr)₃B₂ of tetragonal U₃Si₂ type with homogeneity range at 29-40 at\%Mo, 31-20 at\%Cr, and 40 at\%B. X-ray powder diffraction data for the two compounds were given as well as their lattice parameters. The character of phase equilibria at 1000°C was also examined and no change was observed compared with the one at the temperature of 1400°C.

Kolomytsev et al [69Kol] reported a substantially different result on the phase equilibria of the system. The isothermal section at 1000°C was determined for up to 50 at\%B concentration (Figure 3.27) on the basis of X-ray diffraction, microhardness and metallographic data. Apart
from the binary phases, a ternary compound (T-phase) was observed with tetragonal structure and concentration ranging at 33-34 at% B and 20-48 at% Mo. The d-spacings obtained from X-ray diffraction were presented, however a full structure analysis and how the tetragonal structure was decided was not presented.

In addition, the Mo corner of the Mo-Cr-B system was studied by Zakharov et al [82Zak] giving the combined solubility information of B and Cr in Mo in the solid state.

The ternary compound (Mo, Cr)\textsubscript{3}B\textsubscript{2} is iso-structural with FeMo\textsubscript{2}B\textsubscript{2} and was described using the
same sublattice formula with Cr on one of the transitional metal sublattices and Cr and Mo mixing on the other. With this model, the three-phase region connecting the ternary phase matches extremely well with the experimental result with homogeneity of the compound ranging at 40-29.3 at%Mo, 20-30.7 at%Cr and 40 at%B comparing with experimental data of 40-29 at%Mo, 20-31 at%Cr and 40 at%B from Kuzma [69Kuz]. The parameters of the counterphases used in the calculation are listed in the appendix together with the other thermodynamic data for the compounds and the solution phases.

A calculation of the isothermal section at 1000°C for the system has also been made and the general feature remains the same as the isothermal section at 1400°C, supporting Kuzma's result [69Kuz]. The composition range of the ternary compound becomes slightly smaller at 1000°C than that at 1400°C and the directions of the tie lines are only slightly shifted from those at the higher temperature.
3.4.4 The Fe-Ni-B System

Literature Review

There have been no extensive studies on the ternary Fe-Ni-B system except a few isothermal sections, which will be reviewed here. A metastable phase \((\text{Fe}, \text{Ni})_{23} \text{B}_6\) has been reported by a number of workers and will also be reviewed below.

An isothermal section at 800°C were reported by Kuz'ma and Koval [68Kuz] for the whole composition range (Figure 3.29) on the basis of X-ray diffraction and microstructural analysis.

Figure 3.29  Experimentally determined isothermal section of the Fe-Ni-B system at 800°C from Kuz'ma et al [68Kuz].
results. Another isothermal section at the same temperature for boron content up to 33.3 at% was given by Stadelmaier and Pollock [69Sta] (Figure 3.30) via metallographic and X-ray analysis techniques. Complete miscibility was reported between the two binary compounds Fe$_2$B and Ni$_2$B. The solubility limit of Fe in Ni$_2$B at 800°C was reported to be 45 at%Fe by Kuz'ma et al [68Kuz], which was later confirmed by Stadelmaier et al’s measurement [69Sta]. Both reports presented a region of three-phase equilibrium between (Fe,Ni)$_2$B, (Fe,Ni)$_3$B, and fcc phase with slightly different compositions for the phases in equilibrium (see Table 3.13 for comparison). The solubilities of the third component in the two monoborides FeB and NiB are both limited (~5 at%). A liquidus projection was superimposed on the isothermal section by Stadelmaier and Pollock [69Sta] but no exact data were provided as for the four phase reaction.

![Figure 3.30](image)

Figure 3.30 Experimentally determined isothermal section of the Fe-Ni-B system at 800°C by Stadelmaier and Pollock [69Sta].

An isothermal section of the Fe-Ni-B system at 925°C was given by van Loo and van Beek [89Loo] based on diffusion couple experiments with a combination of X-ray powder diffraction, optical microscopy, SEM and EPMA analyses. Their phase diagram resembles the previous isothermal sections at 800°C [68Kuz, 69Sta]. The three phase equilibrium was established between M$_2$B (10 at%Ni), M$_3$B (25 at%Ni), and fcc (40 at%Ni). The compositions of the equilibrium phases in the three phase region were included in Table 3.13 for comparison.

A metastable $\gamma$-phase (Fe,Ni)$_2$B$_6$ was reported to form as a primary phase in an alloy Fe$_{10}$Ni$_{70}$B$_{20}$ and has the same crystalline structure as the Cr$_{23}$C$_6$ [69Sta]. Only (Fe,Ni)$_3$B was found in an
alloy of Fe_{25}Ni_{55}B_{20}. An interesting discovery about the \( M_{23}B_6 \) phase is that alloys which did not show the phase on cooling did not produce it on annealing, whereas specimens containing the phase on cooling still show this phase after annealing for 300 hours at 800°C. This suggests that the \( M_{23}B_6 \) phase is almost a stable, i.e., a very strong metastable phase. Another investigation [82Mul] on crystallization phenomena in the metallic glass \( Fe_{40}Cr_{40}B_{20} \) also revealed the existence of the \( M_{23}B_6 \) phase by TEM results.

Using an atom probe Delargy et al [83Del] showed that in a Ni-based super alloy IN939 the \( M_{23}C_6 \) phase contains significant amount of boron (up to 1.5%B), which increases the stability of the phase. It has been known for a long time that boron substitutes for carbon in \( M_{23}C_6 \). Apart from the roles boron may perform on stabilizing the carbide/matrix interface, it may also make the \( M_{23}C_6 \) more stable with respect to sigma phase formation.

An \((Fe_{0.25}Ni_{0.75})_4B\) (\(\tau\)-phase) was observed with a cubic \( Cr_{23}B_6 \) type, among the other crystalline phases in the study of crystallisation process and structures of amorphous states in the Fe-Ni-B alloys [85War]. However it was not certain as to whether the phase should be considered as a stable or a metastable phase.

A solidification study of an \( Fe_{40}Ni_{40}B_{20} \) at high undercooling was conducted by Vitta et al [90Vit]. This composition lies in the two-phase field of gamma phase and the compound \((Fe, Ni)_3B\) in the ternary equilibrium diagram at 1073 K. Examinations of the alloy microstructure revealed that primary \( M_3B \) was present in a eutectic matrix of gamma phase and \((Fe, Ni)_3B\) in the solidified alloy at an undercooling up to 80 K. At an undercooling of 140 K \( M_3B \) was no longer evident and \((Fe, Ni)_{23}B_6\) in addition to \((Fe, Ni)_3B\) and gamma phase were revealed by X-ray diffraction.

An \( M_{23}B_6 \) phase was found on a Philips diffractometer in crystallized \((Fe_{100-x}M_x)_{83}B_{17}\) glasses, where \( M = Cr, Ni, Mo \) etc. [84Ber]. For the Fe-Ni-B alloys in particular, the \((Fe, M)_{23}B_6\) phase was present in the composition range of 0-50\%Ni depending on the heating rate. The primary \((Fe, M)_{23}B_6\) phase was observed over a wide range of alloying compositions containing the elements (e.g. Cr, Ni) which form substitutional solutions in \( M_{23}C_6 \) crystals. Those elements (e.g. Mo), which form interstitial \( M_{23}B_6 \) crystals due to their larger size misfit, form primary \((Fe, M)_{23}B_6\) with low solute additions.

There has been little work in the literature regarding the thermodynamics of the \( M_{23}B_6 \) phase.
Efforts was made by the present author to estimate the values for the enthalpy and entropy of this phase on the basis of the established thermodynamic data from other related systems including Fe-C-B by Ohtani et al [88Oht]. The experimental observations as reviewed provide useful information for the estimation.

The Calculation

The calculation of the Fe-Ni-B phase diagram concentrated on the isothermal sections of the system up to 33.3 at%B at 800° and 925°C where the best fit with the experimental data was obtained. The calculated results of the three phase equilibrium between fcc, M$_3$B, and M$_2$B are compared with the experimentally measured values in Table 3.13.

Table 3.13 Comparison between the calculated (in bold) and experimental data on the three-phase equilibrium in the Fe-Ni-B system at 800°C.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Compositions ( at%)</th>
<th>Temp. ( °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe</td>
<td>Ni</td>
</tr>
<tr>
<td>fcc</td>
<td>55</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>62</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>65</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td>M$_3$B</td>
<td>45</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>25</td>
</tr>
<tr>
<td>M$_2$B_tetr</td>
<td>55</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>46</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>57</td>
<td>10</td>
</tr>
</tbody>
</table>
The calculation also showed another three phase region between bcc, fcc, and $M_2B$ phases at the Fe-rich corner of the isothermal diagram, which agrees with experiment [68Kuz, 69Sta]. The isothermal section of the Fe-Ni-B system at 800°C is plotted in Figure 3.31.

The thermodynamic parameters were obtained for bcc, fcc, $M_3B$, and $M_2B$ and the data are listed in the appendix. The bcc and fcc phases were represented using the regular solution model. The $M_3B$ phase was modelled with a suitable interaction term between the stable Ni$_3$B and the metastable Fe$_3$B. The $M_2B$ phase was similarly modelled except that the two end compound phases are both stable. A continuous $M_2B$ compound exist across the metallic composition range as the crystalline structures of Fe$_2$B and Ni$_2$B are both tetragonal (see Figure 3.31).

![Figure 3.31](image-url)  
*Figure 3.31*  Calculated isothermal section of the Fe-Ni-B system at 800°C from the present work.
3.4.5 The Cr-Ni-B System

Literature Review

The most characteristic feature of the Cr-Ni-B system is that there is no substantial solubility of the metallic component in the binary borides, which has been established by the experimental results from Chepiga et al [72Che] and Lugscheider et al [74Lug]. Isothermal sections have been determined using X-ray diffraction and metallography over the whole composition range for the ternary system at 800°C (Figure 3.32, [72Che]), and at 1000°C (Figure 3.33, [74Lug]).

Figure 3.32 Experimentally determined isothermal section of the Cr-Ni-B system at 800°C by Chepiga et al [72Che].
The Cr-Ni-B phase diagram has been calculated for composition range up to 50 at%B. Because there is very little solubility of the third component in any of the phases in this system, the calculation was simply based on the component binary systems. The thermodynamic descriptions for the counter phases were defined by subtracting 2 kJ.mol\(^{-1}\) from the free energy of the stable phase or phases of the same stoichiometry. The calculated phase diagram at 1000°C is shown in the Figure 3.34.
3.5 Characterisations of Quaternary Systems

3.5.1 The Fe-Cr-Mo-B System

Literature Review and the Calculation

Details concerning the constitution of the Fe-Cr-Mo-B quaternary system are quite limited. Takagi et al. [86Tak, 87Tak] examined the liquid phase in sintered alloys and made an investigation on the Mo₂FeB₂ type phase in alloys with five levels of Mo content, corresponding to Mo/B atomic ratios from 0.7 to 1.1, three levels of Cr content at 0, 5 and 10 wt%Cr and a fixed
boron level of 5 wt%B. Alloy partitioning in the Mo₂FeB₂ type phase was measured using chemical analysis [86Tak]. Kim et al [89Kim] studied the phases which were formed in a rapidly solidified Fe₇₀Cr₁₈Mo₂B₁₀ alloys and obtained structural identification and chemical analysis of the various phases which were present.

A later work was conducted by Kim et al [91Kim] on the microstructural changes in a rapidly solidified melt spun Fe₇₀Cr₁₈Mo₂B₁₀ ribbons after annealing at various temperatures using a combination of differential scanning calorimetry, X-ray diffractometry, TEM, and energy dispersive X-ray (EDX) microanalysis. It was found that the as-solidified melt spun ribbons consist of primary crystalline particles of bcc ferrite with an amorphous matrix. After annealing for 2 hours at 500° or 600°C, the amorphous phase crystallises into a mixture of Cr-rich primitive tetragonal M₃B boride particles and bcc ferrite grains. When annealed for 2 hours at 700° and 800°C, the microstructure transforms into a mixture of Cr-rich orthorhombic M₂B and Mo-rich fcc M₂₃B₆ particles embedded in a matrix of bcc ferrite. At an annealing temperature of 900°C, the bcc ferrite matrix is replaced by fcc austenite, which transforms to dislocated lath martensite on cooling from the annealing temperature. After annealing for 2 hours at 950° and 1000°C, M₂₃B₆ boride particles are replaced by Mo-rich primitive tetragonal M₃B₂ particles, a microstructure very similar to that of the same alloy after rapid solidification followed by extrusion at this annealing temperature.

Calculations for the quaternary system were made on the basis of the binary and ternary characterisations presented in the previous sections of the thesis. So that calculations could be made for the ternary phase M₃B₂, counterphase parameters were chosen for the metastable compounds Cr₂FeB₂, Fe₂CrB₂ and Fe₃B₂ on the basis that the heat of transformation to the stable phases was 2 kJ.mol⁻¹ and their entropy of formation was equivalent to that of the stable mixture of phases. Such parameters ensured that the counterphase remained metastable in the appropriate area.

The experimental results from Takagi et al [86Tak] are shown in Figure 3.35 and compared with the present calculations. The two sets of data are in very good agreement at higher Cr content and in fair agreement with each other at lower Cr content with error levels of < ±5 at% for any of the elements.

The present calculations can also be compared to the phases observed by Kim et al [89Kim] in
PHASE DIAGRAM ASSESSMENTS

Figure 3.35  Comparison of the alloy partitioning in the phase $\text{M}_3\text{B}_2$ between the calculated results (open circles with dotted lines) from this work and the experimental data (half filled circles with solid lines) from Takagi et al [86Tak]. a) B contents; b) Cr contents; c) Mo contents; d) Fe contents in $\text{M}_3\text{B}_2$ as a function of Mo/B atomic ratio.
PHASE DIAGRAM ASSESSMENTS

c) Mo contents

d) Fe contents
PHASE DIAGRAM ASSESSMENTS

the Fe_{70}Cr_{18}Mo_{2}B_{10} alloy. They [89Kim] reported that amorphous melt spun ribbon, heat treated
at 950°C and extruded at the same temperature, contained three phases on subsequent
examination at room temperature: a martensitic Fe-rich matrix, the M_{2}B_{orth} phase, and the
M_{3}B_{2} phase. The results for the transition metal ratio Fe:Cr:Mo in each of the phases were
reported. The ratios were then converted into atomic compositions of the elements assuming the
ideal stoichiometry of the compounds and negligible solubility of boron in the Fe-based matrix.
The comparison is shown in Table 3.14.

Table 3.14  Mole fractions and compositions of the phases in equilibrium at 1000°C of the alloy
Fe_{70}Cr_{18}Mo_{2}B_{10}. (The calculated results in bold; experimental results from [89Kim].)

<table>
<thead>
<tr>
<th>Phase</th>
<th>Mole %</th>
<th>Fe</th>
<th>Cr</th>
<th>Mo</th>
<th>B</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>fcc</td>
<td>71.5</td>
<td>90.0</td>
<td>9.8</td>
<td>.07</td>
<td>.006</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>87.0</td>
<td>12.0</td>
<td>1.0</td>
<td>.000</td>
<td></td>
<td>[89Kim]</td>
</tr>
<tr>
<td>M_{2}B_{orth}</td>
<td>21.2</td>
<td>20.3</td>
<td>44.8</td>
<td>1.54</td>
<td>33.3</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>31.0</td>
<td>34.7</td>
<td>1.0</td>
<td>33.3</td>
<td></td>
<td>[89Kim]</td>
</tr>
<tr>
<td>M_{3}B_{2}</td>
<td>7.3</td>
<td>18.4</td>
<td>19.4</td>
<td>22.2</td>
<td>40.0</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>16.8</td>
<td>19.2</td>
<td>24.0</td>
<td>40.0</td>
<td></td>
<td>[89Kim]</td>
</tr>
</tbody>
</table>

As the temperature during extrusion rises from 950°C to somewhat above 1000°C, calculations
were made for equilibrium at 1000°C. The calculated results (Table 3.14) show that three phases
in equilibrium, the gamma (Fe, Cr) solid solution, the M_{2}B_{orth} phase, and the M_{3}B_{2} phase are
in good agreement with Kim et al [89Kim], which confirms that the originally unknown
tetragonal phase is M_{3}B_{2}. A comparison with the chemical compositions is very good for the
gamma solid solution and the M_{3}B_{2} phase, but gives somewhat higher Cr concentrations for the
M_{2}B_{orth} phase. Of importance is the formation of the gamma phase at 1000°C, as it is the
transformation of gamma to alpha on subsequent cooling which gives rise to the lath martensite
A phase mole fraction versus temperature plot for the same alloy composition has also been made as shown in Figure 3.36, where solidus and liquidus temperature are shown as 1127°C and 1274°C respectively. The transformation between δ (bcc) solid solution phase and γ (fcc) solid solution phase occurs at 1111°C and between γ (fcc) and α (bcc) solid solution phase at 857°C.

Figure 3.36  Calculated phase mole fraction versus temperature for the alloy Fe70Cr18Mo2B10. On the figure, 1 liquid; 2 solid solution phase, bcc; 3 M3B2 boride; 4 M₂B_orth boride; 5 solid solution phase, fcc.
3.5.2 The Fe-Cr-Ni-B System

**Literature Review and the Calculation**

Since no experimental data was uncovered by the present author, the calculation of this quaternary system was based purely on its component sub-systems. The ternary compounds include the $\text{M}_3\text{B}$ based in the Fe-Ni-B system and the $\text{M}_3\text{B}_2$ based in the Cr-Ni-B system.

3.6 Summary

Phase diagrams of boron-containing binary (Fe-B, Cr-B, Mo-B, and Ni-B), ternary (Fe-Cr-B, Fe-Mo-B, Cr-Mo-B, Fe-Ni-B, and Cr-Ni-B) systems in the Fe-Cr, Mo, Ni-B system have been thermodynamically characterised. A literature review has been made on experimental phase diagram and thermodynamic data of the relevant systems. Previous assessments on some of the alloy systems have been considered and part of the results were taken into account in the present work. The calculated phase diagrams have been presented and compared with the available experimental results where good agreements were found. A thermodynamic database has been established as a result of phase diagram assessments. The database is necessary in providing useful information, such as phase compositions of an alloy at extrusion temperature. Prediction of phase formation in high pressure gas atomised powders, utilising the available database, will be performed in the following chapter, and the prediction results will help explain phase evolution during rapid solidification so as to ensure that the desired microstructure is obtained in the consolidated alloys. The phase equilibrium information also makes it possible to define the compositions of test alloys specified by the alloy selection criteria, which take into account a series of variables, to study the effect of these variables in a systematic manner. Test alloy design based on the characterised phase diagrams of alloy systems of interest will be presented in Chapter VI.
4.1 Introduction

High pressure gas atomisation (HPGA) was chosen as an alternative processing route to chill block melt spinning (CBMS), the technique used in the initial study of the Fe-Cr-Mo-B alloys, in order to achieve bulk production. The purpose of employing rapid solidification in processing alloys is to suppress the formation of primary compounds, in favour of an amorphous structure or supersaturated solid solution, so that fine borides will precipitate in the solid solution matrix during subsequent consolidation and heat treatment. Amorphous ribbons were successfully produced in the initial investigation of the Fe$_{70}$Cr$_{18}$Mo$_2$B$_{10}$ using CBMS technique. The possible structure in an alloy of a particular composition after gas atomisation, however, can be either amorphous or supersaturated fcc/bcc solid solutions, when the powder sizes are small, or mixtures of intermetallic phases with solid solutions, when the powder sizes are fairly large. It is, therefore, necessary to understand how phase formation is related with parameters such as powder size and alloy composition in order to obtain alloys with the preferred phases and microstructure.

Since there is no experimental data available for the iron based alloys via this process, this chapter will attempt to predict the phase formation in the high pressure gas atomised powders using a combined thermodynamic and kinetic approach. Computer programming and software development for the calculations will be discussed, and the modelling techniques will be explained. The input data for the solidification calculations will also be presented.
4.2 Application of the Combined Thermodynamic and Kinetic Approach

It has been previously considered that the controlling factor in an undercooled alloy system is the growth rate of the competing structures [86Boe]. However this assumption presupposes that the nucleation of all the different phases is kinetically feasible and that nucleation rates are comparable. Such an assumption may not necessarily be true and justification has to be made to validate the model treatment.

By assuming that phase formation during rapid solidification is controlled by a nucleation step, Saunders and Miodownik [88Sau2] used a combined thermodynamic and kinetic approach (Section 2.4.6) originally for the evaluation of glass forming range in binary and ternary metallic alloy systems. The results of their work proved the model to be very satisfactory. Further development of this approach [88Sau1] and its extension by the present author et al [89Pan] in modelling the phase formation in gas atomised liquid aluminium alloys also achieved realistic results.

The quantitative success of this approach in predicting phase formation suggests that the metastable structures which are observed in rapidly quenched alloys may often be predominantly controlled by nucleation rather than by growth rate effects. This is strongly supported by the detailed experimental study of icosahedral phase formation in Al-Mn alloys by Bendersky and Ridder [86Ben], which again indicated the validity of the approach.

The computation procedure discussed in Chapter II (Section 2.4.6) was applied in the prediction of phase formation in the high pressure gas atomised powders. Calculations were carried out for the alloy compositions of interest for all the phases which are likely to form in atomised powders of specified powder size. The powder diameter range considered was between 1-100 μm, the commonly observed powder sizes in the atomisation process. The critical nucleation temperature at which the phase reached the necessary number of nuclei for its formation was determined as a function of powder size, and the critical undercooling obtained as the difference between the melting temperature of the phase and the critical nucleation temperature. The phase which is most likely to form is by definition the one with the highest critical nucleation temperature. The hierarchy for the competing phases is then given by the order of the critical nucleation temperature.
Phase formation in rapidly solidified powders can also be defined in terms of cooling rate which can be calculated as a function of powder size. The computation procedure, therefore, can be applied to other rapid solidification processes, for instance chill block melt spinning. It also means that the phase formation results predicted for gas atomised powders can be verified by experimental data available from CBMS when the cooling rate of the process is known.

4.3 Computer Programming for Solidification Studies: 
Software Development Based on MTDATA

Prediction of nucleation for solidification studies of multicomponent systems was carried out by incorporating MTDATA software, designed at National Physical Laboratory, U.K., to enable phase equilibria to be calculated for higher order systems. The algorithm of the computation is expressed in a flowchart (Chart 4.1). An application module was created in connection with MTDATA, which calls a number of subroutines in the 'TRANSITION MODULE' and each of which can perform a sequence of thermodynamic calculations. A macro file 'APP.101' (Appendix II) was used to run the application programme and to make the initial setting of the calculation.

On entry of the application subroutine 'ITR101' (Appendix III) the powder diameter is entered and thereafter the critical number of nuclei is defined. The composition of the alloy is then input via the 'TRANSITION MODULE'. The calculation starts with calling the 'TRANSITION MODULE' to find the equilibrium between the liquid and one of the solid phases. The liquidus temperature of the solid solution or compound phases is defined as the temperature at which the mass of the liquid has been depleted by a small percentage (10^{-2}%). The composition of the solid solution phase is defined at the same time as the liquidus temperature is defined, and this composition is taken as the composition of the nuclei solidified from the liquid throughout the nucleation process, assuming that diffusion is prohibited in the undercooled powders during the nucleation process. Upon finding the liquidus temperature of the phase, the nucleation calculation will be carried through until the critical nucleation temperature is found. Phases can be included in or excluded from the calculation by classifying their status as either 'normal' or 'absent' through a setting procedure in the 'TRANSITION MODULE'.

The thermodynamic quantities needed at various stages of the nucleation calculation are obtained by calling the 'MULTIPHASE' subroutine in the MTDATA main software. Such data include the
Chart 4.1  Flowchart of the nucleation programme for solidification studies.

START: MTDATA

APPLICATION MODULE?

CALL APP.101

MACRO FILE

A

SUBROUTINE ITR101

SET PARAMETERS

GET VARIABLE VALUES FROM MACRO INPUT

COMPUTE CRITICAL NUMBER OF NUCLEI Ncrit,d

DEFINE TEMP STEP SIZE

DO LOOP FOR SOLID PHASES IN TURN

CALL SUBROUTINE TRANSN

PHASE EQUILIBRIUM CALC:
DEFINE MELTING TEMP Tm;
COMPOSITION OF SOLUTION AT Tm

DO LOOP FOR SOLID SOLUTIONS

START WITH Tm

B

C

D

109
Chart 4.1  Flowchart of the nucleation programme for solidification studies (continued).

1. Define temp step size
2. Call subroutine multiphase
3. Compute diffusion coefficient
4. Calculate nucleation rate
5. Calculate number of nuclei
6. Summation of number of nuclei
7. Total number of nuclei > Ncrit,d?
   - No: D
   - Yes: B
   - B: Print Tcrit,d and undercooling (Tm - Tcrit,d)
     - Back to transition module
     - Return to MTDATA
   - D: Continue with thermodynamic calculation: Gibbs energy of solid phase; partial free energy of liquid
integral Gibbs free energy of the solid solution and compound phases at their respective compositions, partial free energy of the liquid phase at its given composition (see Figure 2.3). The driving force of the solidification, from which the heat of fusion $\Delta H_m^f$ is derived, is calculated from the value of the integral energy of the solid phase and the partial free energy of the liquid at the alloy composition. The heat of fusion $\Delta H_m^f$ is determined from the relation $H = G + TS$ whereby the entropy of the driving force is first derived from the driving force difference at very small temperatures intervals (in this work 0.1 K) as $S = -\frac{dG}{dT}$. 
Predicting Phase Formation

The initial procedure is to calculate the stable or metastable liquidus points from which the nucleation integration of the relevant solution and compound phases starts. The number of nuclei formed during each step is summed to give the total nucleant population formed within the time taken from $T_M$, the liquidus temperature, to the current value of temperature, $T$. The critical nucleation temperature will be given when the accumulated nucleant population reaches the critical number of nuclei defined in the beginning of the calculation. Three time steps were implemented in the stepping sequence depending on the summated nucleant population, the step size being larger when the nucleant population is very small and decreasing as the critical nucleant population is approached. This procedure was adopted to save computer time during the calculation. The likely error incurred by adopting different step sizes in the calculation was checked, through a comparison with the calculated answers using a very small step size throughout the temperature range, and found to be less than 0.5°C in $T_{\text{crit},d}$.

The nucleation calculation is conducted for each of the solid phases in turn and the critical nucleation temperatures are obtained at the end of the calculation. The phase with the highest critical temperature is the one which forms first in the specified rapid solidification condition defined by the powder size therefore the cooling rate. When the formation of all the crystalline phases is suppressed, the alloy with this particular composition will form a glass under the defined solidification condition. The glass forming range of an alloy can therefore be predicted by the same computation.

The programming language used for the application module (and MTDATA) is FORTRAN 77.

4.4 Thermodynamic and Thermophysical Data Used in Solidification Calculations

4.4.1 Thermodynamic Database

The thermodynamic data required in the solidification study were taken from the phase diagram characterisation results (Chapter III) for the relevant systems, starting with the liquidus temperature of each solid phase. Therefore, the solidification study can be treated as an application of thermodynamics and phase diagrams, and the nucleation calculation can be combined with phase diagram calculations. The calculation results on the alloy system of particular interest in this work will be discussed in Chapter VIII.
An MTDATA database was created and the thermodynamic data for the relevant systems were loaded into the database, after being converted into MTDATA loading file format from its original THERMO-CALC format with the help of a conversion programme created by Dinsdale [90Din].

4.4.2 Thermophysical Data

The thermophysical data of the gases (helium, argon, and nitrogen are the commonly employed in the HPGA process) required in the solidification calculations are listed in Table 4.1.

Table 4.1 Thermophysical properties of gases used in the atomisation. Data for an estimated effective temperature of 400 to 500 K are taken from Handbook of Chemistry and Physics [82Crc].

<table>
<thead>
<tr>
<th>Property</th>
<th>Symbol</th>
<th>Unit</th>
<th>Gas</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Conductivity</td>
<td>K</td>
<td>W m⁻¹ K⁻¹</td>
<td>0.20</td>
<td>0.02</td>
<td>0.038</td>
<td></td>
</tr>
<tr>
<td>Specific Heat</td>
<td>c</td>
<td>J m⁻³ K⁻¹</td>
<td>950</td>
<td>950</td>
<td>950</td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>ρ</td>
<td>kg m⁻³</td>
<td>0.18</td>
<td>1.8</td>
<td>1.28</td>
<td></td>
</tr>
<tr>
<td>Viscosity</td>
<td>μ</td>
<td>Pa s</td>
<td>2.5x10⁻⁵</td>
<td>3x10⁻⁵</td>
<td>2.3x10⁻⁵</td>
<td></td>
</tr>
</tbody>
</table>

Another important parameter is the diffusion coefficient of transition metals in liquid Fe, which can be derived based on the glass forming temperature T_g, as explained in detail in Section 2.4.6. An experimentally determined glass forming temperature of ~720K was used in the solidification calculations of the present investigation.
5.1 Introduction

The Eshelby method provided a rigorous theoretical basis for modelling elastic properties of alloys in terms of their microstructural features. Information on phase formations during rapid solidification and microstructure evolution during subsequent processing, complemented with an understanding of elastic properties in relation to the microstructure parameters, will make it possible to design alloys with the optimum phase compositions and structure morphology which provide the best performance.

This chapter will tackle the problem of modelling the elastic properties of alloys with particulate composite structures using Eshelby's equivalent inclusion method. A computation algorithm and programming procedures for the modelling calculations will be presented. Data input will be discussed. Young's modulus of the various phases will be derived based on the model calculations and experimental data available from the literature. The prediction of Young's moduli for the designed test alloys will be explained.

5.2 Calculation Procedures of Eshelby Method

5.2.1 Input of Elastic Stiffness Tensor

Young's modulus of a composite, according to the procedures outlined in Section 2.5.4, can be calculated based on the elastic constants of the matrix ($C_M$) and the inclusion ($C_i$). Below is a
brief account for how the two tensors are derived from the common technical moduli (Young's modulus of matrix \(E_M\) and the inclusion phase boride \(E_I\)), and the value of Poisson's ratio of the matrix.

The elastic stiffness tensor \(C_{ijkl}\) is in general a fourth rank tensor, which relates two second rank tensors: the stress \(\sigma_{ij}\) and the strain \(\varepsilon_{kl}\). The same is true for the compliance tensor \(C^{-1}_{ijkl}\), which in theory can be determined by matrix inversion of the stiffness tensor. The generalised form of Hooke's Law may therefore be written as:

\[
\sigma_{ij} = C_{ijkl} \varepsilon_{kl} \quad \text{or} \quad \varepsilon_{ij} = C^{-1}_{ijkl} \sigma_{kl}
\]  

\(...(5.2.1)\)
\(...(5.2.2)\)

The usual convention for designating components of elastic stiffness and elastic compliance uses only two subscripts instead of four. The subscripts in the contracted notation simply denote the row and column in the matrix of components in which they fall:

\[
\sigma_{11} = C_{11} \varepsilon_{11} + C_{12} \varepsilon_{12} + C_{13} \varepsilon_{13} + C_{14} \gamma_{23} + C_{15} \gamma_{13} + C_{16} \gamma_{12}
\]
\[
\sigma_{23} = C_{41} \varepsilon_{11} + C_{42} \varepsilon_{12} + C_{43} \varepsilon_{13} + C_{44} \gamma_{23} + C_{45} \gamma_{13} + C_{46} \gamma_{12}
\]

where \(\gamma_{ij}\) denotes shear strain. The presence of symmetry in the crystal further reduces the number of independent component constants with many of these elastic constants becoming either equal or zero. There are only three independent components in the case of cubic crystals and they observe the following relationship:

\[
C_{11} = C_{22} = C_{33}
\]
\[
C_{12} = C_{21} = C_{13} = C_{31} = C_{23} = C_{32}
\]
\[
C_{44} = C_{55} = C_{66}
\]  

\(...(5.2.4)\)
and all others are zero. The stiffness tensor for a cubic crystal can thus be simplified as:

\[
\begin{pmatrix}
C_{33} & C_{12} & C_{12} & 0 & 0 & 0 \\
C_{12} & C_{33} & C_{12} & 0 & 0 & 0 \\
C_{12} & C_{12} & C_{33} & 0 & 0 & 0 \\
0 & 0 & 0 & C_{44} & 0 & 0 \\
0 & 0 & 0 & 0 & C_{44} & 0 \\
0 & 0 & 0 & 0 & 0 & C_{44}
\end{pmatrix}
\]

The modelling of elastic properties in this study is based on the assumption that the designed test alloys are effectively elastically isotropic. This assumption is reasonable because the individual anisotropies of the grains in the polycrystalline alloys average out in the bulk.

The coefficient \( C_{ij} \) for isotropic crystals can be obtained through the other various elastic constants including the Young’s modulus \( E \), the shear or rigidity modulus \( G \), the bulk modulus \( K \), and the Poisson’s ratio \( v \) (the ratio of lateral contraction to longitudinal extension in uniaxial tension). These constants and the \( C_{ij} \) are interrelated for isotropic crystals according to following formulae [75Cot]:

\[
K = \frac{E}{3(1 - 2v)}, \quad \ldots \text{(5.2.5)}
\]

\[
G = \frac{E}{2(1 + v)}, \quad \ldots \text{(5.2.6)}
\]

\[
C_{11} = K + \frac{4}{3} G, \quad C_{12} = K - \frac{2}{3} G, \quad C_{44} = G \quad \ldots \text{(5.2.7)}
\]

The number of independent components is reduced to two as a result of the symmetry conditions. The input data in the Eshelby calculation include the modulus of the matrix \( (E_M) \), the modulus of the inclusion \( (E_I) \), and the Poisson’s ratio of the matrix \( (v) \). The stiffness tensor for the matrix \( (C_M) \) as well as for the inclusion phase \( (C_I) \) can then be calculated using the relations listed above. In this work a Poisson’s ratio value of 0.3 was taken from Metals Handbook [78ASM] for the Fe-based solid solution matrix and 0.24 recommended by [91Mio] for the borides.

The concepts of stiffness and compliance tensors follow the standard textbook approach [57Nye,
MATHEMATICAL MODELLING OF ELASTIC MODULI

Alternatively the stiffness constants can be derived through the Lame's constant $\lambda$. The constant $C_{ij}$ is in this case given in a briefer format:

\[
\begin{align*}
    C_{12} &= \lambda \\
    C_{11} &= 2G + \lambda \\
    C_{44} &= (C_{11} - C_{12})/2
\end{align*}
\]

where

\[
\lambda = \frac{vE}{(1+v)(1-2v)}
\]

5.2.2 Calculation of Eshelby's Tensor

The Eshelby's tensor is calculated in the beginning of the programme, after input of the matrix Poisson's ratio and the aspect ratio of the inclusion, using the formula given in Table 2.1.

5.2.3 Calculation of Composite Compliance Tensor

The matrix $B$ has to be first calculated via Equation (2.5.13), where a series of matrix calculations including inversion of matrices are performed. The compliance tensor of the composite is then calculated using Equation (2.5.16). The Young's modulus of the composite is obtained through Equation (2.5.17).

The matrix algebra in this calculation, for instance the multiplication and inversion of $6 \times 6$ matrices, is conveniently simplified via an application of FORTRAN loops in the programme, in addition to the simplifications due to the symmetry of the matrices.

5.3 Computer Programming for the Modulus Prediction

A computer programme has been written to perform the calculations of Young's modulus via the Eshelby approach by translating the computation procedure into FORTRAN language (Appendix IV). The algorithm is outlined in a flowchart (Chart 5.1). This programme can predict Young's modulus of a composite at any volume fraction and specific aspect ratio of the inclusion for given elastic constants of both the matrix and the inclusion.
MATHEMATICAL MODELLING OF ELASTIC MODULI

Chart 5.1  Flowchart of the programme for the effective modulus of composites.

START

INPUT MODULUS DATA OF MATRIX'S AND INCLUSION'S

INPUT VOLUME FRACTION OF INCLUSION

INPUT: POISSON'S RATIO OF MATRIX INCLUSION'S ASPECT RATIO

ASPECT RATIO > 1000

COMPUTE ESHELBY'S TENSOR FOR A PARTICULATE COMPOSITE

COMPUTE ESHELBY'S TENSOR FOR A FIBRE COMPOSITE

COMPUTE MATRIX B

B = FUNC ( S, C, C, t )

COMPUTE MATRIX C

C⁻¹ = FUNC ( S, C, M, C, B )

COMPUTE MATRIX C

C = C⁻¹

WRITE MATRIX C

STOP

\[ E_{\text{COMP}} = \frac{1}{c_{3}^{-1}} \]
5.4 Modelling of Elastic Properties Using Eshelby Method

5.4.1 Estimation of Young’s Modulus of Boride

There is scarcely any reported data on the elasticity of borides (either M$_2$B$_{orth}$ Cr-rich boride or M$_3$B$_2$ Mo-rich boride). The elastic modulus value of the boride inclusions present in the initial test alloy (RR) was therefore estimated using the following method.

A Young’s modulus value for an Fe+ ~10 at%Cr alloy of ~213 GPa [72Les] was used to approximate the Young’s modulus value of the matrix for the purpose of a preliminary calculation. The composition of the matrix in the first test alloy can be found in Table 3.14. The

![PROPERTY COMPARISON/Young's Modulus](image)

**Figure 5.1** Comparison of the estimated Young’s modulus of boride with the literature [66Ame].

119
effect of 0.07 at%Mo in the matrix was taken to be negligible. A volume fraction of 30% for the borides (measured value using Quantimet analysis in the initial investigation [91Sma]) was input and a random orientation with boride aspect ratio close to 1 was assumed.

According to Eshelby's model, to give a Young's modulus of the composite material around 255-270 GPa (as obtained from mechanical testing in the initial investigation on the Fe$_{70}$Cr$_{18}$Mo$_2$B$_{10}$ alloy [91Sma]), a value of around 420 GPa has to be assumed for the mean value of Young's modulus of the boride inclusion.

Such a value compares quite well (Figure 5.1) with the general band for boride and carbide from literature [66Ame]. However, better data for the modulus of matrix is clearly necessary in order to achieve more confidence in the modulus prediction.

5.4.2 Determination of Young’s Modulus of Fe-based Matrix

Eshelby's approach was used to analyse the elastic moduli of some thirty Cr carbon steels from the literature listed in Table 1.1. The moduli as measured were plotted against volume percentage of carbide in Figure 5.2a, b (a, full scale; b, expanded scale for 0→25 vol% of carbide). Eshelby curves were plotted on the same figure with two levels of modulus value estimated for the Cr matrix (200→210 GPa) and for the carbide (250→430 GPa). The modified moduli of these steels, as listed in Table 1.1, by taking away the effect of Cr from the measured moduli by a factor of 0.5 for 1 wt% Cr (a value according to experiment [72Les]), were plotted in Figure 5.3a, b together with the same Eshelby curves as in Figure 5.2. The scales in Figure 5.3a, b follow those in Figure 5.2a, b respectively for the benefit of presentation.

A comparison between the Figure 5.2 and Figure 5.3 shows that the modified moduli fall more readily into the range defined by the two Eshelby curves than the moduli as measured. Several conclusions can be drawn from this comparison:

(i) Eshelby's approach describes the effect of carbides on the moduli of the steels fairly accurately;
(ii) The effect of Cr content on the moduli of steels can be approximated by a factor of 0.5 for the percentage of Cr in the alloy;
(iii) The estimated values of the moduli of the matrix and the carbides are both at an
Figure 5.2  Young's moduli of Cr carbon steels vs. volume percentage of carbide, compared with Eshelby curves. a) full scale; b) expanded scale for 0→25 vol% of carbide.
MATHEMATICAL MODELLING OF ELASTIC MODULI

Figure 5.3  Modified Young's moduli of Cr carbon steels by deducting the effect of Cr, vs. volume percentage of carbide, compared with Eshelby curves. a) full scale; b) expanded scale for 0→25 vol% of carbide.
acceptable level;

(iv) The modulus of the pure Fe with no Cr can be extrapolated as 200 to 210 GPa.

The conclusion (ii) is particularly useful in that the Young's modulus for the matrix of the designed test alloys can be estimated based on the Cr content in the matrix available from the phase diagram calculations. The success in modelling the moduli of Cr steels with carbides via Eshelby's approach encourages the application of the model in the present work.

5.5 Prediction of Young's Moduli of Designed Test Alloys

Young's moduli of the designed test alloys can be calculated using Eshelby method, based on the estimated values for the Young's modulus of the boride and matrix, together with the measured volume fractions of the boride. The predicted moduli will be presented in Chapter VIII, following the tensile test results of the model alloys, with discussion of these results presented afterwards.
6.1 Introduction

The initial investigation conducted on the base alloy Fe_{70}Cr_{18}Mo_{2}B_{10} (RR) indicated that the alloy contains a distribution of two types of borides (M_{2}B_{orth} Cr-rich and M_{3}B_{2} Mo-rich) in a martensitic matrix. In order to study the roles played by the various microstructural features present in the alloy, so as to understand how the properties can be improved, it is necessary to prepare model alloys which contain well-defined proportions of specific combinations of phases with specified compositions. For example, the function of each individual boride can be understood only when the two types of borides are separated. The effect of amount of boride present in the alloys, on the other hand, can be monitored by designing a series of test alloys with selected levels of borides. This will allow the analyses of the mechanical testing results in terms of the microstructure variables and subsequent selections of alloys with the optimum properties.

Model alloy compositions can be selected only if the phase equilibria are clearly defined. The thermodynamic phase diagram calculations discussed in the Chapter III serve this purpose well by providing accurate information on the proportion and chemistry of relevant phases particularly for the area where there is a lack of experimental data.

6.2 General Selection Criteria for Test Alloys

The model alloy selection was based on the phase equilibrium information at the consolidation temperature (950–1000°C), which ultimately determines the phase and structure in the as
consolidated alloys (assuming a knowledge of the cooling rate following consolidation).

The microstructure variables which are likely to affect the properties of the rapidly solidified Fe-TM-B alloys include:

(i) composition and type of matrix, which can be:
   a) martensitic,
   b) austenitic, or
   c) ferritic;

(ii) amount and type of boride, which can be:
   a) an M₂B₉ orthorhombic Cr-rich ternary boride or
   b) an M₃B₂ Mo-rich quaternary boride.

Nonequilibrium phases, which may have formed during rapid solidification, appear to be removed by the consolidation treatment and associated annealing.

The effect of matrix structure on the properties of the rapidly solidified alloys can be studied by designing test alloys with the respective matrix of interest. Martensite was formed after extrusion in the base alloy because the equilibrium matrix phase at the extrusion temperature is an austenite, which transforms on cooling. However alternative matrices can be considered in order to ensure optimum properties. If alloy compositions are chosen to be in the phase region where bcc and M₂B₉ orth phases are in equilibrium at the extrusion temperature, the matrix in alloys upon consolidation will be ferritic. A stable austenite is another possible matrix with the aim of achieving corrosion resistant alloys.

The matrix compositions in some of the designed model alloys were chosen to be the same as that in the base alloy Fe₇₀Cr₁₈Mo₂B₁₀ (RR) so that a fair comparison can be made of the effect of different borides without bringing in an additional matrix composition variable.

For a given matrix, model alloy compositions were calculated to yield two different levels of boride: 30 mol%, same as in the base alloy; and 15 mol%, to look at the effect of halving the amount of the boride. The effects of the two borides, M₂B₉ orth and M₃B₂, present in the base alloy (RR) can be separated by choosing specific alloy systems. The criteria for test alloy compositions in each chosen system will be presented in the following sections.
A number of other factors, in addition to the structure variables discussed above, were also taken into account in order not to introduce any possible complications. The sigma phase is prone to form in the Fe-TM-B systems, and this tends to embrittle the alloys. The test alloy compositions were therefore selected to avoid its formation at lower temperatures. In addition, the selection of model alloy compositions included consideration of the processing conditions to avoid technical difficulties. For example, the liquidus temperatures in alloys containing $M_3B_2$ phase tends to be very high because of the high melting point of the Mo-rich boride and this raises the temperature required to generate a suitable superheat during atomisation as well as increases the tendency to contamination. Therefore liquidus temperature of all the processed alloys were checked and constrained to lie at reasonable values.

6.3 Selection Criteria for Test Alloy Compositions in Specific Systems

6.3.1 Test Alloys in the Fe-Cr-B System

Test alloys in the Fe-Cr-B ternary system were chosen so that the $M_3B_2$ Mo-rich boride was excluded and the effect of the $M_2B_{\text{orth}}$ Cr-rich boride on the elastic properties could be studied. It is possible to separate the two borides $M_2B_{\text{orth}}$ Cr-rich and $M_3B_2$ Mo-rich, which both existed in the original Fe$_{70}$Cr$_{18}$Mo$_2$B$_{10}$ alloy, because the latter is a ternary compound which only exists in Mo-containing systems.

Different levels of boride content were designed to study the effect of amount of boride on the properties of the alloys with a particular type of matrix, which could be either martensite or ferrite. The effect of each matrix can be studied by selecting test alloys of the matrix with the same level of borides. In addition, the martensite matrix in the model alloys can be designed the same as that in the base alloy so that pair comparison can be made between properties of alloys with different borides on a matrix of the same composition.

6.3.2 Test Alloys in the Fe-Cr-Ni-B System

Ni-containing systems were considered in order to achieve corrosion resistant alloys with austenitic matrix after consolidation. A wide range of alloys in the quaternary Fe-Cr-Ni-B system present ausenitic matrix at the extrusion temperature of 950–1000°C. However, the selection of
the compositions of the model alloys, and the matrix composition in particular, was restricted by the following criteria:

(i) sufficiently low martensite transformation temperature;
(ii) good corrosion resistance;
(iii) high matrix modulus with combinations of Ni and Cr content;
(iv) avoidance of the likely formation of sigma phase.

The primary criterion is that the austenite does not transform into martensite on cooling from the extrusion temperature, and that the matrix structure is maintained to room temperature. The trend of martensite transformation temperature in this system was examined [91Mio] via the $T_0$ (gamma→alpha) temperature to ensure the selected model alloys have a sufficiently low martensitic transformation temperature $M_s$. On the other hand, a stable austenite containing at least 12 at%Cr is necessary in order to achieve corrosion resistant alloys. However while corrosion resistance is improved with an increase in Cr content, the martensite transformation temperature is raised. These two criteria, therefore, are not easy to satisfy simultaneously.

The selection of the matrix composition was also affected by the variation of modulus with the combination of Cr and Ni content. Experimental values for the modulus of steels [47Rob] to discover the effect of Ni and Cr combinations is bedeviled by the simultaneous presence of other element, but examination of the trend indicate that combination of 14Cr 18Ni (in atomic, plus carbides) give useful values [91Mio].

The tendency for the formation of the brittle sigma phase in this alloy system has been avoided to noting the position of the (gamma + alpha + sigma) field. This has also been checked using the phase diagram calculation method and the temperature at which sigma phase becomes one of the equilibrium phases is approximately lower than 300°C. The phase, therefore, will be kinetically unlikely to precipitate during cooling after consolidation.

A target matrix composition was, therefore, eventually settled at 12 at%Cr and 16 at%Ni (close to the stainless steel) at the extrusion temperature (950~1000°C). The amount of M$_2$B$_{\text{orth}}$ borides were chosen to be 15 and 30 mol%.
6.3.3 Test Alloys in the Fe-Cr-Mo-B System

Alloys with compositions in the two phase region (matrix fcc plus M\textsubscript{3}B\textsubscript{2}) of the Fe-Cr-Mo-B system were selected to exclude the M\textsubscript{2}B boride in order to study how the M\textsubscript{3}B\textsubscript{2} phase affects the elastic properties by comparison with the results from the original Fe\textsubscript{70}Cr\textsubscript{18}Mo\textsubscript{2}B\textsubscript{10} alloy.

The liquidus temperatures of the alloys in the Fe-Cr-Mo-B system are considerably higher than those in the Fe-Cr-B because of the high melting element Mo. The two levels of boride content were therefore set at 15 and 25 mol% (instead of 15 and 30 mol% for other test alloys) having taken their liquidus factors into account. The matrix phase at the extrusion temperature is austenitic but is expected to transform into martensite during cooling after the extrusion.

6.4 The Calculation Procedures

The characterised phase diagrams of the Fe-Cr-B, Fe-Cr-Mo-B, and Fe-Cr-Ni-B systems and the established thermodynamic database provided the information necessary to calculate the tie lines of phase equilibria in the selection of test alloy compositions. The calculation procedures for each of the alloy systems are presented below. The designed alloy compositions, in both weight and atomic percentages, are listed in Table 6.1 together with the structure of the matrix, type and amount of the boride in the alloys.
### Table 6.1 Designed alloy compositions with the matrix structure at room temperature, boride type and amounts. Alloy compositions are given in both atomic and weight percentages.

<table>
<thead>
<tr>
<th>Alloy Code</th>
<th>Alloy System</th>
<th>Composition (at% (wt% in brackets))</th>
<th>Matrix Structure (at RT)</th>
<th>Borides +Mole%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SU1</td>
<td>Fe-Cr-B</td>
<td>Fe$<em>{70}$Cr$</em>{20}$B$<em>{10}$ (Fe$</em>{77.3}$Cr$<em>{20.6}$B$</em>{2.14}$)</td>
<td>Martensite</td>
<td>M$_2$B, 30</td>
</tr>
<tr>
<td>SU2</td>
<td></td>
<td>Fe$<em>{65}$Cr$</em>{25}$B$<em>{10}$ (Fe$</em>{72.1}$Cr$<em>{25.8}$B$</em>{2.15}$)</td>
<td>Ferrite</td>
<td>M$_2$B, 30</td>
</tr>
<tr>
<td>SU3</td>
<td></td>
<td>Fe$<em>{80}$Cr$</em>{15}$B$<em>{5}$ (Fe$</em>{84.3}$Cr$<em>{14.7}$B$</em>{1.02}$)</td>
<td>Martensite</td>
<td>M$_2$B, 15</td>
</tr>
<tr>
<td>SU4</td>
<td></td>
<td>Fe$<em>{75}$Cr$</em>{20}$B$<em>{5}$ (Fe$</em>{79.3}$Cr$<em>{19.7}$B$</em>{1.02}$)</td>
<td>Ferrite</td>
<td>M$_2$B, 15</td>
</tr>
<tr>
<td>SU5</td>
<td>Fe-Cr-Ni-B</td>
<td>Fe$<em>{55}$Cr$</em>{24}$Ni$<em>{11}$B$</em>{10}$ (Fe$<em>{60}$Cr$</em>{24.6}$Ni$<em>{12.7}$B$</em>{2}$)</td>
<td>Austenite</td>
<td>M$_2$B, 30</td>
</tr>
<tr>
<td>SU6</td>
<td></td>
<td>Fe$<em>{63}$Cr$</em>{18}$Ni$<em>{14}$B$</em>{5}$ (Fe$<em>{66}$Cr$</em>{17.6}$Ni$<em>{15.4}$B$</em>{1}$)</td>
<td>Austenite</td>
<td>M$_2$B, 15</td>
</tr>
<tr>
<td>SU7</td>
<td>Fe-Cr-Mo-B</td>
<td>Fe$<em>{72}$Cr$</em>{12}$Mo$<em>{6}$B$</em>{10}$ (Fe$<em>{75.5}$Cr$</em>{11.7}$Mo$<em>{10.6}$B$</em>{2.03}$)</td>
<td>Martensite</td>
<td>M$_3$B$_2$, 25</td>
</tr>
<tr>
<td>SU8</td>
<td></td>
<td>Fe$<em>{81}$Cr$</em>{9}$Mo$<em>{4}$B$</em>{6}$ (Fe$<em>{83.2}$Cr$</em>{8.6}$Mo$<em>{7.08}$B$</em>{1.19}$)</td>
<td>Martensite</td>
<td>M$_3$B$_2$, 15</td>
</tr>
<tr>
<td>RR</td>
<td>Fe-Cr-Mo-B</td>
<td>Fe$<em>{70}$Cr$</em>{18}$Mo$<em>{2}$B$</em>{10}$ (Fe$<em>{76}$Cr$</em>{18.2}$Mo$<em>{3.73}$B$</em>{2.1}$)</td>
<td>Martensite</td>
<td>M$<em>2$B+$M_3$B$</em>{2.30}$</td>
</tr>
</tbody>
</table>

#### 6.4.1 Calculations for Fe-Cr-B Alloys

The selection of test alloy compositions in the Fe-Cr-B systems was done on the calculated isothermal section of the system at the extrusion temperature, 1000°C (Figure 6.1). Once the tie line of the equilibrium between the boride and the matrix phase is determined, the composition of the alloy for a chosen amount of borides can be calculated using the lever rule.

The tie lines which connect the matrix and borides as defined on the isothermal section of the ternary system were used in the selection of model alloy compositions. By choosing tie lines at different level of Fe:Cr ratio the matrix in the alloy can be either fcc or bcc at the extrusion temperature. While alloys with compositions on a particular tie line have the same matrix, each
Figure 6.1 Calculated isothermal section of the Fe-Cr-B system at 1000°C.

The selected four alloys, nominated as SU1, SU2, SU3 and SU4, in the Fe-Cr-B system form a composition matrix with two levels of borides and two types of matrix. The composition matrix of the above four alloys in relation to the tie lines between the boride and the matrix phase is
shown in Figure 6.2.

Figure 6.2  Composition matrix of the designed alloys (SU1→SU4) in relation to the tie lines of the equilibrium between the boride and the solid solution matrix phase on the isothermal section of the Fe-Cr-B system at 1000°C.

6.4.2 Calculations for Fe-Cr-Ni-B Alloys

Calculations were carried out and the two alloy compositions which provide an austenitic matrix at the extrusion temperature with 12 at%Cr and 16 at%Ni were obtained. Two levels of boron concentration were intended to provide 15 and 30 mol% $M_2B_{\text{orth}}$ borides because the austenitic phase contains a substantially low level of boron in this alloy system.
The mole fractions of the equilibrium phases as a function of temperature for the two proposed compositions have been obtained from thermodynamic calculation and plotted as shown in Figure 6.3 and Figure 6.4. It should be noted that the two phase (fcc + M₂B_orth) are maintained in equilibrium over a fairly wide temperature range around the extrusion temperature, which is an advantage. It can also be noted from these two plots that the sigma phase forming temperature is sufficiently low (~300°C).

Figure 6.3  Mole fraction of equilibrium phases as a function of temperature for the proposed test alloy SU5: Fe_{55}Cr_{24}Ni_{11}B_{10}.
6.4.3 Calculations for Fe-Cr-Mo-B Alloys

The selected test alloys in the Fe-Cr-Mo-B system were chosen to lie in the two-phase region, fcc and $M_3B_2$. The choice of the test alloy compositions was confined by the phase compositions in the initial test alloy $\text{Fe}_{70}\text{Cr}_{18}\text{Mo}_2\text{B}_{10}$. In order to keep the compositions of the matrix and the Mo-rich boride the same as those in the base alloy, test alloys in the Fe-Cr-Mo-B system were chosen to lie on the two phase boundary (fcc and $M_3B_2$) defined by the three phase triangle between the
matrix and the two borides in the base alloy (Figure 6.5). The end compositions of the equilibrium triangle were derived from the calculated results at 1000°C as listed in Table 3.14. The position of the base alloy (RR) in the tie triangle, as shown in Figure 6.5, corresponds to fcc, 71.5; M₂B_orth, 21.2; and M₃B₂, 7.3 mol%. The compositions at which alloys contain certain amount of the M₃B₂ boride were calculated using the lever rule. Two levels of boride content at 15 and 25 mol% (instead of 15 and 30 mol% for the other test alloys) were chosen with alloys at two boron concentration of 6 and 10 at%B to maintain viable liquidus temperatures.

Figure 6.5 Tie triangle of the three phase equilibrium between fcc, M₂B_orth, and M₃B₂ of the original alloy Fe₇₀Cr₁₈Mo₂B₁₀ (RR). The two phase equilibrium between fcc and M₃B₂ is represented as a ruled surface a₁a₂b₁b₂. The designed test alloy SU7 and SU8 correspond to positions where the fcc phase is in equilibrium with 25 and 15 mol% M₃B₂.
The mole fractions of the equilibrium phases at various temperatures have been plotted for the chosen alloy compositions in this system and are shown in Figure 6.6 and Figure 6.7. The two phase region (fcc + M\textsubscript{3}B\textsubscript{2}) exists over a temperature band of 200°C around the extrusion temperature, and the matrix phase is expected to transform into martensite during the subsequent cooling after the extrusion. Low sigma forming temperatures are again obtained in this composition.

Figure 6.6 Mole fraction of equilibrium phases as a function of temperature for the proposed test alloy SU7: Fe\textsubscript{72}Cr\textsubscript{12}Mo\textsubscript{6}B\textsubscript{10}.
Figure 6.7 Mole fraction of equilibrium phases as a function of temperature for the proposed test alloy SU8: Fe$_{81}$Cr$_{9}$Mo$_{4}$B$_{6}$.

6.5 Volume Fraction of Borides in Designed Alloys

The mole fraction of a boride in a test alloy is normally different from its volume fraction due to the difference in density and mean atomic weight between the matrix and boride phase. The difference is often not large, and can be estimated from the lattice parameter data and compositions of the phases. The volume fractions of borides in the test alloys, designed in terms of boride mole fraction, can be calculated based on these data.
6.5.1 Theoretical Density of Matrix and Borides

The theoretical density of the matrix and borides were calculated based on the composition of the phase, crystalline structure and lattice parameter data using the following equation:

\[
\rho = \frac{(\text{Mean atomic weight}) \cdot (\text{Number of atoms per unit cell})}{(\text{Atomic volume}) \cdot (\text{Avogadro constant})} \quad \ldots (6.5.1)
\]

The mean atomic weight can be derived from the composition of the phase and the atomic weight of each component element; the number of atoms per unit cell is defined by the crystalline structure of the phase and the atomic volume can be derived from the lattice parameters of the phase. The density unit from the above equation is g.cm\(^{-3}\). The method is explained by Cullity [78Cu1].

In the base alloy Fe\(_7\)Cr\(_{18}\)Mo\(_2\)B\(_{10}\), for example, the compositions of the M\(_2\)B\(_{\text{orth}}\) phase were obtained from the equilibrium calculation (see Table 3.14) as:

M\(_2\)B\(_{\text{orth}}\): Fe 20.3  Cr 44.8  Mo 1.54  B 33.3 (at%)

The mean atomic weight (M\(_{M2B_{\text{orth}}}\)) of the phase can then be calculated:

M\(_{M2B_{\text{orth}}}\) = \[20.3 \times 55.85 + 44.8 \times 52 + 1.54 \times 95.94 + 33.3 \times 10.81\]/100 = 39.71

The crystalline structure of M\(_2\)B\(_{\text{orth}}\) data, according to X-ray measurement results by Kim [89Kim] are as follows:

M\(_2\)B\(_{\text{orth}}\): orthorhombic; \(a=14.583, b=7.379, c=4.245 \, \text{Å}\)

The number of atoms per unit cell of M\(_2\)B\(_{\text{orth}}\) is 48, a value given in the Pearlson's Handbook of Crystallographic Data for Intermetallic Phases by Villars and Calvert [85Vil]. The density of the boride phase, therefore, is derived as follows:

\[
\rho_{M2B_{\text{orth}}} = \frac{39.71 \times 48}{14.583 \times 7.379 \times 4.245 \times 6.02357 \times 10^{-1}} = 6.928 \, \text{(g.cm}^{-3}\text{)}
\]
The same procedure is followed in the theoretical density calculation for the matrix and other phases concerned in the Fe-TM-B systems. The lattice parameter and the crystalline structure data used were taken from experimental results of Kim [89Kim], Baliga [91Bal], and the Pearson's Handbook of Crystallographic Data for Intermetallic Phases [85Vil].

6.5.2 Calculation of Volume Fraction of Borides

The theoretical density values of the borides and the matrix calculated in the above fashion were used to convert mole fractions of the borides into volume fractions knowing the mean atomic weight of each phase.

If an alloy consists of two phases, fcc as matrix with mole percentage as \((f_{\text{cc}}, \text{mol}%)\) and \(M_2B_{\text{orth}}\) with mole percentage of \((M_2B_{\text{orth}}, \text{mol}%)\), (here of course, \(f_{\text{cc}}, \text{mol}% + M_2B_{\text{orth}}, \text{mol}% = 100\%\)), their theoretical densities being \(\rho_{\text{fcc}}\) and \(\rho_{M_2B_{\text{orth}}}\), the mean atomic weights \(M_{\text{fcc}}\) and \(M_{M_2B_{\text{orth}}}\) the volume fraction of the boride is, therefore,

\[
M_{2B_{\text{orth}},\text{vol}%) = \frac{M_2B_{\text{orth}},\text{mol}% \times M_{M_2B_{\text{orth}}} / \rho_{M_2B_{\text{orth}}}}{(f_{\text{cc}},\text{mol}% \times M_{\text{fcc}} / \rho_{\text{fcc}}) + (M_2B_{\text{orth}},\text{mol}% \times M_{M_2B_{\text{orth}}} / \rho_{M_2B_{\text{orth}}})}
\]

...(6.5.2)

The density of the alloy can also be derived as its atomic weight divided by its atomic volume,

\[
\rho_{\text{alloy}} = \frac{M_{M_2B_{\text{orth}}} + M_{\text{fcc}}}{(f_{\text{cc}},\text{mol}% \times M_{\text{fcc}} / \rho_{\text{fcc}}) + (M_2B_{\text{orth}},\text{mol}% \times M_{M_2B_{\text{orth}}} / \rho_{M_2B_{\text{orth}}})}
\]

...(6.5.3)

It was found through calculations performed via the procedures discussed above that the volume percentage of borides in most of the designed test alloys are approximately 2~3% lower than its mole percentage level. This is very useful in the design of alloy compositions with specific target volume percentages. The mole percentage is normally easy to calculate from the composition of an alloy, on the condition that the stoichiometry of the compound is known, and that the solubility of boron in the (Fe, TM)-based matrix is negligible. The alloy composition can then be simply obtained to achieve the required level of volume amount of borides.
6.6 Summary

Phase equilibrium calculations serve as a convenient tool in locating the compositions specified by the alloy selection criteria, which takes into account the properties required in the application and alloy processing conditions. The composition matrix defined from the established tie line information in the relevant systems provides a useful basis in the determination of the effects of various phases and microstructure on the properties of the alloys. The experimental procedures on the production and processing, mechanical testing, and examinations of the designed model alloys will be presented in the following chapter. The examination and testing results on the model alloys produced will be correlated with the theoretically predicted phase equilibria, phase formation, and elastic property data, as will be seen in Chapter VIII.
7.1 Production and Processing of Test Alloys

7.1.1 Production of Test Alloys

The test alloys were produced by Ross and Catherall Ltd, Foundry Division of Sheffield (RC), following the designed model alloy compositions.

7.1.2 Liquidus and Solidus of Designed Model Alloys

The liquidus and solidus of the designed test alloys were calculated, using the thermodynamic data listed in the appendix, and the results are shown in Table 7.1. These results can be used to determine the actual processing temperatures in gas atomisation by taking into account superheat requirements. Note that the liquidus temperatures for all the model alloys are low enough to avoid some processing problems due to high melting temperature.

7.1.3 Processing of Test Alloys

The base alloy (RR) was initially processed via chill block melt spinning (CBMS) and later via high pressure gas atomisation (HPGA) to test the alternative processing route. As has been discussed earlier, HPGA has been considered as a more practical route for mass production, although CBMS was the only available rapid solidification route at the time when the initial experiments on the test alloy RR were conducted.
### Table 7.1 Calculated liquidus and solidus of the test alloys.

<table>
<thead>
<tr>
<th>Alloy Code</th>
<th>Composition</th>
<th>Liquidus (°C)</th>
<th>Solidus (°C)</th>
<th>Primary Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>SU1</td>
<td>Fe\textsubscript{70}Cr\textsubscript{20}B\textsubscript{10}</td>
<td>1251</td>
<td>1120</td>
<td>bcc</td>
</tr>
<tr>
<td>SU3</td>
<td>Fe\textsubscript{80}Cr\textsubscript{15}B\textsubscript{5}</td>
<td>1405</td>
<td>1123</td>
<td>bcc</td>
</tr>
<tr>
<td>SU 2</td>
<td>Fe\textsubscript{65}Cr\textsubscript{25}B\textsubscript{10}</td>
<td>1221</td>
<td>1133</td>
<td>bcc</td>
</tr>
<tr>
<td>SU4</td>
<td>Fe\textsubscript{75}Cr\textsubscript{20}B\textsubscript{5}</td>
<td>1391</td>
<td>1132</td>
<td>bcc</td>
</tr>
<tr>
<td>RR</td>
<td>Fe\textsubscript{70}Cr\textsubscript{18}Mo\textsubscript{2}B\textsubscript{10}</td>
<td>1274</td>
<td>1127</td>
<td>M\textsubscript{3}B\textsubscript{2}</td>
</tr>
<tr>
<td>SU5</td>
<td>Fe\textsubscript{55}Cr\textsubscript{24}Ni\textsubscript{11}B\textsubscript{10}</td>
<td>1148</td>
<td>1101</td>
<td>fcc</td>
</tr>
<tr>
<td>SU6</td>
<td>Fe\textsubscript{63}Cr\textsubscript{18}Ni\textsubscript{14}B\textsubscript{5}</td>
<td>1324</td>
<td>1098</td>
<td>fcc</td>
</tr>
<tr>
<td>SU7</td>
<td>Fe\textsubscript{72}Cr\textsubscript{12}Mo\textsubscript{6}B\textsubscript{10}</td>
<td>1482</td>
<td>1210</td>
<td>M\textsubscript{3}B\textsubscript{2}</td>
</tr>
<tr>
<td>SU8</td>
<td>Fe\textsubscript{81}Cr\textsubscript{9}Mo\textsubscript{4}B\textsubscript{6}</td>
<td>1386</td>
<td>1189</td>
<td>bcc</td>
</tr>
</tbody>
</table>
EXPERIMENTAL PROCEDURES

All the designed alloys were processed via HPGA to produce powders from the cast ingots at the University of Surrey, Foundry Laboratory. An example of HPGA processing conditions for a typical model alloy in this investigation (alloy code: RCX440) is shown in Table 7.2.

Table 7.2  HPGA processing conditions for a typical model alloy[410].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy Processed</td>
<td>Fe_{80.3}Cr_{14.9}B_{4.8} (SU3/RCX440)</td>
</tr>
<tr>
<td>Charge</td>
<td>4 kg</td>
</tr>
<tr>
<td>Melt used</td>
<td>3.02 kg</td>
</tr>
<tr>
<td>Atomisation Rate</td>
<td>3 kg min^{-1}</td>
</tr>
<tr>
<td>Gas</td>
<td>Oxygen free Nitrogen</td>
</tr>
<tr>
<td>Atomising Gas Pressure</td>
<td>2 MPa to 3.4 MPa</td>
</tr>
<tr>
<td>Crucible</td>
<td>Zircon</td>
</tr>
<tr>
<td>Stopper Rod</td>
<td>Boron Nitride</td>
</tr>
<tr>
<td>Diameter of nozzle</td>
<td>d_{melt} = 3 mm</td>
</tr>
<tr>
<td>Temperature of Melt</td>
<td>T_{melt} = 1600 °C</td>
</tr>
<tr>
<td>Melt Superheat</td>
<td>ΔT_{SUP} = 200 °C</td>
</tr>
</tbody>
</table>

The atomised powders were sieved and canned in vacuum tight cans inside a glove box fitted with argon. The size distribution of the powders was determined by a laser granulometer (Malvern MaterSizer, Model ST1800). An example of the analysed particle size distribution of the HPGA powders produced (alloy code: RCX442) is shown in Figure 7.1.

The atomised powders were then degassed, canned, soaked at 950°C for 2 hours, and then extruded into 5 mm diameter consolidated bar, with an extrusion ratio of 10:1. The temperature during the extrusion process can rise as high as 1050°C and this is why an average temperature of 1000°C was used in the calculation of phase compositions of the test alloys.
EXPERIMENTAL PROCEDURES

1/6/90 RR3 (Elbow and collection box) (100μm)

Dispersant : Water
Additives : Drop of Nonidet P42
Ultrasound : 40%
Pump speed : 60%
Stir speed : 60%

Notes:

3755 2207 1fu360μm

<table>
<thead>
<tr>
<th>High Under Size %</th>
<th>High Under Size %</th>
<th>High Under Size %</th>
<th>High Under Size %</th>
<th>High Under Size %</th>
<th>High Under Size %</th>
</tr>
</thead>
<tbody>
<tr>
<td>600 100</td>
<td>203 99.5</td>
<td>68.5 72.2</td>
<td>22.4 15.8</td>
<td>7.82 1.0</td>
<td>2.64 0.0</td>
</tr>
<tr>
<td>544 100</td>
<td>184 99.2</td>
<td>67.2 65.7</td>
<td>21.0 13.4</td>
<td>7.48 0.7</td>
<td>2.29 0.0</td>
</tr>
<tr>
<td>493 100</td>
<td>166 98.8</td>
<td>56.2 58.9</td>
<td>19.0 11.3</td>
<td>6.48 0.5</td>
<td>2.17 0.0</td>
</tr>
<tr>
<td>446 100</td>
<td>151 98.2</td>
<td>50.9 52.1</td>
<td>17.2 9.4</td>
<td>5.82 0.3</td>
<td>1.97 0.0</td>
</tr>
<tr>
<td>404 100</td>
<td>137 97.2</td>
<td>46.6 43.5</td>
<td>15.6 7.7</td>
<td>5.27 0.2</td>
<td>1.78 0.0</td>
</tr>
<tr>
<td>366 100</td>
<td>124 95.8</td>
<td>41.6 39.6</td>
<td>14.1 6.1</td>
<td>4.77 0.1</td>
<td>1.61 0.0</td>
</tr>
<tr>
<td>332 99.9</td>
<td>112 93.9</td>
<td>37.9 34.3</td>
<td>12.8 5.0</td>
<td>4.33 0.0</td>
<td>1.46 0.0</td>
</tr>
<tr>
<td>301 99.9</td>
<td>102 91.2</td>
<td>34.3 29.6</td>
<td>11.6 4.9</td>
<td>3.92 0.0</td>
<td>1.32 0.0</td>
</tr>
<tr>
<td>273 99.9</td>
<td>92 91.6</td>
<td>31.1 25.3</td>
<td>10.5 4.5</td>
<td>3.55 0.0</td>
<td>1.20 0.0</td>
</tr>
<tr>
<td>247 99.6</td>
<td>83.4 85.6</td>
<td>28.2 21.7</td>
<td>9.32 2.2</td>
<td>3.29 0.0</td>
<td>1.00 0.0</td>
</tr>
<tr>
<td>224 99.7</td>
<td>75.6 78.3</td>
<td>25.5 18.6</td>
<td>8.63 1.6</td>
<td>2.92 0.0</td>
<td>0.90 0.0</td>
</tr>
</tbody>
</table>

Source = Sample
Focal length = 300
Presentation = 2207

Figure 7.1 An example of HPGA particle size distribution [91Bal].
EXPERIMENTAL PROCEDURES

Gas atomised powder with nominal composition the same as the base composition Fe_{70}Cr_{18}Mo_{2}B_{10} was made at Osprey and followed by alternative hot isostatic pressing at 950–1050°C (assigned as HIP7–HIP11). Different hipping temperatures were chosen in order to study their effect on the alloy properties. Comparisons will be made on the effect of the two different consolidation routes on the properties of the alloys with the same compositions. The hipping conditions for the Fe_{70}Cr_{18}Mo_{2}B_{10} alloy are listed in Table 7.3.

Table 7.3 Hipping conditions for Osprey powders of Fe_{70}Cr_{18}Mo_{2}B_{10}.

<table>
<thead>
<tr>
<th>FOR HIP7–HIP11:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Osprey powder</td>
</tr>
<tr>
<td>Heating at 4 °C/min</td>
</tr>
<tr>
<td>Hold at (950–1050 ± 10)°C at 15000 psi for 1–2 hrs</td>
</tr>
<tr>
<td>Then cool at 4 °C/min to 750°C</td>
</tr>
<tr>
<td>And afterwards cool to Room Temp. at 8 °C/min</td>
</tr>
</tbody>
</table>

HIPPING TEMPERATURE AND TIME FOR

<table>
<thead>
<tr>
<th>HIP</th>
<th>Temp. (°C)</th>
<th>Time (hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HIP7</td>
<td>1050°C</td>
<td>2hrs</td>
</tr>
<tr>
<td>HIP8</td>
<td>950°C</td>
<td>1hr</td>
</tr>
<tr>
<td>HIP9</td>
<td>1000°C</td>
<td>1hr</td>
</tr>
<tr>
<td>HIP10</td>
<td>1050°C</td>
<td>1hr</td>
</tr>
<tr>
<td>HIP11</td>
<td>1050°C</td>
<td>1hr</td>
</tr>
</tbody>
</table>

Alloys SU1–SU8 and RR were re-coded in the format of RCX### used by Ross & Catherall. ‘RC’ stands for Ross and Catherall, ‘X’ for extrusion, and ‘###’ is a specific number for different compositions. The equivalent notation is given in Table 7.4. The advantage of maintaining two sets of nominations for the model alloys is that it is easier to differentiate between the designed compositions and those of the actual test alloys produced.

An alloy of the base composition (Fe_{70}Cr_{18}Mo_{2}B_{10}) was also carburised by adding graphite in the crucible before atomisation [91Bal], and was designated as RCX445C after extrusion.
Table 7.4 Correspondence of the two sets of alloy codes and their nominal compositions. Compositions are given in both at% and wt%.

<table>
<thead>
<tr>
<th>Designed Alloy Code</th>
<th>Extruded Alloy Code</th>
<th>Nominal Composition (at%)</th>
<th>Nominal Composition (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SU1</td>
<td>RCX442</td>
<td>Fe70 Cr20 B10</td>
<td>Fe77.3 Cr20.6 B2.14</td>
</tr>
<tr>
<td>SU2</td>
<td>RCX443</td>
<td>Fe65 Cr25 B10</td>
<td>Fe72.1 Cr25.8 B2.15</td>
</tr>
<tr>
<td>SU3</td>
<td>RCX440</td>
<td>Fe80 Cr15 B5</td>
<td>Fe84.3 Cr14.7 B1.02</td>
</tr>
<tr>
<td>SU4</td>
<td>RCX441</td>
<td>Fe75 Cr20 B5</td>
<td>Fe79.3 Cr19.7 B1.02</td>
</tr>
<tr>
<td>RR</td>
<td>RCX445</td>
<td>Fe70 Cr18 Mo2 B10</td>
<td>Fe76 Cr18.2 Mo3.73 B2.1</td>
</tr>
<tr>
<td>HIP7–11</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SU5</td>
<td>RCX472</td>
<td>Fe55 Cr24 Ni11 B10</td>
<td>Fe60 Cr24.6 Ni12.7 B2</td>
</tr>
<tr>
<td>SU6</td>
<td>RCX470</td>
<td>Fe63 Cr18 Ni14 B5</td>
<td>Fe66 Cr17.6 Ni15.4 B1</td>
</tr>
<tr>
<td>SU7</td>
<td>RCX478</td>
<td>Fe72 Cr12 Mo6 B10</td>
<td>Fe75.5 Cr11.7 Mo10.8 B2.03</td>
</tr>
<tr>
<td>SU8</td>
<td>RCX477</td>
<td>Fe81 Cr9 Mo4 B6</td>
<td>Fe83.2 Cr8.6 Mo7.05 B1.19</td>
</tr>
</tbody>
</table>

Note: (i) HIP7–11: Osprey powder hipped at various temperatures; (ii) RCX###: Surrey powders atomised and extruded.

7.1.4 Analysed Compositions of Test Alloys

The as consolidated test alloys were analysed at Ross and Catherall LTD, and Metallurgical Testing Service (Midland) Limited (MTS). Table 7.5 gives the analysis results for the alloys investigated in this thesis, with details of impurity levels where applicable. All compositions are in weight percent (wt%). The composition for the carburised RCX445C is also found in the table; this alloy will be discussed later.
Table 7.5 Analysed compositions of consolidated alloys.

<table>
<thead>
<tr>
<th>Nominal Composition Code</th>
<th>Composition Code</th>
<th>Fe</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
<th>B</th>
<th>C</th>
<th>Si</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe80Cr15B5 RCX440 Bal</td>
<td></td>
<td>15.1</td>
<td>---</td>
<td>---</td>
<td>1.22</td>
<td>.014</td>
<td>.48</td>
<td>.19</td>
<td></td>
</tr>
<tr>
<td>Fe75Cr20B5 RCX441 Bal</td>
<td></td>
<td>17.1</td>
<td>---</td>
<td>---</td>
<td>1.14*</td>
<td>.016</td>
<td>.44</td>
<td>.19</td>
<td></td>
</tr>
<tr>
<td>Fe70Cr20B10 RCX442 Bal</td>
<td></td>
<td>22.1</td>
<td>---</td>
<td>---</td>
<td>2.00</td>
<td>.034</td>
<td>.46</td>
<td>.11</td>
<td></td>
</tr>
<tr>
<td>Fe65Cr25B10 RCX443 Bal</td>
<td></td>
<td>26.3</td>
<td>---</td>
<td>---</td>
<td>1.78</td>
<td>.054</td>
<td>.44</td>
<td>.45</td>
<td></td>
</tr>
<tr>
<td>Fe70Cr18Mo2B10 RCX445 Bal</td>
<td></td>
<td>16.6</td>
<td>3.79</td>
<td>---</td>
<td>2.03</td>
<td>.045</td>
<td>.46</td>
<td>.17</td>
<td></td>
</tr>
<tr>
<td>HIPped RCX445C Bal</td>
<td></td>
<td>19.2</td>
<td>3.42</td>
<td>---</td>
<td>2.18</td>
<td>.09</td>
<td>.05</td>
<td>.041</td>
<td></td>
</tr>
<tr>
<td>RCX445C Bal</td>
<td></td>
<td>17.8</td>
<td>3.73</td>
<td>---</td>
<td>2.00</td>
<td>.063</td>
<td>.24</td>
<td>.039</td>
<td></td>
</tr>
<tr>
<td>Fe55Cr24Ni11B10 RCX472 Bal</td>
<td></td>
<td>16.8</td>
<td>---</td>
<td>14.8</td>
<td>2.00</td>
<td>.021</td>
<td>.50</td>
<td>.15</td>
<td></td>
</tr>
<tr>
<td>Fe63Cr18Ni14B5 RCX470 Bal</td>
<td></td>
<td>23.7</td>
<td>---</td>
<td>12.1</td>
<td>1.04</td>
<td>.040</td>
<td>.18</td>
<td>.038</td>
<td></td>
</tr>
<tr>
<td>Fe61Cr3Mo4B6 RCX477 Bal</td>
<td></td>
<td>8.5</td>
<td>6.75</td>
<td>---</td>
<td>1.42</td>
<td>.023</td>
<td>.24</td>
<td>.059</td>
<td></td>
</tr>
<tr>
<td>Fe72Cr12Mo3B10 RCX478 Bal</td>
<td></td>
<td>10.9</td>
<td>9.33</td>
<td>---</td>
<td>2.10</td>
<td>.04</td>
<td>.31</td>
<td>.073</td>
<td></td>
</tr>
</tbody>
</table>

* Low B content due to increased porosity in sample analysed.

7.2 Heat Treatment

In order to examine the hardenability of the alloys and its effect on the elastic properties, various heat treatments were performed on selected test alloys.

Extruded alloys RCX442, RCX445 and one of the HIPped alloys were heated up to 1000°C and held at the temperature for 1 hour. The rods were subsequently cooled in water, oil, air, and in a furnace. Hardness tests were then made on these specimens. The oil quenched specimens were followed by tempering at 400°C for 5 hours (to release internal stress) and then machined.
into test pieces to examine their tensile properties. The hardness of these heat treated specimens were measured after tempering to check any significant change.

The Ni-containing test alloys were annealed into the austenitic region and maintained at 1000°C for 4 hours or longer in order to remove any possible metastable phases present in the consolidated alloys, and to allow the composition of the matrix to approach equilibrium before oil quenching the specimens. The likelihood of formation of metastable phases in the atomised powders has been studied using the combined thermodynamic and kinetic approach discussed in Section 2.4.6 and Chapter IV, and the calculation results will be discussed in a later section.

Test alloys containing Mo-rich boride were also heat treated at 1000°C for 4 hours and followed by oil quench. Mechanical testing and hardness measurements were made on the heat treated specimens to compare with the results obtained from the base alloy as well as the other model alloys designed in this investigation.

Heat treatment on the carburised RCX445C was followed by water quench after maintaining at 1000°C for 1 hour and tempering after at 600°C for 4 hours (air cool allowed).

7.3 Hardness Measurement

Indentation hardness is a resultant effect of several basic elastic and plastic properties but appears to be fairly closely related to the other mechanical properties. Measurements of hardness provide a very useful and efficient method for checking the efficiency of various metallurgical treatments, such as heat treatment, and therefore can be very important for routine inspection.

Hardness can be defined as resistance to localized indentations of a surface by a standard indentor under standard conditions [64Twe]. The actual depth involved in the hardness test varies with the material and mode of indentation but must be kept below a certain maximum depth relative to thickness of section. If the maximum depth is exceeded then the elastic deformation volume and, possibly, the plastically deformed volume too, will reach right through the material and will be affected by the supporting background. A safe rule is to ensure the thickness of the test piece is larger than eight times the depth of impression. The location of the
impression should also be away from the edge of the test piece, because the deformation spreads laterally. The centre of the impression should always be three times its own diameter from any edge of the specimen or the edge of an adjacent impression. Otherwise the impression will be distorted and inaccuracy consequently produced.

All the test specimen for hardness measurements were mounted in bakelite. The surface of the specimen were given a fairly fine polish so as to make the image of the impression clearer and its reading easier hence increase the accuracy of the test.

The standard Vickers diamond square pyramid was used in the macro hardness test. A load of 50 kg was selected and kept the same for all the hardness measurements. Two diagonal readings of a resultant impression from a Vickers square pyramid diamond indentor were taken at three different locations on the sample surface and the average value of VPN was taken. More readings were taken if there was too big a difference between the results from the three tests.

7.4 Tensile Testing

7.4.1 Testing Conditions

Tensile testing was performed on an Instron 1195 Universal tensile testing machine. A load of 100 kN was used and a loading speed of 0.05 mm.min⁻¹ applied, following the loading conditions used in the initial testing of the Fe₇₀Cr₁₈Mo₂B₁₀ alloy. The tension test pieces used in the present investigation were round specimens with threaded ends (Figure 7.2). The diameter of the reduced section was 5.06 mm. An extensometer calibrator was used to calibrate strain measurement which was made by an extensometer with initial gauge length of 12.4 mm. The extensometer utilises a mechanical leverage system to amplify the dimensional change over a predetermined gauge length. Load is measured through calibrated load cells incorporating electronic strain sensing devices. The electronic signal is amplified and recorded automatically on a chart. From the load-strain chart obtained from the tensile tests, Young's modulus of elasticity, elastic limit and yield point, or proof strength were determined.
EXPERIMENTAL PROCEDURES

RCX478), and the Ni-containing alloys (RCX470 and RCX472). The samples for tensile test pieces were taken from the extruded bars at various position. The tensile results will be presented in the following chapter.

Figure 7.2  Tensile test piece used in the present investigation.

7.4.2 Elasticity of Model Alloys

Hooke's Law states that, in the elastic range of a material, strain is proportional to stress. The modulus of elasticity is a measure of the ratio of stress to strain, or the gradient of the stress-strain graph in the elastic range. The stress-strain graph over the elastic range was extended from the straight section on the tensile curve where stress is about proportional to strain.

The ideal scale is such that the extension line is inclined at about 45°. This emphasizes the curvature and enables the coordinates to be read with equal accuracy. Appropriate strain scales were therefore used in the strain calibration during the tensile testing in relation to this investigation so that more accurate measures for the modulus could be obtained.

Sometimes the curve did not pass through zero and the readings for load and strain have to be adjusted to take into account the offset of the intercept. Some of the test alloys, although possessing elasticity, did not strictly obey Hooke's Law. For these alloys, the slope of the tangent to the stress-strain curve at the origin or at low stress was taken to be the modulus of elasticity.
EXPERIMENTAL PROCEDURES

7.4.3 Other Tensile Properties

The Proof Strength (PS) at 0.1% strain were calculated from the tensile curve of each of the specimen based on the elastic modulus slope. The Ultimate Tensile Strength (UTS), the maximum stress a material can sustain without fracture, was determined by dividing maximum load by the original cross-sectional area of the specimen.

The elongation of the test alloys, as a measure of a material to undergo deformation without rupture, was readily obtainable from the tensile tests. It was taken as the proportionate increase in length of the gauge length of a tensile piece immediately before fracture, and usually given as a percentage value.

7.4.4 Accuracy of Tensile Measurement

The relative uncertainty of the tensile results was estimated based on the relative uncertainty of the direct measurement including that of the load (P), strain (e), and tensile specimen diameter (d). The term uncertainty here represents the extreme width of the range of possible values for the testing results.

The differential calculus offers a considerably simplification of the propagation of uncertainty. If a most general case of a compound function is given in the form [62Bai]:

\[ z = x^a y^b \] ...

...(7.4.1)

where a and b may be positive or negative, integral or fractional powers. Differentiating both sides gives:

\[ \frac{dz}{z} = a \frac{dx}{x} + b \frac{dy}{y} \] ...

...(7.4.2)

By taking the differentials to be finite differences, the above formula becomes:

\[ \frac{\delta z}{z} = a \frac{\delta x}{x} + b \frac{\delta y}{y} \] ...

...(7.4.3)
EXPERIMENTAL PROCEDURES

The maximum value for $\delta z/z$ (a pessimistic but safe approach) is given by choosing similar signs throughout. A realistic assessment of the absolute uncertainty $\delta z$ can be simply evaluated by multiplying by a computed value $z_0$.

Following the above analysis, the relative uncertainty of the measured Young’s modulus can be derived as:

$$\frac{\delta E}{E} = \frac{\delta P}{P} + 2 \frac{\delta d}{d} + \frac{\delta e}{e}$$

...$(7.4.4)$

This formula suggests that the relative uncertainty of the measured Young’s modulus can be estimated from the relative uncertainty of the load, strain, and tensile specimen diameter.

The precision of these measurements is confined by the data recording scale, which is subdivided at finite intervals, in addition to the precision of the instrument used in the measurement. It is a common practice, and justified by its convenience, to use the finest scale division as a measure of the maximum range of uncertainty of the direct reading from either a micrometer or the tensile chart. For example, the absolute uncertainty of the diameter of a tensile specimen ($\delta d$) measured with a micrometer can be estimated as ±0.005 mm.

The relative uncertainty of the measured elongation ($\delta e/e$), therefore, is the sum of the relative uncertainty of the extensometer with the relative uncertainty related to the finest scale division of strain on the tensile chart. The non-linearity of the extensometer used in strain measurement was 0.25%, a value given in the specifications from the manufacturer [69Ins]. The uncertainty of the extensometer calibrator was given as ±0.0005 mm, an insignificant contribution which can be dropped, compared to the finest scale division of strain (0.01%) on the tensile chart.

The load weighing linearity for the load cells ($\delta P/P$) was quoted in the manual of the Instron tensile machine [81Ins] as ‘±0.5% of indicated load or ±0.25% of recorder scale in use, whichever is greater’. The finest scale division for the load was 0.2 kN on the tensile chart and the full scale used was 20 kN for the majority of the test. The tensile machine used in the present investigation was calibrated on a regular base, hence the systematic error was considered very small and therefore not included in the estimation of the uncertainty of tensile measurement.
The maximum limit for the uncertainty of the Young’s modulus, UTS (also PS), and elongation, taking one significant figure to quote the overall percentage, were estimated as ±8%, ±3%, and ±5% respectively.

7.5 Metallographic Examination

7.5.1 Sample Preparation

Samples for microstructural examination were cut from the extruded bars and mounted in conducting bakelite. Sample preparation was based on a program used in the previous work by Rolls-Royce plc. Some alterations were made on the original sample preparation program. DP DUR was used previously in step 6, and severe scratches occurred on the surface of the samples. Therefore Pan W was used instead in the latter sample polishing procedure. Less pressure (90 instead of 120) proved to be helpful in reducing the borides pull-out effect. The actual preparation program is shown in Table 7.6.

Table 7.6 Sample preparation route for metallography study (modified version).

<table>
<thead>
<tr>
<th>Step</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base</td>
<td>ZrO</td>
<td>SiC</td>
<td>SiC</td>
<td>SiC</td>
<td>Pet.M</td>
<td>Pan.W</td>
<td>DP.Mol</td>
</tr>
<tr>
<td>Grain</td>
<td>120</td>
<td>320</td>
<td>500</td>
<td>1000</td>
<td>6μm</td>
<td>6μm</td>
<td>1μm</td>
</tr>
<tr>
<td>Lubrication</td>
<td>H₂O</td>
<td>H₂O</td>
<td>H₂O</td>
<td>H₂O</td>
<td>Blue</td>
<td>Blue</td>
<td>Blue</td>
</tr>
<tr>
<td>Speed</td>
<td>300</td>
<td>300</td>
<td>300</td>
<td>300</td>
<td>150</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>Pressure</td>
<td>150</td>
<td>150</td>
<td>150</td>
<td>150</td>
<td>150</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Time</td>
<td>2’</td>
<td>3’</td>
<td>3’</td>
<td>3’</td>
<td>6’</td>
<td>2’</td>
<td>5’</td>
</tr>
</tbody>
</table>
A backscattered detector on the Cambridge 100 SEM (or 250 SEM) allowed observation of any segregation and intermetallic phases without the need to etch the sample. When etching was required, Vilellas Reagent was used as detailed below (Table 7.7). The etching reagent was made not long before use in order to limit the possible inaccuracy arisen from the vaporisation of the ingredients and therefore the etching effects.

**Table 7.7  Vilellas Reagent.**

**Vilellas Reagent**

Composition: 100 ml Ethanol or Methanol, 1 g Picric acid, and 5 ml Hydrochloric acid;

Mixing:

i) Use approved fume cupboard,

ii) Wear eye protection and gloves,

iii) Dry picric acid on filter paper before weighing then add to ethanol or methanol,

iv) Add hydrochloric acid slowly while stirring;

Use: Immersion etch for 10 to 50 seconds depending on the variation of the agent made each time, then wash in water followed by acetone to dry;

Hazards:

i) Explosive _ do not crush dry picric acid crystals,

ii) Flammable,

iii) Corrosive,

iv) Toxic.
7.5.2 Examination of Microstructure

Previous examination showed that the microstructure in rapidly solidified alloys were very fine. The size of the boride particles ranged at around 1 μm and a high magnification (x15000) was needed. In order to achieve an SEM image at such a magnification and a high resolution, a high accelerating voltage and a short working distance would normally be required. However it is very difficult to achieve microstructure images of magnetic materials under scanning microscopy where the electron beam interacts with the magnetic field originated from the sample. Many problems occurred due to the magnetic effects. The bigger the size of the sample, the shorter the working space, the stronger the magnetic effect will be on the image.

In order to avoid these difficulties, samples were demagnetised just before being put into the chamber. They were also cut into very small sizes to further diminish this negative effect. The working distance was chosen to be as long as possible while still giving a reasonable resolution of the image. The aperture was adjusted to be very small, and the voltage very low, in this case 15 kV. The spot size was reduced to 240 μm in order to eliminate the interaction between the electron beam and the sample surface. Although the sample was mounted in bakelite, aluminium tape and silver paint were used to improve conductivity.

The total time that the sample remained in the microscope chamber was kept as short as possible. Cutting out the mild steel die also helped in obtaining a stable image for a longer time in the chamber. Re-demagnetising the specimen after its being inside the chamber for a while also helped in getting round the problem. When demagnetising a specimen, repeating the same procedure often gave a better result. One of the practical ways of taking a good microphotograph of the test alloys in the present study was to take the photograph at a newly focused area after having set up the microscope at a different area.

Different machines need different setting when working with these samples. On the SEM 100, for example, a working distance of 16 mm, spot size of level 4.2 and a beam voltage of 25 kV were used in order to produce fairly workable images. A Jeol JSM35CF was also tried with the hope of getting a higher resolution, but the difficulties due to the magnetic effect remained.
EXPERIMENTAL PROCEDURES

7.5.3 Measurement of Volume Fraction of Borides

Volume fractions of borides in the test alloys were measured using quantitative metallography techniques. The first method tried was a Cambridge Image Analyser 'Quantimet 970'. It provides a software package which allows the area fraction of the particles to be measured by setting a grey level threshold to pick-up particles against a matrix background. The specimen can be installed in a SEM through which a live image is obtained for the image analysis. Factors which are likely to introduce errors in the measurements include: (i) the quality, in particular the contrast, of the structure image; (ii) subjective judgement involved in picking up particular image features. The Quantimet routine proves to be favourable on images with very good contrast, but did not give reliable results in the present investigation due to the difficulties in obtaining high quality microstructure image of the model alloys.

The measurement was eventually made using the 'point counting' method, one of the widely used for the determination of the relative amount of phases in quantitative metallography. In this method, a grid is superimposed on the microstructure or a photograph of it, and the number of intersections of the grid lines which lie in each phase is determined. The proportion by volume of each phase is then, in principle, considering the quantitative relationships between the features observed on a surface and those present in the bulk, the same as the ratio of intersections lying in that constituent to the total number of intersections [67Che].

It is obvious that the percentage estimation of phases by this method involves a large number of measurements, either manually or with the help of semi-automatic devices. This extremely laborious method was preferred in the determination of volume fraction of borides in the present investigation in favour of its higher reliability over the Quantimet routine.

The accuracy of point counting in metallographic investigations have been evaluated before [60Gla], and the possibility of assigning a definite probability distribution to minimise the number of observations to be made has been examined. A structure is considered having only two constituents existing in proportions (p) and (1-p). The probabilities that any particular point will be in one or other of the two constituents will be (p) and (1-p) respectively. A binomial distribution was assumed and checked. The standard deviation (σ) of the binomial distribution
EXPERIMENTAL PROCEDURES

is given by:

\[ \delta = \sqrt{\frac{p(1-p)}{n}} \] ...(7.5.1)

For any given value of p, the proportion of a particular constituent of the microstructure, the standard deviation \( \delta \) can be calculated from the number of points counted \( n \). The limit of the absolute uncertainty was then estimated to be ±1 vol% of borides, for a total number of points counted of 2352, following the above treatment.

The analysis was carried out on SEM microphotographs taken previously. Backscattered images of the test alloys in the present study proved to be the best, due to the contrast in the borides brought about by the large atomic weight difference between different phases. Photographs taken from several areas on the specimen surface were analysed and a mean value was taken.

7.6 Examination of Porosity in Consolidated Alloys

7.6.1 Examination of Porosity via Metallography

Cavities were found on the microstructure images of a number of specimens in the preliminary examinations on the test alloys. These were firstly thought to be due to pull-out of borides during the sample preparation procedure. Modifications have been made in the sample preparation procedures in order to eliminate this effect, as discussed in the metallographic sample preparation section. Samples which were prepared using the modified polishing routine were examined under the electron microscope and the porosity due to incomplete consolidation in the test alloys were examined using the image analysis method. The uncertainty of porosity measurement was ±1 vol%, same as that of volume fraction of borides as estimated in Section 7.5.3. The accuracy in reality could be lower considering the higher uncertainty involved in the subject judgement of differentiating porosity from borides.
7.6.2 Examination of Porosity via Density Measurement

A simple density measurement was thought to be an effective way of testing whether there was any significant level of porosity present in the extruded alloys.

The method used in density measurement was based on the Archimedes principle whereby the weight change raised from the immersion of a bulk material equals the weight of the liquid by the same volume of the bulk material. The specimen was first weighed and then put into a beaker of water with volume large enough to allow the sample to be emersed, and the weight change was measured by setting the scale at zero before putting the specimen in. The density of water was taken as 1 kg.m\(^{-1}\) and therefore the volume of the sample is simply equal to the weight change. A simple calculation provides the density of the alloy. Two density values were obtained from the ingot (\(\rho_0\)) and the consolidated alloys (\(\rho_1\)), and the level of porosity could then be derived from these measured values:

\[
\text{vol}\% \text{ of porosity} = \frac{\rho_0}{\rho_1} - 1.
\]

The accuracy of the digital scale used in the density measurement was ±0.005 g. The absolute uncertainty of the density measurement was thus estimated to be ±0.01 kg.m\(^{-3}\), following the treatment discussed in Section 7.4.4. The relative uncertainty for the porosity calculated from the measured density is twice the relative uncertainty of the measured density, and the absolute uncertainty was therefore ±0.3 vol\%. These are the maximum possible error ranges, and some of the density measurement results were more accurate due to bigger size samples used where smaller relative error was introduced.

Note also that the accuracy given above is based on the assumption that the ingots were 100% dense. This is not true because most ingots had significant porosity too. Therefore the porosity derived through density measurement may not be realistic.
8.1 Introduction

The objective of this project is to achieve a better understanding of the effect of microstructural features on the elastic properties of alloys processed via rapid solidification, in order to explore the potential of the alloys of the chosen class with changes in composition, processing condition, and microstructure. A theoretical approach, incorporating thermodynamic characterisations of alloy systems involved, prediction of phase formation in rapid solidified alloys, and modelling of elastic modulus of in situ composite structured materials, helps in providing a useful guide to this problem. As has been shown in the previous chapters, prediction of nucleation of various phases in high pressure gas atomised powders is useful in understanding phase formation occurred in the rapidly solidified alloys, in order to ensure that the desired microstructure is achieved. Eshelby's approach is used in evaluating the effect of phase and microstructural variables on the elastic properties of the alloys in this investigation. A series of test alloys have been designed using the phase equilibrium information obtained from thermodynamic characterisations of the relevant phase diagrams.

This chapter will present the predicted results of phase equilibria, phase formation, and elastic modulus of the designed model alloys, as well as metallographic examination and mechanical testing results on the test alloys produced. Thermodynamically calculated phase equilibria in the model alloys will be discussed with respect to metallography and EDX (Energy Dispersive X-ray spectroscopy) analysis results, and predicted phase formation in gas atomised powders complemented by the observed microstructure of consolidated alloys. Eshelby's approach will be used in analysing the measured elastic modulus data from tensile test on the model alloys, and the correlation established between the Young's modulus of the alloys and the
RESULTS AND DISCUSSION

microstructure variables, such as matrix and inclusion, will make it possible to derive the optimum alloys that produce the target properties.

In addition, the effect of different processing routes and conditions on the mechanical properties will be discussed with reference to the measured data obtained from tensile test, and the results will be used to design an optimum fabrication route.

8.2 Phase Equilibria in Designed Test Alloys

8.2.1 Calculated Phase Compositions in Test Alloys

The calculated compositions of the equilibrium phases in the designed alloys at consolidation temperature (1000°C) are listed in Table 8.1.

Table 8.1 Calculated proportions and compositions of equilibrium phases for the model alloys at 1000°C.

<table>
<thead>
<tr>
<th>Alloy Code</th>
<th>Phase</th>
<th>Amount (mol%)</th>
<th>Composition (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Fe</td>
<td>Cr</td>
</tr>
<tr>
<td>SU1</td>
<td>fcc</td>
<td>70</td>
<td>90.7</td>
</tr>
<tr>
<td></td>
<td>M2B_orth</td>
<td>30</td>
<td>21.8</td>
</tr>
<tr>
<td>SU2</td>
<td>fcc</td>
<td>85</td>
<td>90.4</td>
</tr>
<tr>
<td></td>
<td>M2B_orth</td>
<td>15</td>
<td>21.2</td>
</tr>
<tr>
<td>SU3</td>
<td>bcc</td>
<td>70</td>
<td>85.4</td>
</tr>
<tr>
<td></td>
<td>M2B_orth</td>
<td>30</td>
<td>17.3</td>
</tr>
<tr>
<td>SU4</td>
<td>bcc</td>
<td>85</td>
<td>85.2</td>
</tr>
<tr>
<td></td>
<td>M2B_orth</td>
<td>15</td>
<td>17.1</td>
</tr>
</tbody>
</table>
Table 8.1 Calculated proportions and compositions of equilibrium phases for the model alloys at 1000°C (continued).

<table>
<thead>
<tr>
<th>Alloy Code</th>
<th>Phase</th>
<th>Amount (mol%)</th>
<th>Composition (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RR</td>
<td>fcc</td>
<td>71.5</td>
<td>Fe: 90.0 Cr: 9.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mo: &lt;.07 Ni: ---</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>B: &lt;.006</td>
</tr>
<tr>
<td>M₂B_orth</td>
<td>21.2</td>
<td></td>
<td>Cr: 20.3 Mo: 44.8</td>
</tr>
<tr>
<td>M₃B₂</td>
<td>7.3</td>
<td></td>
<td>Fe: 18.4 Cr: 19.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mo: 22.2 Ni: ---</td>
</tr>
<tr>
<td>SU5</td>
<td>fcc</td>
<td>70</td>
<td>Fe: 71.9 Cr: 12.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mo: --- Ni: 15.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>B: &lt;.007</td>
</tr>
<tr>
<td>M₂B_orth</td>
<td>30</td>
<td></td>
<td>Cr: 15.6 Mo: 51.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Fe: --- Ni: 0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>B: 33.3</td>
</tr>
<tr>
<td>SU6</td>
<td>fcc</td>
<td>85</td>
<td>Fe: 71.3 Cr: 12.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mo: --- Ni: 16.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>B: &lt;.007</td>
</tr>
<tr>
<td>M₂B_orth</td>
<td>15</td>
<td></td>
<td>Cr: 15.7 Mo: 51.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Fe: --- Ni: 0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>B: 33.3</td>
</tr>
<tr>
<td>SU7</td>
<td>fcc</td>
<td>75</td>
<td>Fe: 90.0 Cr: 10.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mo: &lt;.09 Ni: ---</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>B: &lt;.005</td>
</tr>
<tr>
<td>M₃B₂</td>
<td>25</td>
<td></td>
<td>Cr: 18.2 Mo: 18.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Fe: 23.7 Ni: ---</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>B: 40.0</td>
</tr>
<tr>
<td>SU8</td>
<td>fcc</td>
<td>85</td>
<td>Fe: 91.9 Cr: 8.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mo: &lt;.09 Ni: ---</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>B: &lt;.006</td>
</tr>
<tr>
<td>M₃B₂</td>
<td>15</td>
<td></td>
<td>Cr: 18.9 Mo: 14.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Fe: 26.2 Ni: ---</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>B: 40.0</td>
</tr>
</tbody>
</table>

8.2.2 Discussion on Phase Equilibria in the Fe₇₀Cr₁₈Mo₂B₁₀ Alloy

The thermodynamic calculation for the Fe₇₀Cr₁₈Mo₂B₁₀ alloy following the characterisations of phase diagrams revealed that the equilibrium phases at the extrusion temperature were the solid solution phase fcc, Cr-rich M₂B_orth and Mo-rich M₃B₂ boride, which explained why martensite was found in the extruded alloy and clarified the identity of the Mo-rich boride phase.

The predicted ratios of the metallic components Fe:Cr:Mo and the EDX (Energy Dispersive X-ray spectroscopy) analysis results obtained on a Philips 400T microscope [91Bal] for the Fe₇₀Cr₁₈Mo₂B₁₀ alloy produced via various processing routes are compared in Table 8.2. All
samples were prepared using ion beam thinning except one (indicated as 'c, i' in the table) which was prepared using electrochemical jet polishing technique. A special analysis (indicated as 'c, ii' in the table) was obtained from extracted borides which were examined under TEM by Baliga [91Bal]. Some previous analysis results on the Fe$_{70}$Cr$_{18}$Mo$_2$B$_{10}$ test alloy by Kim [89Kim] are also included in Table 8.2 for comparison. Very good agreement is found in the data, which confirms the accuracy of the phase composition results predicted from phase diagram calculations as well as the validity of the thermodynamic database obtained from the phase diagram characterisations for the relevant sub-systems.

Table 8.2 Comparison between the calculated (in bold) atomic ratios of the metallic components and EDX analysis results [89Kim, 91Bal] of matrix and borides for an Fe$_{70}$Cr$_{18}$Mo$_2$B$_{10}$ alloy produced via different processing routes.

<table>
<thead>
<tr>
<th>Composition of Alloy Analysed, at%</th>
<th>Matrix Fe : Cr : Mo</th>
<th>Boride (i) M$<em>2$B$</em>{ortho}$ Fe : Cr : Mo</th>
<th>Boride (ii) M$_3$B$_2$ Fe : Cr : Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$<em>{70}$Cr$</em>{18}$Mo$<em>2$B$</em>{10}$</td>
<td>90.0 : 9.87 : 0.07</td>
<td>30.5 : 67.2 : 2.3</td>
<td>30.7 : 32.3 : 37.0</td>
</tr>
<tr>
<td>a(RCX445)</td>
<td>87.0 : 12.0 : 1.0</td>
<td>45.2 : 53.3 : 1.5</td>
<td>29.0 : 33.0 : 38.0</td>
</tr>
<tr>
<td>b(Hipped 8–11)</td>
<td>85.5 : 13.9 : 0.6</td>
<td>45.0 : 53.6 : 1.4</td>
<td>29.0 : 30.0 : 41.0</td>
</tr>
<tr>
<td>c(Extruded ribbon)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>i</td>
<td>85.5 : 12.8 : 1.7</td>
<td>42.4 : 55.1 : 2.5</td>
<td>26.9 : 30.6 : 42.5</td>
</tr>
<tr>
<td>ii</td>
<td>46.2 : 51.9 : 1.9</td>
<td></td>
<td>25.3 : 29.0 : 45.7</td>
</tr>
<tr>
<td>d(Extruded ribbon)</td>
<td>87.0 : 12.0 : 1.0</td>
<td>46.5 : 52.0 : 1.5</td>
<td>28.0 : 32.0 : 40.0</td>
</tr>
</tbody>
</table>

Note: Analysis data in the table were obtained from:

- a Extruded gas atomised powder (Surrey) [91Bal];
- b Hipped gas atomised powder (Osprey) [91Bal];
- c Extruded melt spun ribbon (Surrey) [91Bal];
  - i Electrochemical jet polished
  - ii Extracted boride
- d Extruded melt spun ribbon (Oxford) [89Kim].
8.2.3 Discussion on Phase Equilibria in Designed Fe-TM-B Test Alloys

A comparison was made between the predicted and the EDX analysis results for the ratio of the transition metal components Fe:Cr of both the matrix and the boride in the designed Fe-Cr-B test alloys (Table 8.3). The experimental results were obtained from the extruded gas atomised powders on a Philips 400T microscope by Baliga [91Bal]. It should be noted that there is some difference between the designed model alloy compositions (Table 6.1) and the analysed compositions of the extruded gas atomised powders (Table 7.5), which means that the phase compositions of the test alloys were in fact different from those of the designed model alloys as shown in Table 8.1. The calculated values of phase compositions in Table 8.3 correspond to the

Table 8.3 Comparison between the calculated (in bold) atomic ratios of the metallic components and EDX analysis results [91Bal] of matrix and borides in the designed Fe-Cr-B test alloys (RCX440→443).

<table>
<thead>
<tr>
<th>Composition of Alloy Analysed, at%</th>
<th>Matrix Fe : Cr</th>
<th>Boride (i) M2B_orth Fe : Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe_{69}Cr_{21.6}B_{9.4}</td>
<td>89.5 : 10.5</td>
<td>29.5 : 70.5</td>
</tr>
<tr>
<td>a(RCX442)</td>
<td>86.5 : 13.5</td>
<td>45.0 : 55.0</td>
</tr>
<tr>
<td>Fe_{65.8}Cr_{25.8}B_{8.4}</td>
<td>83.8 : 16.2</td>
<td>24.3 : 75.7</td>
</tr>
<tr>
<td>a(RCX443)</td>
<td>74.0 : 26.0</td>
<td>45.0 : 55.0</td>
</tr>
<tr>
<td>Fe_{78.8}Cr_{15.3}B_{5.9}</td>
<td>91.5 : 8.47</td>
<td>35.0 : 65.0</td>
</tr>
<tr>
<td>a(RCX440)</td>
<td>82.5 : 17.5</td>
<td>38.0 : 62.0</td>
</tr>
<tr>
<td>Fe_{77.1}Cr_{17.3}B_{5.6}</td>
<td>89.5 : 10.5</td>
<td>29.8 : 70.2</td>
</tr>
<tr>
<td>a(RCX441)</td>
<td>82.0 : 18.0</td>
<td>39.5 : 60.5</td>
</tr>
</tbody>
</table>

Note: Analysis data in the table were obtained from:
  a Extruded gas atomised powder (Surrey) [91Bal].
RESULTS AND DISCUSSION

analysed compositions and not to the designed compositions. Even so the experimentally analysed ratios of the transition metal components for the Fe-Cr-B test alloys show a consistent deviation from the calculated Fe and Cr content in the matrix and boride. Two factors may account for this deviation: (i) insufficient soaking time prior to consolidation, which resulted in that the phases did not reach their equilibrium compositions at the extrusion temperature; (ii) insufficient diffusion of metallic components, leaving a composition gradient near the interface between the matrix and the boride. The movement of the composition lines connecting the alloy and the matrix is consistent with the fact that metallic elements diffuse more slowly than boron, and in the SU5 alloy the phase compositions moved closer to the equilibrium levels after longer annealing at the extrusion temperature.

Comparison between the calculated atomic ratios of the metallic components and EDX analysis results [91Bal] of the matrix and borides in the designed Fe-Cr-Ni-B test alloys (RCX470 and RCX472) is shown in Table 8.4. The calculations were made using the compositions obtained from the chemical analysis results (Table 7.5), where the analysed compositions in wt% have been converted into at%, as shown in Table 8.4.

Table 8.4 Comparison between the calculated (in bold) atomic ratios of the metallic components and EDX analysis results [91Bal] of matrix and borides in the designed Fe-Cr-Ni-B test alloys (RCX470 and RCX472).

<table>
<thead>
<tr>
<th>Composition of Alloy</th>
<th>Matrix</th>
<th>Boride (i)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analysed, at%</td>
<td>Austenite</td>
<td>M₂B_{orth}</td>
</tr>
<tr>
<td>Fe : Cr : Ni</td>
<td>Fe : Cr : Ni</td>
<td></td>
</tr>
<tr>
<td>a(RCX470)</td>
<td>68.5 : 15.2 : 16.3</td>
<td>39.9 : 57.8 : 2.3</td>
</tr>
<tr>
<td>Fe₆₉₉₉Cr₂₄.₁Ni₁₀.₉B₅.₁</td>
<td>68.8 : 18.3 : 12.9</td>
<td>15.8 : 84.2 : 0.0</td>
</tr>
<tr>
<td>b(RCX472)</td>
<td>68.6 : 15.9 : 15.5</td>
<td>32.7 : 66.5 : 0.8</td>
</tr>
<tr>
<td>Fe₆₁.₀Cr₁₆.₆Ni₁₂.₉B₉.₅</td>
<td>75.1 : 6.69 : 18.0</td>
<td>37.8 : 62.2 : 0.0</td>
</tr>
</tbody>
</table>

Note: Analysis data in the table were obtained from:

a Extruded gas atomised powder (Surrey) [91Bal].

b Sample of a(RCX472) annealed @1000°C 4 hrs + oil quench [91Bal].
RESULTS AND DISCUSSION

Metastable $M_{23}B_6$ was found to be present in one of the extruded Fe-Cr-Ni-B alloys (RCX472)\(^{(21)}\). Results from phase formation study on rapidly solidified powders of this system provides a reasonable explanation with regard to the appearance of the metastable phase in only one of the alloys. Details will be presented in the next section.

In order to make a sensible comparison, the RCX472 was annealed at 1000°C for 4 hours followed by oil quench. The metastable phase was expected to transform and the phase compositions to reach their equilibrium level. The X-ray lines for $M_{23}B_6$ did indeed disappear, but matrix composition did not change appreciately because of the very small amount of the boride involved.

The experimental data and calculated results in Table 8.4 present a fairly good agreement. The compositions of the matrix show a better agreement for both alloys. The calculated ratios for $M_2B_{\text{orth}}$ in the annealed RCX472 are very close to the EDX analysed values but not for the boride in the other alloy. The very high Ni content in the boride of RCX470 alloy, according to the calculation, requires a high diffusion of Ni which is not easy to achieve for the short equilibrium time allowed during the extrusion. The Ni content in the boride, therefore, tend to remain lower than its theoretical level. The Ni partition in the Cr boride $M_2B_{\text{orth}}$, on the other hand, is theoretically zero because Ni is only found in $M_2B_{\text{tet}}$ in the Fe-Ni-B and Cr-Ni-B phase diagrams. The amount of Ni detected in the EDX analysis must be Ni picked up from the underlying matrix in the sample.

Table 8.5 shows the comparison between the calculated atomic ratios of the metallic components and EDX analysed results [91Bal] of the matrix and borides in the designed Fe-Cr-Mo-B test alloys RCX477 and RCX478. The analysed compositions of the alloys (Table 7.5) were used in the calculations. The agreement found between the two sets of component ratios is satisfactory for all the phases. The appearance of the $M_2B_{\text{orth}}$ phase in one of the alloys (RCX477) was confirmed by recalculating the phase equilibrium using the analysed alloy composition, although these two alloys were initially designed with the intension to produce test alloys with only $M_3B_2$ boride in a matrix of martensite (Table 8.1). The EDX analysis detected $M_2B_{\text{orth}}$ as present but with no information on the quantity of the phase. According to the phase equilibrium calculation, the amount of the Cr boride in the test alloy is only 0.97 mol\%, due to the slight composition difference from the intended alloy. Such a small amount is not expected to introduce much error in the subsequent analysis of the mechanical properties of the alloy.
Table 8.5 Comparison between the calculated (in bold) atomic ratios of the metallic components and EDX analysis results [91Bal] of matrix and borides in the designed Fe-Cr-Mo-B test alloys (RCX477 and RCX478).

<table>
<thead>
<tr>
<th>Composition of Alloy Analysed, at%</th>
<th>Matrix</th>
<th>Boride (i)</th>
<th>Boride (ii)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe : Cr : Mo</td>
<td>Fe : Cr : Mo</td>
<td>Fe : Cr : Mo</td>
</tr>
<tr>
<td>Fe$<em>{73.5}$Cr$</em>{11.1}$Mo$<em>{5.14}$B$</em>{10.26}$</td>
<td>92.2 : 7.75 : 0.05</td>
<td>36.9 : 61.3 : 1.8</td>
<td>32.5 : 33.3 : 34.2</td>
</tr>
<tr>
<td>a(RCX477)</td>
<td>86.1 : 9.8 : 4.1</td>
<td>60.1 : 34.7 : 4.7</td>
<td>39.2 : 21.7 : 39.1</td>
</tr>
<tr>
<td>Fe$<em>{80.3}$Cr$</em>{8.8}$Mo$<em>{3.8}$B$</em>{7.1}$</td>
<td>93.3 : 6.65 : 0.05</td>
<td>----</td>
<td>33.6 : 31.1 : 35.3</td>
</tr>
<tr>
<td>a(RCX478)</td>
<td>90.7 : 7.6 : 1.7</td>
<td>----</td>
<td>54.3 : 15.5 : 30.2</td>
</tr>
</tbody>
</table>

Note: Analysis data in the table were obtained from:

a Extruded gas atomised powder (Surrey) [91Bal].

8.3 Predicted Phase Formation in Gas Atomised Powders and Discussion

The undercoolings and critical nucleation temperatures of the phases of interest in gas atomised powders of specified compositions were predicted using the solidification programme described in Section 4.3. The results are shown in Table 8.6a, b, c for the designed alloy compositions (a: SU1→SU4; b: RR and SU7→SU8; c: SU5→SU6).

The computations produced the critical nucleation temperature, $T_{\text{crit,d}}$, for each competing phase as a function of atomised powder diameter, d. The tables present the results of such computations for three representative powder diameters (d = 100, 10 and 1 µm), the usual powder size range found in the atomised alloys in this study (see Figure 7.1). The calculated melting points (liquidus temperatures) of the solid solution phases and the borides, by suspending all the other solid phases in the calculation, are also given in the tables. The highest critical nucleation temperature $T_{\text{crit,d}}$ at each powder diameter is underlined to highlight the predominant phase.
RESULTS AND DISCUSSION

The undercooling (ΔT) of a phase at a certain powder size is defined as the difference between the melting temperature (T_M) and the critical nucleation temperature (ΔT = T_M - T_{crit,d}). The calculated results confirmed that the undercoolings of various phases become larger as the powder size becomes smaller.

The critical nucleation temperature T_{crit,d} is a very important parameter, which determines the sequence of nucleation (or suppression) among the competing phases. The calculated critical nucleation temperature for the model alloy RR was plotted against the powder size, which can

Table 8.6a  Predicted critical nucleation temperatures and undercoolings for the competing phases at various powder diameters of the designed Fe-TM-B alloys atomised in nitrogen. The highest T_{crit,d} at each powder diameter is underlined.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Phase</th>
<th>T_M(K)</th>
<th>T_{crit,d} (ΔT = T_M - T_{crit,d})</th>
<th>d=100µm</th>
<th>d=10µm</th>
<th>d=1µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe_{70}Cr_{20}B_{10}</td>
<td>M_{2}B_orth</td>
<td>1280</td>
<td>949 (331)</td>
<td>902 (378)</td>
<td>823 (457)</td>
<td></td>
</tr>
<tr>
<td>(SU1)</td>
<td>bcc</td>
<td>1518</td>
<td>1258 (260)</td>
<td>1222 (295)</td>
<td>1154 (364)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>fcc</td>
<td>1510</td>
<td>1253 (257)</td>
<td>1221 (289)</td>
<td>1174 (336)</td>
<td></td>
</tr>
<tr>
<td>Fe_{65}Cr_{25}B_{10}</td>
<td>M_{2}B_orth</td>
<td>1333</td>
<td>983 (350)</td>
<td>931 (402)</td>
<td>846 (487)</td>
<td></td>
</tr>
<tr>
<td>(SU2)</td>
<td>bcc</td>
<td>1485</td>
<td>1254 (231)</td>
<td>1218 (267)</td>
<td>1147 (338)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>fcc</td>
<td>1462</td>
<td>1218 (244)</td>
<td>1185 (277)</td>
<td>1144 (318)</td>
<td></td>
</tr>
<tr>
<td>Fe_{80}Cr_{15}B_{5}</td>
<td>M_{2}B_orth</td>
<td>1063</td>
<td>768 (295)</td>
<td>726 (337)</td>
<td>653 (410)</td>
<td></td>
</tr>
<tr>
<td>(SU3)</td>
<td>bcc</td>
<td>1669</td>
<td>1399 (270)</td>
<td>1364 (305)</td>
<td>1298 (371)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>fcc</td>
<td>1653</td>
<td>1389 (264)</td>
<td>1349 (304)</td>
<td>1291 (362)</td>
<td></td>
</tr>
<tr>
<td>Fe_{75}Cr_{20}B_{5}</td>
<td>M_{2}B_orth</td>
<td>1107</td>
<td>798 (309)</td>
<td>752 (355)</td>
<td>675 (432)</td>
<td></td>
</tr>
<tr>
<td>(SU4)</td>
<td>bcc</td>
<td>1663</td>
<td>1393 (270)</td>
<td>1364 (299)</td>
<td>1301 (362)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>fcc</td>
<td>1626</td>
<td>1364 (262)</td>
<td>1328 (298)</td>
<td>1272 (354)</td>
<td></td>
</tr>
</tbody>
</table>
Table 8.6b  Predicted critical nucleation temperatures and undercoolings for the competing phases at various powder diameters of the designed Fe-TM-B alloys atomised in nitrogen. The highest $T_{\text{crit},d}$ at each powder diameter is underlined.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Phase</th>
<th>$T_M$ (K)</th>
<th>$T_{\text{crit},d}$ ($\Delta T = T_M - T_{\text{crit},d}$), (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$d=100\mu m$</td>
</tr>
<tr>
<td>Fe$<em>{70}$Cr$</em>{18}$Mo$<em>2$B$</em>{10}$</td>
<td>M$<em>2$B$</em>{\text{orth}}$</td>
<td>1316</td>
<td>962 (354)</td>
</tr>
<tr>
<td>(RR)</td>
<td>M$_3$B</td>
<td>1434</td>
<td>1097 (337)</td>
</tr>
<tr>
<td></td>
<td>M$_3$B$_2$</td>
<td>1541</td>
<td>1002 (539)</td>
</tr>
<tr>
<td></td>
<td>bcc</td>
<td>1518</td>
<td>1258 (260)</td>
</tr>
<tr>
<td></td>
<td>fcc</td>
<td>1510</td>
<td>1253 (257)</td>
</tr>
<tr>
<td>Fe$<em>{72}$Cr$</em>{12}$Mo$<em>6$B$</em>{10}$</td>
<td>M$<em>2$B$</em>{\text{orth}}$</td>
<td>1365</td>
<td>971 (394)</td>
</tr>
<tr>
<td>(SU7)</td>
<td>M$_3$B</td>
<td>1603</td>
<td>1222 (381)</td>
</tr>
<tr>
<td></td>
<td>M$_3$B$_2$</td>
<td>1753</td>
<td>1166 (587)</td>
</tr>
<tr>
<td></td>
<td>bcc</td>
<td>1530</td>
<td>1268 (262)</td>
</tr>
<tr>
<td></td>
<td>fcc</td>
<td>1520</td>
<td>1261 (259)</td>
</tr>
<tr>
<td>Fe$_{81}$Cr$_9$Mo$_4$B$_6$</td>
<td>M$<em>2$B$</em>{\text{orth}}$</td>
<td>1202</td>
<td>838 (364)</td>
</tr>
<tr>
<td>(SU8)</td>
<td>M$_3$B</td>
<td>1465</td>
<td>1101 (364)</td>
</tr>
<tr>
<td></td>
<td>M$_3$B$_2$</td>
<td>1575</td>
<td>1019 (556)</td>
</tr>
<tr>
<td></td>
<td>bcc</td>
<td>1653</td>
<td>1370 (283)</td>
</tr>
<tr>
<td></td>
<td>fcc</td>
<td>1640</td>
<td>1373 (267)</td>
</tr>
</tbody>
</table>

be seen to have a strong resemblance to the conventional CCT diagrams for steels, as shown in Figure 8.1. It is clearly seen from this plot that the solid solution fcc or bcc phase show considerably higher critical nucleation temperatures than the borides over the powder size range of interest. Same trend has been observed from the calculated results of all the Fe-Cr-B and other Fe-Cr-Mo-B alloys. Hence these supersaturated solutions will predominantly form in the atomised powders whereas the borides consequently be suppressed.
Figure 8.1 Variation of critical nucleation temperatures for the competing phases with the size of atomised powders. Powder diameter \(d\): \(\mu\)m; Alloy code: RR.

It should be pointed that the predicted cooling rate felt by the smaller diameter powders 1→10 \(\mu\)m are of the order of magnitude of rates in melt spinning \((10^7 \text{ K sec}^{-1})\), and amorphous ribbon was produced at these rates in the original alloy RR. According to the calculations in the present work, on the other hand, gas atomisation produces amorphous powders only in very small particles \((\text{powder diameter } d<1 \mu\text{m})\). However, the calculations in the present work are still of importance because the sequence in the formation of the competing phases in gas atomised powders should not be affected by this difference, and this difference in turn indicates that the gas atomised powders of a normal size range should be expected to contain a mixture of amorphous or supersaturated solution phases, which is precisely the desired microstructure.

Although there was a need in a little more experimental data on the phase and microstructure of the as-atomised powders from the iron-based systems in the present investigation, the
RESULTS AND DISCUSSION

nucleation calculation nevertheless provided a theoretical criterion which helped ensure that amorphous or supersaturated solid solutions were formed after the rapid solidification. The observed microstructure of test alloys after consolidation, however, can be indirectly used to verify the nucleation calculation results. Details will be presented in the following section (Section 8.4).

Table 8.6c Predicted critical nucleation temperatures and undercoolings for the competing phases at various powder diameters of the designed Fe-TM-B alloys atomised in nitrogen. The highest $T_{\text{crit},d}$ at each powder diameter is underlined.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Phase</th>
<th>$T_M$(K)</th>
<th>$T_{\text{crit},d}$ ($\Delta T = T_M - T_{\text{crit},d}$), (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$d=100\mu\text{m}$</td>
</tr>
<tr>
<td>Fe$<em>{55}$Cr$</em>{24}$Ni$<em>{11}$B$</em>{10}$</td>
<td>M$_{23}$B$_6$</td>
<td>1196</td>
<td>977 (219)</td>
</tr>
<tr>
<td>(SU5)</td>
<td>M$<em>{23}$B$</em>{\text{orth}}$</td>
<td>1387</td>
<td>1004 (383)</td>
</tr>
<tr>
<td></td>
<td>M$_3$B</td>
<td>1263</td>
<td>974 (289)</td>
</tr>
<tr>
<td></td>
<td>bcc</td>
<td>1198</td>
<td>945 (253)</td>
</tr>
<tr>
<td></td>
<td>fcc</td>
<td>1237</td>
<td>1027 (210)</td>
</tr>
<tr>
<td>Fe$<em>{63}$Cr$</em>{19}$Ni$_{14}$B$_5$</td>
<td>M$_{23}$B$_6$</td>
<td>973</td>
<td>789 (184)</td>
</tr>
<tr>
<td>(SU6)</td>
<td>M$<em>{23}$B$</em>{\text{orth}}$</td>
<td>1142</td>
<td>811 (331)</td>
</tr>
<tr>
<td></td>
<td>M$_3$B</td>
<td>1057</td>
<td>800 (257)</td>
</tr>
<tr>
<td></td>
<td>bcc</td>
<td>1342</td>
<td>1096 (246)</td>
</tr>
<tr>
<td></td>
<td>fcc</td>
<td>1381</td>
<td>1138 (243)</td>
</tr>
</tbody>
</table>

Examination of one of the Fe-Cr-Ni-B alloys (alloy code: SU5) after atomisation showed the presence of an additional phase corresponding to the stoichiometry M$_{23}$B$_6$ [91Bal], which has been previously observed in rapidly solidified Fe-Ni-B alloys ([69Sta, 82Mul, 84Ber, 85War, 90Vit], see Section 3.4.4), as well as in rapidly solidified amorphous Fe$_{70}$Cr$_{18}$Mo$_2$B$_{10}$ ribbons after annealing for 2 hours at 700°, 800°, and 900°C ([91Kim], see Section 3.5.1). This extra phase was
thermodynamically characterised and solidification calculations were performed to check the possibilities for the formation of this phase in the alloys quoted in the literature. Initial calculations were in agreement with the observed behaviour in the ternary Fe-Ni-B system [91Pan] and calculations were then extended to the quaternary alloys.

The $T_{\text{crit},d}$ values for the Fe-Cr-Ni-B alloys given in Table 8.6c show that the supersaturated solid solution is still the predominant phase regardless of powder size. However, the metastable $M_{23}B_6$ phase (M here includes Fe, Cr, and Ni) in alloy SU5 becomes increasingly competitive over the rest of the borides as the powder diameter becomes smaller (Figure 8.2a). In alloy SU6, on the other hand, the critical nucleation temperature of the metastable phase, as well as the other borides, appear to be consistently lower than those of the solid solution phases.

![Figure 8.2a](image)

**Figure 8.2a**  Variation of critical nucleation temperatures for the competing phases in the atomised powders. Powder diameter: $\mu$m. a) Alloy code: SU5, $M_{23}B_6$ observed.
RESULTS AND DISCUSSION

Figure 8.2b  Variation of critical nucleation temperatures for the competing phases in the atomised powders. Powder diameter: μm. b) Alloy code: SU6, M_{23}B_{6} not observed.

over the whole powder diameter range of interest, until the glass forming temperature is reached (Figure 8.2b). Comparison between the two plots suggests that the metastable M_{23}B_{6} is much more likely to form in alloy SU5 than in SU6, which serves as a reasonable explanation for its appearance observed in the former and the absence in the latter alloy.

There remains a question as to whether the M_{23}B_{6} phase forms as secondary phase due to partitioning during growth at elevated consolidation temperature, or as a primary phase in the solidification. This question can not be answered without examination data on the as-atomised powders. However, the predicted nucleation between the competing phases reflects the tendency in the formation of the phase, which is believed to be similar in either a rapid solidification process, or a high temperature recrystallisation/phase transformation process. The relative
RESULTS AND DISCUSSION

tendency for the appearance of the $\text{M}_{23}\text{B}_6$ phase in the consolidated alloys can be, therefore, determined by the same calculation results as shown above, regardless of during which process the phase formation actually takes place.

8.4 Microstructure of Consolidated Alloys

8.4.1 Observed Microstructure

The microstructure of the consolidated model alloys was observed through secondary or backscattered images under SEM. All the microphotographs (Figure 8.3a–j, see the next five pages) show a fine distribution of boride (the grey particles on the photos) on a solid solution matrix. Various degree of porosity is present in all the alloys (the dark points on the photos). The sizes of boride particles vary with each alloy but measured at an order of 1 μm. There is no indication of significantly elongated borides in the images of the extruded samples. Aspect ratios of borides are taken as approximately 1 for the borides mostly appeared to be spherical.

The size of the boride particles present in the consolidated alloys implies that the borides are most likely formed as a secondary phase during the consolidation process, rather than a primary phase formed during the rapid solidification, which would appear much coarser due to the growth effect. This observation indirectly verified the predicted phase formation in the gas atomised powders presented in the previous section (Section 8.3).
Figure 8.3a, b  SEM microphotographs showing the microstructure of model alloys processed via HPGA followed by extrusion. a) RCX440; b) RCX441.
Figure 8.3c, d  SEM microphotographs showing the microstructure of model alloys processed via HPGA followed by extrusion. c) RCX442; d) RCX443.
Figure 8.3e, f  Microphotographs showing the microstructure of model alloys processed via HPGA followed by extrusion or hipping. e) RCX445; f) HIP9.
RESULTS AND DISCUSSION

Figure 8.3g, h  SEM microphotographs showing the microstructure of model alloys processed via HPGA followed by extrusion. g) RCX470; h) RCX472.
Figure 8.3i, j  SEM microphotographs showing the microstructure of model alloys processed via HPGA followed by extrusion. i) RCX477; j) RCX478.
8.4.2 Volume Fractions of Borides

Volume fractions of borides in the test alloys were measured using point counting on the microphotographs of backscattered images obtained under SEM. The point counting results on the volume fractions of borides in the consolidated alloys are presented in Table 8.7.

The measured volume fractions of borides, as given in Table 8.7, were compared with the predicted phase equilibria (Table 8.1) in the designed test alloys. It should be born in mind that the volume fraction of borides is, in theory, not equal to the mole fraction. However, the volume percentage of borides can be estimated to be 2–3% lower than the mole percentage in number for most of the designed test alloys, as has been explained in a previous section (Section 6.5.2).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>RCX440</th>
<th>RCX441</th>
<th>RCX442</th>
<th>RCX443</th>
<th>RCX445</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured</td>
<td>10</td>
<td>13</td>
<td>28</td>
<td>20</td>
<td>25</td>
</tr>
<tr>
<td>Calculated</td>
<td>13</td>
<td>13</td>
<td>27</td>
<td>27</td>
<td>27</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Alloy</th>
<th>RCX470</th>
<th>RCX472</th>
<th>RCX477</th>
<th>RCX478</th>
<th>HIP8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured</td>
<td>14</td>
<td>31</td>
<td>19</td>
<td>23</td>
<td>30</td>
</tr>
<tr>
<td>Calculated</td>
<td>13</td>
<td>27</td>
<td>13</td>
<td>23</td>
<td>27</td>
</tr>
</tbody>
</table>

Note: The absolute uncertainty of the measurement: ±1 vol% (see Section 7.5.3).

Note also that there exists a difference between the designed alloy compositions (on which results in Table 8.1 are based) and the analysed compositions of the test alloys produced (see Table 7.5). Among the various alloying elements, boron is the most important because the amount of borides is primarily determined by the boron content in the alloy (see Section 6.4).
RESULTS AND DISCUSSION

It was found, as a result of the comparison, that the measured amount of borides were consistent with the analysed boron compositions in the test alloys. This indicates the validity of the calculated phase equilibria, and at the same time supports the quantitative measurement of volume fraction of borides.

8.4.3 Porosity in Consolidated Alloys

The porosity levels in the extruded alloys were measured using point counting on the backscattered microphotographs obtained under SEM. The results are listed in Table 8.8.

Table 8.8 Measured level of porosity in the test alloys.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>RCX440</th>
<th>RCX441</th>
<th>RCX442</th>
<th>RCX443</th>
<th>RCX445</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity (vol%)</td>
<td>~3</td>
<td>~5</td>
<td>~2</td>
<td>~10</td>
<td>~3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Alloy</th>
<th>RCX470</th>
<th>RCX472</th>
<th>RCX477</th>
<th>RCX478</th>
<th>HIP8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity (vol%)</td>
<td>~5</td>
<td>~8</td>
<td>~7</td>
<td>~2</td>
<td>~1</td>
</tr>
</tbody>
</table>

Note: The absolute uncertainty of the measurement: ~ ±1 vol% (see Section 7.6.2).

The measured densities of the ingot and the consolidated alloys are listed in Table 8.9 together with the respective analysed compositions. It can be seen that there is generally a difference between the analysed compositions of the test alloys in their ingot form and as extruded. The comparison between the two sets of density data, therefore, also depends on the difference in density arising from this composition change. However the porosity values given in Table 8.9 were estimated through the difference between the measured densities, assuming that the composition difference between the ingot and the consolidated alloys was small enough to be
RESULTS AND DISCUSSION

negligible. Although the results showed that there was actually some degree of porosity in most consolidated alloys, these porosity levels were much lower than those measured via metallography (see Table 8.8). It can be concluded that results obtained through metallography provides a more realistic description for the level of porosity in the consolidated alloys, particularly when there is a significant level of porosity in the ingots.

Table 8.9 Measured density ($\rho$) of the test alloys with the estimated level of porosity.

<table>
<thead>
<tr>
<th>Alloy Code</th>
<th>Composition (Fe + wt%)</th>
<th>$\rho$ (kg.m$^{-1}$)</th>
<th>As extruded Composition (Fe + wt%)</th>
<th>$\rho_1$ (kg.m$^{-1}$)</th>
<th>Estimated Porosity (vol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RCX440</td>
<td>Cr$<em>{14.9}$B$</em>{1.22}$</td>
<td>7.65</td>
<td>Cr$<em>{15.1}$B$</em>{1.22}$</td>
<td>7.56</td>
<td>1.2</td>
</tr>
<tr>
<td>RCX441</td>
<td>Cr$<em>{20.05}$B$</em>{1.14}$</td>
<td>7.58</td>
<td>Cr$<em>{17.1}$B$</em>{1.14}$</td>
<td>7.50</td>
<td>1.1</td>
</tr>
<tr>
<td>RCX442</td>
<td>Cr$<em>{20.69}$B$</em>{2}$</td>
<td>7.57</td>
<td>Cr$<em>{22.1}$B$</em>{2}$</td>
<td>7.49</td>
<td>1.1</td>
</tr>
<tr>
<td>RCX443</td>
<td>Cr$<em>{25.86}$B$</em>{1.78}$</td>
<td>7.48</td>
<td>Cr$<em>{26.3}$B$</em>{1.78}$</td>
<td>7.42</td>
<td>0.9</td>
</tr>
<tr>
<td>RCX445</td>
<td>Cr$<em>{18.32}$Mo$</em>{3.8}$B$_{2.03}$</td>
<td>7.55</td>
<td>Cr$<em>{16.6}$Mo$</em>{3.79}$B$_{2.03}$</td>
<td>7.59</td>
<td>0.0</td>
</tr>
<tr>
<td>HIPped</td>
<td>Cr$<em>{18.32}$Mo$</em>{3.8}$B$_{2.03}$</td>
<td>7.55</td>
<td>Cr$<em>{19.2}$Mo$</em>{3.42}$B$_{2.18}$</td>
<td>7.58</td>
<td>0.0</td>
</tr>
<tr>
<td>RCX470</td>
<td>(not available)</td>
<td>---</td>
<td>Cr$<em>{16.8}$Ni$</em>{14.8}$B$_{2.0}$</td>
<td>7.83</td>
<td>---</td>
</tr>
<tr>
<td>RCX472</td>
<td>---</td>
<td>---</td>
<td>Cr$<em>{23.7}$Ni$</em>{12.1}$B$_{1.04}$</td>
<td>7.68</td>
<td>---</td>
</tr>
<tr>
<td>RCX477</td>
<td>---</td>
<td>---</td>
<td>Cr$<em>{8.5}$Mo$</em>{6.75}$B$_{1.42}$</td>
<td>7.75</td>
<td>---</td>
</tr>
<tr>
<td>RCX478</td>
<td>---</td>
<td>---</td>
<td>Cr$<em>{10.9}$Mo$</em>{9.33}$B$_{2.1}$</td>
<td>7.55</td>
<td>---</td>
</tr>
</tbody>
</table>

Note: The absolute uncertainty of the measurement (see Section 7.6.1):

±0.01 kg.m$^{-1}$ for the density;

±0.3 vol% for the porosity.
8.5 Tensile Test Results

The tensile test results, including the Young's modulus (E), 0.1% Proof Strength (0.1%PS), Ultimate Tensile Strength (UTS) and failure strain (\(e_{\text{Failure}}\)) of the test alloys as extruded, hipped and heat treated are listed in Table 8.10a–e. All heat treatment was at 1000°C for 1 hour followed by oil quench (designated in the tables as 'OQ'), except those specified otherwise. The relative uncertainty of these tensile results were evaluated (see Section 7.4.4) as ±8% for E, ±3% for UTS and PS, and ±5% for \(e_{\text{Failure}}\). A summary of the tensile data is shown in Figure 8.4.

Table 8.10a  Tensile data for extruded Fe-Cr-B alloys.

<table>
<thead>
<tr>
<th>ALLOY</th>
<th>ROUTE</th>
<th>E (GPa)</th>
<th>0.1%PS (MPa)</th>
<th>UTS (MPa)</th>
<th>(e_{\text{Failure}}) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Fe}<em>{80}\text{Cr}</em>{15}\text{B}_{5})</td>
<td>RCX440</td>
<td>182</td>
<td>288</td>
<td>686</td>
<td>12.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>191</td>
<td>278</td>
<td>721</td>
<td>16.0</td>
</tr>
<tr>
<td>(\text{Fe}<em>{70}\text{Cr}</em>{20}\text{B}_{10})</td>
<td>RCX442</td>
<td>230</td>
<td>497</td>
<td>1066</td>
<td>7.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>227</td>
<td>487</td>
<td>1054</td>
<td>9.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>230</td>
<td>497</td>
<td>1044</td>
<td>6.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>249</td>
<td>487</td>
<td>1019</td>
<td>6.9</td>
</tr>
<tr>
<td>(\text{Fe}<em>{75}\text{Cr}</em>{20}\text{B}_{5})</td>
<td>RCX442+OQ</td>
<td>268</td>
<td>977</td>
<td>1281</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>257</td>
<td>975</td>
<td>1278</td>
<td>3.2</td>
</tr>
<tr>
<td>(\text{Fe}<em>{85}\text{Cr}</em>{25}\text{B}_{10})</td>
<td>RCX441</td>
<td>181</td>
<td>388</td>
<td>689</td>
<td>12.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>219</td>
<td>387</td>
<td>676</td>
<td>18.0</td>
</tr>
<tr>
<td>(\text{Fe}<em>{85}\text{Cr}</em>{25}\text{B}_{10})</td>
<td>RCX441+OQ</td>
<td>216</td>
<td>377</td>
<td>630</td>
<td>10.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>240</td>
<td>373</td>
<td>582</td>
<td>10.5</td>
</tr>
<tr>
<td>(\text{Fe}<em>{65}\text{Cr}</em>{25}\text{B}_{10})</td>
<td>RCX443</td>
<td>215</td>
<td>615</td>
<td>943</td>
<td>8.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>157</td>
<td>622</td>
<td>995</td>
<td>7.5</td>
</tr>
</tbody>
</table>
### RESULTS AND DISCUSSION

**Table 8.10b** Tensile data for alloys with the base composition Fe$_{70}$Cr$_{18}$Mo$_2$B$_{10}$.

<table>
<thead>
<tr>
<th>ALLOY ROUTE</th>
<th>E (GPa)</th>
<th>0.1%PS (MPa)</th>
<th>UTS (MPa)</th>
<th>$e_{\text{Failure}}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$<em>{70}$Cr$</em>{18}$Mo$<em>2$B$</em>{10}$</td>
<td>Hip@950°C</td>
<td>254</td>
<td>1094</td>
<td>1268</td>
</tr>
<tr>
<td>@1000°C</td>
<td>260</td>
<td>995</td>
<td>1392</td>
<td>0.87</td>
</tr>
<tr>
<td>@1000°C</td>
<td>254</td>
<td>1119</td>
<td>1467</td>
<td>1.21</td>
</tr>
<tr>
<td>@1050°C</td>
<td>255</td>
<td>1069</td>
<td>1616</td>
<td>1.30</td>
</tr>
<tr>
<td>Fe$<em>{70}$Cr$</em>{18}$Mo$<em>2$B$</em>{10}$</td>
<td>RCX445+</td>
<td>229</td>
<td>925</td>
<td>1258</td>
</tr>
<tr>
<td>Temper</td>
<td>250</td>
<td>984</td>
<td>1333</td>
<td>3.8</td>
</tr>
<tr>
<td>RCX445+OQ</td>
<td>252</td>
<td>1129</td>
<td>1338</td>
<td>6.4</td>
</tr>
<tr>
<td></td>
<td>290</td>
<td>1193</td>
<td>1328</td>
<td>3.7</td>
</tr>
</tbody>
</table>

Note: (i) Alloy composition: Fe$_{84}$Cr$_{17.8}$Mo$_{3.73}$B$_{2.63}$, in wt%;
(ii) Heat treatment: @1000°C 1hr water quench + 600°C 4hr temper.

**Table 8.10c** Tensile data for carburised Fe$_{70}$Cr$_{18}$Mo$_2$B$_{10}$ alloys.

<table>
<thead>
<tr>
<th>ALLOY ROUTE</th>
<th>E (GPa)</th>
<th>0.1%PS (MPa)</th>
<th>UTS (MPa)</th>
<th>$e_{\text{Failure}}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$<em>{70}$Cr$</em>{18}$Mo$<em>2$B$</em>{10}$+C</td>
<td>RCX445$_{+HT}$</td>
<td>266</td>
<td>1034</td>
<td>1492</td>
</tr>
<tr>
<td>RCX445$_{+HT}$</td>
<td>230</td>
<td>995</td>
<td>1243</td>
<td>0.87</td>
</tr>
</tbody>
</table>

Note: (i) Alloy composition: Fe$_{84}$Cr$_{17.8}$Mo$_{3.73}$B$_{2.63}$, in wt%;
(ii) Heat treatment: @1000°C 1hr water quench + 600°C 4hr temper.
### Table 8.10d Tensile data for extruded Fe-Cr-Mo-B alloys.

<table>
<thead>
<tr>
<th>ALLOY</th>
<th>ROUTE</th>
<th>E  (GPa)</th>
<th>0.1%PS (MPa)</th>
<th>UTS (MPa)</th>
<th>e_Failure (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe_{81}Cr_{9}Mo_{4}B_{6}</td>
<td>RCX477</td>
<td>190</td>
<td>945</td>
<td>1342</td>
<td>12.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>202</td>
<td>930</td>
<td>1318</td>
<td>11.0</td>
</tr>
<tr>
<td></td>
<td>RCX477+OQ</td>
<td>242</td>
<td>895</td>
<td>1273</td>
<td>9.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>248</td>
<td>860</td>
<td>1273</td>
<td>7.2</td>
</tr>
<tr>
<td>Fe_{70}Cr_{10}Mo_{8}B_{12}</td>
<td>RCX478</td>
<td>203</td>
<td>1134</td>
<td>1721</td>
<td>4.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>237</td>
<td>1193</td>
<td>1691</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>RCX478+OQ</td>
<td>248</td>
<td>1079</td>
<td>1666</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>262</td>
<td>1069</td>
<td>1666</td>
<td>3.5</td>
</tr>
</tbody>
</table>

### Table 8.10e Tensile data for extruded Fe-Cr-Ni-B alloys.

<table>
<thead>
<tr>
<th>ALLOY</th>
<th>ROUTE</th>
<th>E  (GPa)</th>
<th>0.1%PS (MPa)</th>
<th>UTS (MPa)</th>
<th>e_Failure (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe_{63}Cr_{18}Ni_{14}B_{5}</td>
<td>RCX470</td>
<td>133</td>
<td>358</td>
<td>726</td>
<td>10.0</td>
</tr>
<tr>
<td>(Matrix: fcc)</td>
<td></td>
<td>138</td>
<td>348</td>
<td>709</td>
<td>19.0</td>
</tr>
<tr>
<td>Fe_{55}Cr_{24}Ni_{11}B_{10}</td>
<td>RCX472</td>
<td>206</td>
<td>608</td>
<td>1159</td>
<td>8.0</td>
</tr>
<tr>
<td>(Matrix: fcc)</td>
<td></td>
<td>227</td>
<td>572</td>
<td>1144</td>
<td>9.5</td>
</tr>
<tr>
<td></td>
<td>RCX472+OQ</td>
<td>199</td>
<td>487</td>
<td>945</td>
<td>8.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>216</td>
<td>472</td>
<td>895</td>
<td>15.2</td>
</tr>
</tbody>
</table>
Figure 8.4  Summary of tensile data (UTS, VPN and Young's modulus vs. elongation), [91Mio].
8.6 Analysis of the Effect of Consolidation Conditions on Mechanical Properties

8.6.1 Effect of Hipping Temperature

A comparison was made of the tensile data of alloys processed via Hot Isostatic Pressing (HIPping) atomised powders at different temperatures to analyse the effect of hipping temperature on the mechanical properties. The hipping conditions are listed in Table 7.3 and the tensile results for the hipped alloys in Table 8.10b.

No significant difference was found in Young’s modulus, nor proof strength for alloys processed at different hipping temperatures. However there is a fairly consistent increase in the UTS and failure strain with an increase in hipping temperature. A high hipping temperature, therefore, appeared to optimise the overall tensile properties at no loss in elastic modulus. This is probably due to a denser and more homogeneous structure achieved in the alloys as a result of consolidation at a higher temperature.

8.6.2 Effect of Consolidation Route

Another comparison was made between the mechanical properties of the hipped and the extruded alloys of the same composition to examine the effect of different consolidation routes on the properties of the alloys. The alloys chosen for the comparison are RCX445 versus HIPped both of nominally the same composition Fe70Cr18Mo2B10. There is a small difference, however, in real compositions in the two alloys (see Table 7.5) because of the different atomised powders used (Osprey powders for the hipped alloys and Surrey powders the extruded). The tensile properties of the alloys are listed in Table 8.10b and c.

A comparison between the Young’s modulus from the two sets of data shows that the hipped alloys have in general higher Young’s modulus (254–260 GPa compared to 229–250 GPa) whereas the extruded ones exhibit a much higher elongation (4–6% compared to 0.7–1.3%) with the UTS only slightly lower than alloys consolidated at a lower hipping temperature. After being oil quenched, however, the extruded alloys show a marked improvement in proof strength and a Young’s modulus at a level close to or higher than the hipped while maintaining the high elongation before the treatment.
RESULTS AND DISCUSSION

The improvement in mechanical properties, particularly in the Young's modulus, obtained from the tensile tests on such heat-treated specimens of the extruded alloys, implied that the rate of cooling after extrusion could be an important variable. The cooling conditions following the fabrication process were investigated through examinations of hardenability and the equivalent cooling rate was found to lie between those of oil quench and air cool (see the next section). An improvement in mechanical properties can, therefore, be expected by an increase in the rate of cooling following consolidation.

The porosity level in the hipped alloy appears to play an important role in the performance of the alloys. It can be seen from the microstructure examination of the consolidated materials that there is a higher degree of porosity in the extruded alloys (~3 vol%), compared to the hipped ones (~1 vol%, see Table 8.8). Apparently hipping proved to be a more efficient processing route in producing denser materials than extrusion. Further discussions on the effect of porosity on the elastic properties based on Eshelby method will be presented in Section 8.9.5.

The difference in the real compositions of the two groups of alloys may have contributed to the difference in the mechanical properties. According to the chemical analysis results (Table 7.5), the chromium, boron, and in particular the carbon content, are higher in the hipped alloys than those in the extruded alloys (HIPped: Cr19.2/B2.18/C0.09 wt%, compared to the extruded RCX445: Cr16.6/C0.045/B2.03, wt%). The higher boron content would result in better performance with high boride in the alloy, and the chromium and carbon may improve the elastic modulus of the alloy through improving the modulus of the matrix. No evidence was found for any tetragonality in the matrix phase for any of the extruded alloys produced in Surrey even after oil-quenching. This correlates with the consistently lower carbon content of these extruded alloys and may be a significant factor in the lower hardness, yield strength, and UTS observed.

A check was made on the maximum adiabatic heating due to extrusion process, with specific reference to the possibility of locally exceeding the calculated solidus temperature of the alloys [91Bal]. A considerable temperature rise (ΔT) was predicted, and for some alloys the predicted ΔT suggests the solidus would be exceeded, but the calculation does not include any heat loss to the container and no metallographic evidence for melting has been detected.[91Bal].
8.7 Correlation of Hardness with Elastic Modulus

8.7.1 Hardness of Consolidated Alloys

The hardness measurement results of the consolidated Fe-Cr-B, Fe-Cr-Ni-B, and the Fe-Cr-Mo-B alloys are listed in Table 8.11 (in bold to differentiate from those of the heat treated). Extruded alloys RCX440 and RCX441 which were designed with 5 at%B have a hardness value of HV 210–220 whereas RCX442 and RCX443, with 10 at%B, of HV 320–330, which is consistent with the respective amount of borides in the alloys. The hardness of the quaternary Fe-Cr-Mo-B alloys has a much higher value of HV 400–600 which is probably due to the existence of the Mo-rich boride phase in the alloy.

8.7.2 Hardness of Alloys after Heat Treatment

The hardness of the heat treated alloys are listed in Table 8.11 together with their heat treatment history. There is a consistent increase in hardness among the quenched alloys and the increase can be as high as HV ~160 as in the case of the extruded RCX442. Tempering at 400°C for 5 hours followed by furnace cool did not decrease the hardness level of the alloys (RCX442 and RCX445). Discussion on how hardness and heat treatment correlate with elastic properties of alloys will be presented in the following section.

The observed hardness (see Table 8.11) of the consolidated test alloys as received and after a series of heat treatment (annealing at 1000°C followed by oil, air and furnace cool) provide the data necessary to determine the actual cooling conditions following consolidation process. There is a consistent hardness increase in all alloys being oil quenched. Measured hardness of the HIPped, RCX442 and RCX445 as received and after various heat treatment was plotted in Figure 8.5. It was shown in this plot that the cooling condition following extrusion lies between air cooling and furnace cooling.
### RESULTS AND DISCUSSION

Table 8.11 Measured hardness of the test alloys as extruded and after various heat treatment.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Composition (at%)</th>
<th>Hardness (VPN)</th>
<th>Processing route or Heat treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>HIPped</td>
<td>Fe\textsubscript{70}Cr\textsubscript{18}Mo\textsubscript{2}B\textsubscript{10}</td>
<td>652</td>
<td>As received</td>
</tr>
<tr>
<td></td>
<td></td>
<td>665</td>
<td>1000°C 1hr + oil quench</td>
</tr>
<tr>
<td></td>
<td></td>
<td>653</td>
<td>1000°C 1hr + air cool</td>
</tr>
<tr>
<td></td>
<td></td>
<td>639</td>
<td>1000°C 1hr + furnace cool</td>
</tr>
<tr>
<td>RCX440</td>
<td>Fe\textsubscript{80}Cr\textsubscript{15}B\textsubscript{5}</td>
<td>210</td>
<td>As received</td>
</tr>
<tr>
<td>RCX441</td>
<td>Fe\textsubscript{75}Cr\textsubscript{20}B\textsubscript{5}</td>
<td>219</td>
<td>As received</td>
</tr>
<tr>
<td>RCX442</td>
<td>Fe\textsubscript{70}Cr\textsubscript{20}B\textsubscript{10}</td>
<td>326</td>
<td>As received</td>
</tr>
<tr>
<td></td>
<td></td>
<td>424</td>
<td>1000°C 1hr + oil quench</td>
</tr>
<tr>
<td></td>
<td></td>
<td>437</td>
<td>1000°C 1hr + oil quench + temper</td>
</tr>
<tr>
<td></td>
<td></td>
<td>384</td>
<td>1000°C 1hr + air cool</td>
</tr>
<tr>
<td></td>
<td></td>
<td>282</td>
<td>1000°C 1hr + furnace cool</td>
</tr>
<tr>
<td>RCX443</td>
<td>Fe\textsubscript{65}Cr\textsubscript{25}B\textsubscript{10}</td>
<td>323</td>
<td>As received</td>
</tr>
<tr>
<td>RCX445</td>
<td>Fe\textsubscript{70}Cr\textsubscript{18}Mo\textsubscript{2}B\textsubscript{10}</td>
<td>421</td>
<td>As received</td>
</tr>
<tr>
<td></td>
<td></td>
<td>470</td>
<td>1000°C 1hr + oil quench</td>
</tr>
<tr>
<td></td>
<td></td>
<td>475</td>
<td>1000°C 1hr + oil quench + temper</td>
</tr>
<tr>
<td></td>
<td></td>
<td>454</td>
<td>1000°C 1hr + air cool</td>
</tr>
<tr>
<td></td>
<td></td>
<td>328</td>
<td>1000°C 1hr + furnace cool</td>
</tr>
<tr>
<td>RCX470</td>
<td>Fe\textsubscript{55}Cr\textsubscript{24}Ni\textsubscript{11}B\textsubscript{10}</td>
<td>412</td>
<td>As received</td>
</tr>
<tr>
<td>RCX472</td>
<td>Fe\textsubscript{63}Cr\textsubscript{18}Ni\textsubscript{14}B\textsubscript{5}</td>
<td>306</td>
<td>As received</td>
</tr>
<tr>
<td>RCX477</td>
<td>Fe\textsubscript{81}Cr\textsubscript{9}Mo\textsubscript{4}B\textsubscript{6}</td>
<td>423</td>
<td>As received</td>
</tr>
<tr>
<td>RCX478</td>
<td>Fe\textsubscript{72}Cr\textsubscript{12}Mo\textsubscript{6}B\textsubscript{10}</td>
<td>552</td>
<td>As received</td>
</tr>
</tbody>
</table>
Figure 8.5  

Hardness of consolidated alloys (HIPped, RCX442, and RCX445) as received and after heat treatment. O.Q. = Oil Quench; A.C. = Air Cool; A.R. = As Received; F.C. = Furnace Cool.

8.7.3 Analysis of Modulus with Respect to Observed Hardness

Tensile tests on quenched specimens exhibited a marked improvement in mechanical properties for some alloy compositions, particularly in the Young's modulus, emphasising that the alloy hardness is a critical factor. It is generally considered, however, that the modulus of an alloy does not alter with a change in hardness due to heat treatment. How the hardness is related to the modulus of an alloy is still not clear. Miłownik [91Mio] has attempted to explain the indirect effect of alloy hardness on the elastic modulus observed from alloy systems of interest in this investigation, and this will be discussed below.

As it is usually taken that there are no significant changes in modulus with heat treatment in steels, the effect of heat treatment and the hardenability of these alloys must indirectly reflect
other changes in structure which in turn affect modulus. A magneto-strictive effect which is exhibited in Fe-Cr alloys, as discussed in the literature survey (Section 2.5.6), could provide a mechanism for the correlation of alloy hardness with modulus.

According to the analysis of elastic properties of Fe-Cr alloys from the literature, the modulus of these alloys containing little or no carbon shows a marked elastic modulus anomaly which is absent in alloys containing higher carbon content (Figure 2.7). The figure also shows that the magnetostriction and magneto-damping effects are maximum around 10 wt%Cr, which is approximately where the chromium content lies for the matrix of the model alloys in this investigation.

Following the above argument, if there is a reasonably large magneto-strictive effect in these alloys, this would account for the fact that the modulus seems to scale with an increase in hardness. It is however obviously necessary to differentiate between the overall hardness of the alloy and the hardness of the matrix, as it is largely the latter which will be a measure of domain mobility. Tests on alloys which have had their matrix hardness changed appreciably by quenching, but where the boride volume fraction is unchanged, may therefore provide some interesting information to test the role of magnetostriction. It could also lead to a different philosophy in designing the matrix composition, since there would be an additional advantage in reducing the intrinsic magneto-strictive coefficient.

There have been considerable difficulties in quantitative metallography, due to the interference from magnetic effects with imaging of microstructure. The increased sensitivity of the model alloys to magnetic interference is however consistent with the hypothesis reached earlier, that the lower moduli of these alloys can be attributed to mobile magnetic domains.

A magneto-strictive mechanism might also provide a basic explanation for the role of carbon, which clearly acts as an appreciably hardening agent and enhances the tetragonality of martensite. It has already been noted previously that the presence of martensite per se cannot provide an adequate explanation. As the alloys atomised at Surrey have a lower carbon content than the alloys produced by Osprey, this suggests that the low modulus in the Surrey alloys may have its origin in mobile magnetic domains which are capable of being pinned as the result of an oil quench plus tempering treatment. This should be confirmed by examinations on alloys involving the addition of carbon, which is expected to increase the pinning of domains in
addition to raising the hardness and UTS.

The main implication of the magnetostriction effect is that an analysis of the observed modulus results of the model alloys are likely to require additional variables for the matrix modulus which not only depends on Cr content, as already described, but also possibly on locking domains. The possibility that the modulus of the matrix phase can be varied by heat treatment also has implications for the application of Eshelby theory to the modulus of the alloys, since the modulus of the matrix can no longer be considered a constant. The modulus of the matrix, in practice, could be considerably low, and the value used in Section 5.4.1 is therefore a maximum bound.

8.8 Predicted Young’s Moduli of the Fe-TM-B Alloys

For the preliminary prediction of the Young’s moduli of the Fe-TM-B alloy, the Young’s modulus of the matrix is estimated based on the value for bcc α-Fe (around 208 GPa [72Les]), and various effect of alloying elements in the matrix. Boron content in the matrix is in general very low for all the designed alloys (0.06–0.018 at%B), and has been taken as negligible in terms of its effect on the Young’s modulus of the matrix. The Mo content in the matrix is also low (~0.08 at%Mo) in all the Mo-containing alloys, and therefore the Young’s moduli of the matrix are taken to depend mainly on the Cr content in these alloys. The increase in the matrix modulus due to Cr is given by a factor of 0.5 GPa for the Cr percentage (Section 5.4.2). In addition to the effect of Cr on the modulus of the matrix, the effect of Ni, according to Leslie [72Les], is to reduce the Young’s modulus of steels by 2 GPa per atomic percent of Ni. The Cr and Ni compositions in the matrix of the test alloys are taken from results of the phase equilibrium calculations (Table 8.1), and the equivalent Young’s modulus for the matrix (E_{Matrix}) was derived assuming simple addition of the two contributions.

The Young’s modulus of the boride is taken as 420 GPa, an estimated value obtained at the earlier stage of this work (Section 5.4.1). The measured volume fractions of borides in the test alloys (Table 8.7) are input in the Eshelby calculations. The aspect ratio of the boride inclusions is taken as 1 owing to the spherical appearance of the boride particles observed in the test alloys of the present study. The Poisson’s ratio of 0.33 for the Fe-based matrix and 0.24 for the borides are used in the prediction. The calculated moduli are given in Table 8.12.
Table 8.12 Predicted Young’s moduli of the designed alloys using Eshelby’s model.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Cr, Ni at% in Matrix</th>
<th>$E_{\text{Matrix}}$ GPa</th>
<th>Vol% Boride</th>
<th>$E_{\text{Boride}}$ GPa</th>
<th>Predicted $E_{\text{Alloy}}$, GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>RCX440</td>
<td>Cr$_{14.5}$</td>
<td>215</td>
<td>10</td>
<td>420</td>
<td>230</td>
</tr>
<tr>
<td>RCX441</td>
<td>Cr$_{14.8}$</td>
<td>215</td>
<td>14</td>
<td>420</td>
<td>236</td>
</tr>
<tr>
<td>RCX442</td>
<td>Cr$_{9.32}$</td>
<td>213</td>
<td>28</td>
<td>420</td>
<td>257</td>
</tr>
<tr>
<td>RCX443</td>
<td>Cr$_{9.63}$</td>
<td>213</td>
<td>20</td>
<td>420</td>
<td>244</td>
</tr>
<tr>
<td>RCX445</td>
<td>Cr$_{9.87}$</td>
<td>213</td>
<td>25</td>
<td>420</td>
<td>252</td>
</tr>
<tr>
<td>RCX470</td>
<td>Cr$<em>{12.2}$Ni$</em>{16.5}$</td>
<td>181</td>
<td>14</td>
<td>420</td>
<td>203</td>
</tr>
<tr>
<td>RCX472</td>
<td>Cr$<em>{12.4}$Ni$</em>{15.7}$</td>
<td>183</td>
<td>31</td>
<td>420</td>
<td>235</td>
</tr>
<tr>
<td>RCX477</td>
<td>Cr$_{10.0}$</td>
<td>213</td>
<td>19</td>
<td>420</td>
<td>241</td>
</tr>
<tr>
<td>RCX478</td>
<td>Cr$_{9.87}$</td>
<td>213</td>
<td>24</td>
<td>420</td>
<td>250</td>
</tr>
<tr>
<td>HIP8–11</td>
<td>Cr$_{9.87}$</td>
<td>213</td>
<td>30</td>
<td>420</td>
<td>260</td>
</tr>
</tbody>
</table>

The predicted modulus values are high compared to the measured values from tensile test (see Table 8.10). More accurate results will not be achieved unless the effect of phase and microstructure variables on the modulus of alloys is understood. Further modelling based on the Eshelby method using modified input of constituent variables is presented in the next section, following analyses of the effect of microstructural features on alloy modulus.

8.9 Discussion on the Effect of Phase and Microstructure Variables on Alloy Modulus

8.9.1 Effect of Matrix Composition

The Young’s modulus for the matrix has been initially estimated based on the empirical relation taking into account Cr and Ni content in the matrix. In the preliminary prediction of Young’s moduli for the designed model alloys, Eshelby calculations have been based on such estimated modulus values of the matrix. However the experimental data obtained from tensile test of the designed alloys are in most cases lower than the predicted ones, indicating that some additional
RESULTS AND DISCUSSION

factors have to be taken into account in the model treatment.

If the low modulus values obtained from mechanical testing of the extruded Fe-Cr-B alloys are attributed to the omission of Mo boride, there would be no reason why alloys containing molybdenum (RCX445) also showed a low modulus and UTS, when it is clear from microscopic and X-ray examination that the phases present are identical to those present in the base alloy. By contrast, powders produced by Osprey and subsequently hipped exhibited hardness and Young's modulus close to those obtained with the base alloy. It is apparently essential to take into account both major and minor elements in the matrix.

The chemical analysis suggests that the most obvious difference lies in minor changes in nitrogen and particularly carbon content (see Table 7.5). The Surrey alloys are higher in nitrogen but substantially lower in carbon content than the equivalent powders produced by Osprey (the base composition consists of 0.1 wt% C). Carbon could therefore be playing a more significant role than previously otherwise expected. Checks have been made [91Bal] to establish whether there is any nitrogen segregation to the interfaces between boride particles and the matrix, on the assumption that this might reduce the transfer of elastic strain implicit in Eshelby's model. No evidence was found for local enrichment in nitrogen. Where changes were observed in the chromium content, this could be correlated with a reaction with the crucible, which was also the likely source of any silicon pick-up. The latter was also likely to contribute to the observed lower Young's modulus considering the deteriorating effect of silicon suggested by Leslie [72Les].

No evidence was found for any tetragonality in the matrix phase for any of the alloys produced in the Surrey atomiser, even after oil-quenching. This correlates with the consistently lower carbon content of these alloys, and also indicates that carbon content may be a significant factor in the lower hardness, yield strength, and UTS observed. Experiments have been conducted to carburise alloy RCX445 in order to check this hypothesis. The low tensile data, however, obtained on RCX445C, does not eliminate the possible effect of carbon because the carbon addition was much higher than the amount intendedπ.

π The quantity of graphite used to carburise RCX445 was chosen to be considerably larger than a theoretically necessary amount owing to the anticipated difficulties in practice. Unfortunately the carbon content in the carburised alloy turned out to be unexpectedly high.
RESULTS AND DISCUSSION

Estimation of the Young's modulus of the matrix, after having taken into account all the above mentioned factors, is therefore not straightforward. A lower-upper bound of 160 ~ 215 GPa was considered as an estimated range of moduli for the matrix.

8.9.2 Effect of Nature of Matrix

Comparisons were made between the results obtained in this work which relate to (a) alloys designed with a ferritic matrix and Cr boride, (b) alloys with a transformed austenitic matrix and equal amount of the same boride. Mechanical properties (mean values of the measured Young's modulus, UTS, and elongation) for each of these alloys are compared in Figure 8.6. For the low boron alloys (RCX440 and RCX441, 5 at%B), no significant difference was observed in their mechanical properties. However, for the high boron alloys (RCX442 and RCX443, 10 at%B), those

![Figure 8.6](image-url)  

**Figure 8.6** Comparison of mechanical properties between model alloys with a ferritic and a transformed austenitic matrix.
RESULTS AND DISCUSSION

with a transformed austenitic matrix showed a higher Young’s modulus, higher UTS at roughly the same level of elongation.

While tensile test results of most of the heat treated alloys exhibited improvements in overall mechanical properties and the elastic modulus in particular, alloys of high boron, 10 at%B with a transformed austenitic matrix (RCX442) appear to be more advantageous than those of low boron, 5 at%B with a ferritic one (RCX441), considering the higher increase in the UTS after the alloys being quenched (Figure 8.7).

![Graph showing mechanical properties comparison](image)

**Figure 8.7** Comparison of mechanical properties (before and after oil quench) between alloys designed with a ferritic and a transformed austenitic matrix.

Mechanical properties of the extruded alloys designed with a stable austenitic matrix at room temperature (alloy code: RCX470 and RCX472) were compared with those of the similar level of
RESULTS AND DISCUSSION

boron content with a martensitic matrix (alloy code: RCX477 and RCX478) in Figure 8.8. It is clearly shown that austenitic alloys exhibit significantly lower UTS. Although this was compensated by good elongations and fairly good modulus for those with high boron content, such alloys would only be considered when the major selection criterion is for adequate corrosion resistance.

![Comparison of mechanical properties between model alloys designed with an austenitic matrix at room temperature and a martensitic matrix.](image)

Figure 8.8  Comparison of mechanical properties between model alloys designed with an austenitic matrix at room temperature and a martensitic matrix.

It can be concluded, form comparisons made between tensile data of test alloys designed with different matrices, that a martensitic or a transformed austenitic matrix has to be considered if a high modulus is the primary concern in designing alloys.
8.9.3 Effect of Boride Type

In the initial treatment of Eshelby modelling, an estimated modulus for the borides was used in predicting the Young’s modulus for the alloys which actually contains a mixture of two types of borides (Cr-rich $M_2B_{\text{orth}}$ and Mo-rich $M_3B_2$). These two borides, however, may not necessarily have the same effect on the modulus of the alloys.

The alloy with the base composition in the initial investigation showed a considerably higher Young’s modulus than the test alloys which contain only the $M_2B_{\text{orth}}$ Cr-rich borides designed

![Comparison of tensile properties between alloys with Cr- and Mo-borides.](image)

**Figure 8.9** Comparison of tensile properties between alloys with Cr- and Mo- borides.
RESULTS AND DISCUSSION

in the present work. This suggests an important function played by the existence of Mo-boride in the alloy. The most obvious conclusion would be that Mo boride has a higher Young's modulus value than Cr one. This could be proven by comparing tensile properties of alloys containing only the Cr-boride with those containing only the Mo-ones.

However, the comparison between the elastic properties of the two groups of materials (Figure 8.9) shows that Mo-containing $\text{M}_3\text{B}_2$ boride are not more effective than the Cr borides in terms of increasing the modulus. These alloys have nevertheless exhibited a significantly higher hardness and UTS. Better tensile results were again obtained from alloys after quenching but it was now clear that neither of the two borides was, when separated, as effective as the borides present in the base alloy. The co-existence of the two must, therefore, be a critical factor.

8.9.4 Effect of Boride Amount

Test alloys have been designed with different levels of borides so that comparisons could be made between tensile results of the alloys to derive the effect of amount of boride on the elastic properties for a given matrix.

All the Young's modulus data obtained from tensile test of the model alloys were plotted in Figure 8.10. Eshelby curves were calculated using the estimated ranges of moduli for the matrix: a lower-upper bound of 160 ~ 215 GPa for the matrix, taking into account the magnetostriction effect; and the predicted value of 420 GPa for the borides (Section 6.4.1), allowing the uncertainty of ±40 GPa for the estimation. The comparison between Eshelby curves and the experimental points shown in Figure 8.10 allows a satisfactory explanation for the majority of the available results, considering a fairly large scatter observed among the Young's modulus data from tension test results.

Eshelby's approach produced a correct trend in alloy elastic modulus with volume fraction of borides. However the accuracy of the correlation is difficult to assess because of the large scatter band in the tensile data observed. This suggests that a further crucial factor has to be considered, usually the effect of porosity. This effect has also been modelled using Eshelby method, as will be discussed in the next section.
RESULTS AND DISCUSSION

Figure 8.10 Comparison between Eshelby curves and tensile test results of model alloys with various boride content. The estimated Young's modulus range was taken for the matrix (160–215 GPa) and the borides (420±40 GPa).

8.9.5 Effect of Porosity

Examination of the microstructure of the consolidated test alloys designed in this investigation revealed the presence of a considerable degree of porosity or consolidation defects. A significant contribution to the deterioration of the elastic properties might therefore be due to the incomplete consolidation. Estimation of this effect was made using Eshelby method by treating the voids as an imaginary inclusion with the same function as a normal inclusion phase, such as a distribution of a boride phase, except that the Young's modulus of the voids was taken as zero. The contribution due to the voids was taken as the difference between the modulus of the solid material and the calculated modulus value of the imaginary material containing voids.
Eshelby calculations in the estimation of the effect of the voids were based on the measured porosity in the consolidated alloys. An average modulus value of 190 GPa for the matrix was used in the calculations. The Young's moduli obtained from tensile test of the model alloys were modified by deducting the contribution due to the voids from the measured results. Examples of this modification procedure taken from some of the model alloys are shown in Table 8.12a.

Table 8.12a Modification of Young's modulus by deducting the effect of porosity based on Eshelby method.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>E_{Alloy} GPa</th>
<th>Vol%</th>
<th>Predicted E_{Void} GPa</th>
<th>Contribution Due to Voids</th>
<th>Modified E_{Alloy}, GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>RCX440</td>
<td>182</td>
<td>~3</td>
<td>179</td>
<td>11 (=190-179)</td>
<td>193 (=182+11)</td>
</tr>
<tr>
<td>RCX443</td>
<td>157</td>
<td>~10</td>
<td>155</td>
<td>35 (=190-155)</td>
<td>192 (=157+35)</td>
</tr>
<tr>
<td>RCX445</td>
<td>229</td>
<td>~3</td>
<td>179</td>
<td>11 (=190-179)</td>
<td>240 (=229+11)</td>
</tr>
<tr>
<td>RCX477</td>
<td>190</td>
<td>~7</td>
<td>165</td>
<td>25 (=190-165)</td>
<td>215 (=190+25)</td>
</tr>
<tr>
<td>HIP8</td>
<td>254</td>
<td>~1</td>
<td>186</td>
<td>4 (=190-186)</td>
<td>258 (=254+4)</td>
</tr>
</tbody>
</table>

The resultant modulus, modified by deducting the deterioration due to the porosity present in each alloy, was then compared with Eshelby curves in Figure 8.11. The modulus results for the Ni-containing austenitic alloys are exceptionally low and have been excluded from the plot. The modulus points for the heat treated alloys were marked with a different symbol for clearance reason. The modified Young's modulus points appear, in general, to fit better with the Eshelby curves. The majority of the modulus obtained from the heat treated alloys lie above the upper curve of Eshelby's model, which can be explained by an increase in the modulus of the matrix after heat treatment. This is consistent with the hypothesis of the magnetostriction effect discussed in Section 8.7.3. The consistency shown in Figure 8.11 supported the proposed role of porosity, as well as the use of an Eshelby treatment on the correlation of porosity with the observed deficiency in elastic properties.
RESULTS AND DISCUSSION

Figure 8.11 Eshelby curves with Young’s modulus modified by deducting the deterioration due to the porosity present in the test alloys.

8.10 Optimisation of Alloy Compositions

It has been shown clearly, from Eshelby calculations and the testing results obtained in the present work, that a high volume fraction of borides is essential in order to achieve a high elastic modulus. It is therefore desirable to design alloys which contain as high as possible an amount of borides, although the highest volume fraction of borides is restricted by a number of crucial factors as discussed below.

High boron concentration is necessary in order to produce sufficient amount of boride in the alloys. Compositions of alloys could be selected to obtain alloys with equal amount of Mo-boride and Cr-boride in a transformed austenite matrix, following the previously established argument
RESULTS AND DISCUSSION

that the two types of borides are both required for a favoured modulus of the alloy. The boron content, on the other hand, is confined by the liquidus of the alloy, which should not exceed 1480°C (highest liquidus of model alloys already produced without problems) in order to avoid any technical difficulties likely to occur in the processing of the alloys.

The carbon content has to be controlled and the level in the base composition (~0.045 wt%) is so far considered as optimum. A check still needs to be made against whether adding the appropriate amount of carbon to the alloys would (a) further increase the hardness, (b) produce a tetragonal martensite, and (c) increase the modulus. In addition, heat treatable alloys were advantageous as observed from the best results obtained so far.

Two final alloy compositions, based in Fe-Cr-Mo-B system and designated as SU9 and SU10, are determined based on the above analyses. Table 8.13 lists the two alloy compositions, in both weight and atomic percentages, together with the structure of the matrix at room temperature. The calculated proportions and compositions of equilibrium phases in the proposed optimum alloys at 1000°C are given in Table 8.14, and the calculated liquidus and solidus in Table 8.15.

Predictions of Young’s modulus based on Eshelby method are performed for the optimised alloys. The Young’s modulus of the matrix is taken to be 215 GPa, the upper limit of the modulus range previously used for the matrix, as these alloys possess a higher hardness and consequently the magneto-striction effect is expected to diminish. An estimated modulus of

Table 8.13  Designed alloy compositions with the matrix structure at room temperature, boride type and amounts. Alloy compositions are given in both atomic and weight percentages.

<table>
<thead>
<tr>
<th>Alloy Code</th>
<th>Composition (at%)</th>
<th>Composition (wt%)</th>
<th>Matrix structure (Room temp.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SU9</td>
<td>Fe$<em>{68.1}$Cr$</em>{17.7}$Mo$<em>4$B$</em>{10.2}$</td>
<td>Fe$<em>{72.86}$Cr$</em>{17.66}$Mo$<em>{7.34}$B$</em>{2.11}$</td>
<td>Martensite</td>
</tr>
<tr>
<td>SU10</td>
<td>Fe$<em>{67}$Cr$</em>{17}$Mo$<em>4$B$</em>{12}$</td>
<td>Fe$<em>{72.8}$Cr$</em>{17.2}$Mo$<em>{7.47}$B$</em>{2.53}$</td>
<td>Martensite</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

Table 8.14 Calculated proportions and compositions of equilibrium phases for the proposed optimum alloys at 1000°C.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Phase</th>
<th>Amount (mol%)</th>
<th>Composition (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Amount</td>
<td>Fe</td>
</tr>
<tr>
<td>SU9</td>
<td>fcc</td>
<td>73.0</td>
<td>87.5</td>
</tr>
<tr>
<td></td>
<td>M₂B_orth</td>
<td>12.6</td>
<td>16.7</td>
</tr>
<tr>
<td></td>
<td>M₃B₂</td>
<td>14.4</td>
<td>14.2</td>
</tr>
<tr>
<td>SU10</td>
<td>fcc</td>
<td>67.3</td>
<td>90.1</td>
</tr>
<tr>
<td></td>
<td>M₂B_orth</td>
<td>16.0</td>
<td>20.4</td>
</tr>
<tr>
<td></td>
<td>M₃B₂</td>
<td>16.7</td>
<td>18.4</td>
</tr>
</tbody>
</table>

Table 8.15 Calculated liquidus and solidus of the proposed optimum alloys.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Nominal composition</th>
<th>Liquidus (°C)</th>
<th>Solidus (°C)</th>
<th>Primary phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Code</td>
<td>(at%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SU9</td>
<td>Fe₆₈.₁Cr₁₇.₇Mo₄B₁₀₂</td>
<td>1400</td>
<td>1132</td>
<td>M₃B₂</td>
</tr>
<tr>
<td>SU10</td>
<td>Fe₆₇Cr₁₇Mo₄B₁₁₂</td>
<td>1445</td>
<td>1127</td>
<td>M₃B₂</td>
</tr>
</tbody>
</table>

450 GPa is used here for the borides. This value is chosen to be higher than the predicted modulus of 420 GPa (Section 5.4.1) in order to take into account the combined effect of the two borides. The total volume fraction of borides is estimated based on the calculated mole fractions of the borides. It was also assumed that on average a ~3 vol% porosity is inevitable in the alloys. The prediction results for the moduli of the two proposed optimum alloys are listed in Table 8.16. The Young’s moduli of the optimised alloys are expected to reach 270 GPa, the target modulus, after a simple heat treatment at 1000°C for 1 hour followed by oil quench.
RESULTS AND DISCUSSION

Table 8.16  Predicted range of Young's modulus for the proposed optimum alloys.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Vol% Boride</th>
<th>$E_{\text{Alloy, Due to Boride}}$</th>
<th>Vol% Porosity to Voids</th>
<th>$E_{\text{Alloy, Due to Voids}}$</th>
<th>Predicted $E_{\text{Alloy}}$, GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>SU9</td>
<td>26</td>
<td>260</td>
<td>~3</td>
<td>-13</td>
<td>247</td>
</tr>
<tr>
<td>SU10</td>
<td>30</td>
<td>267</td>
<td>~3</td>
<td>-13</td>
<td>254</td>
</tr>
</tbody>
</table>

8.11 Summary

It has been shown that the predicted phase equilibria and phase formation in the selected Fe-TM-B alloys are supported by metallography and EDX results, which confirmed the concept of using phase equilibrium calculations in alloy design.

The effect of different processing routes and conditions on the mechanical properties has been discussed and the results used to design an optimum fabrication route. The hardenability observed in some of the test alloys has been analysed and an interesting indirect effect on the modulus of the alloys attributed to magneto-strictive effects.

An evaluation of the contribution to elastic modulus made by (a) composition and nature of matrix, (b) type and amount of borides, and (c) porosity present in the test alloys has been carried out with the help of Eshelby modelling. This has allowed a better understanding of the correlation between the elastic properties and the microstructure constituents in the alloys, and made it possible to suggest the optimised alloy compositions.

It is important to point out that the value in the mechanical property modelling lies not only in optimising the structure parameters to utilise the property potentials to a maximum extent, but also in defining the property limit that one can achieve by simply varying the morphology of the alloy microstructure.
9.1 Conclusions

[i] Successful phase equilibrium calculations have been made in the Fe-Cr-B, Fe-Cr-Mo-B and Fe-Cr-Ni-B systems. This has allowed the selection of model alloys to test the effect of specific combinations of phase and microstructural variables, including type, amount, and composition of matrix and borides.

[ii] Nucleation behaviour during solidification in high pressure gas atomised powders has been predicted using a combined thermodynamic and kinetic approach for the designed model alloys. Critical nucleation temperatures for the supersaturated solid solution phases and compounds were determined at various powder diameters as well as the undercooling for each phase. The prediction provides a useful theoretical basis to ensure amorphous phase or supersaturated solutions are produced in the alloys upon rapid solidification.

[iii] Elastic moduli of in situ metal matrix composite structures have been modelled as a function of microstructural parameters by making use of Eshelby’s equivalent inclusion method. Values for the moduli of boride and matrix in the test alloys were estimated based on Eshelby’s model, and the effective Young’s moduli of the designed test alloys predicted.

[iv] An evaluation of the contribution to the effective modulus made by (a) composition and nature of matrix; (b) type and amount of borides, and (c) porosity present in the test alloys has allowed a better understanding of the correlation between elastic properties and microstructural constituents in the alloys. Optimum alloy compositions to achieve the target modulus in the
CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

present alloy system have been calculated.

[v] It has been shown that thermodynamic calculations and computer modelling of alloy properties serve as a convenient tool in locating the compositions which comply with alloy selection criteria and subsequently designing alloys with improved properties by optimum microstructure. The method has proved to be cost-effective for exploring the potentials in alloys of this class by separating the effect of various phase and structure variables on the properties, and by limiting the necessary number of alloys to be examined.

[vi] A critically assessed database for the Fe-TM-B alloys has been established, and is available for further calculations in such systems.

9.2 Suggestions for Further Work

[i] The final test alloys recommended as a result of this study need to be examined to confirm the expected mechanical properties.

[ii] Experiments to test the hypothesis concerning magnetic effect on the modulus of the Fe-based alloys should be conducted. The experimental results are expected to reveal whether the modulus of an alloy is determined in some way by mobile magnetic domains.

[iii] Phase equilibria in the Fe-Cr-Mo-B-C system should be studied since carbon appears to have a significant effect on modulus. This can be done by extending the database obtained from the present work with additional data from the relevant carbon systems.

[iv] The cost-effectiveness in alloy design demonstrated in this thesis could be applied further in the search for better performance from materials based on alloys with a lower density matrix.
<table>
<thead>
<tr>
<th>Year</th>
<th>Reference</th>
</tr>
</thead>
</table>
REFERENCES


REFERENCES

65Has: M. Hasegawa and M. Okamoto, Nippon Kinzoku Gakkaishi, 29, 328 (1965).
66Ame: The Amer. Ceramic Soc., Engineering Properties of Selected Ceramic Materials, Battelle
REFERENCES

Memorial Inst., Columbus Lab, Ohio (1966).


REFERENCES

Ceram., 657; [Trans. from Poroshkovaya Metallurgiya, 8(80), 66] (1969).


REFERENCES


REFERENCES

80Hil: M. Hillert, CALPHAD, 4, 1 (1980).
REFERENCES


REFERENCES


87Gus: P. Gustafson, ibid, D80 (March 1987).


REFERENCES


REFERENCES


APPENDIX I

Thermodynamic Parameters for the Fe-Cr-Mo-Ni-B Systems

OUTPUT FROM GIBBS ENERGY SYSTEM ON THERMO-CALC

ALL DATA IN SI UNITS
FUNCTIONS VALID FOR 298.15<T<6000.00K UNLESS OTHERWISE STATED

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>STABLE REFERENCE STATE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 B</td>
<td>RHOMB</td>
</tr>
<tr>
<td>2 Cr</td>
<td>BCC</td>
</tr>
<tr>
<td>3 Fe</td>
<td>BCC</td>
</tr>
<tr>
<td>4 Mo</td>
<td>BCC</td>
</tr>
<tr>
<td>5 Ni</td>
<td>FCC</td>
</tr>
</tbody>
</table>

LIQUID
CONSTITUENTS  B, Cr, Fe, Mo, Ni

G(LIQUID, B)-G(RHOMB, B) = 50200-21.38T+GHSERB
G(LIQUID, Cr)-G(BCC, Cr) =
  298.15<T<2180.00 :  24335.9-11.42T+2.3762*10^{21}T^7+GHSERCr
  2180.00<T<6000.00 : 18405-8.562T+2.8853*10^{32}T^9+GHSERCr
G(LIQUID, Fe)-G(BCC, Fe) =
  298.15<T<1811.00 : 12040.2-6.558T-3.6752*10^{21}T^7+GHSERFe
  1811.00<T<6000.00 : 14544.8-8.011T-2.2960*10^{31}T^9+GHSERFe
G(LIQUID, Mo)-G(BCC, Mo) =
  298.15<T<2896.00 : 41616.8-14.609T+4.0358*10^{22}T^7+GHSERMo
  2896.00<T<6000.00 : 34262.1-11.942T+4.61045*10^{33}T^9+GHSERMo
APPENDIX

\[
G(\text{LIQUID, Ni}) - G(\text{FCC, Ni}) =
\begin{align*}
298.15 < T < 1728.00 : & \quad 16414.7 - 9.3977T - 3.8232 \times 10^{-21}T^2 + \text{GHSERNi} \\
1728.00 < T < 6000.00 : & \quad 18290.9 - 10.537T - 1.1275 \times 10^3T^9 + \text{GHSERNi}
\end{align*}
\]

\[
G(\text{LIQUID, B, Cr; } 0) = -165600 + 34T \\
G(\text{LIQUID, B, Cr; } 1) = -10000 \\
G(\text{LIQUID, B, Cr; } 2) = 20000 \\
G(\text{LIQUID, B, Fe; } 0) = -140000 + 42.834T \\
G(\text{LIQUID, B, Fe; } 1) = -1500 \\
G(\text{LIQUID, B, Fe; } 2) = 20000 \\
G(\text{LIQUID, B, Mo; } 0) = -208000 + 40T \\
G(\text{LIQUID, B, Mo; } 1) = -15000 \\
G(\text{LIQUID, B, Mo; } 2) = 20000 \\
G(\text{LIQUID, B, Ni; } 0) = -120000 + 38T \\
G(\text{LIQUID, B, Ni; } 1) = 15500 \\
G(\text{LIQUID, B, Ni; } 2) = 15000
\]

\[
G(\text{LIQUID, Cr, Fe; } 0) = -14550 + 6.65T \\
G(\text{LIQUID, Cr, Mo; } 0) = +15810 - 6.714T \\
G(\text{LIQUID, Cr, Mo; } 1) = -6220 \\
G(\text{LIQUID, Cr, Ni; } 0) = -1276 - 5.3873T \\
G(\text{LIQUID, Cr, Ni; } 1) = +2699 \\
G(\text{LIQUID, Fe, Mo; } 0) = -6973 - 37T \\
G(\text{LIQUID, Fe, Mo; } 1) = -9424 + 4.502T \\
G(\text{LIQUID, Fe, Ni; } 0) = -18378.9 + 6.03912T \\
G(\text{LIQUID, Fe, Ni; } 1) = +9228.1 - 3.5464T \\
G(\text{LIQUID, Mo, Ni; } 0) = -17573 + 13.807T
\]

**BCC**

**CONSTITUENTS** B, Cr, Fe, Mo, Ni

\[
G(\text{BCC, B}) - G(\text{RHOMB, B}) = G_{\text{BBCC}} \\
G(\text{BCC, Cr}) - G(\text{BCC, Cr}) = G_{\text{HSERCr}} \\
G(\text{BCC, Fe}) - G(\text{BCC, Fe}) = G_{\text{HSERFe}} \\
G(\text{BCC, Mo}) - G(\text{BCC, Mo}) = G_{\text{HSERMo}} \\
G(\text{BCC, Ni}) - G(\text{BCC, Ni}) = G_{\text{NiBCC}}
\]
APPENDIX

\[ G(\text{BCC}, \text{B, Cr}; 0) = -140000 + 49T \]
\[ G(\text{BCC}, \text{B, Fe}; 0) = -1000 - 5T \]
\[ G(\text{BCC}, \text{B, Mo}; 0) = -92000 + 20T \]

\[ G(\text{BCC}, \text{Cr, Fe}; 0) = 20500 - 9.68T \]
\[ G(\text{BCC}, \text{Cr, Mo}; 0) = 28890 - 7.962T \]
\[ G(\text{BCC}, \text{Cr, Mo}; 1) = 5974 - 2.428T \]
\[ G(\text{BCC}, \text{Cr, Ni}; 0) = 21310 - 13.6585T \]
\[ G(\text{BCC}, \text{Cr, Ni}; 1) = 25800 - 7.827T \]
\[ G(\text{BCC}, \text{Fe, Mo}; 0) = 36818 - 9.141T \]
\[ G(\text{BCC}, \text{Fe, Mo}; 1) = -362 - 5.724T \]
\[ G(\text{BCC}, \text{Fe, Ni}; 0) = -965.63 - 1.28726T \]
\[ G(\text{BCC}, \text{Fe, Ni}; 1) = 1789.03 - 1.92912T \]
\[ G(\text{BCC}, \text{Mo, Ni}; 0) = 23430 + 13.807T \]

**ADDITIONAL CONTRIBUTION FROM MAGNETIC ORDERING**

\[ f(t) \text{ below Curie Temperature} = \]
\[ 1 - 0.905299383t - 0.153008346t^3 - 0.00680037095t^9 - 0.00153008346t^{15} \]

\[ f(t) \text{ above Curie Temperature} = \]
\[ -0.0641731208t^{5} - 0.00203724193t^{15} - 4.27820805 \times 10^{-4}t^{-25} \]

\[ T_C(\text{BCC, B}) = 0 \]
\[ T_C(\text{BCC, Cr}) = -311.5 \]
\[ T_C(\text{BCC, Fe}) = 1043 \]
\[ T_C(\text{BCC, Mo}) = 0 \]
\[ T_C(\text{BCC, Ni}) = 575 \]
\[ \beta(\text{BCC, B}) = 0 \]
\[ \beta(\text{BCC, Cr}) = -0.008 \]
\[ \beta(\text{BCC, Fe}) = 2.22 \]
\[ \beta(\text{BCC, Mo}) = 0 \]
\[ \beta(\text{BCC, Ni}) = 0.85 \]

\[ T_C(\text{BCC, Cr, Fe}; 0) = 1650 \]
\[ T_C(\text{BCC, Cr, Fe}; 1) = 550 \]
\[ T_C(\text{BCC, Cr, Ni}; 0) = 2373 \]
\[ T_C(\text{BCC, Cr, Ni}; 1) = 617 \]
\[ T_C(\text{BCC, Fe, Mo}; 0) = 335 \]
\[ T_C(\text{BCC, Fe, Mo}; 1) = 526 \]
\[ T_C(\text{BCC, Fe, Ni}; 0) = 0 \]
\[ \beta(\text{BCC, Cr, Fe}; 0) = -0.85 \]
\[ \beta(\text{BCC, Cr, Ni}; 0) = +4 \]
\[ \beta(\text{BCC, Fe, Mo}; 0) = 0 \]
\[ \beta(\text{BCC, Fe, Ni}; 0) = 0 \]
APPENDIX

FCC

CONSTITUENTS B, Cr, Fe, Mo, Ni

\[ G(\text{FCC}, B) - G(\text{RHOMB}, B) = \text{GBFCC} \]
\[ G(\text{FCC}, \text{Cr}) - G(\text{BCC}, \text{Cr}) = \text{GCrFCC} \]
\[ G(\text{FCC}, \text{Fe}) - G(\text{BCC}, \text{Fe}) = \text{GFeFCC} \]
\[ G(\text{FCC}, \text{Mo}) - G(\text{BCC}, \text{Mo}) = \text{GMoFCC} \]
\[ G(\text{FCC}, \text{Ni}) - G(\text{FCC}, \text{Ni}) = \text{GHSERNi} \]

\[ G(\text{FCC}, \text{B}, \text{Fe}; 0) = 21000 - 15T \]
\[ G(\text{FCC}, \text{B}, \text{Ni}; 0) = -16500 \]

\[ G(\text{FCC}, \text{Cr}, \text{Fe}; 0) = 10833 - 7.477T \]
\[ G(\text{FCC}, \text{Cr}, \text{Fe}; 1) = 1410 \]
\[ G(\text{FCC}, \text{Cr}, \text{Ni}; 0) = 8347 - 12.1038T \]
\[ G(\text{FCC}, \text{Cr}, \text{Ni}; 1) = 29895 - 16.3838T \]
\[ G(\text{FCC}, \text{Fe}, \text{Mo}; 0) = 28347 - 17.691T \]
\[ G(\text{FCC}, \text{Fe}, \text{Ni}; 0) = -12054 + 3.174T \]
\[ G(\text{FCC}, \text{Fe}, \text{Ni}; 1) = 11082 - 4.451T \]
\[ G(\text{FCC}, \text{Fe}, \text{Ni}; 2) = -725.8 \]
\[ G(\text{FCC}, \text{Mo}, \text{Ni}; 0) = +4803.7 - 5.96T \]
\[ G(\text{FCC}, \text{Mo}, \text{Ni}; 1) = 10880 \]

ADDITIONAL CONTRIBUTION FROM MAGNETIC ORDERING

\[ f(\tau) \text{ below Curie Temperature} = 1 - 0.860338755\tau^1 - 0.17449124\tau^2 + 0.00775516624\tau^3 - 0.0017449124\tau^{15} \]
\[ f(\tau) \text{ above Curie Temperature} = -0.0426902268\tau^5 - 0.0013552453\tau^{15} - 2.84601512 \times 10^{-4}\tau^{25} \]

\[ T_c(\text{FCC}, \text{B}) = 0 \]
\[ T_c(\text{FCC}, \text{Cr}) = -1109 \]
\[ T_c(\text{FCC}, \text{Fe}) = -201 \]
\[ T_c(\text{FCC}, \text{Mo}) = 0 \]
\[ T_c(\text{FCC}, \text{Ni}) = 633 \]
\[ \beta(\text{FCC}, \text{B}) = 0 \]
\[ \beta(\text{FCC}, \text{Cr}) = -2.46 \]
\[ \beta(\text{FCC}, \text{Fe}) = -2.1 \]
\[ \beta(\text{FCC}, \text{Mo}) = 0 \]
\[ \beta(\text{FCC}, \text{Ni}) = 0.52 \]

\[ T_c(\text{FCC}, \text{Cr}, \text{Ni}; 0) = -3605 \]
\[ T_c(\text{FCC}, \text{Fe}, \text{Ni}; 0) = +2133 \]
\[ \beta(\text{FCC}, \text{Cr}, \text{Ni}; 0) = -1.91 \]
\[ \beta(\text{FCC}, \text{Fe}, \text{Ni}; 0) = +9.55 \]
APPENDIX

\[ T_c(\text{FCC, Fe, Ni}; 1) = -682 \]
\[ T_c(\text{FCC, Fe, Ni}; 2) = 0 \]
\[ T_c(\text{FCC, Fe, Ni}; 3) = 0 \]

\[ \beta(\text{FCC, Fe, Ni}; 1) = +7.23 \]
\[ \beta(\text{FCC, Fe, Ni}; 2) = +5.93 \]
\[ \beta(\text{FCC, Fe, Ni}; 3) = +6.18 \]

\[ \text{Cr}_2\text{B}_4 \]
2 SUBLATTICES, SITES .429 : .571
CONSTITUENTS Cr : B

\[ G(\text{Cr}_3\text{B}_4, \text{Cr}) - 0.571*G(\text{RHOMB}, \text{B}) - 0.429*G(\text{BCC}, \text{Cr}) = -44750 + 4T + 0.429*\text{GHSERCr} + 0.571*\text{GHSERB} \]

\[ \text{Cr}_2\text{B}_3 \]
2 SUBLATTICES, SITES .625 : .375
CONSTITUENTS Cr, Mo : B

\[ G(\text{Cr}_3\text{B}_3, \text{Cr}) - 0.375*G(\text{RHOMB}, \text{B}) - 0.625*G(\text{BCC}, \text{Cr}) = -40300 + 4.15T + 0.625*\text{GHSERCr} + 0.375*\text{GHSERB} \]
\[ G(\text{Cr}_3\text{B}_3, \text{Mo}) - 0.375*G(\text{RHOMB}, \text{B}) - 0.625*G(\text{BCC}, \text{Mo}) = -48785 + 4.9T + 0.625*\text{GHSERMo} + 0.375*\text{GHSERB} \]

\[ \text{CrB} \]
2 SUBLATTICES, SITES .5 : .5
CONSTITUENTS Cr, Fe, Mo : B

\[ G(\text{CrB}, \text{Cr}) - 0.5*G(\text{RHOMB}, \text{B}) - 0.5*G(\text{BCC}, \text{Cr}) = -47608 + 4.86T + 0.5*\text{GHSERCr} + 0.5*\text{GHSERB} \]
\[ G(\text{CrB}, \text{Fe}) - 0.5*G(\text{RHOMB}, \text{B}) - 0.5*G(\text{BCC}, \text{Fe}) = -30000 + 6.35T + 0.5*\text{GHSERFe} + 0.5*\text{GHSERB} \]
\[ G(\text{CrB}, \text{Mo}) - 0.5*G(\text{RHOMB}, \text{B}) - 0.5*G(\text{BCC}, \text{Mo}) = -57300 + 4.5T + 0.5*\text{GHSERMo} + 0.5*\text{GHSERB} \]
APPENDIX

CrB₂
2 SUBLATTICES, SITES .333 : .667
CONSTITUENTS Cr : B

\[ G(\text{CrB}_2, \text{Cr} : \text{B}) - 0.667^* G(\text{RHOMB}, \text{B}) - 0.333^* G(\text{BCC}, \text{Cr}) = -38000 + 1.75T + 0.333^* \text{GHSERCr} + 0.667^* \text{GHSERB} \]

CrB₄
2 SUBLATTICES, SITES .2 : .8
CONSTITUENTS Cr : B

\[ G(\text{CrB}_4, \text{Cr} : \text{B}) - 0.8^* G(\text{RHOMB}, \text{B}) - 0.2^* G(\text{BCC}, \text{Cr}) = -25000 + 2.279T + 0.2^* \text{GHSERCr} + 0.8^* \text{GHSERB} \]

FeB
2 SUBLATTICES, SITES .5 : .5
CONSTITUENTS Cr, Fe, Mo : B

\[ G(\text{FeB}, \text{Cr} : \text{B}) - 0.5^* G(\text{RHOMB}, \text{B}) - 0.5^* G(\text{BCC}, \text{Cr}) = -44608 + 4.86T + 0.5^* \text{GHSERCr} + 0.5^* \text{GHSERB} \]
\[ G(\text{FeB}, \text{Fe} : \text{B}) - 0.5^* G(\text{RHOMB}, \text{B}) - 0.5^* G(\text{BCC}, \text{Fe}) = -33000 + 6.35T + 0.5^* \text{GHSERFe} + 0.5^* \text{GHSERB} \]
\[ G(\text{FeB}, \text{Mo} : \text{B}) - 0.5^* G(\text{RHOMB}, \text{B}) - 0.5^* G(\text{BCC}, \text{Mo}) = -48300 + 4.5T + 0.5^* \text{GHSERMo} + 0.5^* \text{GHSERB} \]

ADDITIONAL CONTRIBUTION FROM MAGNETIC ORDERING
f(t) below Curie Temperature =
\[ 1 - 8.60338755t^{-1} - 17449124t^{3} - 0.00775516624t^{9} - 0.0017449124t^{15} \]
f(t) above Curie Temperature =
\[ -0.0426902268t^{-5} - 0.013552453t^{15} - 2.84601512*10^{4}t^{-25} \]

Tc(FeB, Fe : B) = 600 \[ \beta(\text{FeB}, \text{Fe} : \text{B}) = 1.03 \]
APPENDIX

M₂B_ORTH
2 SUBLATTICES, SITES .667 : .333
CONSTITUENTS  Cr, Fe, Mo : B

\[ G(M₂B_ORTH, Cr : B) - 0.333*G(RHOMB, B) - 0.667*G(BCC, Cr) = -37675 + 4T + 0.667*GHSERCr + 0.333*GHSERB \]

\[ G(M₂B_ORTH, Fe : B) - 0.333*G(RHOMB, B) - 0.667*G(BCC, Fe) = -21500 + 3.62T + 0.667*GHSERFe + 0.333*GHSERB \]

\[ G(M₂B_ORTH, Mo : B) - 0.333*G(RHOMB, B) - 0.667*G(BCC, Mo) = -40720 + 5.04T + 0.667*GHSERMo + 0.333*GHSERB \]

M₂B_TETR
2 SUBLATTICES, SITES .667 : .333
CONSTITUENTS  Cr, Fe, Mo, Ni : B

\[ G(M₂B_TETR, Cr : B) - 0.333*G(RHOMB, B) - 0.667*G(BCC, Cr) = -37075 + 4T + 0.667*GHSERCr + 0.333*GHSERB \]

\[ G(M₂B_TETR, Fe : B) - 0.333*G(RHOMB, B) - 0.667*G(BCC, Fe) = -24175 + 3.62T + 0.667*GHSERFe + 0.333*GHSERB \]

\[ G(M₂B_TETR, Mo : B) - 0.333*G(RHOMB, B) - 0.667*G(BCC, Mo) = -46720 + 5.04T + 0.667*GHSERMo + 0.333*GHSERB \]

\[ G(M₂B_TETR, Ni : B) - 0.333*G(RHOMB, B) - 0.667*G(FCC, Ni) = -22600 + 6.08T + 0.667*GHSERNi + 0.333*GHSERB \]

\[ G(M₂B_TETR, Cr, Fe : B; 0) = 7650 \]
\[ G(M₂B_TETR, Cr, Mo : B; 0) = 1750 \]
\[ G(M₂B_TETR, Cr, Ni : B; 0) = +10000 \]

ADDITIONAL CONTRIBUTION FROM MAGNETIC ORDERING
\[ f(\tau) \text{ below Curie Temperature} = 1 - 0.860338755\tau^{-1} - 0.17449124\tau^{-2} - 0.00775516624\tau^{-9} - 0.0017449124\tau^{15} \]
\[ f(\tau) \text{ above Curie Temperature} = -0.0426902268\tau^{-5} - 0.0013552453\tau^{-15} - 2.84601512*10^{-4}\tau^{-25} \]

\[ T_C(M₂B_TETR, Fe : B) = 1018 \]
\[ T_C(M₂B_TETR, Cr, Fe : B; 0) = -1622 \]

\[ \beta(M₂B_TETR, Fe : B) = 1.91 \]
\[ \beta(M₂B_TETR, Cr, Fe : B; 0) = -4.007 \]
APPENDIX

\[ T_{C}(M_2B_{TETR}, Cr, Fe : B; 1) = 3150 \]
\[ \beta(M_2B_{TETR}, Cr, Fe : B; 1) = -1.1926 \]
\[ T_{C}(M_2B_{TETR}, Cr, Fe : B; 2) = 3269 \]
\[ \beta(M_2B_{TETR}, Cr, Fe : B; 2) = .1828 \]

**M_{23}B_{6}**

2 SUBLATTICES, SITES .7931 : .2069

CONSTITUENTS Cr, Fe, Ni : B

\[
G(M_{23}B_{6}, Cr : B)-0.7931*G(BCC, Cr)-0.2069*G(RHOMB, B) = -16000-1.0T+.7931*GHSERCr+.2069*GHSERB
\]
\[
G(M_{23}B_{6}, Fe : B)-0.7931*G(BCC, Fe)-0.2069*G(RHOMB, B) = -10345-1.0T+.7931*GHSERFe+.2069*GHSERB
\]
\[
G(M_{23}B_{6}, Ni : B)-0.7931*G(FCC, Ni)-0.2069*G(RHOMB, B) = -9152-1.0T+.7931*GHSERNi+.2069*GHSERB
\]

G(M_{23}B_{6}, Fe, Ni : B; 0)= -17500+10T

**M_{3}B**

2 SUBLATTICES, SITES .75 : .25

CONSTITUENTS Cr, Fe, Mo, Ni : B

\[
G(M_{3}B, Cr : B)-0.25*G(RHOMB, B)-0.75*G(BCC, Cr) = -25000+3.00T+.25*GHSERB+.75*GHSERCr
\]
\[
G(M_{3}B, Fe : B)-0.25*G(RHOMB, B)-0.75*G(BCC, Fe) = -15950+1.29T+.25*GHSERB+.75*GHSERFe
\]
\[
G(M_{3}B, Mo : B)-0.25*G(RHOMB, B)-0.75*G(BCC, Mo) = -30000+3.78T+.25*GHSERB+.75*GHSERMo
\]
\[
G(M_{3}B, Ni : B)-0.25*G(RHOMB, B)-0.75*G(FCC, Ni) = -17500+3.32T+.25*GHSERB+.75*GHSERNi
\]

G(M_{3}B, Fe, Mo : B; 0) = -19500
G(M_{3}B, Fe, Ni : B; 0) = -4900+2T
G(M_{3}B, Fe, Ni : B; 0) = +2500
G(M_{3}B, Cr, Ni : B; 0) = +7000
APPENDIX

M₃B₂ (Tetragonal)
3 SUBLATTICES, SITES 4 : 2 : 4
CONSTITUENTS Cr, Fe, Mo, Ni : Cr, Fe, Ni : B

\[ G(M₃B₂, Cr : Cr : B) - 0.4G(RHOMB, B) - 0.6G(BCC, Cr) = \]
\[ -36762 + 4.29T + 0.4GHSECr + 0.4GHSEB \]

\[ G(M₃B₂, Fe : Cr : B) - 0.4G(RHOMB, B) - 0.2G(BCC, Cr) - 0.4G(BCC, Fe) = \]
\[ -29530 + 3.31T + 0.4GHSEFe + 0.2GHSECr + 0.4GHSEB \]

\[ G(M₃B₂, Mo : Cr : B) - 0.4G(RHOMB, B) - 0.2G(BCC, Cr) - 0.4G(BCC, Mo) = \]
\[ -45290 - 2T + 0.4GHSMo + 0.2GHSECr + 0.4GHSEB \]

\[ G(M₃B₂, Cr : Fe : B) - 0.4G(RHOMB, B) - 0.4G(BCC, Cr) - 0.2G(BCC, Fe) = \]
\[ -34300 + 1.93T + 0.4GHSECr + 0.2GHSEFe + 0.4GHSEB \]

\[ G(M₃B₂, Fe : Fe : B) - 0.4G(RHOMB, B) - 0.6G(BCC, Fe) = \]
\[ -21445 + 5T + 0.6GHSEFe + 0.4GHSEB \]

\[ G(M₃B₂, Mo : Fe : B) - 0.4G(RHOMB, B) - 0.2G(BCC, Fe) - 0.4G(BCC, Mo) = \]
\[ -55000 + 5T + 0.4GHSMo + 0.2GHSEFe + 0.4GHSEB \]

\[ G(M₃B₂, Cr : Ni : B) - 0.4G(RHOMB, B) - 0.2G(FCC, Ni) - 0.4G(BCC, Cr) = \]
\[ -35820 + 3.51T + 0.4GHSECr + 0.2GNI + 0.4GHSEB \]

\[ G(M₃B₂, Fe : Ni : B) - 0.4G(RHOMB, B) - 0.2G(FCC, Ni) - 0.4G(BCC, Fe) = \]
\[ -24341 + 2.41T + 0.4GHSEFe + 0.2GNI + 0.4GHSEB \]

\[ G(M₃B₂, Ni : Cr : B) - 0.4G(RHOMB, B) - 0.4G(FCC, Ni) - 0.2G(BCC, Cr) = \]
\[ -30487 + 5.47T + 0.4GNI + 0.2GHSECr + 0.4GHSEB \]

\[ G(M₃B₂, Ni : Fe : B) - 0.4G(RHOMB, B) - 0.4G(FCC, Ni) - 0.2G(BCC, Fe) = \]
\[ -22997 + 4.14T + 0.4GNI + 0.2GHSEFe + 0.4GHSEB \]

\[ G(M₃B₂, Ni : Ni : B) - 0.4G(RHOMB, B) - 0.6G(FCC, Ni) = \]
\[ -20210 + 6.58T + 0.6GNI + 0.4GHSEB \]

Mo₂B₅
2 SUBLATTICES, SITES 32 : 68
CONSTITUENTS Mo : B

\[ G(Mo₂B₅, Mo : B) - 0.68G(RHOMB, B) - 0.32G(BCC, Mo) = \]
\[ -49742 + 4.98T + 0.32GHSMo + 0.68GHSEB \]
MoB
2 SUBLATTICES, SITES .5 : .5
CONSTITUENTS Cr, Fe, Mo : B

\[ G(\text{MoB}, \text{Cr} : \text{B}) - 0.5G(\text{RHOMB, B}) - 0.5G(\text{BCC, Cr}) = \]
\[ -37608 + 4.86T + 0.5G_{\text{HSERCr}} + 0.5G_{\text{HSERB}} \]
\[ G(\text{MoB}, \text{Fe} : \text{B}) - 0.5G(\text{RHOMB, B}) - 0.5G(\text{BCC, Fe}) = \]
\[ -23000 + 6.35T + 0.5G_{\text{HSERFe}} + 0.5G_{\text{HSERB}} \]
\[ G(\text{MoB}, \text{Mo} : \text{B}) - 0.5G(\text{RHOMB, B}) - 0.5G(\text{BCC, Mo}) = \]
\[ -58300 + 4.5T + 0.5G_{\text{HSERMo}} + 0.5G_{\text{HSERB}} \]

MoB\textsubscript{2}
2 SUBLATTICES, SITES .38 : .62
CONSTITUENTS Mo : B

\[ G(\text{MoB}_2, \text{Mo} : \text{B}) - 0.62G(\text{RHOMB, B}) - 0.38G(\text{BCC, Mo}) = \]
\[ -47938 + 2.22T + 0.38G_{\text{HSERMo}} + 0.62G_{\text{HSERB}} \]

MoB\textsubscript{4}
2 SUBLATTICES, SITES .2 : .8
CONSTITUENTS Mo : B

\[ G(\text{MoB}_4, \text{Mo} : \text{B}) - 0.8G(\text{RHOMB, B}) - 0.2G(\text{BCC, Mo}) = \]
\[ -33688 + 4.5T + 0.2G_{\text{HSERMo}} + 0.8G_{\text{HSERB}} \]

Ni\textsubscript{4}B\textsubscript{3}
2 SUBLATTICES, SITES .571 : .329
CONSTITUENTS Ni : B

\[ G(\text{Ni}_4\text{B}_3, \text{Ni} : \text{B}) - 0.329G(\text{RHOMB, B}) - 0.571G(\text{FCC, Ni}) = \]
\[ -22000 + 6.85T + 0.32G_{\text{HSERNi}} + 0.68G_{\text{HSERB}} \]
APPENDIX

NiB
2 SUBLATTICES, SITES 5:5
CONSTITUENTS Ni : B

\[ G(\text{NiB}, \text{Ni : B}) - 0.5^*G(\text{RHOMB, B}) - 0.5^*G(\text{FCC, Ni}) = -20100 + 6.23T + 0.5^*\text{GHSERNi} + 0.5^*\text{GHSERB} \]

\[ \mu \_\text{PHASE} \]
3 SUBLATTICES, SITES 7:2:4
CONSTITUENTS Cr, Fe : Mo : Cr, Fe, Mo

\[ G(\mu \_\text{PHASE}, \text{Cr : Mo : Cr}) - 11^*G(\text{BCC, Cr}) - 2^*G(\text{BCC, Mo}) = 7^*\text{GCrFCC} + 2^*\text{GHSERMo} + 4^*\text{GHSERCr} + 130000 - 100T \]

\[ G(\mu \_\text{PHASE}, \text{Fe : Mo : Cr}) - 4^*G(\text{BCC, Cr}) - 7^*G(\text{BCC, Fe}) - 2^*G(\text{BCC, Mo}) = 7^*\text{GFeFCC} + 2^*\text{GHSERMo} + 4^*\text{GHSERFe} + 130000 - 100T \]

\[ G(\mu \_\text{PHASE}, \text{Cr : Mo : Fe}) - 7^*G(\text{BCC, Cr}) - 4^*G(\text{BCC, Fe}) - 2^*G(\text{BCC, Mo}) = 7^*\text{GCrFCC} + 2^*\text{GHSERMo} + 4^*\text{GHSERFe} + 130000 - 100T \]

\[ G(\mu \_\text{PHASE}, \text{Fe : Mo : Fe}) - 11^*G(\text{BCC, Fe}) - 2^*G(\text{BCC, Mo}) = 7^*\text{GFeFCC} + 2^*\text{GHSERMo} + 4^*\text{GHSERFe} + 39475 - 6.032T \]

\[ G(\mu \_\text{PHASE}, \text{Cr : Mo : Mo}) - 7^*G(\text{BCC, Cr}) - 6^*G(\text{BCC, Mo}) = 7^*\text{GCrFCC} + 6^*\text{GHSERMo} + 130000 - 100T \]

\[ G(\mu \_\text{PHASE}, \text{Fe : Mo : Mo}) - 7^*G(\text{BCC, Fe}) - 6^*G(\text{BCC, Mo}) = 7^*\text{GFeFCC} + 6^*\text{GHSERMo} - 46663 - 5.891T \]

\[ G(\mu \_\text{PHASE}, \text{Cr, Fe : Mo : Mo; 0}) = -45000 \]

RHOMB_B
CONSTITUENTS B

\[ G(\text{RHOMB} \_B, B) - G(\text{RHOMB, B}) = \text{GHSERB} \]
APPENDIX

SIGMA (σ)
3 SUBLATTICES, SITES 8 : 4 : 18
CONSTITUENTS  Fe, Ni : Cr, Mo : Cr, Fe, Mo, Ni

\[
\begin{align*}
G(\text{SIGMA, Fe : Cr : Cr}) &= 22G(\text{BCC, Cr}) - 8G(\text{BCC, Fe}) = 8G_{\text{FeFCC}} + 22G_{\text{HSERCr}} + 92300 - 95.96T \\
G(\text{SIGMA, Fe : Mo : Cr}) &= 18G(\text{BCC, Cr}) - 8G(\text{BCC, Fe}) - 4G(\text{BCC, Mo}) = 8G_{\text{FeFCC}} + 4G_{\text{HSERMo}} + 18G_{\text{HSERCr}} + 488480 - 360T \\
G(\text{SIGMA, Fe : Cr : Fe}) &= 4G(\text{BCC, Cr}) - 26G(\text{BCC, Fe}) = 8G_{\text{FeFCC}} + 4G_{\text{HSERCr}} + 18G_{\text{HSERFe}} + 117300 - 95.96T \\
G(\text{SIGMA, Fe : Mo : Fe}) &= 26G(\text{BCC, Fe}) - 4G(\text{BCC, Mo}) = 8G_{\text{FeFCC}} + 22G_{\text{HSERMo}} + 83326 - 69.618T \\
G(\text{SIGMA, Fe : Cr : Ni}) &= 4G(\text{BCC, Cr}) - 8G(\text{BCC, Fe}) - 18G(\text{FCC, Ni}) = 8G_{\text{FeFCC}} + 4G_{\text{HSERCr}} + 18G_{\text{NiBCC}} \\
G(\text{SIGMA, Fe : Mo : Ni}) &= -18G(\text{FCC, Ni}) - 8G(\text{BCC, Fe}) - 4G(\text{BCC, Mo}) = 8G_{\text{FeFCC}} + 4G_{\text{HSERMo}} + 18G_{\text{NiBCC}} + 408600 - 200T \\
G(\text{SIGMA, Ni : Cr : Cr}) &= 22G(\text{BCC, Cr}) - 8G(\text{FCC, Ni}) = 8G_{\text{HSERNi}} + 22G_{\text{HSERCr}} + 173460 - 188T \\
G(\text{SIGMA, Ni : Cr : Fe}) &= 4G(\text{BCC, Cr}) - 18G(\text{BCC, Fe}) - 8G(\text{FCC, Ni}) = 8G_{\text{HSERNi}} + 4G_{\text{HSERCr}} + 18G_{\text{HSERFe}} \\
G(\text{SIGMA, Ni : Mo : Cr}) &= 4G(\text{BCC, Mo}) - 18G(\text{BCC, Cr}) - 8G(\text{FCC, Ni}) = 8G_{\text{HSERNi}} + 4G_{\text{HSERCr}} + 18G_{\text{HSERMo}} - 131651 \\
G(\text{SIGMA, Ni : Mo : Fe}) &= 4G(\text{BCC, Mo}) - 18G(\text{BCC, Fe}) - 8G(\text{FCC, Ni}) = 8G_{\text{HSERNi}} + 4G_{\text{HSERMo}} + 18G_{\text{HSERFe}} + 386423 \\
G(\text{SIGMA, Ni : Mo : Mo}) &= 22G(\text{BCC, Mo}) - 8G(\text{FCC, Ni}) = 8G_{\text{HSERNi}} + 22G_{\text{HSERMo}} + 85662 \\
G(\text{SIGMA, Ni : Mo : Ni}) &= 4G(\text{BCC, Mo}) - 26G(\text{FCC, Ni}) = 8G_{\text{HSERNi}} + 4G_{\text{HSERMo}} + 18G_{\text{NiBCC}} - 16385 \\
G(\text{SIGMA, Ni : Mo : Fe}) &= 4G(\text{BCC, Mo}) - 26G(\text{FCC, Ni}) = 8G_{\text{HSERNi}} + 4G_{\text{HSERMo}} + 18G_{\text{NiBCC}} - 16385
\end{align*}
\]


APPENDIX

\[ G(\Sigma, \text{Fe}, \text{Ni}, \text{Mo}; 0) = -164570 - 10^4 T \]

\[ G(\Sigma, \text{Fe}, \text{Cr}, \text{Mo}; 0) = -148000 \]

\[ G(\Sigma, \text{Fe}, \text{Mo}, \text{Cr}, \text{Mo}; 0) = 121000 \]

\[ G(\Sigma, \text{Fe}, \text{Cr}, \text{Fe}, \text{Mo}; 0) = 570000 \]

\[ G(\Sigma, \text{Fe}, \text{Mo}, \text{Fe}, \text{Mo}; 0) = 222909 \]

<table>
<thead>
<tr>
<th>SYMBOL</th>
<th>VALUE / FUNCTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 ( R )</td>
<td>8.3145100E+00</td>
</tr>
<tr>
<td>2 RTLNP</td>
<td>( R^<em>T^</em>\ln(9.8692327*10^{-6}P) )</td>
</tr>
<tr>
<td>3 GHSERB</td>
<td>0.0</td>
</tr>
<tr>
<td>4 GHSERCr</td>
<td>0.0</td>
</tr>
<tr>
<td>5 GHSERFe</td>
<td>0.0</td>
</tr>
<tr>
<td>6 GHSERMo</td>
<td>0.0</td>
</tr>
<tr>
<td>7 GHSERNi</td>
<td>0.0</td>
</tr>
<tr>
<td>8 GBBCC</td>
<td>50208 - 13.472T + GHSERB</td>
</tr>
<tr>
<td>9 GBFCC</td>
<td>43514 - 12.217T + GHSERB</td>
</tr>
<tr>
<td>10 GCrFCC</td>
<td>7284 + 1.63T + GHSERCr</td>
</tr>
<tr>
<td>11 GMoFCC</td>
<td>15200 + 63T + GHSERMo</td>
</tr>
<tr>
<td>12 GNiBCC</td>
<td>8715.084 - 3.556T + GHSERNi</td>
</tr>
</tbody>
</table>
APPENDIX II

The Micro File APP.101

:Application loading, please wait ...
APPLIC DEFINE DATA ********
!
:^[2][0;0H
:^[6^[3 ^^[7mA P P L I C A T I O N 1 0 1^[m
:^[4 ^^[7mA P P L I C A T I O N 1 0 1^[m
:^[m^[B
SET USER_V(APPLICATION_CODE)= 101
USER_V(APPLICATION_NAME)= "Demonstration User Application 101"
USER_V(PURPOSE)="Application Interface at Surrey University"
USER_V(................................................. 11
USER_V(POWDER DIAMETER)= "^[1mTo be set^[m"
USER_V(---------------------)="-----------------------------"
USER_V(BOUNDARIES)=1
USER_V(PERCENT IN)=0.01
USER_V(N CRIT D)="To be calculated"
!
LIST SY P ! SET
: PLEASE ENTER PHASE NUMBER FOR LIQUID
USER_V(K LIQUID)=********
!
list sy set !
:
: ENTER POWDER DIAMETER (in μm)
SET USER_V(POWDER DIAMETER) ********
!
APPENDIX

: ENTER NUMBER FOR EITHER GLASS-FORMING(1) OR NOT(0)
: SET USER_V(K GLASS)=1
!
:
: ENTER GLS-FORMING TEMP... [Enter 0 for non-glass-forming]
SET USER_V(GLS-FORMING TEMP)=********
!
; ENTER TEMP-STEPPING FACTOR ...
;    — ranging from 1000 (accurate but slower)
;    to 0.01 (faster but less accurate)
: SET USER_V(TEMP-STEPPING FACTOR)=1
!
: ENTER GAS NUMBER: Helium(0), Argon(1), Nitrogen(2)... 
SET USER_V(N GAS) = ********
!
:
RANGE T ********
; MAX TEMPERATURE
    ******
; MIN TEMPERATURE
    ******
; TOLERANCE IN PHASE BOUNDARY
!
:
list sy p
!
list sy co
!
:
: NOW enter alloy composition at APPLICATION MODULE ...
: (N.B. You can also classify phase absent at APPLICATION MODULE)
APPENDIX III

The Nucleation Subroutine ITR101

C

SUBROUTINE ITR101()
C
C AN APPLICATION MODULE USING THE TRANSITION MODULE.
C SUBROUTINE ITR101 CORRESPONDS TO ITRANS = 101.
C THIS MODULE FINDS A TEMPERATURE AT WHICH THE MASS OF THE
C LIQUID HAS BEEN DEPLETED BY PCENT PERCENT. IT PRODUCES TIELINES,
C AT THIS POINT (IN MASS FRACTION OR MOLE FRACTION DEPENDING ON
C WEIGHT(0) DEFINED OR UNDEFINED).
C NOTE THAT IF PCENT IS TOO NEAR ZERO THE TIELINES WILL BE
C UNRELIABLE.
C IT ALSO PRODUCES THE ENTHALPY AND HEAT CAPACITY AT THE POINT.
C IT ALSO DOES MULTIPHASE CALCULATIONS ON EACH INDIVIDUAL PHASE.
C
C AT ENTRY,
C IPRINO, THE PRINT LEVEL REQUIRED.
C TMAX, THE MAXIMUM TEMPERATURE TO BE CONSIDERED.
C TMIN, THE MINIMUM TEMPERATURE TO BE CONSIDERED.
C ACC, THE ACCURACY REQUIRED IN THE BOUNDARY TEMPERATURE.
C KLIQ, THE NUMBER OF THE LIQUID PHASE.
C NBDY = 1, THE NUMBER OF PHASE BOUNDARIES TO BE FOUND
C AT EACH COMPOSITION.
C PCENT, THE PERCENTAGE OF THE LIQUID MASS TO BE USED UP.
C INQSTP = 2, THE BOUNDARY TEMPERATURE IS TO BE FOUND AT
C A GIVEN COMPOSITION
C ITRANS = 8.
APPENDIX

C OUT, FILE OUTPUT DEVICE NUMBER.
C OUTVDU, SCREEN OUTPUT DEVICE NUMBER.
C
C AFTER A CALL OF SUBROUTINE TRASN THE FOLLOWING WILL HAVE
C BEEN SET (THESE APPEAR IN DIRECTIVE DIRTRR).
C
C TBDY(1), TEMPERATURE AT WHICH PCENT PER CENT OF LIQUID MASS
C HAS BEEN TRANSFORMED.
C ITIE(1,2), ITL THE NUMBER OF TIELINES, IE NUMBER OF PHASES PRESENT.
C ITIE(2,2)...ITIE(ITL+1,2), THE PHASE NUMBERS OF PHASES PRESENT AT 1ST
C BOUNDARY.
C TIELN(I,J,2), I=1, ITL, J=1,NELEX-NEXTRA,
C THE COMPONENT MASS OR MOLE FRACTIONS OF PHASES PRESENT,
C TOGETHER WITH THE PHASE MASS (NOT MOLES) FOR 1ST PHASE BOUNDARY.
C ENTHPY(1), THE ENTHALPY AT THE POINT.
C HEATCP(1), THE HEAT CAPACITY AT THE POINT.
C
C AFTER A CALL OF SUBROUTINE SGMCC0 (A SINGLE MULTIPHASE
C CALCULATION) PERHAPS FOR EACH PHASE CONSIDERED INDEPENDENTLY
C THE FOLLOWING INFORMATION IS AVAILABLE.
C (THE VARIABLES ARE TO BE FOUND IN DIRECTIVE DIR3.FOR)
C NCOMP - THE NUMBER OF COMPONENTS PRESENT,
C MUREF(1) ... MUREF(NCOMP), THE CHEMICAL POTENTIALS OF COMPONENTS
C WITH RESPECT TO THE REFERENCE PHASE,
C ACTREF(1) ... ACTREF(NCOMP), THE ACTIVITIES OF COMPONENTS
C WITH RESPECT TO THE REFERENCE PHASE,
C GFEREF, THE GIBBS ENERGY WITH RESPECT TO REFERENCE PHASE.
C
DOUBLE PRECISION T1,T2
DOUBLE PRECISION ACC,TACC
DOUBLE PRECISION TMAX,TMIN,RCOUNT,LIQSUM,LIQSM2
INTEGER INQSTP
C
LOGICAL LSET(5)
C
INCLUDE 'DIR0.FOR '
INCLUDE 'DIR2A.FOR'
APPENDIX

INCLUDE 'DIR3.FOR'
INCLUDE 'DIR5.FOR'
INCLUDE 'DIR6.FOR'
INCLUDE 'DIRAPP.FOR'
INCLUDE 'DIRTRR.FOR'

COMMON /TOCMP1/MODULE,LCALC
DOUBLE PRECISION RMXAMT
DOUBLE PRECISION OLDAMT(NLXMXD),OLDWGT(NLXMXD)
INTEGER OLDIPN(M2MAXD), OOIPN(M2MAXD)

C

C ** PARAMETERS FOR NUCLEATION CALC. ADDED LI-MEI **
DOUBLE PRECISION DO, Q, PI, CL, CG, A0, RCONST, NVNUCL
DOUBLE PRECISION KI, U, RO, MU, XSTEP, TSTEP

INTEGER KLIQ
DOUBLE PRECISION PCENT
DOUBLE PRECISION POWDIA
DOUBLE PRECISION TEMP1, ENTHDL

C

C **ADDED OCT 89, LI-MEI**
DOUBLE PRECISION NCRITD, TISO, HI
DOUBLE PRECISION TMELT, TSTART, TCHECK, TSUP, DTI, TF
DOUBLE PRECISION GPLIQS, DGSOL, DSSOL, NOREF, JTREF
DOUBLE PRECISION GPLIQ(M2MAXD), GSOL
DOUBLE PRECISION HMF, DGSOL1, DGSOL2, GSTAR
INTEGER INDEX, NGAS, NGLS, RKLIQ
DOUBLE PRECISION DI
DOUBLE PRECISION EH, FT, TGLS, ETA, KBOLTZ, TFCTOR

C

C ** DO NOT OVERWRITE VARIABLES IN THESE DIRECTIVES
C EXCEPT WHERE INDICATED **

C

C AT ENTRY TO THIS SUBROUTINE A PROBLEM WILL HAVE BEEN DEFINED.
DOUBLE PRECISION ARRAY AGCIN(N2MAXD, NLXMXD) CONTAINS THE
ABOUNDANCE EQUATION ARRAY, IE AGCIN(I,J) I=1, NCOM,
J=1, NELMIN, WHERE NCOM IS THE TOTAL NUMBER OF SPECIES
APPENDIX

C AND NELMIN IS THE TOTAL NUMBER OF COMPONENTS BEFORE
C ANY HAVE BEEN DECLARED ABSENT.
C THE INTEGER ARRAY ICMP(I), I=1, NELEMIN IS SUCH THAT
C ICMP(I) = 0 IF THE COMPONENT HAS BEEN CLASSIFIED ABSENT
C ICMP(I) = 1 IF THE COMPONENT IS PRESENT.
C IPHS(I) = 0, 1 IF PHASE DECLARED ABSENT, PRESENT
C AMOUNT(I), I=1, NELMIN CONTAINS THE AMOUNTS IN MOLES
C OF THE NONABSENT AND ABSENT COMPONENTS.
C NELEX-NEXTRA ARE THE NUMBER OF COMPONENTS THAT HAVE NOT BEEN
C DECLARED ABSENT.
C
C ** SET PARAMETERS **
C ** VALUES TAKEN FROM [62SAX]:

\[
D_0 = 9.4D-8 \\
Q = 45.1D3 \\
\]

C

\[
\pi = 3.1415926D0 \\
R_{\text{CONST}} = 8.31451D0 \\
N_{\text{VNUCL}} = 5.0D28 \\
\]

C ** A0, CL, U SHOULD BE ALTERED FOR CALC. OF DIFFERENT ALLOYS **
C A0: atomic diameter of the alloy;
C CL: specific heat (per unit volume) of the liquid alloy;
A0 = 0.4D-9
CL = 2.4D6
C
C ** SET GAS PARAMETERS **
C ** No. FOR DIFFERENT GAS: He=0, Ar=1, N=2 **
NGAS = GETNUM('N GAS')
IF (NGAS.EQ.0) THEN
CG = 950.0
KI = 0.2
RO = 0.18
MU = 2.5D-5
ENDIF
IF (NGAS.EQ.1) THEN
CG = 950
KI = 0.02
ENDIF
RO = 1.8
MU = 3.0D-5
ENDIF
IF (NGAS.EQ.2) THEN
  CG = 950
  KI = 0.038
  RO = 1.28
  MU = 2.3D-5
ENDIF
U = 1000.0
XSTEP = 1D-5
TSTEP = 1D-2
KBOLTZ = 138D-23

C

RNBDY = GETNUM('BOUNDARIES')
IF(RNBDY.EQ.UNDEF) GOTO500
NBDY = RNBDY
PCENT = GETNUM('PERCENT IN')
IF(PCENT.EQ.UNDEF) GOTO500
RKLIQ = GETNUM('K LIQUID')
IF(RKLIQ .LT. 0.0 .OR. RKLIQ .EQ. UNDEF) GOTO500
KLIQ = RKLIQ
POWDIA = 1D-6*GETNUM('POWDER DIAMETER')
NGLS = GETNUM('K GLASS')
TGLS = GETNUM('GLS-FORMING TEMP')
TFCTOR = GETNUM('TEMP-STEPPING FACTOR')

C

** Ncrit,d CALC., ADDED LI-MEI,
C ** AND TIME GAP TISO UNDER ISOTHERMAL COOLING**
NCRITD = ((4*PI/3)*(POWDIA/2.0)**3)**(-1)
C
WRITE(OUTVDU, *)' Ncrit, d ', NCRITD
HI = 2*KI/POWDIA+0.6*(U/POWDIA)**0.5*(KII**2*CG)**(1/3)*
* (RO/MU)**(1/6)
TISO = POWDIA*CL*100/(6*HI*600)

C

IF(POWDIA.EQ.UNDEF) GOTO500
TMAX = VALRNG(1, 1)
APPENDIX

IF(TMAX.EQ.UNDEF) GOTO500
TMIN = VALRNG(1, 2)
IF(TMIN.EQ.UNDEF) GOTO500
IF(TMAX.LT.TMIN) THEN
  T = TMIN
  TMIN = TMAX
  TMAX = T
ENDIF

C **
C ** ADDED LI-MEI, NOV 89, TO CALC NUCLEATION FOR EACH SOLID PHASE
C ONE BY ONE WITH LIQ PHASE **
C
CC WRITE(OUTVDU, *) 'MMIN ', MMIN
DO 1000 K=1, MMIN
  OLDIPN(K)=IPHSIN(K)
1000 CONTINUE
DO 4100 IJ = 1, MMIN
  IF (IJ.EQ. KLIQ) GOTO 4100
  IF (OLDIPN(IJ) .EQ. 0) GOTO 4100
  WRITE(*, *) PHASE ', PNMEIN(IJ)
CC WRITE(OUTVDU, *) 'IPHSIN(jJ) ', Il'HSINQJ)
4110 CONTINUE
IPHSIN(KLIQ) =1
C
C ** LIQ PHASE CLASSIFIED IN HERE! **
C
DO 4110 JJ = 1, MMIN
  IF (JJ.NE.IJ) IPHSIN(JJ) = 0
  IF (JJ.EQ.IJ) IPHSIN(JJ) = 1
CC WRITE(OUTVDU, *) 'IPHSIN(JJ) ', IPHSIN(JJ)
4110 CONTINUE
IPHSIN(KLIQ) = 1
C
C ** SET PARAMETERS SINCE CLASSIFICATIONS HAVE BEEN CHANGED **
PRVACT = .FALSE.
PRVSOL = .FALSE.
C
TEMP(1) = TMAX
T = TMAX
ACC = VALRNG(2, 1)
IF(ACC.EQ.UNDEF)GOTO500
IF(ISPRNG(2).NE.-1)GOTO500
INQSTP = 2

C
C IMAX - NUMBER OF SETS OF TRANSITIONS TO BE PERFORMED,
C
C IMAX = 1
C
C ***CHECK OK IF COMPONENTS CLASSIFIED ABSENT***
C CHECK WEIGHT CF AMOUNT
C
RMXAMT = 0.0D+0
NNMAX = 0
DO 1100 K=1, MMIN
   OOPN(K) = IPHSIN(K)
1100 CONTINUE
DO 10 I = 1, NELMIN
   OLDAMT(I) = AMOUNT(I)
   OLDWGT(I) = WEIGHT(I)
   IF (ICMP(I) .EQ. 0) GO TO 10
   IF (AMOUNT(I).GT.RMXAMT) THEN
      RNDCkW = AMOUNT(I)
      NNMA)C =I
   ENDIF
10 CONTINUE
T1 = TMAX
T2 = TMIN
TACC = ACC
DO 50 ICNT = 1, IMAX
   IF(ICNT.GT.1) THEN
      IF (ICMP(ICNT-1).EQ.0) GO TO 50
   ENDIF
   RCOUNT = ICNT
   IF (ICNT.GE.2) T1 = TBDY(1) + 20.0D+0
20 INFORM = 0
INPT = INPTIN
IF (IPRINO.GT.-1) THEN
   IF (INQSTP.NE.1) THEN
      WRITE (OUT, *) 'Component moles and masses'
      WRITE (OUTVDU, *) 'Component moles and masses'
      DO 30 I = 1, NELMIN
         IF (AMOUNT(I).NE.UNDEF) WEIGHT(I) = AMOUNT(I)*CMMSIN(I)
         IF (AMOUNT(I).EQ.UNDEF) WRITE (OUT, *) 'undef'
         IF (AMOUNT(I).EQ.UNDEF) WRITE (OUTVDU, *) 'undef'
         IF (AMOUNT(I).NE.UNDEF) WRITE (OUT, *) AMOUNT(I), WEIGHT(I)
         IF (AMOUNT(I).NE.UNDEF) WRITE (OUTVDU, *) AMOUNT(I), WEIGHT(I)
      CONTINUE
   END IF
   WRITE (OUT, 9020) NBDY
   WRITE (OUTVDU, 9020) NBDY
   END IF
   CALL TRANSN(INPT, INQSTP, Ti, 72, TACC, NBDY, KLIQ, PCENT, +LIQSUM, LIQSM2, +IFLAG, IFAIL)
   IF (IFAIL. NE. 0) RETURN
   IF (IFLAG .EQ. 2) THEN
      WRITE(OUTVDU, *)' PHASE BOUNDARY NOT FOUND'
      WRITE(OUT, *)' PHASE BOUNDARY NOT FOUND'
      GOTO 4100
   END IF
   IF (IFLAG. EQ. 1) Ti = T1 + 50.0D+0
   IF (IFLAG.EQ.1) GO TO 20
C
DO MULTIPHASE CALCULATIONS ON INDIVIDUAL PHASES
C IE CHANGE PHASE CLASSIFICATIONS AND AMOUNTS
C
   TEMP(I) = TBDY(I)
C ** ADDED OCT 89, NUCLEATN CALC. LI-MEI **
APPENDIX

TMELT = TBDY(1)
WRITE(*, *)' Tmelt =', TMELT

4000 NOREF = 0
TSUP = 0
TSTART = TMELT
DO 4010, J = 1, 9000
IF (NOREF.LT. 1.0D-3) TF = TISO/(TFCTOR*5.0D0)
IF (NOREF.GT. 1.0D-3) TF = TISO/(TFCTOR*5.0D1)
IF (NOREF.GT. 1.0D-1) TF = TISO/(TFCTOR*1.0D3)
TSTART = TSTART - TSUP
DTI = TSTART - 298.15
TSUP = TP*6*HI*DTI/(POWDIA*CL)

C WRITE(OUTVDU, *)' TSUP ', TSUP
C TCHECK = TSTART - TSUP/2
C WRITE(OUTVDU, *)' TCHECK ', TCHECK
C WRITE (OUT, *)' TCHECK ', TCHECK
C
INDEX = 0
C ** CALCULATE DG BETWEEN LIQ & SOL **
C ** BY CALLING MULTIPHASE
C **
NT = 1
4055 TEMP(1) = TCHECK
DO 2200 K = 1, MMIN
C
C ** IPHSIN(KK) TO BE DEFINED TO DO NUCL CALC ONE BY ONE **
IF(OOIPN(KK).EQ.0)GOTO 2200
WRITE(OUT, *)'0 PHASE ', PNMEIN(KK)
DO 2300 KK = 1, MMIN
IF(KK.NE.K)IPHSIN(KK) = 0
IF(KK.EQ.K)IPHSIN(KK) = 1
2300 CONTINUE
C ** ADDED LI-MEI, SET COMPOSITION FOR MULTIPHASE CALC **
IF(K.EQ.KLIQ) GOTO 4017
DO 4027, I = 1, NELMIN
IF(ITIE(2, I).NE.KLIQ)THEN
AMOUNT(I) = TIELN(1, I, 2)
ELSE
AMOUNT(I) = TIELN(2, I, 2)
ENDIF
4027 CONTINUE
GOTO 4047
4017 DO 4037, I = 1, NELMIN
   AMOUNT(I) = OLDAMT(I)
4037 CONTINUE
C
C SET MODULE=3 FOR MULTIPHASE CALCULATIONS
C
4047 MODULE = 3
C
C ***NB*** IT IS ESSENTIAL TO SET PRVACT = .FALSE.
C IF CLASSIFICATIONS HAVE BEEN CHANGED
C
   PRVACT = .FALSE.
   PRVSOL = .FALSE.
C
C CALL MULTIPHASE CALCULATION
C
   CALL SGMCC0
C
C CALCULATE ENTHALPY AND HEAT CAPACITY
C
   ISTATE = 1
   NT = 1
   TEMP1 = TEMP(I)
C ** ADDED OCT 89, LI-MEI **
   TEMP1 = TCHECK
C
   WRITE(OUTVDU, *) 'TEMP1 ', TEMP1
C **
C RESET MODULE = 6 IN CASE MORE TRANSITION CALCULATIONS
C MAY BE REQUIRED
C
   MODULE = 6
C
C STORE AWAY REQUIRED QUANTITIES
C EG GFE, GIBBS ENERGY, MUREF, ACTREF
C
CC WRITE(OUT, *)' GFEREF, GFEREF
CC WRITE(OUTVDU, *)' GFEREF, GFEREF
C ** ADDED OCT 89, LI-MEI **
   IF (K .GT. 1) GSOL = GFEREF
C **
   I = 0
   DO 2400 II = 1, NELMIN
   IF (ICMP(II).EQ.0)GOT02400
   I = I + 1
CC WRITE(OUT, *)' CMPT, MUREF, ACTREF'
CC WRITE(OUT, *)CNMEIN(II), MUREF(I), ACTREF(I)
CC WRITE(OUTVDU, *)' CMPT, MUREF, ACTREF'
CC WRITE(OUTVDU, *)CNMEIN(II), MUREF(I), ACTREF(I)
C ** ADDED OCT 89, LI-MEI **
   IF (K .EQ. 1) GPLIQ(II) = MUREF(I)
C **
2400 CONTINUE
2200 CONTINUE
C
C ** ADDED OCT 89, LI-MEI **
C ** TO CALCULATE DG **
   GPLIQS = 0
   DO 4030, II = 1, NELMIN
C **NOT ONLY FOR SOLUTION PHASES: TIELN(2, II, 2) IS ALWAYS **
C ** THE SECOND PHASE COMPOSITION; 1 IS FOR LIQ **
   IF(ITIE(2, 2).NE.KLIQ)THEN
      GPLIQS = GPLIQS + GPLIQ(II)*TIELN(1, II, 2)
   ELSE
      GPLIQS = GPLIQS + GPLIQ(II)*TIELN(2, II, 2)
   ENDIF
4030 CONTINUE
   DGSOL = -GSOL + GPLIQS
C WRITE(OUTVDU, *)' DGSOL ', DGSOL

APPENDIX

243
C **

C

C ** ADDED OCT 89, LI-MEI **
C ** CALCULATE DS FROM DG BETWEEN LIQ & SOL **

IF (INDEX .EQ. 1) THEN
   DGSOL2 = DGSOL
   TCHECK = TCHECK - 0.1
   INDEX = 0
ELSE
   DGSOL1 = DGSOL
   TCHECK = TCHECK + 0.1
   INDEX = 1
GOTO 4055
ENDIF

DSSOL = (DGSOL1-DGSOL2)/0.1
WRITE(OUT, *)' DSSOL ', DSSOL
WRITE(OUT, *)' DGSOL1, DGSOL2 ', DGSOL1, DGSOL2

HMF = DGSOL1 + TCHECK*DSSOL
WRITE(OUT, *)' HMF ', HMF

IF (DGSOL1**2 .LT. 1D-20) THEN
   JTREF = 0
GOTO 1300
ENDIF

GSTAR = 16.0D0*PI/3.0D0*(0.45D0*FIMF)**3/DGSOL1**2

C ***************

IF (NGLS.NE.1) THEN
   DI = D0*EXP(-Q/(RCONST*TCHECK))
C ** DI is liquid diffusion coefficient **
ELSE
C !! SORT OUT THE SIZE OF THE NUMBERS LATER !!

C ** For glass-forming alloys **
EH = 13.83D0*TGLS - 1400.0D0
FT = 0.03D0* EXP(EH/(RCONST*TGLS)) * EXP(-EH/(RCONST*TCHECK))
ETA = 10D12* EXP(-1.0D0/0.03D0) * EXP(1.0D0/FT)
APPENDIX

\[ DI = \frac{KBOLTZ \times TCHECK}{(6.0D0 \times PI \times ETA \times AO)} \]

ENDIF

WRITE (OUT, *)' GSTAR ', GSTAR

C **

JT = DI*NVNUCL/AO**2*EXP(-GSTAR/(RCONST*TCHECK))

C ** REWRITE THE ABOVE EQUATION **

JTREF = LOG(6.3D0*5.0D0/16.0D0)+39.0D0*LOG(1D1)-LOG(NCRITD)

* -GSTAR/(RCONST*TCHECK)

WRITE(OUT, *)' LN(JTREF) ', JTREF

JTREF = EXP(JTREF)

WRITE(OUT, *)' JTREF, JTREF

1300 NOREF = NOREF + JTREF*TF

WRITE(OUTVDU, *)' JT-NUCLEATN RATE ', JTREF

WRITE(OUT, *)' NO OF NUCLEI ', NOREF

IF (NOREF .GT. 1.0D0) GOTO 4089

IF (TCHECK LT. TGLS) GOTO 4089

C ** Tcrit = TCHECK **

4010 CONTINUE

C ** RESET PARAMETERS FOR ANOTHER NUCL CALC **

PRVACT = .FALSE.

PRVSOL = .FALSE.

50 CONTINUE

C **

C RESTORE ORIGINAL PHASE CLASSIFICATIONS AND AMOUNTS

C ** ADDED OCT 89, LI-MEI **

4089 WRITE(*, *)' Tcrit, d =', TCHECK

WRITE(*, *)' Tbdy-Tcrit, d =', TMELT-TCHECK

IF (TCHECK .LT. TGLS) THEN

WRITE(*, *)' Glass forming'

C WRITE(OUT, '*')' Glass forming'

ENDIF

DO 2100 K = 1, MMIN
APPENDIX

IPHSN(K) = OLDIPH(K)

2100 CONTINUE
   DO 40 I = 1, NELMIN
       AMOUNT(I) = OLDAMT(I)
       WEIGHT(I) = OLDMWT(I)
   40 CONTINUE

C
C **ADDED SEPT 90, LI-MEI **
C **RESET PARAMETERS SINCE CLASSIFICATIONS HAVE BEEN CHANGED**
   PRVACT = .FALSE.
   PRVSOI = .FALSE.

C
C **DO FOR ANOTHER SOLID PHASE: **
4100 CONTINUE
C **SET PARAMETERS AGAIN**
   PRVACT = .FALSE.
   PRVSOI = .FALSE.
   RETURN

500 WRITE(OUT, *)' ***FAIL, a variable is undefined'
   WRITE(OUT, *) IPSRNG(2), RNBDY, PCENT, TMAX, TMIN, TACC, POWDIA,
   * IPSRNG(2), RNBDY, PCENT, TMAX, TMIN, TACC, POWDIA
   WRITE(OUTVDU, *)' ***FAIL, a variable is undefined'
   WRITE(OUTVDU, *) IPSRNG(2), RNBDY, PCENT, TMAX, TMIN, TACC, POWDIA,
   * IPSRNG(2), RNBDY, PCENT, TMAX, TMIN, TACC, POWDIA

C
9020 FORMAT ( I14, I4, I1 )
   END
APPENDIX IV

The Programme for Eshelby Calculation

C ** PROGRAMME FOR CALCULATING MODULUS OF METAL MATRIX COMPOSITE **
C ** USING ESHELBY METHOD AND BROWN-CLARKE Sijkl PARAMETERS **
C
IMPLICIT DOUBLE PRECISION (A-H, O-Z)
DOUBLE PRECISION IA, IC, EM, EI, EC, UC, A, B, D
DIMENSION S(3, 3, 3, 3), CM(6, 6), CI(6, 6)
DIMENSION II(6, 6), CMI(6, 6), SSII(6, 6), SI(6, 6)
DOUBLE PRECISION INTER(6, 6), DEM(6, 6), INDEM(6, 6), INVER(6, 6)
DIMENSION SS(6, 6), SFSI(6, 6), E(6, 6), CMINV(6, 6), CCINV(6, 6)
PI = 3.1415926
C
C ** DEFINE IDENTITY MATRIX **
DO 10, J = 1, 6
DO 20, K = 1, 6
IF (K .EQ. J) II(J, K) = 1
IF (K .NE. J) II(J, K) = 0
20 CONTINUE
10 CONTINUE
C
C ** INPUT MODULI OF MATRIX (EM) AND INCLUSION (EI) **
WRITE(*, *) 'INPUT EM, –Elastic Modulus of Matrix’
READ (*, *) EM
WRITE(*, *) 'INPUT EI, –Elastic Modulus of Inclusion’
READ(*, *) EI
C
**APPENDIX**

**INPUT VOLUME FRACTION OF THE INCLUSION**

```plaintext
WRITE(*, *) 'INPUT f, Vol Fraction of Inclusion'
READ(*, *) F
WRITE(*, *) 'INPUT vM, Poisson Ratio of Matrix'
READ(*, *) VM
WRITE(*, *) 'INPUT vI, Poisson Ratio of Inclusion'
READ(*, *) VI
WRITE(*, *) 'INPUT p, Finite inclusion aspect ratio'
READ(*, *) P
```

**DEFINE DEFAULT MATRIX CM, CI etc.**

```plaintext
DO 110, I = 1, 6
   DO 120, J = 1, 6
      CM(I, J) = 0
      CI(I, J) = 0
      CMINV(I, J) = 0
      INTER(I, J) = 0
      DEM(I, J) = 0
      INDEM(I, J) = 0
      CMI(I, J) = 0
   120 CONTINUE
```

**INPUT OF MATRIX AND INCLUSION MODULUS TENSOR**

```plaintext
KM = EM/(3*(1-2*VM))
KI = EI/(3*(1-2*VI))
UM = EM/(2*(1+VM))
UI = EI/(2*(1+VI))
CM(1, 1) = KM + (4.0/3.0)*UM
CI(1, 1) = KI + (4.0/3.0)*UI
CM(1, 2) = KM - (2.0/3.0)*UM
CI(1, 2) = KI - (2.0/3.0)*UI
CM(4, 4) = UM
CI(4, 4) = UI
CM(2, 2) = CM(1, 1)
CM(3, 3) = CM(1, 1)
CM(2, 1) = CM(1, 2)
CM(1, 3) = CM(1, 2)
```
APPENDIX

\[
\begin{align*}
CM(3, 1) &= CM(1, 2) \\
CM(2, 3) &= CM(1, 2) \\
CM(3, 2) &= CM(1, 2) \\
CM(5, 5) &= CM(4, 4) \\
CM(6, 6) &= CM(4, 4) \\
CI(2, 2) &= CI(1, 1) \\
CI(3, 3) &= CI(1, 1) \\
CI(2, 1) &= CI(1, 2) \\
CI(1, 3) &= CI(1, 2) \\
CI(3, 1) &= CI(1, 2) \\
CI(2, 3) &= CI(1, 2) \\
CI(3, 2) &= CI(1, 2) \\
CI(5, 5) &= CI(4, 4) \\
CI(6, 6) &= CI(4, 4)
\end{align*}
\]

C ** DEFINE ESHELBY'S FOURTH RANK TENSOR Sijkl **

\[
\begin{align*}
&\text{DO } 113, I = 1, 3 \\
&\text{DO } 123, J = 1, 3 \\
&\text{DO } 133, K = 1, 3 \\
&\text{DO } 143, L = 1, 3 \\
&S(I, J, K, L) = 0 \\
&143 \text{ CONTINUE} \\
&133 \text{ CONTINUE} \\
&123 \text{ CONTINUE} \\
&113 \text{ CONTINUE}
\end{align*}
\]

C

\[
\begin{align*}
&\text{IF} (P \geq 1000) \text{ THEN} \\
&S(1, 1, 1, 1) = (5-4*VM)/(8*(1-VM)) \\
&S(2, 2, 2, 2) = S(1, 1, 1, 1) \\
&S(1, 1, 2, 2) = (-1+4*VM)/(8*(1-VM)) \\
&S(2, 2, 1, 1) = S(1, 1, 2, 2) \\
&S(1, 1, 3, 3) = VM/(2*(1-VM)) \\
&S(2, 2, 3, 3) = S(1, 1, 3, 3) \\
&S(3, 3, 1, 1) = 0 \\
&S(3, 3, 2, 2) = S(3, 3, 1, 1) \\
&S(1, 2, 1, 2) = (3-4*VM)/(8*(1-VM)) \\
&S(3, 1, 3, 1) = 0.25 \\
&S(2, 3, 2, 3) = 0.25
\end{align*}
\]
APPENDIX

GOTO 30
ENDIF

IF ( P .EQ. 1) THEN
  SD1 = (7-5*VM)/(15*(1-VM))
  SD2 = (5*VM-1)/(15*(1-VM))
  SD3 = (4-5*VM)/(15*(1-VM))
  S(1, 1, 1, 1) = SD1
  S(1, 1, 2, 2) = SD2
  S(1, 1, 3, 3) = SD2
  S(2, 2, 1, 1) = SD2
  S(2, 2, 2, 2) = SM
  S(2, 2, 3, 3) = SD2
  S(3, 3, 1, 1) = SD2
  S(3, 3, 2, 2) = SD2
  S(3, 3, 3, 3) = SM
  S(1, 2, 1, 2) = SD3
  S(1, 3, 1, 3) = SD3
  S(2, 3, 2, 3) = SD3
  GOTO 30
END IF

C

Q = 3/(8*PI*(1-VM))
R = (1-2*VM)/(8*PI*(1-VM))
ACOSHP = LOG(P+(P**2-1)**.5)
C
PRINT*, COSHP

IA = 2*PI*P/(P**2-1)**1.5 * (P*(P**2-1)**0.5 - ACOSHP)
IC = 4*PI - 2*IA
T = Q*(4*PI-3*IA)/(3*(P**2-1))
C

S(1, 1, 1, 1) = Q*PI + R*IA + 3.0/4.0*T
S(2, 2, 2, 2) = S(1, 1, 1, 1)
S(1, 1, 2, 2) = Q*PI/3.0 - R*IA + T/4.0
S(2, 2, 1, 1) = S(1, 1, 2, 2)
S(1, 1, 3, 3) = -R*IA - P**2*T
S(2, 2, 3, 3) = S(1, 1, 3, 3)
S(3, 3, 1, 1) = -R*IC - T
APPENDIX

\[ S(3, 3, 2, 2) = S(3, 3, 1, 1) \]
\[ S(3, 3, 3, 3) = Q^*4\pi/3 + R^*IC + 2^*P^*2^*T \]

\[ S(2, 3, 2, 3) = 2^*PI*R - IA*R/2.0 - (1+P^*2)/2^*T \]
\[ S(3, 1, 3, 1) = 2^*PI*R - IA*R/2.0 - (1+P^*2)/2^*T \]
\[ S(1, 2, 1, 2) = Q^*PI/3.0 + R^*IA + T/4.0 \]

\[ \text{TO SIMPLIFY THE S MATRIX} \]

\begin{verbatim}
30 DO 106, I = 1, 6
   DO 206, J = 1, 6
      SS(I, J) = 0
   206 CONTINUE
106 CONTINUE

SS(1, 1) = S(1, 1, 1, 1)
SS(1, 2) = S(2, 2, 1, 1)
SS(1, 3) = S(3, 3, 1, 1)
SS(2, 1) = S(1, 1, 2, 2)
SS(2, 2) = S(2, 2, 2, 2)
SS(2, 3) = S(3, 3, 2, 2)
SS(3, 1) = S(1, 1, 3, 3)
SS(3, 2) = S(2, 2, 3, 3)
SS(3, 3) = S(3, 3, 3, 3)
SS(4, 4) = S(2, 3, 2, 3)
SS(5, 5) = S(3, 1, 3, 1)
SS(6, 6) = S(1, 2, 1, 2)
\end{verbatim}

\[ \text{** MODULI CALCULATIONS ARE BASED ON THE FOLLOWING EQUATIONS :} \]

\begin{verbatim}
500 CONTINUE
C WRITER(*, 4000) 'SS(I, K)', (SS(I, K), K=1, 6)
500 CONTINUE
C
DO 510, J = 1, 6
   DO 520, K = 1, 6
      SFSI(J, K) = SS(J, K) - F*(SS(J, K) - II(J, K))
520 CONTINUE
\end{verbatim}
** APPENDIX **

520 CONTINUE
510 CONTINUE
C
C ** BELOW IS CALCULATION OF [(CM-CI)*SFSI-CM] ***
  DO 530, I=1, 6
  DO 540, J=1, 6
  DO 541, K=1, 6
  INTER(I, J) = INTER(I, J) + CMI(I, K)*SFSI(K, J)
541 CONTINUE
  INTER(I, J) = INTER(I, J) - CM(I, J)
540 CONTINUE
530 CONTINUE
C
C ** TO CALCULATE INVERSE OF INTER(I, J): INVER(I, J) ***
C
  A = INTER(1, 1)**2 - INTER(1, 2)**2
  B = INTER(1, 2)**2 - INTER(1, 1)*INTER(1, 2)
  D = A*INTER(1, 1) + 2*B*INTER(1, 2)
  DO 550, I=1, 6
  DO 560, J=1, 6
  IF (I LE. 3 .AND. J LE. 3) THEN
    IF(I. EQ. J) THEN
      INVER(I, J) = A/D
    ELSE
      INVER(I, J) = B/D
    ENDIF
  ELSE
    IF(I EQ. J) THEN
      INVER(I, J) = 1/INTER(I, J)
    ENDIF
  ENDIF
560 CONTINUE
550 CONTINUE
C
C ** TO CALCULATE INVERSE OF CM ***
  A = CM(1, 1)**2 - CM(1, 2)**2
  B = CM(1, 2)**2 - CM(1, 1)*CM(1, 2)
APPENDIX

\[
D = A \cdot CM(1, 1) + 2 \cdot B \cdot CM(1, 2)
\]

DO 610, I = 1, 6
DO 611, J = 1, 6
IF(I .LE. 3 .AND. J .LE. 3) THEN
  IF (I .EQ. J) THEN
    CMINV(I, J) = A/D
  ELSE
    CMINV(I, J) = B/D
  ENDIF
ELSE
  IF(I .EQ. J) THEN
    CMINV(I, J) = 1/CM(I, J)
  ENDIF
ENDIF
ENDIF
611 CONTINUE
610 CONTINUE
C
C *********************************
C ** ASSUME CMINV IS O.K. THEN **
C ** CALCULATE DEM(I, J) = CMI*CMINV ***
    DO 710, I = 1, 6
    DO 720, J = 1, 6
    DO 730, K = 1, 6
    DEM(I, J) = DEM(I, J) + CMI(I, K) * CMINV(K, J)
730 CONTINUE
720 CONTINUE
710 CONTINUE
C ** CALCULATE INDEM(I, J) = INVER*CMI*CMINV ***
    DO 740, I = 1, 6
    DO 750, J = 1, 6
    DO 760, K = 1, 6
    INDEM(I, J) = INDEM(I, J) + INVER(I, K) * DEM(K, J)
760 CONTINUE
750 CONTINUE
740 CONTINUE
C
C
C ** THEN CALCULATE CCINV: THE COMPLIANCE TENSOR ***

DO 810, I = 1, 6
DO 820, J = 1, 6
CCINV(I, J) = CMINV(I, J) - F*INDEM(I, J)
820 CONTINUE
WRITE(*, 4000) (CCINV(I, J), J=1, 6)
810 CONTINUE

4000 FORMAT(6F8.4)
   EC = 1 / CCINV(3, 3)
   UC = 1 / CCINV(4, 4)
   WRITE(*, *)
   WRITE(*, 4001) EC
   WRITE(*, 4002) UC
   WRITE(*, *)

4001 FORMAT(‘ Elastic modulus of composite = ’, F8.2)
4002 FORMAT(‘ Shear modulus of composite = ’, F8.2)
   WRITE(*, *)STOP? .. (0) OR CONTINUE? .. (1)
   READ(*, *) NY
   IF(NY.NE.0) GOTO99
STOP
END
APPENDIX V

Derivation of Tensor A and B in the Mean Stress Equation

\[ \langle \sigma \rangle_M = A \, \varepsilon^T + B \, \sigma^A \]

As given by Equation (11a) in Withers et al [89Wit],

\[ \langle \varepsilon \rangle_M = f [S - I]^T [(C_M - C_I) [S - f(S - I)] - C_M]^{-1} [C_I \varepsilon^T - (C_I - C_M) \varepsilon^A] \]  \hspace{1cm} (11a)

Because

\[ \langle \sigma \rangle_M = C_M \langle \varepsilon \rangle_M \]

and

\[ \sigma^A = C_M \varepsilon^A \quad \text{hence} \quad \varepsilon^A = C_M^{-1} \sigma^A \]

replacing \( \langle \varepsilon \rangle_M, \varepsilon^A \) in Equation (11a) with \( \langle \sigma \rangle_M \) and \( \sigma^A \) respectively gives:

\[ \langle \sigma \rangle_M = f C_M [S - I]^T [(C_M - C_I) [S - f(S - I)] - C_M]^{-1} C_I \varepsilon^T \]

\[ - f C_M [S - I]^T [(C_M - C_I) [S - f(S - I)] - C_M]^{-1} (C_I - C_M) C_M^{-1} \sigma^A \]

The mean stress was written in Withers et al [89Wit] as Equation (11b):

\[ \langle \sigma \rangle_M = A \, \varepsilon^T + B \, \sigma^A \]  \hspace{1cm} (11b)

Therefore

\[ B = f C_M [S - I]^T [(C_M - C_I) [S - f(S - I)] - C_M]^{-1} (C_M - C_I) C_M^{-1} \]

The expression for tensor A is thus also obtained.