

PHASE SEPARATION IN  
SOME MODEL NICKEL-BASE SUPERALLOYS

by

Sally Anne Hill

Newnham College

A dissertation submitted for the degree of  
Doctor of Philosophy in the University of Cambridge

December 1980

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PREFACE

Department of Metallurgy  
University of Cambridge

This dissertation is submitted for the degree of Doctor of Philosophy in the University of Cambridge. The research described herein was carried out in the Department of Metallurgy and Materials Science, University of Cambridge, between October 1979 and December 1980, under the supervision of Dr. B. Ralph.

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## PREFACE

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$A_n$	coefficient of $n^{\text{th}}$ Fourier cos term	data
$A_n$	major species of binary (A+B) alloy	
REFERENCES	wavenumber term in equation E2.11	123
$B_n$	coefficient of $n^{\text{th}}$ Fourier sine term	
$\bar{B}_n$	mean coefficient of $n^{\text{th}}$ sine terms	
$C_n$	$n^{\text{th}}$ compositional term in sampling domain	
$C_n^R$	reduced compositional term after subtraction of mean, $\bar{c}$	
$C_n^{R'}$	new reduced term after subtraction of Fourier terms	
$\tilde{D}$	interdiffusion coefficient	
E	Young's modulus	
$F_c$	total free energy, Fourier notation	
$F(h)$	elastic free energy	
$F(\omega)$	Fourier transform of discrete data	
$F(\omega)$	Fourier transform of aperiodic function $f(t)$	
$F(\omega), G(\omega)$	Fourier pairs (transforms) of functions $f(t), g(t)$	
$G(h)$	chemical free energy	
$\tilde{J}$	interdiffusional flux	
$\tilde{J}_A$	interdiffusional flux of species A	
$J_k$	nucleation rate	
$J_k^s$	steady state nucleation rate	
K	chemical gradient energy coefficient	

SYMBOLS AND ABBREVIATIONS

Symbols

A	minor species of binary (A+B) alloy
$\bar{A}$	arithmetic mean amplitude
$A_I(\beta)$	Fourier amplitude of wavenumber
$\bar{A}_I(\beta)$	mean Fourier amplitude of wavenumber
$A_n$	coefficient of $n^{\text{th}}$ Fourier cos term
B	major species of binary (A+B) alloy
B	wavenumber term in equation E2.11
$B_n$	coefficient of $n^{\text{th}}$ Fourier sine term
$\bar{B}_n$	mean coefficient of $n^{\text{th}}$ sine terms
$C_n$	$n^{\text{th}}$ compositional term in sampling domain
$C_n^R$	reduced compositional term after subtraction of mean, c
$C_n^{R'}$	new reduced term after subtraction of Fourier terms
$\tilde{D}$	interdiffusion coefficient
E	Youngs modulus
$F_t$	total free energy, Fourier notation
$F(h)$	elastic free energy
$F(v)$	Fourier transform of discrete data
$F(\omega)$	Fourier transform of aperiodic function $f(t)$
$F(\omega), G(\omega)$	Fourier pairs (transforms) of functions $f(t), g(t)$
$G(h)$	chemical free energy phase
$\tilde{J}$	interdiffusional flux phase
$\tilde{J}_A$	interdiffusional flux of species A
$J_k$	nucleation rate component A
$J_k^s$	steady state nucleation rate
K	chemical gradient energy coefficient critical nuclei

$L$	APFIM drift distance
$M$	atomic mobility
$N, n, t$	number of samples
$N_v$	electron vacancy number
$N_v$	number of atoms per unit volume
$Q(h)$	Fourier transform of concentration covariance
$R(\beta)$	amplification factor of wavenumber
$S$	degree of long range order
$T$	temperature
$T_c$	critical temperature
$T_s$	temperature of chemical spinodal
$T_s^*$	temperature of coherent spinodal
$U$	number of B atoms between adjacent A atoms in data chain
$V$	variance
$V_{DC}$	applied standing voltage
$V_P$	additional pulse voltage
$V(h)$	concentration wave
$X_t$	state of system at time $t$
$Y$	function of elastic constants defined by equation E2.9
$Z$	Zeldovitch factor
$a, b$	Bragg-Williams constants
$a, d$	lattice parameters
$a_\gamma$	lattice parameter of $\gamma$ phase
$a_{\gamma'}$	lattice parameter of $\gamma'$ phase
$\bar{c}$	mean composition
$c_A$	concentration of component A
$c_e$	equilibrium concentration
$c_k^o$	metastable equilibrium concentration of critical nuclei

$c_0$	initial concentration
$c_s$	spinodal composition
$d$	particle diameter
$e$	electronic charge
$f$	Helmholtz free energy per unit volume
$f'$	$(\partial f / \partial c)$
$f''$	$(\partial^2 f / \partial c^2)$
$f_A''$	$(\partial^2 f / \partial c^2)$
$f(t), g(t)$	aperiodic functions
$h$	allowed lattice site
$k$	Boltzman's constant
$k_1, k_2, k_3$	constants
$m/ne$	ionic mass-to-charge ratio
$m, t$	size of data sampling unit
$r$	particle radius
$t$	time
$\Delta G_n$	free energy change
$\Phi$	integral free energy
$\Psi(h)$	free energy in concentration wave formulation
$\alpha(h)$	amplification factor, concentration wave formulation
$\alpha_r$	fraction of "correctly" occupied lattice sites
$\beta$	Fourier wavenumber
$\beta_k$	frequency with which critical nucleus exceeds critical size
$n$	percentage lattice misfit
$n$	(phase) hexagonal $Ni_3Ti$
$\gamma$	f.c.c. matrix
$\gamma'$	$L1_2$ -type second phase

$\lambda$	wavelength
$\lambda_c$	critical wavelength
$\lambda_m$	wavelength receiving maximum amplification
$\mu$	chemical potential
$\nu$	Poisson's ratio
$\sigma$	(math.) standard deviation
$\sigma$	(phase) Laves phase
$\tau$	incubation time
$\tau$	data sampling interval
$\omega, \nu$	frequency
*	convolution operator
II(t)	rectangular sampling function
III(t)	infinite impulse train
QAP	Quantitative Atom-Probe
SADP	Selected Area Diffraction Pattern
SFE	Stacking Fault Energy
SIMS	Secondary Ion Mass Spectrometer
STEM	Scanning Transmission Electron Microscope
TEM	Transmission Electron Microscope
VDC	Volume Diffusion Control
b.c.c.	body centred cubic
f.c.c.	face centred cubic

Abbreviations

APB	Anti-Phase (domain) Boundary
APFIM	Atom-Probe Field Ion Microscope
DFFT	Discrete Fast Fourier Transform
DFT	Discrete Fourier Transform
EDS	Energy Dispersive Spectrometry
FFT	Fast Fourier Transform
FIM	Field-Ion Microscope
FT	Fourier Transform
IAP	Imaging Atom-Probe
IC	Interface Control
LRO	Long Range Order
PSR	Plane Stability Ratio
QAP	Quantitative Atom-Probe
SADP	Selected Area Diffraction Pattern
SFE	Stacking Fault Energy
SIMS	Secondary Ion Mass Spectrometer
STEM	Scanning Transmission Electron Microscope
TEM	Transmission Electron Microscope
VDC	Volume Diffusion Control
b.c.c.	body centred cubic
f.c.c.	face centred cubic

Studies of Ni-20.0at.%Cr-14.0at.%Al alloy (Chapter 5) indicate that in this material two populations of modulated second phase  $\gamma'$ , differing in both composition and size, are present. The possibility that these arise from separate spinodal and conventional nucleation

## PHASE SEPARATION IN SOME MODEL NICKEL-BASE SUPERALLOYS

### GENERAL SUMMARY

Many physical properties of high temperature nickel-base superalloys are dictated by features of the underlying two-phase  $\gamma/\gamma'$  microstructure. This dissertation examines mechanisms by which  $\gamma/\gamma'$  distributions are generated in some model superalloys, each model being designed to illustrate a particular feature displayed by more complex commercial materials. The major technique employed in this study is Atom-Probe Field-Ion Microscopy (APFIM). Subsidiary data are provided by Transmission Electron Microscopy.

Background summaries of superalloy microstructure and formal theory of phase transitions are presented in Chapters 1 and 2 respectively. Chapter 3 of the thesis develops an original and quantitative method of data chain analysis suitable for use in APFIM studies of continuous (spinodal) decomposition kinetics. Extensions of the method to studies of other transitions and more general data analysis are discussed.

This new method of APFIM data analysis is employed in Chapter 4 to examine phase separation in rapidly-quenched Ni-14.1at.%Al alloy. It is shown that decomposition proceeds continuously at 625°C. The spinodal reaction is replaced by conventional nucleation as the quench rate is lowered.

Studies of Ni-20.0at.%Cr-14.0at.%Al alloy (Chapter 5) indicate that in this material two populations of modulated second phase  $\gamma'$ , differing in both composition and size, are present. The possibility that these arise from separate spinodal and conventional nucleation

changes is discussed.

#### GENERAL INTRODUCTION

Chapter 5 also demonstrates that  $\gamma'$  phase is nucleated conventionally in Ni-9.1at.%Al-4.4at.%Ti and Ni-8.7at.%Al-2.5at.%Ti alloys. The initial second phase composition is sensitive to service prequench temperature, which suggests that nucleation is highly heterogeneous, decomposition proceeding via a non-equilibrium phase.

A matrix model of alloy PE16 (Chapter 6) shows conventional and wrought forms superalloys are employed for structural and moving homogeneous nucleation. APFIM studies of elemental partitioning reveal that adjustment of the titanium/aluminium ratio in the  $\gamma'$  towards equilibrium apparently follows the rejection from the  $\gamma'$  lattice of species (particularly chromium) which partition to the  $\gamma$  phase. The implications of this observation are examined.

Chapter 7 discusses the general conclusions reached in the thesis and suggests possible future studies based upon the results. Overall, data for the model systems examined suggest that under conditions of high solute supersaturation reaction to  $\gamma/\gamma'$  microstructures may proceed spinodally (continuously) in commercial alloys.

stability has been affected by dispersion strengthening using rare earth oxides, particularly in artifacts produced by powder metallurgical routes (Gessinger and Bonford 1974; Lewis, Parkin and Thompson 1977).

The behaviour of these alloys under given service conditions is often predicted on the basis of empirical measurements of physical and mechanical properties since theoretical assessments are extremely difficult. The understanding and control of microstructure and behaviour may be improved, however, by knowledge of the phase

## GENERAL INTRODUCTION

Nickel-base superalloys possess high strength, good stability with respect to creep and excellent corrosion resistance in a service temperature range of  $550^{\circ}$ - $1300^{\circ}$ C. The alloys are essentially high temperature analogues of the austenitic stainless steels (maximum service temperature  $\sim 800^{\circ}$ C, Decker and deWitt 1965). In various cast and wrought forms superalloys are employed for structural and moving parts in power plant and aeroengines (e.g. Sims 1978) and also in the manufacture of high-temperature pressure vessels.

The early superalloys (service temperature  $650^{\circ}$ - $750^{\circ}$ C, Betteridge and Heslop 1974) exhibited essentially only one solid state precipitation reaction, that is, the formation of ordered  $\gamma'$  phase (based upon  $\text{Ni}_3\text{Al}$ ) from supersaturated solid solution. In subsequent materials alloying additions used to promote an increase in service temperature encouraged the formation of several other phases, both desirable (carbides to prevent grain boundary sliding) and deleterious (brittle Laves phases). Recently yet greater microstructural stability has been effected by dispersion strengthening using rare earth oxides, particularly in artifacts produced by powder metallurgical routes (Gessinger and Bomford 1974; Lewis, Parkin and Thompson 1977).

The behaviour of these alloys under given service conditions is often predicted on the basis of empirical measurements of physical and mechanical properties since theoretical assessments are extremely difficult. The understanding and control of microstructure and behaviour may be improved, however, by knowledge of the phase

transformations by which the complex structure is generated. The present dissertation concentrates upon identification of possible phase transitions by which basic two-phase  $\gamma/\gamma'$  microstructures of superalloys may develop.

The complexity of commercial superalloys renders direct analysis of phase transformation behaviour a non-trivial and difficult problem. The present study therefore approaches the investigation by identifying the operative transition mechanisms in a series of model superalloys of varying complexity, each alloy being designed to illustrate a particular feature of the  $\gamma'$  separation reaction.

The first chapter of this thesis considers the general characteristics of superalloys and discusses the selection of the model systems nickel-aluminium, nickel-chromium-aluminium, nickel-aluminium-titanium, and a PE16 matrix model alloy. Chapter 1 also introduces the mechanisms of phase separation and other transitions which may occur in the alloys. Formal developments of appropriate transition theories are presented in Chapter 2 with particular attention to continuous changes.

Experimentally, studies of precipitation reactions require microanalysis, in order to assess the extent of separation, and measurements of particle sizes, in order to follow growth processes. In the present work these results were obtained principally by various forms of Atom-Probe Field-Ion Microscopy (APFIM, e.g. Mueller 1970a, 1974; Panitz 1975; Waugh and Southon 1979). Subsidiary data were produced by Transmission Electron Microscopy (TEM, e.g. Hirsch, Howie, Nicholson, Pashley and Whelan 1965; Thomas and Goringe 1979). Operational methods are not pursued in detail in the present study,

with the exception of a brief summary in Appendix A of the less common technique of APFIM. General reviews of instrumental techniques have been given by e.g. Mulvey and Webster 1974, Edington 1979 and some examples of investigations which have employed general techniques of microstructural examination are discussed by Ralph 1980.

Once gathered, data must be analysed and presented in a form suitable for direct comparison with compositional and size changes predicted by transition theories. For continuous changes, which are the major subject of this study, the most appropriate representation describes composition profiles in terms of the relative contributions of wavelengths present in the trace. To date no fully quantitative method of such analysis has been presented for APFIM data. Chapter 3 is therefore devoted to development of an original method of analysis by a Fourier transform technique. The route is designed to generate spectral components in a form suitable for comparison with current theories of continuous phase separation. This method is also general, however, and may be applied to other data streams.

The results of experimental investigations and analyses of the model materials are presented and discussed in Chapters 4-6. Specific transformation mechanisms which are identified include spinodal phase separation in binary Ni-14.1at.% Al alloy (analysis of clustering kinetics, Chapter 4) and homogeneous nucleation and growth in PE16 matrix model material (Chapter 6). Observations of alloys of the ternary systems Ni-Cr-Al and Ni-Al-Ti (Chapter 5), however, reveal much more complex behaviour. Also, as factors which exert considerable influence upon engineering properties of alloys, segregation and partitioning effects are examined in some detail. In

particular, the ratio of Ti:Al in the  $\gamma'$  phase of the model PE16 was monitored as a function of ageing time. It was observed that adjustment of the ratio from  $1.1 \pm 0.06$  to  $1.6 \pm 0.05$  occurred in the latter half of the  $\gamma'$  heat treatment, apparently subsequent to the rejection of all but small equilibrium amounts of  $\gamma$ -partitioning elements chromium, iron and molybdenum.

The remaining chapter, Chapter 7, summarises the findings of the investigation, and relates the results to known characteristics of similar commercial materials. Suggestions for further work are also proposed on the basis of these results, both in terms of other modelling studies and more complex studies of early-stage partitioning in industrial alloys.

Reviews of the evolution of the superalloys, studies of the effects of each component of the microstructure and summaries of physical properties may be found in the literature (e.g. Sims 1966; Kotval 1969; Sabol and Stickler 1969; Davies and Johnston 1970; Sims and Hagel 1972; Betteridge and Heslop 1974; Kear 1974; Hammond and Nutting 1977). This dissertation is also limited to examples of microstructure which are pertinent only to wrought material. The microstructural effects of other fabrication methods are again considered in the references (see also e.g. Gessinger and Bowford 1974; and for casting VerSnyder and Shank 1970).

Some topics relevant to the present study of the development of  $\gamma/\gamma'$  microstructures are introduced briefly in the present chapter. Section 1.2 summarises some pertinent features of  $\gamma/\gamma'$  distributions and their development. Specific knowledge of reactions which generate these distributions and the compositions of the participating phases