CHAPTER 1

γ/γ' MICROSTRUCTURES IN NICKEL-BASE SUPERALLOYS

1.1 Introduction

Superalloys, as now developed, comprise a large collection of phases. The main microstructural features are distributions of an ordered γ' phase within a γ matrix. In the commercial alloys additional distributions of such phases as carbides, oxides and borides are found. Whilst these latter distributions are of very considerable consequence in determination of the exact relationships between microstructure and physical properties in such alloys, this dissertation is concerned solely with the evolution of γ/γ' microstructures. 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 Bomford 1974; and for casting VerSnyder and Shank 1970).

Some topics relevant to the present study of the development of γ/γ' microstructures are introduced briefly in the present chapter. Section 1.2 summarises some pertinent features of γ/γ' distributions and their development. Specific knowledge of reactions which generate these distributions and the compositions of the participating phases is particularly important in the much wider and industrially applicable context of the prediction of microstructure. Given the overall alloy composition various algorithms are used to assess the possible tendency of the material to the formation of brittle hexagonal phases such as σ-phase. One predictive method, PHACOMP, is considered very briefly as part of the summary of γ' behaviour. Later in the dissertation (Chapter 6) APFIM analyses of a matrix model of Nimonic PE16 are presented and the position of the matrix with respect to σ-phase formation is compared with the predictions of PHACOMP.

The model systems which have been selected to illustrate particular aspects of transition behaviour to these microstructures are discussed in Section 1.3. The ideas behind phase transition theories which are to be tested in the experimental sections of this thesis are then introduced in Section 1.4. More formal developments of theoretical treatments are reserved for Chapter 2.

1.2 The Phases

1.2.1 Matrix phase - γ

Partitioning or substitution effects in the γ and γ' phases of superalloys are governed principally by electronic considerations (Guard and Westbrook 1959, Rawlings and Staton-Bevan 1975). Thus the face-centred cubic matrix phase is an extended solid solution of the transition elements cobalt, iron, chromium, molybdenum, tungsten and vanadium in nickel (e.g. Sims and Hagel 1972, Betteridge and Heslop 1974) with only traces of γ'- formers. The major strengthening effects of the substituents in the γ phase are solute drag, arising from dissimilarity in atomic size (primarily molybdenum, tungsten and vanadium), and impedance of cross-slip by lowering of stacking fault energy (S.F.E) (cobalt). (see e.g. Guard and Westbrook 1959; Pelloux and Grant 1960; Stoloff and Davies 1965; Copley and Kear 1967). Other contributions may come from modulus changes and short range ordering.

1.2.2 γ' phase

The basic equilibrium γ' phase is $L1_2$ (ordered) Ni_3Al, for which $a_{\gamma'} > a_{\gamma}$. Major substituents on the aluminium sub-lattice are titanium, niobium, tantalum and vanadium. Cobalt may substitute on the nickel sub-lattice and when present in an alloy it is partitioned between nickel sites in both γ and γ' phases. A small tolerance is also demonstrated by γ' towards iron, chromium and molybdenum. These elements are thought to be distributed between the sub-lattices. A variety of spatial and chemical factors such as precipitate size, volume fraction and morphology, lattice and modulus mismatch, anti-phase domain boundary energy and degree of order determine the hardening effect of the second phase.

Two basic morphologies of γ' have been observed. The phase may occur either as distributions of discrete particles or, at grain boundaries, as cellular colonies (e.g. Barlow and Ralph 1979, 1980). Replacement phases with different morphologies have also been found. In alloys of high titanium content γ' phase is only a metastable product and thus at least partial transformation to equilibrium hexagonal (needle-like) η-phase may occur (Betteridge and Heslop 1974). In materials with high niobium contents b.c.c. Nb_3Al-type phase may replace Ni_3Al-type γ' (e.g. Betteridge and Heslop 1974). Unless otherwise stated this dissertation is concerned only with study of the generation of discrete γ'-phase particles of Ni_3Al-type.

The extent of γ/γ' lattice disregistry is adjusted essentially by variation of the matrix content of chromium and molybdenum which expand the γ lattice parameter towards or even beyond that of the γ'. The exact morphology of discrete particles of Ni_3Al-type γ' phase is strongly dependant upon this misfit. In alloys of near-zero misfit the new phase appears as spheres. As mismatch is increased the morphology tends to become cuboidal (Hagel and Beattie 1959, Oblak and Kear 1975, and for model systems, e.g. nickel-chromium-aluminium, Gleiter and Hornbogen 1967a, Chapter 5).

Particle distributions like-wise change with misfit, varying from random arrangement of zero-mismatch second phase to rafts and rods of closely allied particles where there is large strain field interaction (e.g. Ardell, Nicholson and Eshelby 1966; Chellman and Ardell 1974). A convenient description of these modulated microstructures in terms of a radial distribution of precipitates upon a postulated cubic macrolattice has been proposed by Tyapkin and co-workers (Tyapkin, Travina and Kozlov 1973, 1974, 1975; Tyapkin 1977).

The degree of mismatch also determines the exact rate of ($t^{1/3}$) coarsening of γ' (Betteridge and Heslop 1974; Hammond and Nutting 1977). Here, the greater the disregistry, the larger the driving force to reduce total surface area and the faster the ripening. Some studies of the influence of particular elemental species upon γ' distribution have also been made. For example, enrichment of the Ti/Al ratio decreases the γ' coarsening rate (Rogen and Grant 1960; Gibbons and Hopkins 1971).

The presence of γ' distributions has a marked effect upon deformation behaviour of superalloys. At low temperatures the two most relevant modes of dislocation propagation are looping (or bowing) and cutting of particles (e.g. Kelly and Nicholson 1963; Gleiter and Hornbogen 1967a; Copley and Kear 1967; Decker 1969; Ham 1970; Brown and Ham 1971; Kear 1974). The operative mechanism is determined essentially by the magnitude of the interparticle spacing, looping occurring at large precipitate separation and cutting at small spacings. Control of deformation mode is therefore possible by variation of the volume fraction, size and morphology of second phase (discussed above). Some control may also be exerted by alteration of mismatch which influences the effective spacing.

Two examples of the many theoretical treatments of hardening by coherent, ordered precpitates are the work of Gleiter and Hornbogen 1967a (for static systems) and the study of dynamic systems by Copley and Kear 1967. Details of dissociation reactions and slip of dislocations in the γ' phase are discussed further by Kear et al. (Kear, Giamei, Silcock and Ham 1968, Kear, Giamei, Leverant and Oblak 1969a, 1969b; Kear, Oblak and Giamei 1970).

Practical investigations of the relative contributions of various hardening mechanisms have revealed no clearly dominant factor (e.g. Fleischer 1963; Gleiter and Hornbogen 1965a; Gerold and Haberkorn 1966; Phillips 1967, 1968; Decker and Mihalisin 1969; Parker 1970; Raynor and Silcock 1970).

1.2.3 Prediction of γ/γ' dominance : PHACOMP

As stated in section 1.1 (above), PHACOMP (Sims 1966; Woodyatt,

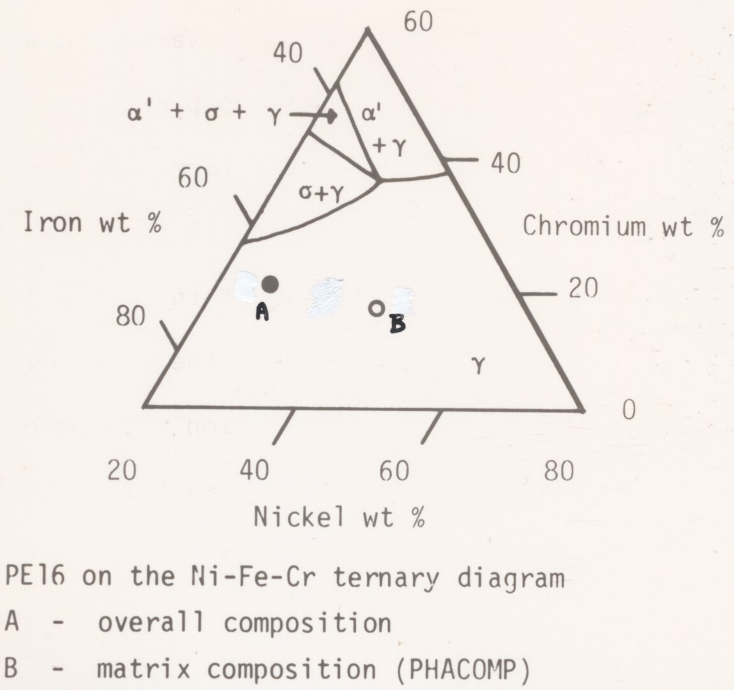

Figure 1.1 Location of Nimonic PE16 on the Ni-Fe-Cr ternary diagram (after Betteridge and Heslop 1974).

Sims and Beattie 1966; Mihalisin, Bieber and Grant 1968; and also Wallace 1975) is one means of assessing which phases are to be expected in a given alloy. The method assumes that, after carbide precipitation, all remaining aluminium, niobium and titanium, plus 10% of the overall chromium content, form γ' phase with nickel. A "mean electron vacancy number", N_v, is then calculated for the remaining composition (examples of individual electron vacancy numbers are Cr,Mo-4.66, Fe-2.66). The value of N_v is compared with 2.52 which is found to be the critical value for σ-phase formation - above this value the brittle phase will form. The result of a calculation of this type for PE16 alloy is shown as point A in figure 1.1 (after Betteridge and Heslop 1974). A is close to the σ field. Point B on this figure represents the overall composition without consideration of concentration changes which accompany phase transitions. Point B clearly does not indicate the true proximity to the σ-phase field.

Sims (1966) highlights some disadvantages of this type of phase assessment. First, it is necessary to assume that no segregation occurs in the material (this is a particular problem in assessment of cast alloy). Second, specific reactions have to be assumed. Third, even with the above approximations, very accurate compositional data are required for each phase because small changes in alloying content for a major phase may be highly significant with respect to a minor phase (e.g. Kriege and Baris 1969; Shimanuki, Masui and Doi 1976). The present study aims to examine the relative importance of these three factors for PE16 (see section 1.1 above).

1.3 Modelling the generation of γ' phase

1.3.1 General Principles

The overall aim of this dissertation is to identify phase transition mechanisms by which γ/γ' distributions may be formed in superalloys. As commercial alloys are complex, this problem is approached by examining the γ/γ' reaction in a series of increasingly complex models. No modelling system can hope to simulate all modes of behaviour. Two important aspects have therefore been selected in the present study: first, identification of the phase transitions which determine the initial distribution of second phase and second, quantification of partitioning of minor alloying elements between γ and γ' phases. The latter determines lattice mismatch, so affecting coarsening behaviour, solid solution strengthening and APB energy.

Four superalloy model systems have been chosen to simulate selected types of microstructure.

1.3.2 Experimental Alloy Systems

1.3.2i Nickel-aluminium

A binary system is particularly useful as the initial model in studies of phase transitions because data concerning phase separation and ordering may be compared directly with available quantitative theories of phase transitions derived essentially for two-component systems. The nickel-aluminium system meets this requirement and also embodies basic γ' formation.

A nominal composition of Ni-14at.%Al was chosen. This corresponds to a volume fraction of 30-40%, so modelling alloys of medium-high volume fraction such as some designed for creep resistance (e.g. Davies and Johnston 1970). The composition is also appropriate because experimental results may be compared with data for isostructural Ni-14at%Ti which already exist in the literature (e.g. Laughlin 1976, Watts and Ralph 1977).

1.3.2ii Nickel-chromium-aluminium

γ and γ' phases in pure binary nickel-aluminium alloys have a relatively high lattice misfit parameter of 0.56% (e.g. Taylor and Floyd 1952a). The next stage of modelling phase transition behaviour is to reduce the mismatch to approximately zero by adding a γ-partitioning element which expands the γ lattice e.g. chromium. Zero lattice mismatch is the second requirement for creep resistance (Davies and Johnston 1970). For purposes of comparison with the behaviour of the first alloy 30-40% volume fraction of γ' was again required. It was assumed as a first approximation that this condition could be met with 14at% of the γ'-former, aluminium. Using tables of lattice mismatch provided by Davies and Johnston 1970 this set the nominal experimental alloy composition at Ni-15.5at%Cr-14.0at%Al.

1.3.2iii Nickel-aluminium-titanium

Most commercial alloys contain both aluminium and titanium partitioned between γ and γ' phases. Thus two alloys of the ternary nickel-aluminium-titanium system were examined. The first, Ni-9.1at%Al-4.4at%Ti, was designed to maintain approximately the same γ' volume fraction as previous models. Ni-8.7at%Al-2.5at%Ti

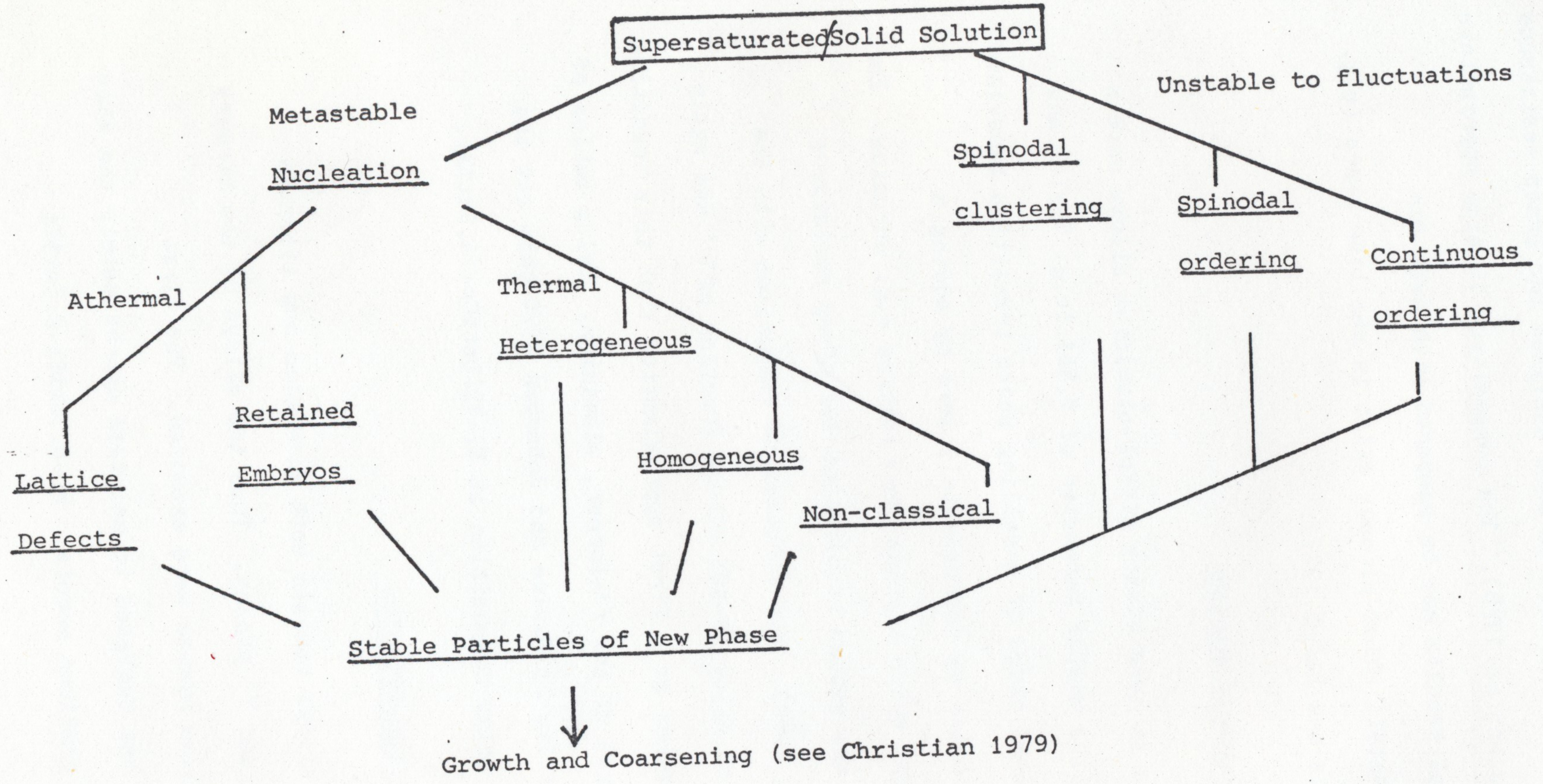

Figure 1.2 Proposed classification scheme.

represented lower volume fraction systems. Mismatch throughout the ternary nickel-aluminium-titanium alloys is slightly greater that in nickel-aluminium system γ/γ' microstructures.

1.3.2iv Commercial alloy: PE16

A close matrix model of alloy PE16, a zero-misfit superalloy, completes the modelling series. The material illustrates some features of partitioning of six major alloying elements: nickel, aluminium, titanium, chromium, iron and molybdenum. The volume fraction of γ' is approximately 10% which is characteristic of weldable superalloys.

1.4 Possible Phase Transitions and their Classification

1.4.1 Introduction: a Mechanistic Approach

Figure 1.2 proposes a classification scheme which may be adopted for studies of γ' phase generation. This classification is based upon a similar route proposed by Christian 1975, 1979. The scheme is mechanistically-based, with initial thermodynamic differentiation between modes of phase separation. All possible decomposition routes which have been found in past studies of both superalloys and model materials are included.

The proposed classification has the advantage that the metallurgical "history" of the material may be followed and kinetic, possibly controlling, factors may be identified. Fully thermodynamic studies (see e.g. Christian 1975, 1979; White and Geballe 1979) take no account of kinetic factors and are indeed impracticable for superalloy studies because sufficient thermodynamic data do not exist.

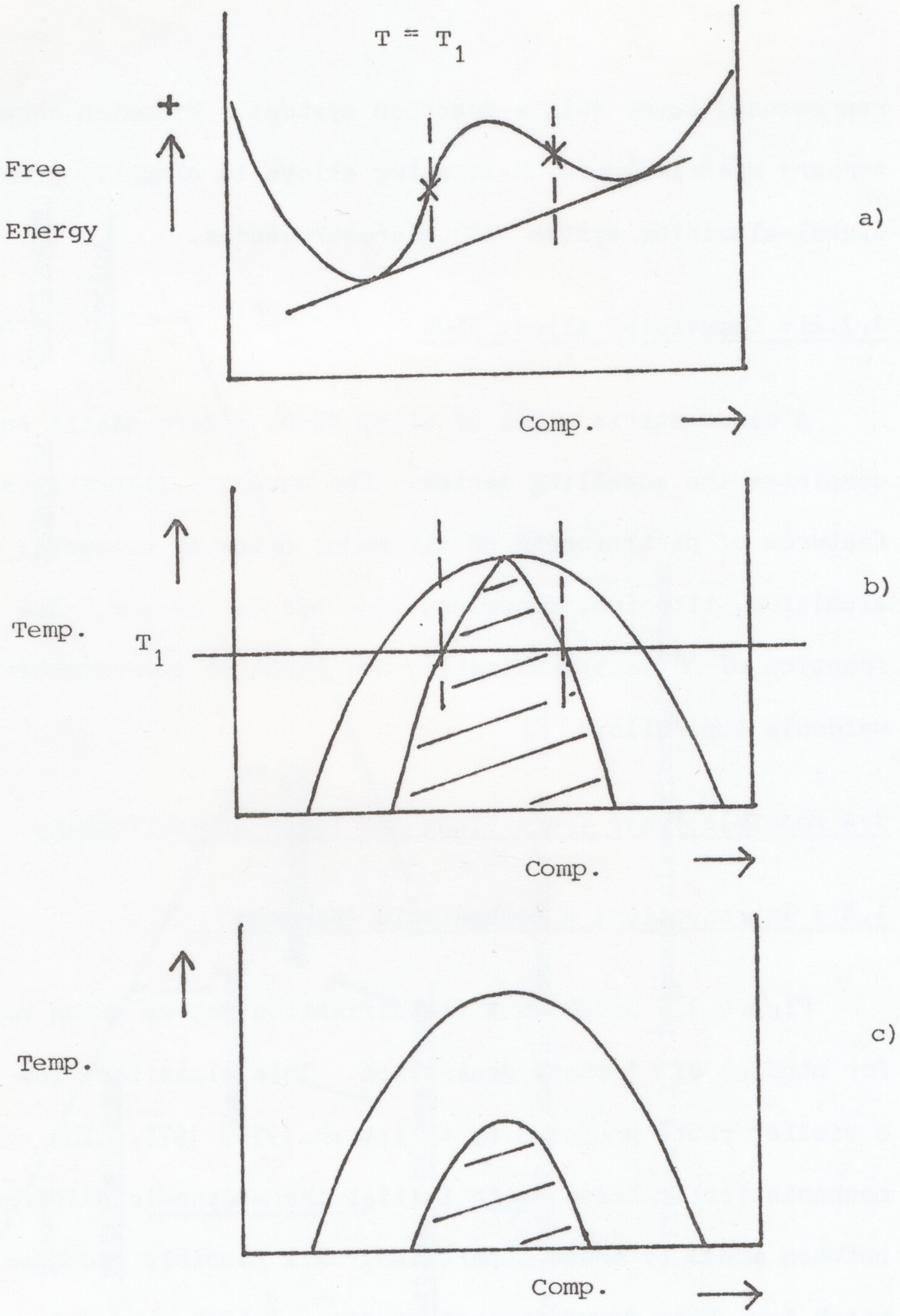

Figure 1.3 Location of the spinodal on a phase diagram:-

a) Appropriate free energy curve, b) phase fields for a system with no lattice strain, c) phase fields for a system with lattice strain.

Morphological studies e.g. Tyapkin, Travina and Kozlov 1975; Tyapkin 1977 also cannot reflect previous microstructure. For example, an aligned, modulated γ' distribution is by no means proof that the original decomposition was periodic. The modulation indicates only that particle/matrix strain field interaction has occurred.

The concept of relative thermodynamic stability, central to the proposed classification scheme, is pursued in the remaining sections of the present chapter. Chapter 2 develops appropriate kinetic theory for one class of these reactions - the unstable or continuous changes. This kinetic theory is suitable for tests of transition behaviour using experimental data and a new route of analysis of compositional data for use with current theories is presented in Chapter 3.

1.4.2 The Basic Thermodynamic Stability Criteria

1.4.2i General principles

For a non-isostructural phase change each phase retains a discrete free energy curve and second phase production must proceed via a reaction intermediate (i.e. must be nucleated). In isostructural changes, however, a single free energy curve relates the two phases. Under some conditions, such as large undercoolings below the transition temperature, the integral free energy curve may take the form shown in figure 1.3a. Here two points of inflexion have been generated at positions in the curve corresponding to

$$\frac{\partial^2 \phi}{\partial c^2} = 0 \qquad \text{....E1.1}$$

where ϕ is the integral free energy. Between these inflexions compositional excursions result in a spontaneous decrease in free energy and a possible immediate propagation of phase separation, although not necessarily to the equilibrium phase. Outside the region of inflexion the reaction is again nucleated i.e. the parent supersaturated solid solution is metastable.

The compositional changes which characterise these reactions are described respectively as "small in degree but large in extent" and "large in degree and small in extent" (Gibbs 1878) and the changes themselves as "continuous" and "nucleated". The phase fields for these reactions are shown on the schematic phase diagram in figure 1.3b. This construction has assumed that there is no strain present.

Figure 1.3c shows phase fields for the case where strain is present in the γ/γ' interface. The strain energy effectively depresses the coherent stability boundary with respect to the incoherent or equilibrium boundary.

1.4.2ii Detailed studies

Some theories of continuous transitions which are relevant to the experimental studies presented later in this dissertation (Chapters 4-6) are reviewed in Chapter 2 below. Various metastable changes are also considered briefly.

Further details of theories of continuous phase transitions and general critical phenomena may be found in the literature (e.g. Landau and Lifshitz 1969; Lines 1973; Christian 1975; Domb and Green 1975; Nagle 1975; White and Geballe 1979). In particular the references consider various methods of differentiating between transitions by definition of a "mathematical order" of reaction. For the thermodynamic criteria adopted above this "mathematical order" corresponds to the first derivative of the integral free energy, Φ, which shows a discontinuity. Thus nucleated reactions have "first order" and (uniquely at T_c) spinodal reactions "second order". Other classifications consider alternative parameters and their behaviour to describe the reaction. For example Landau and Lifshitz 1969 examine symmetry properties and elemental distributions. Some applications of this critical theory to metallurgical studies are discussed by Cook 1976.

Expansions of nucleation theory and studies of other reactions described in the classification diagram (figure 1.2) are again contained in the literature e.g. Christian 1975, 1979.

1.4.3 Microstructures from Continuous Changes

As a result of instability in the parent solid solution phase separation by spinodal change occurs by continuous development of composition waves. In contrast, nucleation produces only discrete regions of second phase (see e.g. Nicholson 1970; Russell 1970).

The exact microstructure which is produced by continuous reactions is determined by the degree of elastic strain in the structure. However, in most metallic systems there is usually a small lattice strain which gives rise to a net preferred direction for the composition wave (see Chapter 2 below). Thus the material shows a characteristic "striated" structure in the electron microscope (e.g. Laughlin, Sinclair and Tanner 1980) which reflects the periodic variation in lattice parameter. The exceptions to striated structure are glass systems where little, if any, strain is present. Similar striated appearances are found in continuously ordering systems (see general references).

As stated above in section 1.4.1, this morphological information alone may not always be interpreted uniquely in terms of phase transition behaviour. However, observations of initial microstructure may often provide valuable supportive evidence in studies of reaction kinetics.

1.4.4 Examples of Continuous Behaviour

Spinodal reactions have been identified in systems as diverse in physical properties as Na_2O-SiO_2 glasses (Cahn and Charles 1965), Cu-Ni-Fe magnet materials (e.g. Livak and Thomas 1971) and aluminium-based systems (e.g. Al-Zn Rundman and Hilliard 1967). Continuous ordering reactions have been observed for a large number of possible lattice transitions (Tanner and Leamy 1974 and reviews Cohen 1970; Khachaturyan 1978; de Fontaine 1979). Examples of transitions are Cu_3Au (A1-$L1_2$), CoPt (A1-$L1_0$) and Ni_2V (A1-D^{25}_{2h} Immm). In many cases, however, more than one continuous change occurs e.g. nickel-titanium alloys (Laughlin 1976; Watts and Ralph 1977). Allen and Cahn (1975, 1976a, 1976b Allen 1977) have devoted considerable attention, both experimental and theoretical, to the study of the rules which determine the sequence of possible reactions in b.c.c. iron-aluminium alloys.

1.5 Summary

In this first chapter features of γ/γ' microstucture in superalloys are reviewed. Four model alloys are chosen in order to investigate particular aspects of separation of the second phase. A scheme for classification of transformation behaviour based upon mechanistic requirements is proposed and the individual transitions which comprise this scheme are introduced. The detailed theories which permit kinetic analysis and identification of transition mechanism are to be pursued in Chapter 2.