CHAPTER 7

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

7.1 Aims

The overall aim of this dissertation is to assess by observation of a series of model alloys which phase separation mechanisms may operate in the generation of γ' phase in commercial superalloys. Four model alloys were chosen from the systems nickel-aluminium (Ni-14.1at.%Al), nickel-chromium-aluminium (Ni-20.0at.%Cr-14.0at.%Al) and nickel-aluminium-titanium (Ni-9.1at.%Al-4.4at.%Ti and Ni-8.7at.%Al-2.5at.%Ti), plus a matrix model of Nimonic alloy PE16 and three distinct modes of general phase separation were identified. Using established theories of continuous transition behaviour (outlined in Chapter 2) and a new method of Fourier analysis designed to extract kinetic data from APFIM composition profiles (presented in Chapter 3) it has been shown that the binary alloy Ni-14.1at.%Al decomposes spinodally at 625^{o}C. The two nickel-aluminium-titanium alloys were found to nucleate γ' heterogeneously, while in the matrix model of PE16 γ' was generated by conventional homogeneous nucleation. The behaviour of the nickel-chromium-aluminium alloy was found to be more complex and results suggested that two populations of γ' phase were produced by separate spinodal and conventional nucleation mechanisms. The details of these results are given in the appropriate experimental chapters (4-6).

In this present chapter the overall implications of these results with respect to general modes and features of γ' phase separation in

superalloys are examined.

7.2 General Phase Transformations of Superalloys

7.2.1 Primary Precipitation

The results summarised in the previous section (7.1) indicate that spinodal phase separation may be possible in the simplest (least alloyed) commercial superalloys. The possibility of spinodal decomposition apparently decreases as the number of alloying additions increases or the supersaturation decreases. Certainly it is to be expected that replacement transitions may occur with large strains and chemical gradient terms and also with low volume fraction of γ'. However, the overall result does indeed support the suggestion of e.g. Merrick 1978 that some alloys which generate fine-scale γ' may do so by spinodal decomposition. One such likely alloy is Nimonic 80A. Qualitative examination by Wood, Mills, Bingham and Bee (1979) certainly suggests that phase separation may be spinodal in 80A but quantitative analysis of reaction kinetics must yet be performed to confirm this idea (see section 7.3 below).

7.2.2 Subsequent Precipitation

In general, once primary γ' formation has occurred secondary γ' (cooling or ageing) may be formed. This produces a finer-scale in-filling between the original γ' particles, which themselves must either be the result of conventional nucleation and/or growth or they must be a coarsening product of a previous continuous transition. In the present investigation it has been shown that primary and secondary γ' may not necessarily have similar compositions. It may be the case that each separate γ' precipitation reaction is governed by solubility

rules of the form which determine the overall equilibrium and non-equilibrium reactions. If this is so, then empirical measurement of γ' compositions over a wide variety of model alloys may permit estimation of the rules which pertain. This in itself would promote improved understanding of the contributions which each γ' distribution may make towards the net alloy hardening and other properties.

One particular property which has at least been touched in passing is the ordering of the γ' lattice. Experimental results for the PE16 matrix model show that, at least under those circumstances, adjustment of the concentration of γ'-formers in the second phase, and therefore the degree of order towards the equilibrium γ' lattice, is dependent upon rejection of chromium from the lattice. The degree of order must influence the APB energy. For an alloy of high volume fraction of γ', variations in APB energy between γ' distributions may result in change of dislocation propagation from cutting to bowing or vice versa, cutting being favoured in the phase of lower APB energy. Where the appearances of γ' distributions are time-dependent such mechanistic variations with time may result in important changes in mechanical properties with time.

7.2.2 Use of Fourier Analysis

In examination of the different transition behaviours displayed by the binary and ternary systems it has been shown that the method of Fourier analysis outlined in Chapter 3 of this dissertation is capable of reflecting the constant wavelength behaviour of spinodal changes and the different spectra of nucleation events. This in

itself has justified the use of this analytical tool.

7.3 Suggestions for Further Work

The new work which may be proposed on the basis of these results falls broadly into three catergories. First, studies of further model systems; second, assessment of the behaviour of more commercial alloys; and third, additional studies such as extensions of the Fourier analysis technique which was proposed in Chapter 3.

7.3.1 Further Modelling Studies

The present study has shown that, under conditions of low solute supersaturation and high lattice mismatch, phase separation by conventional nucleation mechanisms is favoured in superalloys. Several additional model alloys may yet be examined in order to define more closely the conditions for mechanistic transition between nucleation-and-growth and continuous change. First, a nickel-chromium-aluminium alloy of defined zero misfit should be examined to eliminate the role of strain energy considerations (see Chapter 1 above) more closely. Second, a nickel-aluminium-titanium alloy of much greater solute supersaturation than those already studied should be followed. This should show whether a highly depressed miscibilty gap may be found in this system at all. In this case a composition of, say Ni-14at.%Al-7at.%Ti may be suggested and a low ageing temperature of 400^{o}C in order to give the maximum possibility of spinodal behaviour. Lastly, a quaternary alloy of the system nickel-chromium-aluminium-titanium may be investigated in order to follow the effects of yet greater alloying. All of these model studies may employ the experimental and analytical techniques which have already

been applied in the course of the present study. This dissertation has also shown the value of the melt-spinning process for study of continuous reactions after short ageing periods and it is recommended that, where possible, all alloys are examined in the melt-spun or splat-quenched state.

7.3.2 Direct Study of Commercial Alloys

One direct extension of the present work to commercial systems must comprise examination of partitioning behaviour in other alloys of the series designed to model the behaviour of PE16 (Shaw 1980, see Chapter 6) and particularly in the alloy PE16 itself, in order to esablish whether the observed dependency of the Ti/Al ratio of the γ' phase upon chromium content of that phase persists in the commercial alloy. With subsidiary studies of these other alloys and parallel investigation of mechanical properties and the compositional stability of the γ' phase it may be possible to identify any composition change which is associated with stability of the microstructure towards void swelling.

Other experiments may employ presently established techniques in quantitative investigation of transition kinetics in simple alloys, that is, those with few alloying additions. The most promising alloy for spinodal decomposition, Nimonic 80A, has already been mentioned above in section 7.2 and kinetic analyses may be applied to this system as an initial study. Other alloys such as Nimonics 90 and 115 may be studied, but, at least for APFIM analysis, the interpretation of experimental data would be considerably more complex because these alloys contain cobalt for which the single isotope lies within the range of the isotopes of nickel on the mass-to-charge ratio scale.

Further improvements in atom-probe mass resolution should, in principle, overcome this difficulty. However, in Chapter 5 of this thesis investigations of the Fourier spectra of individual QAP traces for the separate elements of a ternary nickel-chromium-aluminium alloy suggested that the essential characteristics of the phase transformation are often contained within each individual trace and that the complete set of elemental traces may not be required. Hence, provided that say aluminium, titanium, nickel and chromium traces reflect all characteristics of partitioning behaviour and precipitate shape, it may not be necessary to monitor the absolute nickel and cobalt contents in the first instance in order to test for reaction kinetics. Thus, other alloys such as Nimonics 90 and 115 may be studied.

It is suggested that this investigation begin by following partitioning in, say, Nimonic 90 and carefully comparing the Fourier characteristics of individual traces in order to ascertain the extent to which the partial trace analysis is applicable. The study may then be generally extended to examination of the effect upon reaction mechanisms and microstructural scale of the products, of segregation to the interface created in the solid/solid state phase change (e.g. Seah and Hondros 1977).

7.3.3 Additional Studies

7.3.3i Development of the Fourier analysis route

Some developments of this analysis such as examination of lattice ordering waves and study of plane-stability-ratio as ways of finding the degree of lattice order within an alloy have already been mentioned in section 3.7 of Chapter 3. In more general terms

extensions which may be anticipated for use of the process include study of EDS traces from STEM analysis, studies of microprobe traces and SIMS traces. In all cases these results may be converted to signals which represent compositional determinations at fixed intervals ranging from 2-200nm. Thus a large range of microstructural periodicities may be examined and structures of cast superalloys and eutectic forms may be studied.

Much interest has been shown in the technique of lattice imaging as a general method of examining spinodal microstructures (e.g. Sinclair, Gronsky and Thomas 1976; Wu and Thomas 1977; Wu Sinclair and Thomas 1978). However, some difficulties are experienced in relating fringe spacing to the exact compositional modulations in the structure (e.g. Spence, Cowley and Gronsky 1979). Since APFIM analyses provide very accurate compositional data it may be envisaged that some new studies of spinodal systems may employ lattice imaging and APFIM techniques in parallel. The Fourier analysis given in this dissertation may then be extended to the lattice imaging data.

7.3.3ii Secondary γ' populations

The analyses of Chapter 5 showed that APFIM is suitable for accurate compositional analysis of different γ' populations within the same alloy. By examination of a series of models of, say, the nickel-chromium-aluminium system it may be possible to assess at least empirically how the compositions of each successive γ' population depend upon the remaining matrix composition. The results of Chapter 5 suggest that the concentration of chromium tolerated by the γ' lattice changes with overall composition and the study of ternary alloys would follow the role played by chromium in determining the γ'

compositions and volume fractions. This study of ternary materials may then be extended to alloys of quaternary and more complex systems and general rules concerning solubility may be found. Then, given the overall alloy composition, it may be possible to assess not only the possibility of σ-formation (PHACOMP) but also the precise nature of γ' populations and their volume fraction. This is turn would considerably improve the possiblity of prediction and understanding of mechanical properties which depend so strongly upon the γ' phase.

Parallel studies of lattice ordering by combined QAP trace studies and PSR measurements (see section 7.3.3 above) would permit examination of the change in the degree of lattice order within the γ' phase as the chromium content is varied.